Magnetic behavior of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ in the electric-field-driven insulator-metal transition

Jolanta Stankiewicz,* Javier Sesé, Joaquín García, Javier Blasco, and Conrado Rillo
*Instituto de Ciencia de Materiales de Aragón, Consejo Superior de Investigaciones Científicas,
 Universidad de Zaragoza, 50009 Zaragoza, Spain*

(Received 16 November 1999)

The magnetization through an electric-field-driven transition from a charge ordered state to a conducting one in polycrystalline $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, with $x=1/3$ and 0.4, have been measured, simultaneously with current-voltage characteristics. These measurements have been performed at several temperatures and magnetic fields in the ranges 20–40 K and 0–3.5 T, respectively. A significant increase in the magnetization, observed at the transition, fits in with a two phase model of insulator-metal transition in this system.

Doped manganese oxides of the $R_{1-x}A_x\text{MnO}_3$ (R is a rare earth and A is an alkali metal element) type show a great variety of behaviors. For some ranges of x and T , the resistivity of some of these oxides decreases by many orders of magnitude in an applied magnetic field.¹ Double exchange interactions, which are essential for the formation of a ferromagnetic metallic (FM) state,² are mediated by holes created when a divalent alkali metal A substitutes a trivalent rare-earth element R . Other interesting phenomena are orbital and charge ordering.³ The latter usually occurs when cations that are smaller than the average cation in perovskite manganese oxides (e.g., $R=\text{Nd}$ or Pr and $A=\text{Sr}$ or Ca) are introduced into a compound. The subsequent lattice distortion leads to localization of Mn e_g electrons.⁴ A periodic pattern of filled ($1-x$ fraction of Mn ions) and empty (x fraction of Mn ions) electron sites may form giving rise to a charge ordered (CO) state. Such states are more stable when the concentration of charge carriers is commensurate with the periodicity of the crystal lattice. In $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ systems, CO states exist for $0.3 \leq x \leq 0.75$.⁵ They form at temperatures below approximately 240 K and are accompanied by a change in lattice structure.⁵ At zero magnetic field, this system is an insulator. For $x \geq 1/3$, it orders antiferromagnetically at approximately 130 K and ferromagnetically (F) below 115 K.^{5,6} The low-temperature state has been described as a canted antiferromagnetic (AF) structure with some fraction of the moments forming a spin-glass state.⁷ However, Jirák *et al.* interpreted their neutron-diffraction results in terms of two phases (F and AF) in about equal proportion.^{5,6}

The CO state in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is rather sensitive to external fields and radiation. Application of magnetic fields,⁸ high electric fields,⁹ irradiation with x rays,^{10,11} or with visible light¹² destroy charge ordering and lead to a conducting state. The transition driven by a magnetic field or by irradiation with x rays is a transition from an insulator to a FM state with a very low resistivity (of about $10^{-3} \Omega \text{ cm}$).^{8,10} The electron-lattice coupling seems to be dominant in charge localization for this system.¹⁰ Furthermore, a phase segregation is likely responsible for the x ray induced insulator-metal transition.¹¹ In this model, exposure to x rays induces aggregation of small ferromagnetic clusters present in the AF phase at low temperatures. A gradual melting of the CO phase follows and a FM phase is formed. On the other hand, the nature of the conducting states obtained by means other

than the application of magnetic field or x ray irradiation is not clear. For instance, the photoinduced transition in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ requires a current flow through the sample to sustain it.¹² Conducting states induced by visible light or electric fields are not stable and collapse into an insulating state after the applied electric field is removed. Formation of filamentary metallic paths inside the system, after a transition driven by a static electric field or by irradiation with light takes place, has been conjectured.^{9,13} Current switching transitions could consequently be used to obtain nanometer FM domains within an insulating antiferromagnetic matrix.⁹ This would certainly be very important for nanoscale production.

The aim of this report is to further elucidate the nature of the electric-field induced conducting states in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$. We have measured, for the first time, dc magnetization simultaneously with current-voltage (I - V) characteristics in polycrystalline $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ samples at several temperatures ($20 \leq T \leq 40$ K) and magnetic fields ($0 \leq H \leq 3.5$ T). A significant rise in magnetization, observed at the transition from the CO to the conducting state, does not fit in with a filamentary (threadlike) picture of the metallic state. In addition, the electric-field induced changes in magnetization are irreversible. A phase segregation seems to provide a better explanation of our results. A presence of metallic inclusions embedded in an insulating matrix has been proposed earlier to explain the transport properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$.¹⁴ In our picture, as-cooled material is in an insulating phase but with significant anisotropic strain which develops below the CO temperature.¹¹ Application of high electric fields leads to the formation of ferromagnetic, quite likely elongated, clusters with the corresponding lattice relaxation along the current path. The resistivity drops abruptly once the percolating current path is established. As current through the sample decreases, small clusters linking large FM clusters disappear under the stress from the surrounding insulating bulk. The large FM clusters remain and give a measurable contribution to the total magnetization of the system.

The $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ samples were prepared by reacting Pr_6O_{11} , CaCO_3 , and MnCO_3 at 1400 °C in air. X-ray analysis showed that all samples were of a single phase. We measured conductivity on rectangular samples ($1 \times 2 \times 4 \text{ mm}^3$) using the “guard-ring” method.¹⁵ The purpose of the guard-ring is to minimize errors due to surface conductivity while

FIG. 1. dc susceptibility in applied field of 0.02 and 3 T for the $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample. Open points correspond to ZFC condition and full points to FC condition. The inset shows data for $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ at $H=0.02$ T. Solid and dashed lines are to guide the eye.

making volume resistivity measurements. The contacts were made with silver paint. A known voltage was applied to the sample, in series with a 1 M Ω load resistor, and the current was monitored by an electrometer. The sample was mounted on an insert of a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer. Special care was taken to ensure good thermal contact between the sample and the surrounding cool helium gas. The temperature was measured with a carbon resistor placed next to the sample and was maintained constant to within 2 K during measurements. Magnetic and resistivity measurements were performed on $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ samples prior to application of a high electric field. Figure 1 shows how dc magnetic susceptibility varies with temperature warming up a zero-field-cooled (ZFC) sample and, subsequently, cooling it down in a magnetic field (FC). A broad peak at around 250 K corresponds to the CO transition in the $x=0.4$ sample. This peak is less evident in $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ shown in the inset of Fig. 1. (We observe also a change in the slope of the resistivity as a function of temperature in the same region.) As temperature decreases, the AF and F transitions follow. At low temperatures, there is notable difference between ZFC and FC data likely arising from cluster glass state.

Figure 2 shows how the current through $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ samples varies with the applied voltage at 30 and 40 K, respectively, both in zero magnetic field and in a field of 3 T. In the low-voltage region, the resistance of $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ is about 10^{10} Ω . As the applied voltage increases, the resistivity drops abruptly by more than four orders of magnitude at some threshold voltage. Current-voltage (I - V) characteristics are hysteretic. Below some voltage V_0 , there is no hysteresis. V_0 decreases and the transition becomes less abrupt as the applied magnetic field H increases. For $H \geq 3$ T, $V_0 = 0$. These I - V characteristics are essentially unchanged throughout the temperature range studied (20–40 K), but the size of the hysteretic region may depend on the experimental history. The $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ data points shown as full squares exhibits an analogous behavior. Here, at the threshold voltage the resistance jumps by about two orders of magnitude and $V_0 = 0$ for $H \geq 5$ T. The slope of the I - V curve for this sample shows that its resistivity decreases

FIG. 2. Current-voltage (I - V) characteristics in magnetic fields of 0 and of 3 T for $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (open circles) and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (full squares) at 30 and 40 K, respectively (upper panel). Corresponding magnetization values are shown in lower panel. The data points were obtained going from low voltage up to 1000 V, and returning to the initial value of V . M_0 is the value of magnetization at zero volts. The error bars shown stands for magnetization errors. Solid lines are to guide the eye.

monotonically as the applied voltage increases. In addition, its zero-voltage resistivity is smaller than observed in the $x = 1/3$ samples. This may arise from the presence of metallic inclusions in zero voltage that grow in size and number as V increases.

The behavior of the magnetization through the transition is also exhibited in Fig. 2. The error bars shown include effects of both residual fields in the SQUID and of Joule heating. We observe a significant rise in magnetization at the same threshold voltage where the current rises abruptly. This change is irreversible. At zero magnetic field, each voltage cycle leads to an additional magnetization increment in $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. Each one of these increments is smaller than the preceding one. We obtain a 30% rise in magnetization after several repeated voltage cycles. However, this magnetization is still well below its FM value. The conducting states achieved in zero magnetic field are of relatively high resistivity; the sample resistance does not fall below 10^6 Ω . On the other hand, current switching leads to states with higher conductivity when magnetic fields of a few teslas are applied. Here, we also observe a significant rise in magnetization as the current rises through the electric-field driven transition. Sometimes, but not always, samples become conducting (of 10^5 Ω) without current switching after cooling down when a magnetic field of approximately 3 T is applied.

FIG. 3. Magnetization as a function of the sample resistance for $x = 1/3$ and $x = 0.4$ at 30 and 40 K, respectively. The inset exhibits M versus magnetic field at 30 and 40 K for $x = 1/3$ and $x = 0.4$, respectively. Solid lines are to guide the eye.

Less resistive samples always show higher magnetization values, independently of how the conducting state is reached.

The variation of magnetization with resistance R in polycrystalline $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is shown in Fig. 3 for a magnetic field of 3 T. Here, data obtained before and after current switching as well as values of M in samples which turned out to be conducting after the application of a magnetic field are included. The magnetization decreases with resistivity monotonically and follows approximately the relation $M = a + b/R^n$, where $n \approx 0.5$ for both compositions (a and b are constants). The inset in Fig. 3 shows how the magnetization varies with applied magnetic field for $x = 1/3$ and $x = 0.4$ samples at 30 and 40 K, respectively. The data points correspond to measurements with no applied electric field as the magnetic field increases (up to 5 T) and then decreases. The magnetization values obtained in the electric-field induced conducting phase are much smaller than the ones in the FM state induced by the application of sufficiently high magnetic fields.

The above results suggest the following scenario for the electric-field induced conducting state in $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. First, we show below that a filamentary picture of conduction would give no observable change in magnetization through the electric-field driven transition, and seems therefore incompatible with our experimental data. Let us consider a resistance drop through the transition from, say, 10^9 to $10^5 \Omega$. In the filamentary picture, this is equivalent to the addition of a parallel component, of about $10^5 \Omega$, in the electrical circuit. This component represents the FM conducting part of sample. The resistivity of the FM state (induced by magnetic field) measured in $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ samples is $\rho_{FM} \approx 10 \Omega \text{ cm}$. The total volume occupied by FM filaments, V_{FM} , can be estimated from the relation $V_{FM}/V_S = \rho_{FM}/\rho_S$, where V_S and ρ_S is the total volume and resistivity of the sample, respectively, in the conducting state. Therefore V_{FM} would be about 0.05% of the sample volume. Such a small variation in magnetization through the transition would be unobserved. (Our estimate gives a lower bound for the magnetization of conducting filaments.) How-

ever, magnetization increases significantly just at the voltage at which the resistivity drops. The change in magnetization is two orders of magnitude larger than the predicted one in the above scenario. Therefore we must conclude that the electric-field induced conducting states are not of filamentary (threadlike) nature. An effective-medium model approximation, in which a field- and temperature-dependent concentration of metallic elongated inclusions in an insulating background accounts for the electronic transport properties of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds,¹⁴ might provide a better explanation of our data. As-cooled $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is in an insulating AF phase. However, a significant anisotropic strain develops in this system below the CO temperature.¹¹ When a high electric field is applied to the sample, ferromagnetic clusters form along the current path. A large lattice relaxation follows the formation of these clusters.^{10,11} The resistivity drops abruptly once the percolating current path is established. The sharp increase in the current through the transition suggests a low percolation threshold. Elongated metallic clusters would produce the observed effect: a large variation in the sample resistivity and a small but significant increase in the magnetization.¹⁴ When the current through the sample decreases, small FM clusters linking larger ones disappear under stress from the surrounding AF insulating bulk. The larger FM clusters however remain and are frozen in giving a measurable contribution to the total magnetization of the system. Repeated application of high voltages may lead to a total increase of 30% in magnetization; however, it is still well below the magnetization value in the bulk FM state. The transition to the conducting state in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is irreversible for applied magnetic fields higher than a few tesla, since the magnetic field destabilizes the CO state. As the FM clusters become larger and more highly ordered, the magnetization increases and the resistivity decreases. Thus we conclude that the electric-field driven transition in polycrystalline $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system leads to the mixed state that is less resistive and more highly magnetized than the CO initial state.

Finally, we would like to make a comment about heating effects in our experiments. One might suspect that the observed irreversibility in M at the transition voltage, in small applied magnetic fields, could arise from magnetic remanence effects. These effects would follow from the initial temperature rise produced by Joule heating on going through the transition and the subsequent cooling that is enforced experimentally. However, the measured variations in M would imply a temperature rise of about 10 K in the presence of a magnetic field, which is quite unlikely for the reasons that follow: (i) we performed magnetization measurements only after the sample temperature was stable at 30 K, as monitored by a carbon resistor placed next to and in good thermal contact with the sample; (ii) the corresponding temperature gradient in the sample is highly unlikely, taking into account the value of the thermal conductivity obtained for parent materials.¹⁶

Part of this research was supported by Project No. MAT 99-0847 of Comisi3n Interministerial de Ciencia y Tecnolog3a (CICYT).

*Electronic address: jolanta@posta.unizar.es

- ¹R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
- ²C. Zener, Phys. Rev. **82**, 403 (1951); P.W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955); P.G. de Gennes, *ibid.* **118**, 141 (1960).
- ³C.H. Chen and S-W. Cheong, Phys. Rev. Lett. **76**, 4042 (1996).
- ⁴J.B. Torrance, P. Laccore, A.I. Nazzal, E.J. Ansaldo, and Ch. Niedermayer, Phys. Rev. B **45**, 8209 (1992).
- ⁵Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratilav, J. Magn. Magn. Mater. **53**, 153 (1985).
- ⁶Z. Jirak, S. Krupicka, V. Nekvasil, E. Pollert, G. Villeneuve, and F. Zounova, J. Magn. Magn. Mater. **15-18**, 519 (1980).
- ⁷H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **52**, R13 145 (1995).
- ⁸Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, J. Phys. Soc. Jpn. **64**, 3626 (1995).
- ⁹A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature (London) **388**, 59 (1997).
- ¹⁰V. Kiryukhin, D. Casa, J.P. Hill, B. Keimer, A. Vigliante, Y. Tomioka, and Y. Tokura, Nature (London) **386**, 813 (1997).
- ¹¹D.E. Cox, P.G. Radaelli, M. Marezio, and S-W. Cheong, Phys. Rev. **57**, 3305 (1998).
- ¹²K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **78**, 4257 (1997); T. Mori, K. Ogawa, K. Yoshida, K. Miyano, Y. Tomioka, and Y. Tokura, J. Phys. Soc. Jpn. **66**, 3570 (1997).
- ¹³K. Ogawa, W. Wei, K. Miyano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **57**, R15 033 (1998).
- ¹⁴M. Jaime, P. Lin, S.H. Chun, M.B. Salamon, P. Dorsey, and M. Rubinstein, Phys. Rev. B **60**, 1028 (1999).
- ¹⁵W. Crawford Dunlap, Jr., in *Methods of Experimental Physics*, edited by K. Lark-Horovitz and V. A. Johnson (Academic Press, New York, 1959), Vol. 6, Part B, p. 39.
- ¹⁶J.L. Cohn, J.J. Neumeier, C.P. Popovicui, K.J. McClellan, and Th. Leventouri, Phys. Rev. B **56**, R8495 (1997).