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## Low-temperature magnetoresistance and magnetic ordering in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$

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**Abstract.** In zero field,  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  shows thermally activated behaviour for all values of  $x$ . For  $x \geq 0.3$  charge ordering occurs at 250 K, with long-range antiferromagnetic ordering at lower temperatures. For a range of compositions ( $0.30 \leq x \leq 0.45$ ) a first-order magnetic-field-induced insulator–metal transition produces changes in resistivity of up to 12 orders of magnitude at low temperatures. These conducting states are metastable, resulting in a large hysteresis in resistivity with changes in both magnetic field and temperature. There is a marked relationship between the resistivity and the magnetic state of the material. Below the charge-ordering temperature, metamagnetic transitions occur which transform the magnetic correlations from either paramagnetic or antiferromagnetic to ferromagnetic. The range of compositions for which these metamagnetic transitions occur, the fields required to induce the ferromagnetic state, and the irreversible changes in the nature of the magnetic ordering all correlate with the field-induced changes in resistivity.

### 1. Introduction

Recently there has been renewed interest in the properties of the rare-earth manganite perovskites  $\text{R}_{1-x}\text{A}_x\text{MnO}_3$  where R is a rare-earth element such as La, Pr, Nd or Y, and A is one of a number of divalent ions including Sr, Ca, Ba and Pb. A range of doping around  $x = 0.3$  can produce materials which have a paramagnetic-to-ferromagnetic (FM) transition which is accompanied by very large decrease in resistivity [1–5]. The application of a magnetic field can also increase the temperature at which long-range ferromagnetic order is observed. As a result these materials can be driven between a low- and a high-conductivity state by the application of a magnetic field. The behaviour exhibited by these materials is usually explained in terms of the double-exchange theory [6–8]. Doping produces an increase in the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio making it easier for electrons to hop between Mn ions and creating a tendency for ferromagnetic interactions rather than the antiferromagnetic (AFM) exchange interactions which dominate if the electrons are more localized. However, more recent work has suggested that in order to calculate resistivities with the correct order of magnitude polaron effects due to strong electron–phonon coupling coming from the Jahn–Teller splitting should also be included in any theoretical model [9].

For certain compositions near 50% doping, there is charge ordering (CO), i.e. a regular arrangement of the Mn ions into a  $\text{Mn}^{3+}/\text{Mn}^{4+}$  sublattice. The resulting restriction in the mobility of the electrons produces an increase in the resistivity. This CO is often accompanied by AFM ordering. Application of a magnetic field can melt the CO lattice leading to a large decrease in resistivity and the reappearance of a FM state. Once again

a magnetic field can be used to switch between a high- and a low-conductivity state. The clearest example of the influence of CO is observed in studies of  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  [10]. This material has a FM transition at 270 K accompanied by a decrease in the resistivity. At 140 K charge ordering occurs with a simultaneous transition into an AFM state and a large increase in resistivity due to the localization of the charge carriers. Below the AFM/CO/localized transition temperature the FM/conducting state can be retrieved by applying a sufficiently large external magnetic field. A degree of hysteresis accompanies this transition suggesting that the phase transition is first order. These effects are very dependent on composition in this material and are restricted to a small range of doping around 50%.

The electronic structure of these materials is also strongly coupled to the lattice. Large magnetovolume effects have been reported, and in the case of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  it has been shown that it is even possible to force a structural phase transition at constant temperature by the application of a magnetic field [11].

## 2. Properties of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$

$\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  forms across the whole range of composition ( $0 \leq x \leq 1$ ) with an orthorhombically distorted perovskite structure. There are a number sources of distortion present in this system [12–17]. For example, a buckling of the  $\text{MnO}_6$  octahedra results from the ionic radii mismatch in this material. The Goldschmidt tolerance factor in this series increases from 0.93 for  $x = 0$  to 1.004 for  $x = 1$  [16]. There is also a Jahn–Teller effect which leads to distortions of the  $\text{Mn}^{3+}\text{O}_6$  octahedra. Previous work has shown that as the strength of these effects varies  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  assumes a variety of structures for different values of  $x$  and temperature. For small values of  $x$  the structure of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  is also sensitive to oxygen content. At 945 K pure  $\text{PrMnO}_3$  undergoes a structural transition from a quasicubic to an O orthorhombic structure and then at around 820 K a cooperative Jahn–Teller effect drives the systems into an O' orthorhombic structure with  $c/\sqrt{2} < a < b$ . The substitution of Ca for Pr weakens this cooperative Jahn–Teller effect. Doping with divalent  $\text{Ca}^{2+}$  ions also creates  $\text{Mn}^{4+}$  ions and there is electron hopping between  $\text{Mn}^{3+}$ - and  $\text{Mn}^{4+}$ -ion sites. For  $0 \leq x \leq 0.3$  the O–O' transition is still observed but there is a rapid decrease in the transition temperature. For  $0.3 \leq x \leq 1.0$  the system is O orthorhombic at high temperature whilst at low temperatures it is compressed pseudotetragonal with  $c/\sqrt{2} < a$  (T) for  $0.3 \leq x \leq 0.75$ , elongated pseudotetragonal  $c/\sqrt{2} > a$  (T') for  $0.75 \leq x \leq 0.9$  and pseudocubic (O) for  $0.9 \leq x \leq 1.0$ . This quasitetragonal distortion occurs over a wide range of composition at nearly the same temperature ( $T \approx 250$  K). It has been suggested that the cooperative Jahn–Teller effect is now too weak to induce an O–O' transition at this temperature. The electrons become more localized with a hopping frequency which is less than the vibrational frequency associated with the Jahn–Teller distortion, and the  $\text{Mn}^{3+}$  lifetime is now long enough to allow ordering of the  $d_{z^2}$  orbitals which produces the O–T transition. At the same time an optimization of elastic and electrostatic energies leads to spatial charge ordering of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions. It appears that the flexibility of the perovskite lattice and the smaller divalent Ca ion allows charge ordering to persist, albeit in a disordered or locally clustered form, for a wide composition range (30% to 70% doping).

The  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  system is also reported to have a complex magnetic phase diagram [12–17].  $\text{PrMnO}_3$  orders antiferromagnetically at  $T_N = 91$  K although the nature of the magnetic order appears to depend on the oxygen stoichiometry [18]. Addition of Ca leads to the appearance of ferromagnetic order for  $0 < x < 0.3$ . For  $x = 0.2$ ,  $T_c = 130$  K. For the  $x = 0.3$  composition, which is situated on the boundary between two crystallographic types, the nature of the magnetic ordering is less clear cut. It has been suggested that a collinear

CE-type AFM structure at  $T_N \approx 130$  K is succeeded by a canted ferromagnetic structure together with an antiferromagnetic component of the CE type at  $T_{CA} \approx 115$  K [17, 19]. For  $0.4 \leq x \leq 1.0$  the ordering is one of a number of possible AFM structures. For  $0.4 \leq x \leq 0.5$  the materials order with a canted AFM structure and a  $T_N$  of around 170 K.  $\text{CaMnO}_3$  has a G-type AFM structure with a  $T_N$  of 110 K.

Initially, work on the field-dependent properties of the  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  system concentrated on the  $x = 0.3$  compound since many of the previous studies of similar systems had shown that the critical concentration of divalent dopant ion should be around  $x = 0.3$ . Huge negative magnetoresistance (MR) has been reported for  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x = 0.3$  [20, 21]. Colossal negative MR has also been reported for the  $x = 0.3$  compound where small amounts of Ca have been replaced by Sr [22, 23]. Similar field-dependent transport properties are observed for the  $x = 0.4$  compound [24]. There is a strong correlation between transport and magnetic properties of this material with the onset of ferromagnetism coinciding with the appearance of the high-conductivity state. A recent neutron diffraction study of the  $x = 0.3$  compound [19] has shown that an application of a magnetic field leads to the breakdown of the both the charge and AFM ordering, with the appearance of a FM metallic state. This correlation can be more easily studied for the  $x = 0.4$  composition where the zero-field AFM state is well defined. The structural and CO transitions around 250 K are decoupled from the AFM ordering which occurs at 170 K. Below 250 K application of a magnetic field drives this system from either a paramagnetic (for  $170 \text{ K} < T < 250 \text{ K}$ ) or AFM (for  $T < 170 \text{ K}$ ) state into a ferromagnetically ordered state.

In this paper we present measurements of resistivity, magnetization and magnetic susceptibility as functions of magnetic field and temperature for a range of compositions of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  of  $0 \leq x < 1$ . Magnetic-field-induced insulator-metal transitions are shown to occur for the range of Ca compositions  $0.30 \leq x \leq 0.45$ . Within this composition range the dramatic changes in the resistivity are accompanied by regions of hysteresis extending over a considerable range of temperature and magnetic field. The high-conductivity states are shown to be metastable at low temperature. We also show that for  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  compounds there is a clear correlation between the ease with which the system can be forced into a ferromagnetic state by the application of a magnetic field, the transport properties in zero field and the appearance of a field-induced conducting state.

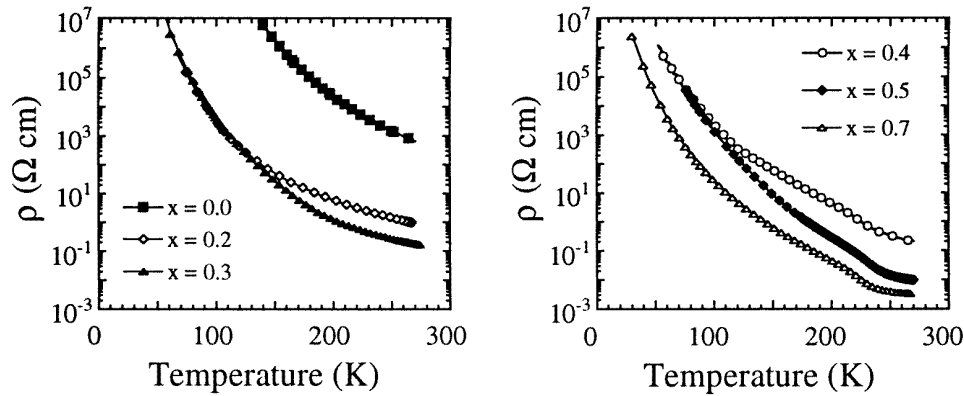
### 3. Sample preparation and experimental details

Polycrystalline samples of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $0 \leq x \leq 1$ ) were prepared by a normal solid-state reaction route. Stoichiometric quantities of  $\text{Pr}_6\text{O}_{11}$ ,  $\text{CaCO}_3$  and  $\text{MnO}_2$  were repeatedly ground and then sintered in air for 12 hours at a temperature of  $1350^\circ\text{C}$  before finally being pressed into pellets and sintered at the same temperature for 24 hours.

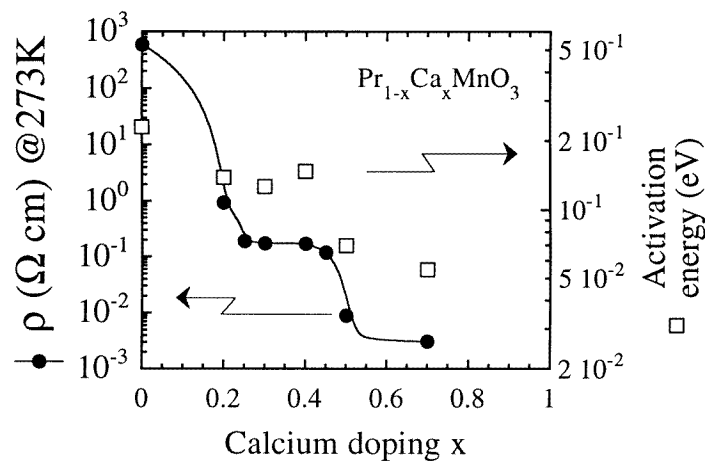
Measurements of the resistivity ( $\rho$ ) in magnetic fields of up to 80 kOe were carried out using a standard dc four-probe method. An excitation current of between 1 and 1000  $\mu\text{A}$  was used, depending on the resistance of the sample. The voltage limit of the current source and input impedance of the voltmeter limited the resistance which could be measured to below  $10^8 \Omega$ . Measurements of the magnetic susceptibility ( $\chi$ ) were made using a mutual inductance technique with an ac driving field of 5 Oe at a frequency of 403 Hz in dc fields of up to 80 kOe. Measurements of the magnetization ( $M$ ) were performed in an Oxford Instruments VSM in applied magnetic fields of up to 120 kOe.

#### 4. Experimental results

The x-ray spectra obtained showed all samples to be nominally single phase. The calculated lattice parameters agree well with published data [16].



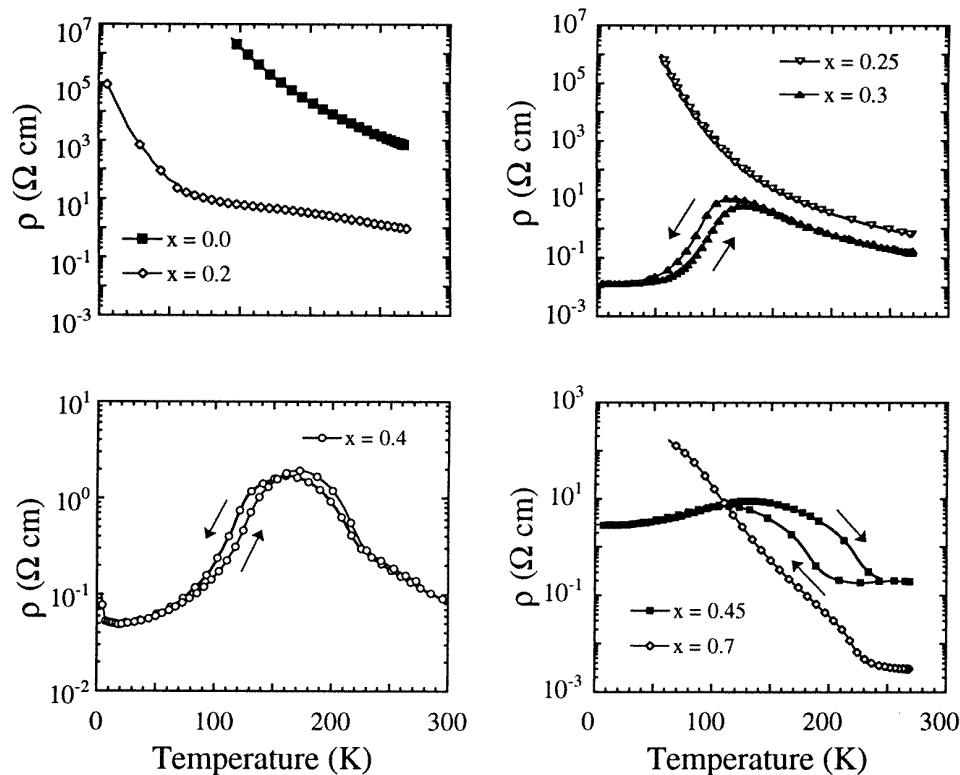
**Figure 1.** Resistivity versus temperature data collected in zero magnetic field for several  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  samples. For  $0.2 \leq x \leq 0.7$  a distinct change in slope at around 250 K indicates the onset of charge ordering.



**Figure 2.** The variation in the zero-field resistivity at 273 K and the activation energy as a function of calcium for doping for the  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  series.

Figure 1 contains curves showing the variation in the resistivity as a function of temperature for several samples with different Ca concentrations. In zero field the magnitude of the resistivity at 273 K decreases from around  $800 \Omega \text{ cm}$  for  $x = 0.0$  to  $0.003 \Omega \text{ cm}$  at  $x = 0.7$  (see figure 2). For all values of  $x$ , the resistivity and  $-\text{d}\rho/\text{d}T$  increase with decreasing temperature. Below  $\simeq 50 \text{ K}$   $\rho$  exceeds the value that we can measure using our voltmeter–current source arrangement. Using an electrometer we have determined that the resistivity of the  $x = 0.4$  compound exceeds  $10^{10} \Omega \text{ cm}$  at 4 K. We have fitted the  $\rho$ – $T$  data

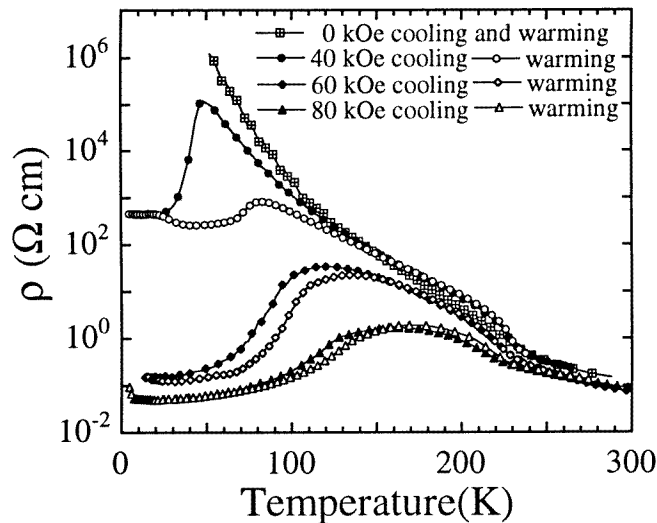
for the whole composition range studied using a simple exponential expression of the form  $\rho = \rho_0 \exp(T_0/T)^p$ , where  $T_0$  is some effective temperature and  $p$  is a positive exponent whose value depends on the details of the conduction mechanism [25]. Reasonable fits have been obtained by fixing  $p = 1$  (nearest-neighbour hopping) and with  $p = 1/4$  (3D Mott hopping). This suggests that conduction occurs primarily by some activated process but does not allow us to draw any firm conclusions about the exact nature of the conduction mechanism at this stage. We have calculated values for the activation energy using  $p = 1$ . For  $x \leq 0.2$  a fit produces a single value for the activation energy over the entire temperature range examined. For higher values of  $x$  there is a distinct change in slope of  $\rho-T$  at around 250 K associated with a structural transition and possibly charge ordering. This leads to an increase in the activation energy below this temperature for each composition. The activation energy at high temperature decreases with increasing  $x$  across the series from 0.2 eV at  $x = 0.0$  to 0.03 eV at  $x = 0.7$  (see figure 2).



**Figure 3.** Resistivity versus temperature data collected in a magnetic field of 80 kOe for several  $Pr_{1-x}Ca_xMnO_3$  samples. The data were taken while cooling the sample in the magnetic field. For  $x = 0.3, 0.4$  and  $0.45$  the data taken during subsequent field warming are also shown. These data demonstrate that for  $0.3 \leq x \leq 0.45$  there is a field-induced transition to a state with low resistivity. The change in slope in  $\rho-T$  at around 250 K for  $x \geq 0.5$  indicates the continuing presence of charge ordering.

In a field of 80 kOe the resistivity initially increases with decreasing temperature for all of the samples studied (see figure 3). For each composition the magnitude of the resistivity at 273 K and 80 kOe is lower than the zero-field value. This reduction corresponds to a

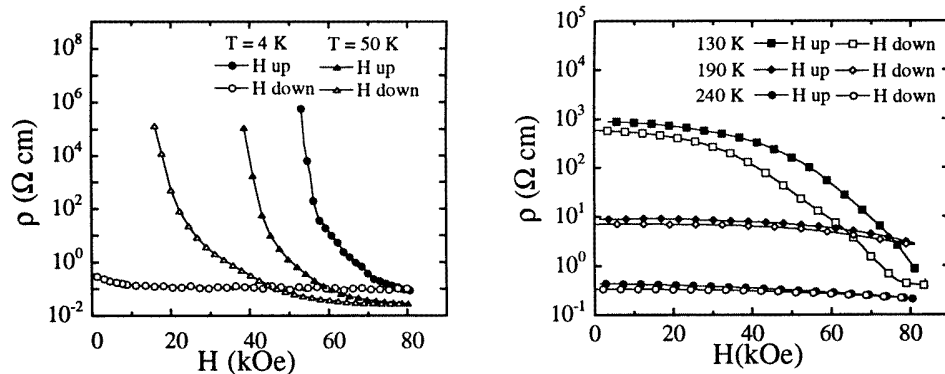
negative MR,  $\Delta\rho/\rho_0$ , where  $\Delta\rho = (\rho_H - \rho_0)$ , of around 3% over a wide composition range. For  $0.5 \leq x \leq 0.7$  a clear feature indicating the onset of charge ordering and a structural transition is present at around 240 K. For a more limited composition range  $0.3 \leq x \leq 0.45$  the resistivity for 80 kOe has a peak at around 150 K and then falls, in some cases by several orders of magnitude. The magnitude of the resistivity observed below 10 K yields negative MR values in excess of 99.999 999%. The details of the magnetotransport and magnetic properties of samples around this critical composition range ( $0.2 \leq x \leq 0.5$ ) are discussed in more detail below.



**Figure 4.** Resistivity versus temperature curves for  $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  taken in several magnetic fields. The data were collected during field cooling (closed symbols) and during subsequent field warming in the same magnetic field (open symbols). For  $H \geq 40$  kOe there is a field-induced fall in the resistivity accompanied by large regions of hysteresis.

Temperature-cycling experiments, in various applied magnetic fields, have been performed on several samples. The results for the  $x = 0.4$  composition are shown in figure 4. This sample exhibits activated behaviour in applied fields of less than 30 kOe although the magnitude of the resistivity decreases slightly with field. In higher fields a peak appears in the resistivity versus temperature data which is followed by a rapid fall in resistivity at lower temperatures. As the applied magnetic field is increased the position of this peak is shifted to higher temperature and the magnitude of the resistivity falls. At 4 K the value of the resistivity can be varied by at least 12 orders of magnitude depending on the value of the applied field. On warming from low temperature in fields greater than 40 kOe there is a further decrease in  $\rho-T$  producing a minimum at around 40 K. The difference between cooling and warming curves shows hysteresis in the data with a width of up to 100 K. Similar results have been obtained for samples with  $x = 0.3$  and  $x = 0.45$ .

Figure 5 shows the resistivity versus magnetic field at fixed temperature for the same  $x = 0.4$  sample. For each loop the sample was first zero-field cooled from room temperature to the measuring temperature. At 4 K the resistivity is initially above the limit which we can measure. As the magnetic field is increased there is a rapid fall in  $\rho-H$  around 50 kOe. The resistivity falls by more than seven orders of magnitude within 5 kOe. A more gradual decrease in  $\rho-H$  by a further two orders of magnitude is observed up to 80 kOe. Sweeping



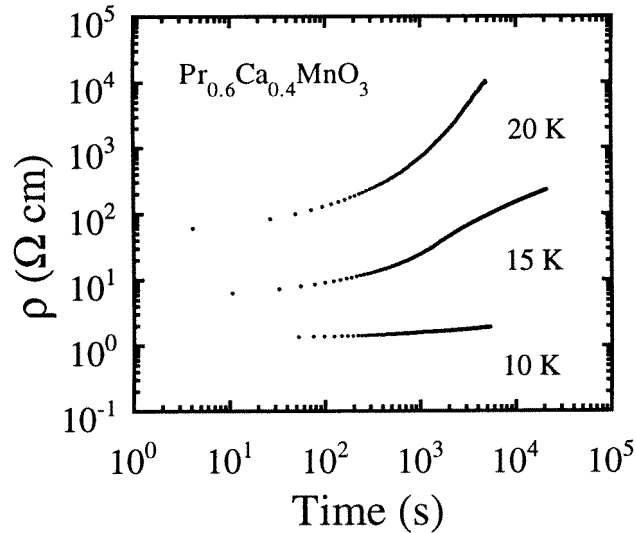
**Figure 5.** Resistivity versus magnetic field curves for  $Pr_{0.6}Ca_{0.4}MnO_3$  taken at several temperatures. The measurements were performed after cooling the sample from 300 K in zero magnetic field. The data were then collected in increasing field (closed symbols) and decreasing field (open symbols). At 4 K a field-induced insulator–metal transition leads to the appearance of a metastable conducting state.  $\Delta\rho/\rho_0$  exceeds 99.99999% at 4 K. Significant hysteresis and large negative magnetoresistance persist up to 130 K.

the field back to 0 kOe produces only a small increase in the magnitude of the resistivity. Around 50 K there is a more gradual appearance of a high-conductivity state for fields of around 40 kOe. At temperatures of up to 130 K the resistivity falls with increasing magnetic field corresponding to a negative MR of 99.9%. There are no discontinuities in the data and the  $\rho$ - $H$  loops open up only for higher fields. At higher temperatures a negative MR still exists but the behaviour is essentially reversible over the entire field range studied and the changes in the value of  $\rho$ - $H$  are much smaller in magnitude. Similar magnetic-field-induced transitions to a state with low resistivity at low temperature have been observed in samples with  $x = 0.3$  and  $x = 0.45$ . The field-induced conducting state observed at low temperatures for  $0.3 \leq x \leq 0.45$  are metastable.

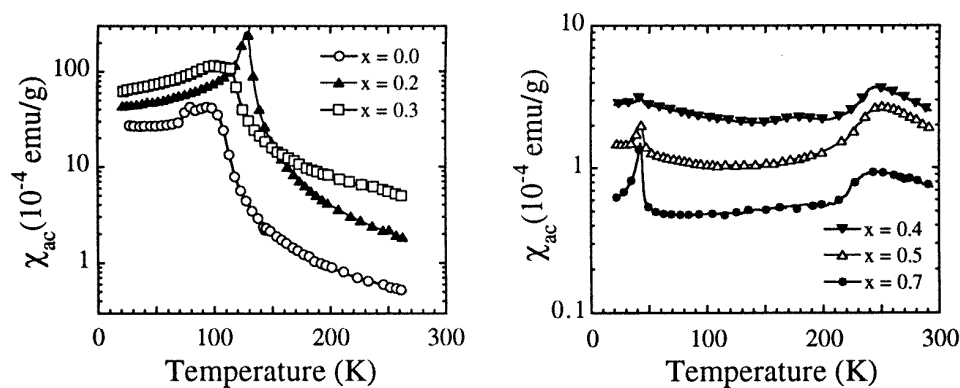
Figure 6 shows the increase in resistivity as a function of time in zero field for the  $x = 0.4$  composition after first cooling the sample to 4 K and applying a field of 80 kOe. Relaxation rates increase rapidly with temperature and the material is returned to a low-conductivity state by annealing at temperatures above 30 K. The conducting state is more stable in the  $x = 0.3$  compound where only a fraction of the original resistivity returns in zero field at 30 K and temperatures of above 100 K are required to recover the original resistivity over a relatively short time-scale.

Magnetization and magnetic susceptibility measurements have been performed in order to investigate the nature of the magnetic ordering with increasing magnetic field and to try to correlate any changes with the transport data. The temperature dependence of the ac susceptibility for several compositions in the range  $0 \leq x \leq 0.7$  are presented in figure 7. The peak in  $\chi_{ac}$ - $T$  at 95 K for the  $x = 0.0$  composition indicates the onset of long-range AFM order. For  $x = 0.1$  (not shown) the peaks at 100 K and 80 K agree well with temperatures at which the FM ordering and spin reorientation are reported to occur [17]. A sharp peak at 130 K in the  $x = 0.2$  data indicates the onset of FM ordering. At  $x = 0.3$  there is an increase in the magnitude of the susceptibility at around 150 K with a maximum which appears to be made up of two separate components. The temperatures of these features correspond well with the previously reported values of  $T_{CA} = 115$  K and  $T_N = 130$  K [17, 19]. For  $0.4 \leq x \leq 0.7$  there is a broad peak in the  $\chi_{ac}$ - $T$  data at around





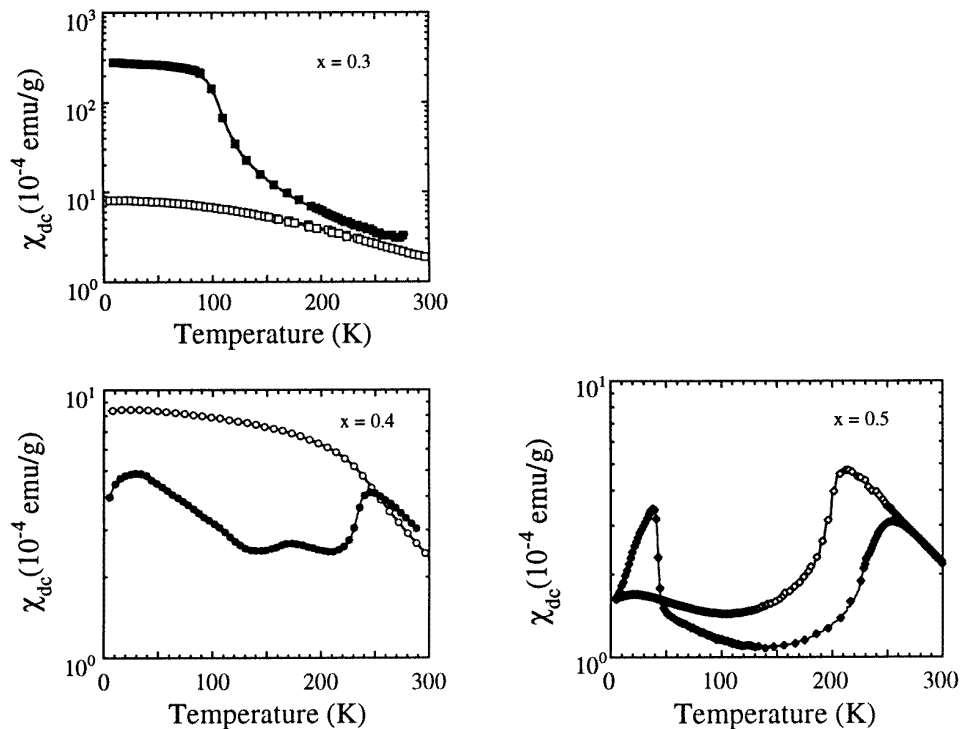
**Figure 6.** Variation in the resistivity as a function of time for  $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  at different temperatures. For each curve the sample was zero-field cooled to 10 K and subjected to an applied magnetic field of 80 kOe. The magnetic field was then reduced to 0 kOe at which point the measurements were begun.



**Figure 7.** ac susceptibility versus temperature curves for several  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  compositions. For  $x \geq 0.4$  the peak seen at around 250 K indicates charge ordering.

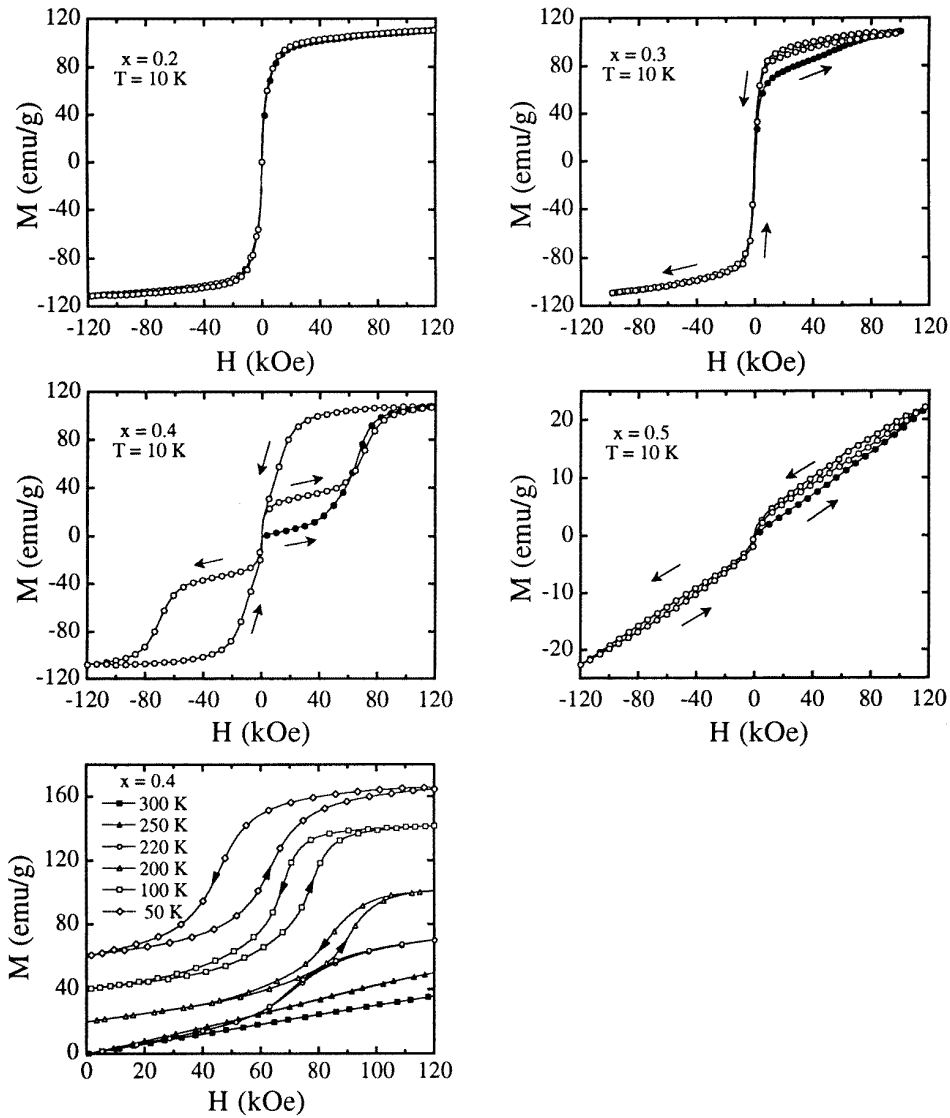
250 K which does not shift noticeably in temperature within this composition range. This maximum is associated with the O–T transition and charge ordering which occurs at this temperature. It should be noted that for  $0 \leq x \leq 0.3$  there are no features in the data from 200 K up to room temperature. A second maximum at around 160 K, which is seen most clearly in the  $x = 0.4$  data, indicates the onset of AFM ordering, whilst a third much sharper feature at 40 K whose magnitude increases with increasing  $x$  might be attributed to a spin reorientation. From these data it is clear that the charge and AFM ordering present in compounds in the doping range  $0.4 \leq x \leq 0.7$  occur at different temperatures.

Low-field  $\chi_{dc}$ - $T$  curves for  $x = 0.3$ – $0.5$  shown in figure 8 agree well with the ac



**Figure 8.** dc susceptibility versus temperature data for  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  where  $x = 0.3, 0.4$  and  $0.5$ . The data were collected during warming in applied magnetic fields of 1 kOe (closed symbols) and 120 kOe (open symbols) after cooling from 300 K in the measuring field.

susceptibility data.  $M-H$  loops taken on zero-field-cooled samples with different Ca concentrations at a temperature of 10 K are shown in figure 9. For  $x = 0.2$  the magnetization increases rapidly, saturating in fields above 20 kOe. The  $x = 0.3$  data contain features which indicate that this composition is in a crossover region of the magnetic phase diagram. The response is essentially FM in character and has much in common with the data for  $x = 0.2$ . However a small degree of hysteresis and the behaviour of the virgin response are evidence for coexistence of an AFM phase at low fields and a metamagnetic transition to a FM state at around 60 kOe. After the initial field sweep the response is essentially ferromagnetic. The data for the  $x = 0.4$  more clearly indicate the presence of a metamagnetic transition from AFM to FM ordering and an irreversible change in the magnetic response of the material. The initial susceptibility agrees well with ac susceptibility data and is characteristic of a AFM ordered state. A sharp increase in the  $M-H$  curve is observed at 50 kOe and the signal continues to increase rapidly up to fields of around 100 kOe and then tends toward saturation. This behaviour is the signature of a metamagnetic transition to FM ordering. As the field is decreased the magnitude of the signal remains almost constant with a sharp increase in  $dM/dH$  at around 20 kOe. The  $M-H$  loop passes close to the origin and then traces out a symmetric path about the origin with an enhanced susceptibility compared to the virgin response at low fields, and a rapid increase (decrease) in  $M$  at around 50 kOe (20 kOe) indicates the continuing presence of a metamagnetic transition. This metamagnetic transition is shifted to higher field with increasing temperature.  $M-H$  loops at higher

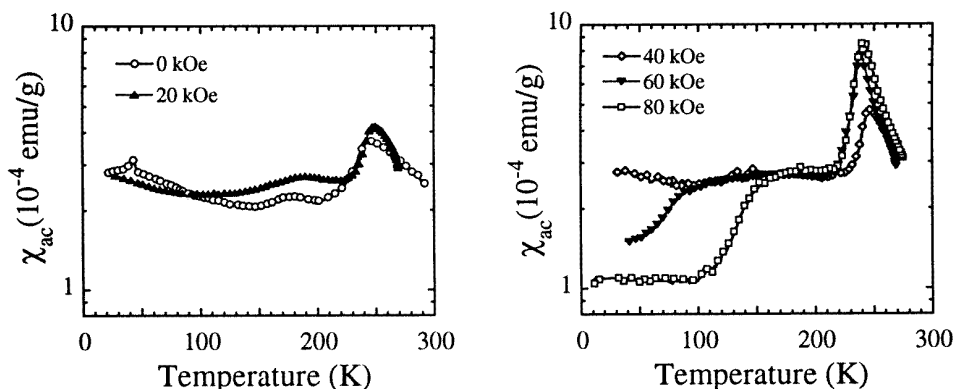


**Figure 9.** Magnetization versus applied magnetic field loops for  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  where  $x = 0.2, 0.3, 0.4$  and  $0.5$  taken at  $10\text{ K}$ . The measurements were performed after cooling the samples from  $300\text{ K}$  in zero magnetic field. The closed symbols indicate the data collected during the initial field sweep. The last panel shows data for the  $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  sample collected above (closed symbols) and below (open symbols) the charge-ordering temperature. Data taken below  $220\text{ K}$  are offset for clarity.

temperatures for the  $x = 0.4$  sample also show that the irreversible behaviour is present in this sample up to temperatures of at least  $220\text{ K}$  (see figure 9). For  $0.2 \leq x \leq 0.4$  the saturation moment lies between  $4.4 \mu_B$  per formula unit for  $x = 0.20$  and  $3.95 \mu_B$  per formula unit for  $x = 0.40$ . This is slightly higher than the mean spin-only value expected for free  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions indicating that the magnetization signal may include a small

contribution from the Pr at low temperatures. For  $x = 0.5$  the  $M-H$  data exhibit a small amount of hysteresis. No metamagnetic transition is observed and there is no tendency toward saturation. The magnitude of the signal at 120 kOe corresponds to only  $0.45 \mu_B$  per formula unit. These data show that the  $x = 0.5$  sample orders into an AFM state and that this ordering is stable even in higher magnetic fields.

$\chi_{dc}-T$  curves taken in magnetic fields of 120 kOe for  $0.3 \leq x \leq 0.5$  are also shown in figure 8. For  $x = 0.3$  and  $x = 0.4$  there is a rapid increase in  $\chi_{dc}-T$  at around 250 K, and at lower temperatures the signals saturate with magnitudes which agree well with the  $M-H$  data taken at various temperatures. These data indicate that for  $x = 0.3$  and  $x = 0.4$  there is a field-induced paramagnetic-to-ferromagnetic transition which occurs at around the  $T_{CO}$ . In contrast, the high-field  $\chi_{dc}-T$  curve for the  $x = 0.5$  sample resembles the low-field  $\chi_{dc}-T$  curve and the  $\chi_{ac}-T$  data, the only difference being the suppression of the low-temperature peak which may correspond to some spin reorientation within the sample. These data indicate that the CO and AFM order seen in the system are more stable at the  $x = 0.5$  composition.



**Figure 10.** ac susceptibility versus temperature data for  $Pr_{0.6}Ca_{0.4}MnO_3$  collected in dc magnetic fields of 0, 20, 40, 60 and 80 kOe. The data were taken during field cooling. The peaks seen at 250 K and 160 K indicate charge ordering and antiferromagnetic ordering respectively. For  $H \geq 40$  kOe the sharp peak at 240 K signals the appearance of ferromagnetic order.

Further evidence of field-induced FM ordering in these materials comes from ac susceptibility measurements performed on the  $x = 0.4$  compound in dc applied fields of up to 80 kOe (see figure 10). These measurements show that for  $H \leq 40$  kOe the charge-ordering peak seen in  $\chi_{ac}-T$  is present at 250 K and is little changed from the zero-dc-field data. However, for  $H_{dc} > 40$  kOe there is a rapid increase in the magnitude of the signal, a change in the shape of the maximum to a sharp peak and a shift of 10 K in the position of the peak to 240 K. This peak coincides with the onset of field-induced ferromagnetic ordering from a paramagnetic state. The rapid fall in  $\chi_{ac}$  seen at lower temperature may be the signature of some spin reorientation which occurs below the FM ordering temperature and is shifted to higher temperatures in magnetic fields. Alternatively it could be due to domain effects such as domain reorientation or pinning which could be present within the FM ordered state.

## 5. Summary

The results presented in this paper show that for  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  there are a range of compositions  $0.3 \leq x \leq 0.45$  for which there is a first-order magnetic-field-induced transition to a conducting state. In zero field this material shows activated behaviour down to 4 K and is never metallic. As a result the changes in conductivity are orders of magnitude larger than those reported in other systems such as Pr–Sr [10], La–Ca [4] or La–Sr [11] manganite. This field-induced transition occurs in a restricted composition range. For low levels of Ca doping, high values for both the activation energy and resistivity indicate that the carriers are localized. For  $x \geq 0.5$  a charge-ordered state is fully established and is stable in fields of up to 120 kOe. This is indicated by the continuing presence, in high fields, of a change in slope in  $\rho$ – $T$  curves, a peak in  $\chi_{ac}$ – $T$  and  $\chi_{dc}$ – $T$  at 250 K, and the onset of AFM ordering at lower temperatures. However, for  $0.3 \leq x \leq 0.45$  there is a significant decrease in the values of both the resistivity and the activation energy. At the same time the AFM state is not fully established. Application of a magnetic field drives the material into a FM ordered state which in turn leads to the appearance of a high-conductivity state at low temperatures. It is not clear whether the magnetic field prevents the formation of a charge-ordered state or melts the charge-ordered state at the FM ordering temperature. It may be that in the  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  there is also a field-induced change in the structure of the material or at least a large magnetovolume effect which in turn leads to the onset of FM and a higher conductivity. Magnetic-field-induced structural changes have recently been reported for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  [11]. This may explain why the field-induced FM ordering temperature of 240 K for  $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  does not shift drastically with field. This possibility is currently being investigated. It is clear that the field-induced transition to a high-conductivity state is closely associated with a field-induced transition to a FM ordered state and that many of the changes in transport properties of these materials correlate well with features in the magnetic data. For example,  $M$ – $H$  and  $\chi_{ac}$ – $T$  measurements on the  $x = 0.4$  compound have shown that applied fields in excess of 40 kOe produce ferromagnetic ordering. It is surely not a coincidence that a field of around 40 kOe is also required to induce the metallic behaviour observed in the material at lower temperatures. At low temperatures, the field required to drive a metamagnetic transition from an AFM to a FM state in  $0.3 < x \leq 0.45$  samples agrees with the field at which the jump to a conducting state is observed. The  $M$ – $H$  loops also show that the initial field sweep produces an irreversible change in the nature of the magnetic ordering of the material whilst the low-temperature  $\rho$ – $H$  loops reveal irreversible changes in the transport properties of the material with the appearance of a metastable conducting state.

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