Insulator–metal transitions in $Pr_{0.7}Ca_{0.3}MnO_3$ induced by a magnetic field

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(Received 3 July 1995; accepted for publication 5 November 1995)

A magnetic field induced insulator to metal transition has been observed in both polycrystalline and single crystals samples of $Pr_{0.7}Ca_{0.3}MnO_3$. Application of a magnetic field leads to a first-order phase transition from an insulating to a conducting state at low temperatures. The hysteresis associated with this transition allows the resistivity at 4 K to be varied by more than eight orders of magnitude depending on the field history of the sample. © *1996 American Institute of Physics.* [S0003-6951(96)01303-8]

Rare-earth (RE) manganites when doped with divalent ions on the RE site exhibit a wide range of magnetic and structural transitions as a function of temperature which themselves lead to large changes in conductivity. When a magnetic field is applied to such a material the conductivity may be further enhanced producing a giant negative magnetoresistance (MR) effect. This letter describes our recent investigations of the $Pr_{1-x}Ca_xMnO_3$ system and concentrates on the particular composition $x=0.3$ where an interesting series of insulator to metal transitions can be induced by both the application of a magnetic field at constant temperature and cooling in the presence of a magnetic field. The hysteresis which is prevalent at such transitions is sufficiently large to allow us to change the conductivity in zero applied field by more than eight orders of magnitude. This material appears to be unusual in adopting a high conductivity state at low temperatures after the application of a magnetic field.

The magnetic properties of $Pr_{1-x}Ca_xMnO_3$ materials[1,2] at low temperatures are determined by ordering of the Mn^{3+}/Mn^{4+} ions, intra- and inter-Mn exchange interactions and by the structural distortions produced by the smaller divalent ions. $PrMnO_3$ has an antiferromagnetic (AFM) ground state. With Ca doping, a ferromagnetic (FM) ground state develops for $x=0.2$. Hole doping also markedly reduces the orthorhombic–orthorhombic structural transition temperature which is associated with a cooperative ordering of the distorted manganese octahedra and occurs in the doping range up to $x=0.3$.[1] Charge/orbital ordering of the Mn ions occurs over a wide composition range from $0.3<x<0.75$ with an ordering temperature of ~250 K. This charge ordering is accompanied by a crystallographic transition from an orthorhombic to tetragonal structure. AFM ordering is observed at 175 K for $x=0.5$ while canted magnetic structures are present for higher and lower Ca doping ($x=0.4$ and 0.6). The $x=0.3$ composition is of particular interest since it lies on the boundary of a charge ordered state and is influenced by a range of magnetic interactions together with structural instabilities. In a neutron powder diffraction experiment AFM ordering was observed to arise at 130 K while a FM contribution becomes evident below 115 K.[2] This was initially assigned to mixed phase behavior given the FM behavior for $x=0.2$ and the canted magnetism (but with identical onset temperature for the AFM and FM contribution), for $x=0.4$. Our single crystal studies of the ac susceptibility for $x=0.3$ clearly show anomalies at both temperatures and the magnetic ordering in this material would be better described as collinear antiferromangnetism below 130 K with a transition to a canted FM structure below 115 K.

A complete description of our experimental studies across the entire $Pr_{1-x}Ca_xMnO_3$ system will be published elsewhere. In this letter we shall concentrate on the unusual transport properties of the $x=0.3$ samples.

The samples we have investigated were prepared by a standard ceramic processing route using base oxides as starting materials. All samples were reacted and sintered in air. No attempt has yet been made to optimize the oxygen stoichiometry. Single crystals were grown using an infrared image furnace from the polycrystalline rods. Large single crystals of volume ~0.5 cc were readily produced using this method. The polycrystalline and single crystal samples were characterized by x-ray diffraction, magnetic susceptibility, and resistivity studies. Reproducibility in all these characterization measurements was found for nominally identical materials and across the range of manufactured compositions. The resistivity measurements were made using a standard four probe technique; a maximum resistance of $\sim 10^8$ Ω could be measured.

Figure 1 presents a series of resistivity versus magnetic field scans at several temperatures for a polycrystalline sample of $Pr_{0.7}Ca_{0.3}MnO_3$. Samples cooled from 250 K in zero magnetic field and then cycled in applied fields of up to 8 T show very peculiar behavior. For a zero field cooled sample (ZFC) the resistance of the sample exceeds our measurement limit between 50 and 4 K. On applying a magnetic field at 4 K the resistivity drops rapidly at 5.5 T by more than seven orders of magnitude within 0.5 T; a more gradual decrease by an additional two orders of magnitude occurs on further increasing the magnetic field from 6 to 8 T. When the field is swept back to zero there is only a slight increase in resistivity (×2) from the high field value induced by the initial field sweep. The resulting conducting state is metastable and this sample can only be returned to its previous behavior by annealing at high temperatures (>150 K). This behavior would suggest that there is a first-order transition from an insulating state to a conducting state induced by an applied magnetic field of 5.5 T. Certainly at 4 K such an

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 0003-6951/96/68(3)/424/3/$6.00

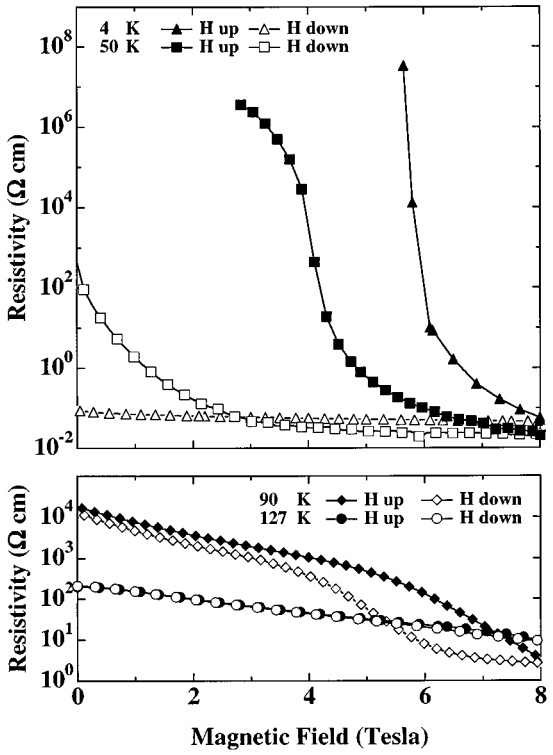

FIG. 1. Resistivity of $Pr_{0.7}Ca_{0.3}MnO_3$ as a function of applied magnetic field for temperatures of 4, 50, 90, and 127 K. The filled symbols refer to measurements as a function of increasing field while the open symbols are for the decreasing field cycle.

applied field is required to manufacture a ''metallic'' state, but once created such a state can exist without the presence of the magnetic field. When a similar field sweep is applied to a ZFC sample at 50 K the transition from an insulating to a metallic state occurs at 4.0 T and is more rounded than observed at lower temperatures. On decreasing the magnetic field the sample attempts to regain its ZFC state; the resistivity rises as the field is reduced, but only a small fraction of the original resistivity returns. At 90 K the resistivity falls with increasing magnetic field but there is no discontinuity in the resistance at any field. A small amount of hysteresis is still present at high fields but he resistivity almost regains its original value on reducing the field. At higher temperatures a negative MR still exists [e.g., $\Delta R/R(0)$ of 95.7% at 8 T and 127 K] but reversible behavior is observed and the changes are much smaller in magnitude.

Figure 2 presents some of our collected data for temperature cycling experiments in various applied magnetic fields. ZFC runs show thermally activated conductivity for all temperatures from room temperature to 50 K. Cooling the sample from high temperature (300 K) in an applied magnetic field produces similar changes in conductivity, but the onset of a high conductivity state occurs at different points in the magnetic field-temperature phase space. At 4 K the resistivity can be forced to vary by at least eight orders of magnitude depending on the field imposed. In fields of less than 2 T the resistivity at 4 K is beyond our measurement limit. Cooling in a field of 3 T produces a maximum resistivity at

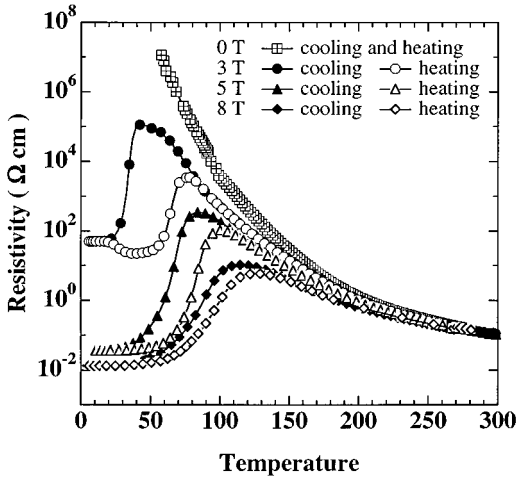

FIG. 2. Resistivity of $Pr_{0.7}Ca_{0.3}MnO_3$ as a function of temperature for applied magnetic fields of 0, 3, 5, and 8 T. The filled symbols refer to measurements as a function of decreasing temperature while the open symbols are for the heating cycle.

~40 K. On warming the sample from 4 K we note a further decrease in resistivity producing a minimum at ~40 K. In higher magnetic fields we again find considerable hysteresis in the conductivity, with each cooling run following a higher resistivity path than the heating cycle. The hysteretic regions vary in width with an observed maximum extent of ~100 K. At high and low temperatures the resistivity is reversible. The temperature at which reversible behavior is maintained at high temperatures varies as a function of applied magnetic field; in a field of 8 T this temperature is ~150 K, but decreases to ~80 K in 3 T.

It is obvious from the above results that the state of the conductivity in this material is very dependent on the temperature and magnetic field history of the sample. Both temperature and magnetic field are important variables for determining or destroying the low temperature/high magnetic field ''metallic'' state. From our low temperature data, it seems likely that there is a phase transition of some sort (structural, magnetic, electronic) which frees some current carriers or drastically increases the mobility of existing carriers. Once this conducting state is created it is metastable and persists after the removal of the applied field.

There are a number of systems which exhibit unusual magnetotransport properties. In the $La_{1-x}Sr_xMnO_3$ system there is also a large degree of interplay between structural instability, magnetic interactions, and large changes in the conductivity of the compound. By an appropriate choice of composition it is possible to arrange for these structural and magnetic transitions to be situated near room temperature. For example, for $x=0.175$ the system has a rhombohedral structure at high temperature which becomes orthorhombic around 285 K. The structural transition can be driven by the application of external magnetic field.[3] At fixed temperature this structural switching is irreversible and produces small irreversible changes in the magnitude of the zero field conductivity. The system orders ferromagnetically below 270 K. The temperature dependence of the resistivity shows acti-

vated behavior at high temperature and the resistivity falls by three orders of magnitude around T_c and is metallic at low temperatures. Application of an external magnetic field around T_c produces a large negative MR, which has been described as a nonmetal–metal transition.[4] However, there is only a moderate, monotonic decrease in the resistivity as the field is increased unlike the discontinuous change observed at low temperatures in the $Pr_{0.7}Ca_{0.3}MnO_3$ compound. The MR is also reversible. The zero field scans of Ref. 4 resemble our high field data presented in Fig. 2 However, the magnitude of the field induced effects reported here dwarves those observed for the La system since we are coming from an insulating state. In addition we find a higher resistivity maximum on a cooling run rather than for a heating cycle, this effect is reversed in the La manganite samples.

Recently Tomioka *et al.*[5] have reported on the magnetic and transport properties of $Pr_{0.5}Sr_{0.5}MnO_3$. Although similar in composition to the system discussed here, the properties of this material and the phenomena observed are quite different. At high temperatures $Pr_{0.5}Sr_{0.5}MnO_3$ shows metallic behavior and is ferromagnetically ordered. On cooling there is a first order phase transition at 140 K into a charge ordered AFM state. Application of a magnetic field shifts this nonmetal–metal transition to progressively lower temperatures and for fields greater than 7 T the material remains metallic down to 0 K. M versus H and ρ versus H curves show that for $T<140$ K there is a critical magnetic field in which a metamagnetic-like transition from an AFM to a FM state occurs together with a change in the conductivity. There is a small degree of hysteresis associated with this transition, but the system always returns to the charge ordered state in zero field. In addition the overall changes in the magnitude of the resistivity are relatively small (10^{-2} Ω cm in 0 T to 10^{-4} Ω cm in a field of 7 T).

The magnitude of the changes in conductivity observed in this work are more reminiscent of metal–insulator transitions in materials such as V_2O_3.[6] However an applied magnetic field is required to drive the transition, and the ground-state has the high conductivity. There are also a number of RE semiconductor systems, such as EuO[7] and EuSe,[8] which exhibit a large negative MR at low temperatures. For EuO, in zero magnetic field, a FM transition at 70 K is accompanied by a 14 orders of magnitude increase in the conductivity of the material. The activated behavior observed at high temperatures gives way to a metallic state at low temperatures. An increase in conductivity by six orders of magnitude is observed around T_c with the application of a magnetic field. In the case of EuSe a small negative MR is reported at high temperatures [$\Delta R/R(0)$ of 5% at 15 T and 297 K]. This is attributed to a decrease in spin disorder scattering in a metallic regime and the carriers are electrons in the conduction band. A rapid increase in the resistivity at low temperatures is attributed to electron trapping due to a strong s–f interaction. In both these systems the large decrease in resistance observed at low temperatures is driven either by changes in the internal magnetic field or by the application of an external magnetic field. Such fields delocalize the trapped electrons and produce a marked increase in carrier mobility. In all cases the carrier concentrations densities $n \approx 5\times10^{19}$ cm^{-3} are some two orders of magnitude lower than those expected for the manganite systems. Again there is little or no hysteresis reported for these changes in conductivity. The zero field conductivity is independent of the magnetic history of the sample.

The large negative MR in the manganites is usually associated with forced alignment of the canted magnetic moments and a net reduction in the scattering or the charge carriers leading to an increase in conductivity. These electronic effects are also strongly influenced, and may themselves influence, the structural arrangement of the ions, hence the possibility of field induced structural phase transitions. It is probably not by chance that the enhancements in the conductivity we have described are associated with a composition of $x=0.3$, since this material lies on a boundary between canted magnetism and ferromagnetism together with a change in the structural properties at low temperatures. The enormous changes in conductivity we observe in this material probably requires some large change in the magnetic or structural properties in an applied magnetic field, such as a metamagnetic phase transition or a magneto-structural rearrangement which will alter the electronic states. It is likely that the mobile charge carriers are not simple holes but a more complicated species involving holes dressed with a series of magnetic and structural excitations.

The novel phenomenon observed for $Pr_{0.7}Ca_{0.3}MnO_3$ reflects an unusual insulator–metal phase transition where a magnetic field is required to force the changes in conductivity. Unusually, the ground state is more conducting than at higher temperatures. The hysteresis associated with the transition is pronounced and allows metastable high conductivity states to be established in zero applied field.

Note added in proof. We have recently become aware of a paper by Tomioka *et al.*[9] on $Pr_{1-x}Ca_xMnO_3$, which contains results similar to those presented in this letter.

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