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Field induced insulator–metal transition in $Pr_{1-x}Ca_xMnO_3$

M.R. Lees[a,*], J. Barratt[a], C.D. Dewhurst[b], G. Balakrishnan[a], C.V. Tomy[a], D. McK. Paul[a]

[a] *Physics Department, University of Warwick, Coventry, CV4 7AL, UK*
[b] *IRC in Superconductivity, University of Cambridge, Cambridge, CB3 OHE, UK*

Abstract

We present a detailed study of the properties of $Pr_{1-x}Ca_xMnO_3$ which shows that for a range of compositions ($0.3 \leqslant x < 0.5$) there is a first-order magnetic field induced insulator–metal transition. In zero field the resistivity ρ of this material shows an activated behaviour and ρ exceeds $10^8\ \Omega$ cm below 50 K. At 4 K, application of magnetic fields of up to 80 kOe, allows ρ to be reduced by at least 8 orders of magnitude depending on the value of the applied field. For the $x = 0.4$ composition the magnetic and charge ordering (CO) effects observed in this material are decoupled. The antiferromagnetic (AFM) ordering at $T_N = 170$ K develops at considerably lower temperatures than the CO state which is observed at $T_{CO} = 250$ K. Below T_{CO}, application of a magnetic field produces metamagnetic transitions. The field transforms the magnetic correlations from either paramagnetic or AFM to ferromagnetic (FM). At temperatures below 25 K the magnetic field produces irreversible changes in the magnetic order of this material. This in turn leads to the formation of long lived conducting states in zero field.

1. Introduction

The substitution of divalent A ions (A = Ca, Sr, etc.) on the rare earth (R) site in $R_{1-x}A_xMnO_3$ compounds produces materials which exhibit a very large reduction in ρ in an applied magnetic field [1–3]. Additional large changes in ρ occur when these compounds undergo magnetic or charge ordering [3–5]. These effects are due to an increase in Mn valence which enhances carrier mobility creating a tendency for ferromagnetic (FM) rather than the antiferromagnetic (AFM) exchange interactions which dominate if carriers are more localised. Such effects have been discussed in terms of the double exchange interaction [6]. However, recent theoretical work suggests that a polaron picture would be a better model for the dominant interactions [7]. The Mn ions can also charge order (CO) into a Mn^{3+}/Mn^{4+} sublattice at $x = 0.5$ [5] producing an increase in ρ and the formation of an AFM ground state. A magnetic field can melt this CO state leading to a decrease in ρ and a FM state. The electronic structure in such materials is also strongly coupled to the lattice structure and it is possible to force a structural phase transition at constant temperature by the application of a magnetic field [8]. The substitution of Ca for Pr in $PrMnO_3$ also shows the influence of CO but the flexibility of the perovskite lattice and the smaller divalent ion allows a degree of CO to persist for $x = 0.3$–0.7. Here we present resistivity (ρ), magnetisation (M) and magnetic susceptibility (χ) measurements on $Pr_{1-x}Ca_xMnO_3$ which demonstrate that for the disordered charge lattice system produced at $x = 0.3$–0.4 doping, the application of a magnetic field produces large changes in ρ, accompanied by extensive regions of hysteresis extending over a considerable range of T and H. Metastable states are formed below 25 K which produce extremely long time constants for the increase in ρ on removal of the magnetic field.

* Corresponding author.

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2. Experimental results and discussion

$Pr_{1-x}Ca_xMnO_3$ forms across the whole composition range, assumes a variety of structures at different temperatures and has a complex magnetic phase diagram [9]. Polycrystalline samples of $Pr_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 1$) were prepared by reacting Pr_6O_{11}, $CaCO_3$ and MnO_2 in air. X-ray spectra showed all the samples to be single phase.

Fig. 1 shows χ_{DC}–T data and Fig. 2 presents ρ–T warming and cooling curves in several magnetic fields for the $x = 0.4$ compound. The broad peak in χ–T at $\sim$250 K is also seen up to $x = 0.7$ whilst there are no obvious features in χ–T above 200 K for $x \leqslant 0.3$. ρ–T shows thermally activated behaviour for all values of x. In zero field the room temperature resistivity ρ decreases from $\sim$800 Ωcm for $x = 0.0$ to $\sim$0.003 Ωcm at $x = 0.5$. The activation energy at high T decreases from 0.2 eV at $x = 0.0$ to 0.07 eV at $x = 0.5$. For $x \leqslant 0.2$ a single value for the activation energy is observed over the entire T range examined. For $0.3 < x \leqslant 0.7$ a change in the slope of ρ–T indicates an increase in the activation energy below 250 K. These features in the χ and ρ data are associated with CO and an orthorhombic to tetragonal structural transition, which occurs at 250 K for $0.3 < x \leqslant 0.7$ [9]. A second maximum in χ–T at 170 K indicates the onset of AFM ordering. For $x = 0.3$–0.4, a sufficiently high magnetic field produces a maximum in ρ–T. At 4 K, ρ can be varied by at least 8 orders of magnitude depending on the value of H. The cooling and warming data show hysteresis with a width of up to 100 K.

Fig. 3 shows ρ–H curves at fixed T for a zero field cooled (ZFC) $x = 0.4$ sample. At 4 K, ρ is initially above 10^8 Ωcm. There is a fall in ρ–H of six orders of magnitude within 5 kOe around $H = 50$ kOe. A more gradual decrease in ρ–H by a further two orders of magnitude is observed up to 80 kOe. Sweeping H to zero produces only a small increase in ρ. At 45 K the transition to the conducting state occurs around 40 kOe and is more gradual. On decreasing H the sample returns to an insulating state. At higher T, ρ falls with increasing H corresponding to a large negative magnetoresistance. The ρ–H loops open up only for higher fields with a very small hysteresis in zero field; there are no discontinuities in the data.

Magnetisation measurements reveal significant changes in magnetic ordering with increasing H. M–H loops taken on a ZFC $x = 0.4$ sample are shown in Fig. 4. The initial slope agrees with χ–T data and is characteristic of an AFM ordered state. A metamagnetic transition to FM ordering is observed at 50 kOe. The saturation

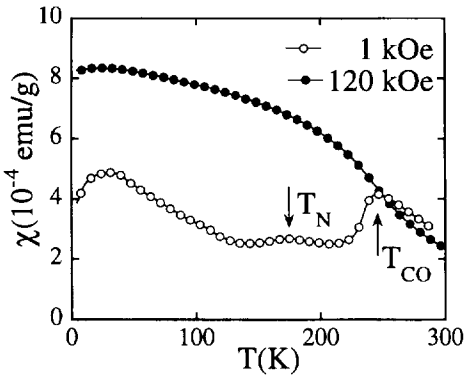

Fig. 1. χ_{DC}–T for $Pr_{0.6}Ca_{0.4}MnO_3$. The sample was zero field cooled and the data collected in applied fields of 1 kOe and 120 kOe.

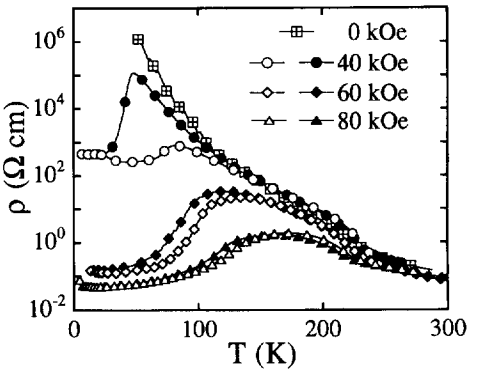

Fig. 2. ρ–T for $Pr_{0.6}Ca_{0.4}MnO_3$ taken in several magnetic fields. ρ was measured while cooling the sample from 300 K under magnetic field (filled symbols) and then during field cooled warming (open symbols).

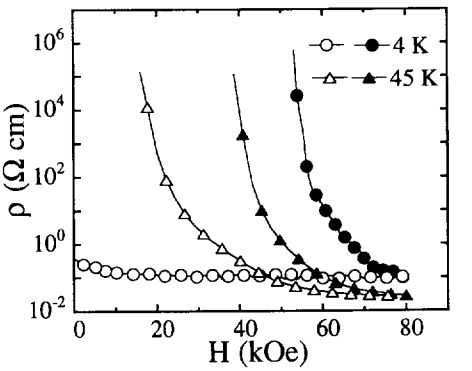

Fig. 3. ρ–H data for $Pr_{0.6}Ca_{0.4}MnO_3$ taken at 4 and 45 K. The data were collected in an increasing (filled symbols) and a decreasing (open symbols) magnetic field after cooling the sample from 300 K in zero field.

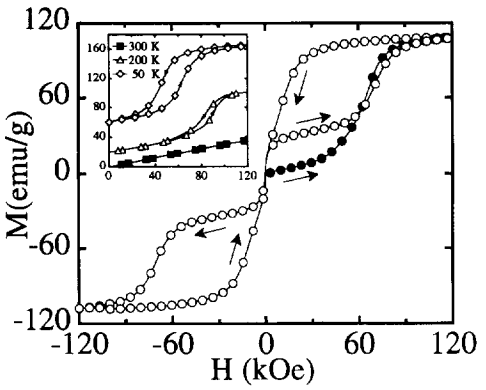

Fig. 4. M–H loop for $Pr_{0.6}Ca_{0.4}MnO_3$ taken at 10 K. The closed symbols indicate the data collected during the initial field sweep. The inset shows the data collected above (filled symbols) and below (open symbols) the charge ordering temperature. This data is offset for clarity. All the measurements were performed after cooling from 300 K in zero field.

moment of $3.95\mu_B$/Mn atom is slightly higher than the mean spin-only value for Mn ions and may be explained by a small contribution from the Pr ions. Following the initial field sweep the M–H loops show an enhanced χ at low fields and a rapid increase (decrease) in M around 50 kOe (20 kOe) indicates the metamagnetic transition from AFM to FM ordering. This transition is shifted to higher fields with increasing T and together with the irreversible behaviour is present up to $T_{CO} = 250$ K. χ_{DC}–T data in 120 kOe (Fig. 1) confirms the appearance of FM behaviour at 250 K in high fields.

For $Pr_{1-x}Ca_xMnO_3$, the influence of CO at 250 K is decoupled from the onset of magnetic order which in zero field occurs at $T_N = 170$ K. A first-order magnetic field induced transition from an insulating to a conducting state occurs for a range of compositions between $x = 0.3$ and 0.5. The changes in ρ are orders of magnitude larger than those observed in other manganite materials. There is a correlation between ρ and the magnetic state of the material. Below T_{CO}, a field transforms the magnetic correlations from either paramagnetic or AFM to FM and leads to a breakdown of the CO state. At 10 K, the metamagnetic transition and the jump to a conducting state are observed at the same value of H. However, as T is increased the conducting state is observed at lower H, whilst the metamagnetic transition shifts to higher fields. The low-T M–H loops (Fig. 4) show that the initial field sweep produces an irreversible change in the magnetic state of the material. The low-T ρ–H loops also indicate the appearance of a metastable conducting state. After application of an 80 kOe field, which for $x = 0.4$ produces a 10^8 decrease in ρ, subsequent relaxation measurements in zero field have shown that at 10 K ρ only doubles in 2 h. Relaxation rates increase with T and ρ rapidly returns to its original value above 30 K. This temperature coincides with the low-T peak in the χ–T data. Various frustration mechanisms in these ceramic materials may help create the metastable states and could also influence the Pr and Mn magnetic configurations [11].

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