Growth, transport, and magnetic properties of $Pr_{0.67}Ca_{0.33}MnO_3$ thin films

S. K. Singh, S. B. Palmer, D. McK. Paul, and M. R. Lees[a)]
Physics Department, University of Warwick, Coventry CV4 7AL, United Kingdom

(Received 23 January 1996; accepted for publication 13 May 1996)

We have grown $Pr_{0.67}Ca_{0.33}MnO_3$ thin films on $LaAlO_3$ using pulsed laser deposition. Below 50 K, a field induced insulator-metal transition results in changes in resistivity of at least 6 orders of magnitude. The field induced conducting state is metastable at low temperature. The temperature dependence of the resistivity exhibits considerable hysteresis in a field of 40 kOe but becomes reversible in a field of 80 kOe. © *1996 American Institute of Physics.* [S0003-6951(96)02128-6]

Negative giant magnetoresistance (GMR) effects have been reported in doped perovskites $Ln_{1-x}A_xMnO_{3\pm\delta}$ (Ln=La, Pr, or Nd and A=Ca, Ba, Sr, or Pb).[1–6] These effects have been observed in thin film, polycrystalline, and single crystal samples. This behavior is usually explained in terms of the double exchange theory.[7] Doping produces a decrease in the Mn^{3+}/Mn^{4+} ratio making it easier for electrons to hop between Mn ions and creating a tendency for ferromagnetic interactions rather than the antiferromagnetic exchange interactions which dominate if the electrons are more localized. However, more recent theoretical work has suggested that in order to obtain quantitative agreement with experimental data, polaron effects due to strong electron-phonon coupling coming from the Jahn–Teller splitting should also be included in any theoretical model.[8]

Within this group of Mn based GMR materials, a number of different types of behavior are observed. In some cases, for example, $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ ($0.1\leqslant x\leqslant 0.4$),[1–3] the materials are metallic ferromagnets. Large field induced changes in conductivity occur at temperatures around the ferromagnetic-paramagnetic transition. In other materials such as $Pr_{1-x}Sr_xMnO_3$ ($x=0.5$), a conducting/ferromagnetic state is replaced at low temperatures, in this case below 140 K, by a charge ordered/antiferromagnetic state and a switch to resistivity which exhibits activated behavior.[6] Application of a magnetic field can melt the charge ordered lattice and lead to the restoration of a conduction/ferromagnetic regime. In the case of $Pr_{1-x}Ca_xMnO_3$ ($0.3\leqslant x\leqslant 0.45$), magnetic and charge ordering transitions occur at different temperatures.[9–11] Evidence for charge ordering is seen at 250 K with a paramagnetic-antiferromagnetic transition at around 160–170 K. The resistivity in zero field exhibits activated behavior at all temperatures. Below the charge ordering temperature the application of a sufficiently high magnetic field induces a transition from either a paramagnetic or antiferromagnetic into a ferromagnetically ordered state. This transition is accompanied by a decrease in the resistivity of the material and at low temperature this results in a field induced insulator-metal transition.[10,11]

In this letter, we report on the growth and properties, including the magnetic field dependence of the electrical resistivity and the magnetization, of textured $Pr_{0.67}Ca_{0.33}MnO_3$ thin films. Field induced changes in the resistivity of at least 6 orders of magnitude have been observed below 50 K in magnetic fields of 80 kOe. These samples also display field history dependent properties which are qualitatively different from those of the corresponding bulk material.

Energy dispersive x-ray spectroscopy (EDXS) analysis of $Pr_{1-x}Ca_xMnO_3$ (PCMO) thin films grown in a pilot study revealed that the films contained a lower concentration of Ca than the target. In order to obtain films with a composition in the range $0.3\leqslant x\leqslant 0.5$ we used an off-stoichiometry target with a composition $Pr_{0.4}Ca_{0.6}Mn_{1.2}O_3$. This target was prepared by a standard solid state reaction technique using 99.9% purity Pr_6O_{11}, $CaCO_3$, and MnO_2 which were repeatedly ground and sintered in air for 24 h at 1300 °C. The PCMO thin films were grown by pulsed laser ablation deposition using an excimer laser with a XeCl gas mixture producing UV radiation ($\lambda=308$ nm). During growth, the laser irradiance at the target was fixed at 1.8 J cm^{-2}. The laser beam was scanned across the surface of a rotating target to prevent severe degradation.[12] Thin films with a thickness of 1400 nm were deposited on (100) $LaAlO_3$ substrates. During growth the substrate temperature was held at 700–750 °C. Depositions were carried out in a 0.1–0.2 mbar atmosphere of flowing oxygen. The films were cooled to room temperature under 1 atm of flowing oxygen. No postgrowth annealing was performed.

The structure of the as-deposited films was examined by x-ray diffraction. Measurements in the normal Bragg geometry show textured growth. Only the (002ℓ) reflections were present in the spectra with the lattice parameter $c=7.55\pm0.05$ Å. This value agrees well with that expected for material with the composition around $Pr_{0.7}Ca_{0.3}MnO_3$.[9] EDXS measurements show the films have a nominal composition of $Pr_{0.67\pm0.03}Ca_{0.33\pm0.03}MnO_3$.

The electrical resistivity of the samples was measured as a function of temperature and magnetic field using a standard dc four probe technique. Data were collected between 4 and 300 K in magnetic fields of up to 80 kOe. The field was applied parallel to the substrate surface and the direction of current flow. The data are shown in Fig. 1.

In zero field, the resistivity of both sets of films increases with decreasing temperature and $d\rho/dT<0$ at all temperatures measured. This suggests that the conduction occurs via an activated process and that the samples exhibit insulating behavior at low temperatures. Below 80 K the resistance of the samples exceeds 10^8 Ω. This is the maximum value we can measure using our existing experimental apparatus. Activa-

a)Electronic mail: phrqr@csv.warwick.ac.uk

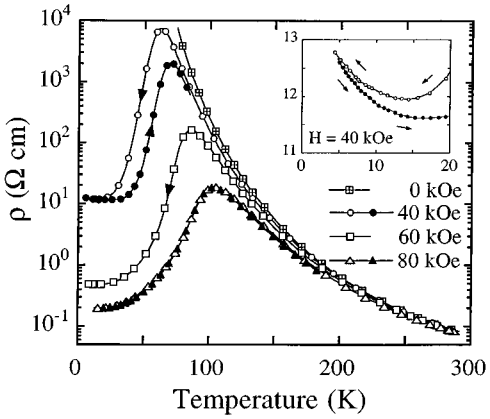

FIG. 1. Resistivity vs temperature curves for a thin film of $Pr_{0.67}Ca_{0.33}MnO_3$ grown on $LaAlO_3$ taken in several magnetic fields. The data were collected during field cooling (open symbols) and during subsequent field warming in the same magnetic field (closed symbols). For $H \geqslant 40$ kOe there is a field induced fall in the resistivity. In $H=40$ kOe the data contain large regions of hystersis, while in $H=80$ kOe the behavior is reversible. The inset shows the low-temperature upturn in the data collected in $H=40$ kOe in more detail.

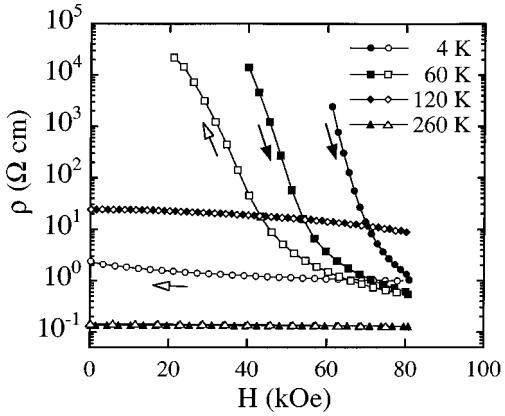

FIG. 2. Resistivity vs magnetic field curves for a thin film of $Pr_{0.67}Ca_{0.33}MnO_3$ taken at several temperatures. The measurements were performed after cooling the sample from 300 K in zero magnetic field. The data were then collected in increasing field (closed symbols) and decreasing field (open symbols). At 4 K, a field induced insulator-metal transition leads to the appearance of a metastable conducting state. $\Delta R/R_0$ exceeds 99.998% at 4 K. At 60 K, significant hysteresis and a large negative magnetoresistance persist, but the sample returns to the insulating state as the field is reduced. $\Delta R/R_0 = 65\%$ and 7.5% at 120 and 260 K, respectively, where the behavior is reversible.

tion energies at temperatures between 200 and 300 K, calculated using a simple exponential expression are ~0.1 eV for applied magnetic fields of up to 80 kOe. There are no features in the data which indicate the presence of charge ordering. Similar results have been observed in bulk samples with a Ca concentration of 30%.[10] Application of a magnetic field of 40 kOe or more produces a peak in ρ-T. This peak shifts to higher temperature with increasing magnetic field. Below this maximum, ρ falls rapidly then flattens off and once again begins to increase at low temperature (see the inset in Fig. 1). Thin-film samples of a number of other $Ln_{1-x}A_xMnO_{3\pm\delta}$ systems with $x=0.3$ are metallic ferromagnets in zero field with temperature independent residual resistivities at low temperature.[6] The zero field resistivity of these PCMO films increases with decreasing temperature and is never metallic. The application of a magnetic field reduces the localization of the carriers but is not necessarily strong enough to offset the continuing localization which occurs as the temperature is lowered. This may be the origin of the low-temperature minimum seen in the ρ-T data taken in 40 kOe. Alternatively, slight variations in the Ca concentration within the films could produce regions in the sample in which the MR is lower. This could be the cause of the low-temperature upturn in ρ-T.

In 40 kOe there is a considerable difference between the ρ-T data taken during cooling and warming. However, the ρ-T behavior in a field of 80 kOe is completely reversible. Previous studies[10,11] carried out on single crystal and bulk polycrystalline samples of $Pr_{1-x}Ca_xMnO_3$ $(0.3 \leqslant x \leqslant 0.5)$ have all revealed significant hysteresis in the ρ-T data collected, even in magnetic fields as high as 80 kOe. At fixed Ca composition and for $H \geqslant 40$ kOe, there is a reduction in the amount of hysteresis observed with increasing field. For samples with $0.3 \leqslant x \leqslant 0.5$ the ρ-T data collected in a field of 80 kOe show that the onset of reversible behavior shifts to increasingly higher temperature with increasing Ca concentration.[10] There are several papers which describe first order, field induced structural or magnetic phase transitions in this class of materials. These report that the degree of hysteresis associated with these transitions decreases with increasing field.[10,11,13] However, there are no reports of a change in the order of the transition in high field so this is probably not the cause of the reversible behavior seen in this case. It seems more likely, that the appearance of reversibility is related to interplay between the morphology of the films and the pinning effects which govern both the variation in size and orientation of ferromagnetic domains present in the material at low temperature and high field, and the way in which the system evolves between a magnetically ordered state and the paramagnetic state as the temperature is varied.

Resistivity versus field measurements at fixed temperature confirm the presence of a field induced switching between an insulating and a conducting state. For each curve shown in Fig. 2 the samples were cooled to the measuring temperature in zero field, then cycled in a magnetic field of 80 kOe. At temperatures above the peak in the ρ-T data the samples show a small negative magnetoresistance, with $\Delta R/R_0 (\Delta R = R_H - R_0)$ in a field $H=80$ kOe of 7.5% and 65% at 260 and 120 K, respectively. At 60 K, ρ initially exceeds 10^4 Ω cm. Above 40 kOe, a rapid fall in ρ is observed. The conducting state is unstable and the sample returns to the insulating state in zero field. At 4 K, a field induced high conductivity state appears in fields in excess of 60 kOe. At this temperature, the conducting state is metastable and the sample remains conducting even after the field is removed.

Magnetization and neutron diffraction data indicate that the origin of the field induced insulator metal transition observed in $Pr_{1-x}Ca_xMnO_3$ is a metamagnetic transition from an antiferromagnetic to a ferromagnetically ordered state which is accompanied by a melting of the charge ordering and the appearance of a conducting state.[10,11] Magnetization measurements were made using a SQUID magnetometer in

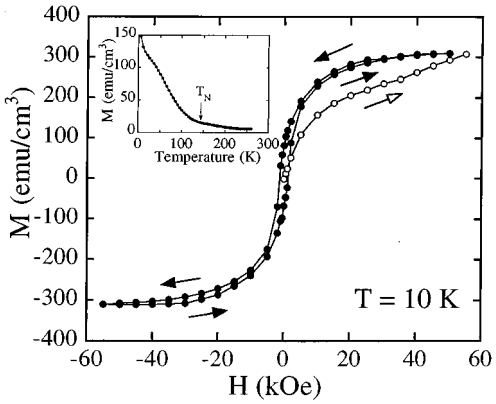

FIG. 3. Magnetization vs applied magnetic field loop for a thin film of $Pr_{0.67}Ca_{0.33}MnO_3$ taken at 10 K. The measurement was performed after cooling the sample from 300 K in zero magnetic field. The open symbols indicate the data collected during the initial field sweep. The inset shows the temperature dependence of the magnetization of the same sample. The data were collected during warming in applied magnetic field of 5 kOe after cooling from 300 K in the measuring field.

magnetic fields of up to 55 kOe over a temperature range of 5–300 K. The field was applied in the plane of the substrate. Magnetization versus temperature measurements (see inset Fig. 3) performed in a field of 5 kOe show the onset of magnetic order at 150 K. There are no features in the data at higher temperature. *M-H* measurements (see Fig. 3) were taken at 10 K on the same sample after zero field cooling. The virgin magnetization curve increases steadily with field with no indication of saturation. For subsequent field cycling it follows the same soft ferromagnetic curve. These magnetization curves are comparable to those reported for bulk samples with $x \approx 0.3$ which suggests that these thin-film samples have similar magnetic behavior.

As a result of the application of a magnetic field, the low-temperature resistivity of these PCMO films varies by at least 6 orders of magnitude. This field induced decrease in resistivity corresponds to a MR of at least 99.998% which compares favorably with the largest even values reported for manganese oxide thin films.[1–6] The abrupt switching from an insulating to conducting state reported here, suggests this class of materials have great potential for use in applications, although at present the operating temperatures are low. In addition, these materials are compatible, both chemically and structurally, with a number of technologically important materials including the cuprate superconductors. It should be possible to grow multilayer structures including PCMO layers where the resistivity of this layer can be switched in a controlled way from an insulator to a metallic conductor by application of a magnetic field. Once established, the metastable nature of the conducting state would allow the PCMO layers to remain conducting in zero field provided the structure was maintained at low temperature. Alternatively, they could be switched back to the insulating state by simply annealing at higher temperatures.

This work was supported in part by the EPSRC, UK. We would like to thank the IRC in Superconductivity, University of Cambridge, Cambridge, UK, for the use of the SQUID magnetometer.

[1] R. von Helmholt, J. Wecker, B. Holzapfel, L. Shultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[2] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993); M. McCormack, S. Jin, T. H. Tiefel, R. M. Fleming, J. M. Philips, and R. Ramesh, *ibid.* **64**, 3045 (1994); S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994); P. Schiffer, A. P. Ramirez, W. Bao, and S. W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[3] H. L. Ju, C. Kwon, Q. Li, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **65**, 2109 (1994).
[4] G. C. Xiong, Q. Li, H. L. Ju, S. N. Mao, L. Senapati, X. X. Xi, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **66**, 1427 (1995); G. C. Xiong, Q. Li, H. L. Ju, R. L. Greene, and T. Venkatesan, *ibid.* **66**, 1689 (1995); G. C. Xiong, S. M. Bagrat, Q. Li, M. Domínguez, H. L. Ju, R. L. Greene, T. Venkatesan, J. M. Byers, and M. Rubinstein, Solid State Commun. **97**, 599 (1995).
[5] J. M. D. Coey, M. Viret, L. Ranno, and K. Ounadjela, Phys. Rev. Lett. **75**, 3910 (1995).
[6] Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **74**, 5108 (1995).
[7] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).
[8] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
[9] Z. Jirak, S. Vritislav, and J. Zajicek, Phys. Status Solidi **52**, 39 (1979); E. Pollert, S. Krupicka, and E. Kumzicova, J. Phys. Chem. Solids **43**, 1137 (1982); Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratislav, J. Magn. Magn. Mater. **53**, 153 (1985).
[10] J. Barratt, M. R. Lees, G. Balakrishnan, and D. McK. Paul, Appl. Phys. Lett. **68**, 424 (1996); M. R. Lees, J. Barratt, G. Balakrishnan, and D. McK. Paul, Phys. Rev. B **52**, 14303 (1995); M. R. Lees, J. Barratt, G. Balakrishnan, and D. McK. Paul, J. Phys. Condens. Matter **8**, 2967 (1996).
[11] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **52**, 13145 (1995); Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, J. Phys. Soc. Jpn. **64**, 3626 (1995).
[12] T. J. Jackson, N. J. Appleyard, N. J. Cooper, D. H. Richards, and S. B. Palmer, Meas. Sci. Technol. **6**, 128 (1995).
[13] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature **373**, 407 (1995).