# Percolative metal-insulator transition in $La_{0.9}Sr_{0.1}MnO_3$ ultrathin films by resistive relaxation

X. J. Chen,[1,2] H.-U. Habermeier,[2] and C. C. Almasan[1]
[1]*Department of Physics, Kent State University, Kent, Ohio 44242, USA*
[2]*Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany*
(Received 18 July 2003; published 14 October 2003)

We report an experimental study of the time dependence of resistivity of a $La_{0.9}Sr_{0.1}MnO_3$ ultrathin film in order to elucidate the underlying mechanism for metal-insulator transition and colossal magnetoresistance (CMR) effect. There is a clear change of sign in the resistive relaxation rate across the metal-insulator transition driven by temperature or magnetic field. When measuring in increasing temperature or decreasing magnetic field, the resistivity increases with time in the metallic state but decreases with time in the insulating state. These relaxation processes indicate that the metal-insulator transition and the associated CMR are a direct result of phase separation and of percolation of the metallic phase.

DOI: 10.1103/PhysRevB.68.132407 PACS number(s): 75.47.Lx, 75.47.Gk, 71.30.+h, 76.60.Es

Mixed-valence manganites of $R_{1-x}A_xMnO_3$ ($R$ is a rare-earth trivalent element and $A$ a divalent dopant) are a particularly important class of materials because of their scientific interest and potential technological applications.[1] For an intermediate doping region, an insulator-metal transition occurs at a temperature $T_{IM}$, marked by a peak in the electrical resistivity $\rho$. The system is insulating ($d\rho/dT<0$) above $T_{IM}$ and metallic ($d\rho/dT>0$) below $T_{IM}$. This phase change is accompanied by a transition from high-temperature paramagnetic (PM) to low-temperature ferromagnetic (FM) state at the Curie temperature $T_C$. Under the application of an external magnetic field, $T_{IM}$ shifts to a higher temperature and the resistivity is strongly suppressed. This gives rise to a huge magnetoresistance, called colossal magnetoresistance (CMR).

Although the theoretical understanding of the CMR phenomenon is still incomplete, double-exchange,[2] electron-phonon coupling,[3] and orbital effects[4] are commonly recognized as its main ingredients. Contrasting ground states can result from the combination of all these internal interactions. A subtle energy balance between some of the competing states may lead to the formation of electronic phase mixtures. Recent studies[5–13] have provided accumulating evidence for the existence of phase separation in manganites. For example, it has been proposed theoretically[5,7] that percolation should play an essential role in the transport properties. Scanning tunneling spectroscopy[12] and magnetic force microscopy[13] have revealed the formation and evolution of percolation networks of metallic and insulating phases across the metal-insulator transition.

In this paper, we use resistive relaxation measurements to reveal the nature of the metal-insulator transition and CMR effect of $La_{0.9}Sr_{0.1}MnO_3$, a compound which belongs to a composition range where the occurrence of phase separation has recently been proposed theoretically.[14] We discover resistive relaxation in both the insulating and metallic regions, with opposite relaxation rates in these two regions and a change of sign across the metal-insulator transition, driven by temperature and magnetic field. These experimental data imply phase separation in both insulating and metallic regions. They also indicate that the metal-insulator transition and the associated colossal magnetoresistance effect are the result of percolation of the metallic clusters imbedded into the insulating matrix.

The 50-Å $La_{0.9}Sr_{0.1}MnO_3$ films used in our experiments were grown on a (100) $SrTiO_3$ substrate with a pulsed laser deposition technique described previously.[15] Because the lattice constant of $SrTiO_3$ is smaller than that of $La_{0.9}Sr_{0.1}MnO_3$, the film grown on $SrTiO_3$ is subject to compressive strain, resulting in a suppression of the charge and orbital ordering (CO) transition temperature $T_{CO}$ as well as a significant enhancement of $T_{IM}$ compared to the bulk.[16,17] The epitaxially strained growth of these ultrathin films has been revealed by high-resolution transmission electron microscopy. The detailed structure analysis is presented elsewhere.[18] Resistivity and magnetoresistivity measurements in zero field and under various magnetic fields up to 14 T have been performed through a conventional four-probe method by using a quantum design physical properties measurement system. The temperature stability was better than 0.01% during the relaxation measurements.

The temperature dependence of the resistivity $\rho(T)$ measured in different applied magnetic fields is shown in Fig. 1. All these data are characterized by hysteresis, which is ex-

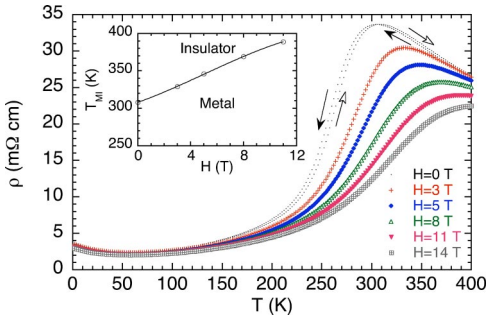


FIG. 1. (Color online) Temperature dependence of the resistivity for a 50-Å $La_{0.9}Sr_{0.1}MnO_3$ ultrathin film under zero field and various magnetic fields measured in a warming run. The zero-field data show a typical resistivity hysteresis, with the arrows indicating the directions of the temperature sweeps. Inset: Temperature—magnetic-field phase diagram. The solid line is the metal to insulator transition boundary.

 

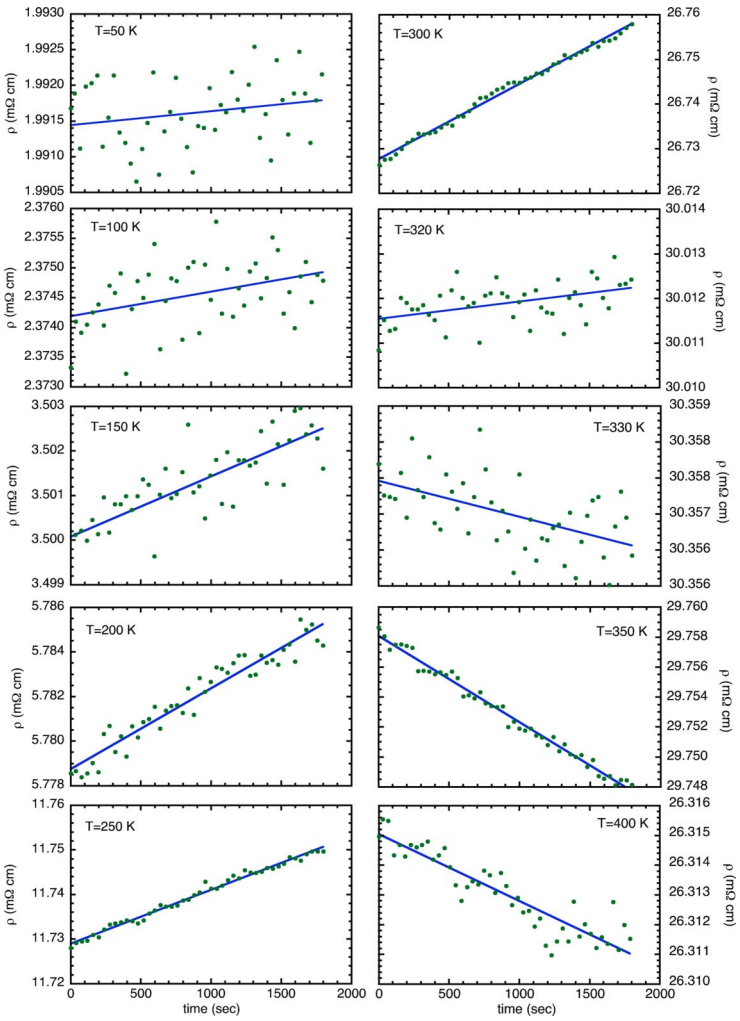


FIG. 2. (Color online) Time dependence of the resistivity for a 50-Å $La_{0.9}Sr_{0.1}MnO_3$ ultrathin film measured in a magnetic field of $H=3$ T at different temperatures, as labeled on the graph, in a warming run. The solid lines are linear fits of the data.

emplified in the figure by the zero-field resistivity curves. Upon cooling from 400 K, the $\rho(T)$ curve exhibits a peak at $T_{IM}=300$ K, signaling the insulator-metal transition. At a lower temperature $T_{CO}\approx 50$ K, $\rho(T)$ displays a minimum, indicating the appearance of a low-temperature FM insulating-like state for $T<T_{CO}$. In this low-temperature state, new structural reflections characteristic of CO appear in neutron[19]- and x-ray[20]-diffraction patterns. In warming from 2 K, the $\rho(T)$ curve is first below the cooling one, it overshoots the cooling curve around 305 K and exhibits a peak (metal-insulator transition) at $T_{MI}=308$ K. Such a behavior gives a clear indication of intrinsic phase inhomogeneity.[11,13] An applied magnetic field $H$ suppresses the resistivity, shifts $T_{MI}(H)$ towards higher temperatures (see inset to Fig. 1), and, hence, gives rise to the CMR effect.

We measured the magnetization as a function of temperature up to 300 K in a magnetic field of 0.5 T using a quantum design superconducting quantum interference device magnetometer. The magnetization is still large ($\sim 70$ emu/cm$^3$) at 300 K compared to its saturation value of $\sim 300$ emu/cm$^3$ at low temperatures. This indicates that the Curie temperature $T_C$ of this film is above 300 K. A lower $T_{IM}$ value compared to $T_C$ has been previously reported in $La_{1-x}Sr_xMnO_3$ thin films.[15,21] A possible explanation for $T_{IM}<T_C$ is the existence of microscopic phase segregation, with FM clusters embedded in PM insulating matrix. The FM clusters are large enough to give a magnetic contribution, but do not percolate for $T>T_{IM}$. Our relaxation data shown below support such a scenario.

Relaxation studies of the resistivity have proven to be a useful tool to investigate the dynamics of the competing superexchange and double-exchange interactions in manganites.[22] The relaxation effect on the resistivity and magnetization of the half-doped manganites $R_{0.5}A_{0.5}MnO_3$ has been studied recently in order to address nonequilibrium phenomena present in these systems.[23–27] Here, we use relaxation studies of the resistivity to elucidate the mechanism responsible for the metal-insulator transition in manganites. Figure 2 shows representative profiles of the relaxation of the resistivity measured in the presence of a magnetic field $H=3$ T at different temperatures in a warming run. The film was initially cooled to 2 K in the presence of the magnetic field. The temperature was then increased to the desired value at which the resistive relaxation measurement was performed. Then, the temperature was stabilized to the next desired value and the resistive relaxation measurement performed again. The resistivity increases with time for $50\leqslant T\leqslant 320$ K and decreases with time for $T\geqslant 330$ K. Figure 3 shows the relaxation of the resistivity measured at a fixed temperature $T=320$ K for various magnetic fields in a de-

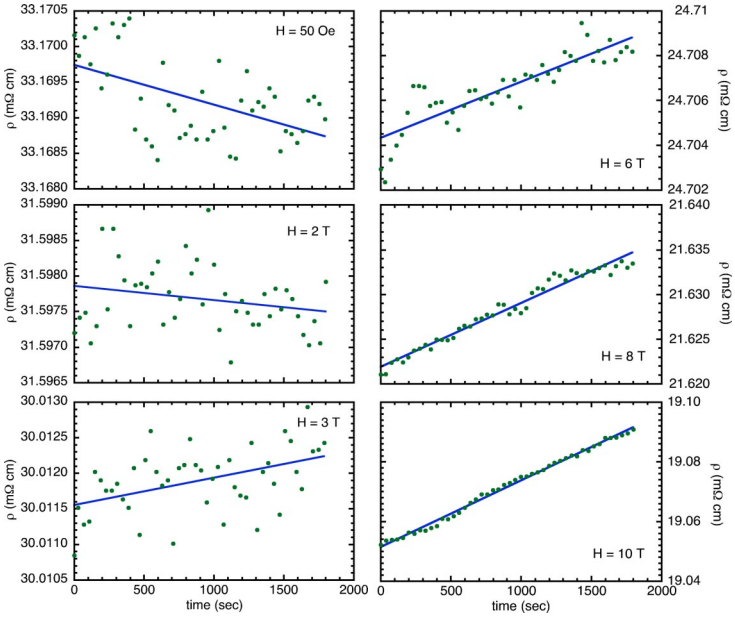


FIG. 3. (Color online) Time dependence of the resistivity of a 50-Å $La_{0.9}Sr_{0.1}MnO_3$ ultrathin film measured at a temperature of 320 K for different applied magnetic fields, as labeled on the graph, in a field decreasing run. The solid lines are linear fits of the data.

creasing field run. The resistivity increases with time for $H \geqslant 3$ T and decreases with time for $H \leqslant 2$ T. As shown in the inset to Fig. 1, the temperature of 320 K is the metal-insulator transition temperature for a field of about 2.2 T. Thus the system is in the metallic state for $H \geqslant 3$ T and $T \leqslant 320$ K, and in the insulating state for $H \leqslant 2$ T and $T \geqslant 320$ K. The decrease (increase) of the resistivity with time in the insulating (metallic) state is, therefore, obtained through both protocols: measuring the resistive relaxation at different $T$ while keeping $H$ fixed or at different $H$ while keeping $T$ fixed.

We performed a linear fit of all relaxation data with $\rho(t) = \rho(t_0) + \eta t$. Here $t$ is the relaxation time, $\rho(t_0)$ is the initial resistivity, and $\eta$ is the resistive relaxation rate, which is the only free parameter. Figures 4(a) and 4(b) show the variation of $\eta$ with $T$ measured at $H = 3$ T, and with $H$ measured at $T = 320$ K, respectively. As shown above, $\eta$ is positive in the metallic state, zero around the metal-insulator transition, as marked by the solid line and dashed region, and negative in the insulating state. The resistive relaxation rate has a maximum in the metallic state around 280 K, as shown in Fig. 4(a). The inset to this figure shows that the absolute value of CMR for the same field of 3 T is maximum around the same temperature. Also, both $\eta$ [see Fig. 4(b)] and the CMR (see Fig. 1), measured at a constant temperature, increase with increasing $H$ in the metallic state. These results indicate that there is a direct correlation between the behavior of the colossal magnetoresistance and the relaxation rate of the resistivity.

It is also interesting to note that $\eta$ decreases with decreasing temperature for $T < 280$ K and approaches zero again at $T = 50$ K [see Fig. 4(a)]. Recalling that there is a minimum in the $\rho(T)$ curve at $T_{CO} \approx 50$ K (see Fig. 1), the relaxation of the resistivity also reveals the transition from the FM metallic state to the FM insulating-like state below 50 K.

One may consider whether the value of $\eta$ includes a contribution which is a result of temperature drift. To verify this point, we calculated the values of $\partial\rho/\partial t$ (hence $\eta$) which would be the result of temperature drift, from $\partial\rho/\partial T$ determined from $\rho$ vs $T$ curves in a magnetic field of 3 T and $\partial T/\partial t$ determined from the time dependence of $T$ recorded during the resistive relaxation measurements. These values of $\eta$ are two orders of magnitude smaller than those determined from the resistive relaxation measurements shown in Fig. 4(a). Thus, the contribution to $\eta$ from temperature drift is negligible.

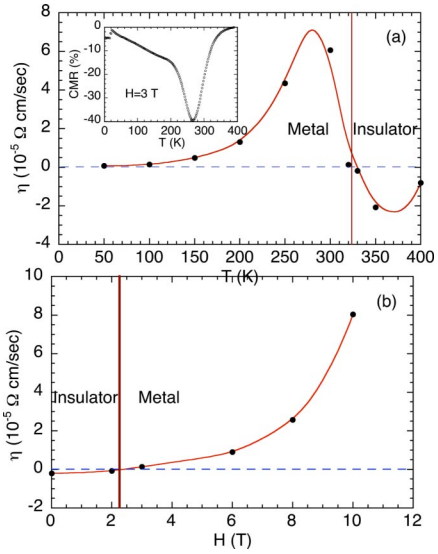


FIG. 4. (Color online) (a) Temperature dependence of the relaxation rate of the resistivity $\eta$ obtained from resistivity vs time measurements in a magnetic field of 3 T for a 50-Å $La_{0.9}Sr_{0.1}MnO_3$ ultrathin film. The vertical line marks the metal-insulator transition temperature for a magnetic field of 3 T. Inset: Temperature dependence of the magnitude of the colossal magnetoresistance (CMR) is equal to $[\rho(3T) - \rho(0)]/\rho(0)$ for a magnetic field of 3 T. (b) Relaxation rate of the resistivity $\eta$ as a function of magnetic field $H$ measured at a temperature of 320 K. The dashed region marks the metal-insulator transition corresponding to this temperature. The dashed lines are guides to the eye.

Next we demonstrate that these resistive relaxation measurements point towards the scenario of phase separation and percolation in this compound. Specifically, these data show that the metal-insulator transition and the CMR effect of manganites are a direct result of intrinsic phase inhomogeneity over the whole measured temperature range and of the evolution of the relative volume of the insulating and metallic phases with temperature or magnetic field. The presence of resistive relaxation up to 400 K indicates that there are FM clusters in the PM region. The existence of FM clusters above $T_C$ has been detected by small-angle neutron-scattering measurements.[10] These conductive FM clusters are embedded into an insulating host matrix. Upon lowering temperature or increasing magnetic field, the FM clusters grow and the ratio of FM metal to PM insulator becomes larger and larger. At a critical temperature or magnetic field, the conducting FM domains become interconnected across the whole sample, the percolation is established. Therefore, the resistivity exhibits a large decrease and the insulator-metal transition takes place. By further lowering temperature or increasing applied magnetic field, the fraction of the FM insulating phase decreases rapidly; accordingly, the fraction of the FM metallic phase increases. The existence of these electronically phase-separated FM insulating and FM metallic phases in the low-temperature FM metallic region has been confirmed by measurements of Mössbauer spectroscopy,[28] muon spin relaxation,[8] and nuclear magnetic resonance.[9]

When the system is warmed from low temperatures or field decreased from high values, the fraction of the FM metallic domains does not decrease as fast as it increased on the cooling run.[13] Therefore, this fraction is larger than its equilibrium value for a certain temperature or magnetic field on both sides of $T_{MI}$. This gives rise to the hysteretic behavior of the resistivity both below and above $T_{MI}$ and to a larger value of the metal-insulator transition temperature, as depicted in Fig. 1. Also, since the fraction of the FM metallic domains is larger than its corresponding equilibrium value, with increasing time the resistivity in the metallic region increases, the metal-insulator transition temperature (the temperature corresponding to the threshold for percolation) shifts to lower temperatures (since the threshold for percolation does not change in time), and the resistivity in the insulating region decreases. As a result, the resistive relaxation rate is positive in the metallic state and negative in the insulating state with a change in sign across the metal-insulator transition, as shown by Fig. 4.

We should emphasize that the results presented are representative for the CMR manganites which have metal-insulator transitions, and not only for ultrathin films of $La_{0.9}Sr_{0.1}MnO_3$. We have found similar resistive relaxations in both insulating and metallic regions of thicker films of the same composition and of bilayer $La_{1.2}Sr_{1.8}Mn_2O_7$ single-crystal manganites.

In summary, our experimental data of $La_{0.9}Sr_{0.1}MnO_3$ ultrathin films clearly show opposite resistive relaxation rates in the paramagnetic insulating state and the ferromagnetic metallic state, with a crossover in the sign of the relaxation rate around the metal-insulator transition. The experimental results provide strong support for the existence of phase separation in both insulating and metallic regions. Our findings, of a remarkable consistency between the effects of temperature and magnetic field, suggest that the metal-insulator transition and the negative colossal magnetoresistance are a result of the percolation of metallic ferromagnetic domains.

We thank G. Cristiani for growing the thin films, H. Zhang and C. L. Zhang for help in transport measurements, and M. Varela and J. Santamaria for TEM studies of our films. The work at KSU was supported by NSF Grant No. DMR-0102415.

[1] J.M.D. Coey, M. Viret, and S. von Molnar, Adv. Phys. **48**, 167 (1999).
[2] C. Zener, Phys. Rev. **82**, 403 (1951).
[3] A.J. Millis, Nature (London) **392**, 147 (1998).
[4] R. Maezono, S. Ishihara, and N. Nagaosa, Phys. Rev. B **58**, 11 583 (1998).
[5] L. Gor'kov and V. Kresin, J. Supercond. **13**, 239 (2000).
[6] G. Varelogiannis, Phys. Rev. Lett. **85**, 4172 (2000).
[7] M. Mayr *et al.*, Phys. Rev. Lett. **86**, 135 (2001).
[8] R.H. Heffner *et al.*, Phys. Rev. Lett. **85**, 3285 (2000).
[9] M.M. Savosta and P. Novák, Phys. Rev. Lett. **87**, 137204 (2001).
[10] J.M. De Teresa *et al.*, Nature (London) **386**, 256 (1997).
[11] M. Uehara *et al.*, Nature (London) **399**, 560 (1999).
[12] M. Fäth *et al.*, Science **285**, 1540 (1999).
[13] L.W. Zhang *et al.*, Science **298**, 805 (2002).
[14] S. Okamoto, S. Ishihara, and S. Maekawa, Phys. Rev. B **61**, 451 (2000).
[15] X.J. Chen *et al.*, Phys. Rev. B **65**, 174402 (2002).
[16] A. Urushibara *et al.*, Phys. Rev. B **51**, 14 103 (1995).
[17] M. Paraskevopoulos *et al.*, J. Phys.: Condens. Matter **12**, 3993 (2000).
[18] X.J. Chen *et al.* (unpublished).
[19] Y. Yamada *et al.*, Phys. Rev. Lett. **77**, 904 (1996).
[20] Y. Endoh *et al.*, Phys. Rev. Lett. **82**, 4328 (1999).
[21] O.J. González *et al.*, J. Magn. Magn. Mater. **222**, 199 (2000).
[22] R. von Helmolt *et al.*, Appl. Phys. Lett. **67**, 2093 (1995).
[23] H. Kawano *et al.*, Phys. Rev. Lett. **78**, 4253 (1997).
[24] V.N. Smolyaninova, C.R. Galley, and R.L. Greene, cond-mat/9907087 (unpublished).
[25] M. Uehara and S.-W. Cheong, Europhys. Lett. **52**, 674 (2000).
[26] J. Lopez *et al.*, Phys. Rev. B **63**, 224422 (2001).
[27] P. Levy *et al.*, Phys. Rev. Lett. **89**, 137001 (2002).
[28] V. Chechersky *et al.*, Low Temp. Phys. **23**, 545 (1997).