Colossal magnetoresistance in the antiferromagnetic $La_{0.5}Ca_{0.5}MnO_3$ system

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We have explored the colossal magnetoresistance (CMR) effect in the antiferromagnetic $La_{0.5}Ca_{0.5}MnO_3$ compound. In the absence of a magnetic field (H), the solid is a canted antiferromagnetic (AFM) insulator. An applied H in the Tesla scale induces a first order AFM to FM phase transition, and correspondingly, an insulator to metal transition. The observed CMR is attributed to the H-induced charge localization-delocalization behavior associated with the AFM–FM transition. At low temperatures ($T<100$ K), the solid remains in the AFM phase, where we have observed a phenomenal one millionfold change in resistivity between 0 and 8 Tesla. The origin of CMR in low T-region is a thermal activation energy gap which is strongly dependent on H.
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The magnetotransport and magnetic properties of the perovskite $La_{1-x}A_xMnO_{3+\delta}$ ($0 \leqslant x \leqslant 1$) system have received a great amount of attention recently after the discovery of the so-called colossal magnetoresistance (CMR) effect in the ferromagnetic phase (FM) of this system.[1–6] Essential to the CMR is the existence of the mixed valence state of Mn, evolving from Mn^{3+} (spin $S=2$) in the parent phase ($x=0$) to Mn^{4+} (spin $S=3/2$) in the end compound such as $CaMnO_3$ (i.e., $A=Ca$). The low energy t_{2g}^3 triplet contributes a local spin of $S=3/2$ to both Mn^{3+} and Mn^{4+}. In addition, Mn^{3+} has an additional electron in the e_g^1 state with its spin parallel to the local spin, whereas the e_g^1 state is empty in Mn^{4+}. Whether the e_g^1 electron is localized or mobile depends on the local spin orientation. If the local spins are aligned as in a FM, the e_g^1 electron will be mobile so as to lower its kinetic energy. However in the AFM configuration, the intra-atomic exchange between the e_g^1 electron and the local spin would forbid the electron transfer, hence, resulting in a charge localization. Because of these reasons, the electron transport in $La_{1-x}A_xMnO_3$ is sensitive to an underlying magnetic structure and its dynamics.[7] It is believed that the origin of CMR is directly related to this sensitivity.

To date, research on CMR has focused on the FM phase, in particular, on $La_{0.67}Ca_{0.33}MnO_3$ and other similar compounds.[1–4] CMR as large as ten-thousandfold has been obtained in polycrystals,[3] single crystals,[8] and epitaxial thin films.[1,2] A maximum MR is generally associated with the FM phase transition. We have studied the CMR effect using a different approach, and have searched for the maximum MR with an emphasis on the AFM phase. As a consequence we have achieved record CMR values of 830 000% at $T=125$ K and 10^8% at $T=57$ K in a well-prepared $La_{0.5}Ca_{0.5}MnO_3$ compound. Coupled with such a dramatic CMR is a field induced AFM–FM first order phase transition. At low T, we have also observed a strongly field dependent activation energy gap in the AFM phase.

The bulk $La_{0.5}Ca_{0.5}MnO_3$ compound was prepared using a solid-state reaction method. Appropriate proportions of La_2O_3, $CaCO_3$, and MnO_2 precursors were thoroughly mixed and then pressed into pellets. The sintering process lasted over a long period of 150 h in an oxygen atmosphere. Two intermediate grindings and mixings were carried out for homogenization. The annealing temperature was 1200 °C for the first two sinterings and was 1300 °C for the last. The sample was cooled to room temperature in more than 8 h. Four-probe magnetoresistance was measured in a cryostat equipped with an 8 T magnet. The magnetization of the sample was measured using the Quantum Design SQUID magnetometer. X-ray diffraction analysis indicated that the sample has a single phase with a cubic perovskite structure. The lattice constant is 7.66 Å.

Figure 1 shows the temperature (T) dependence of resis-

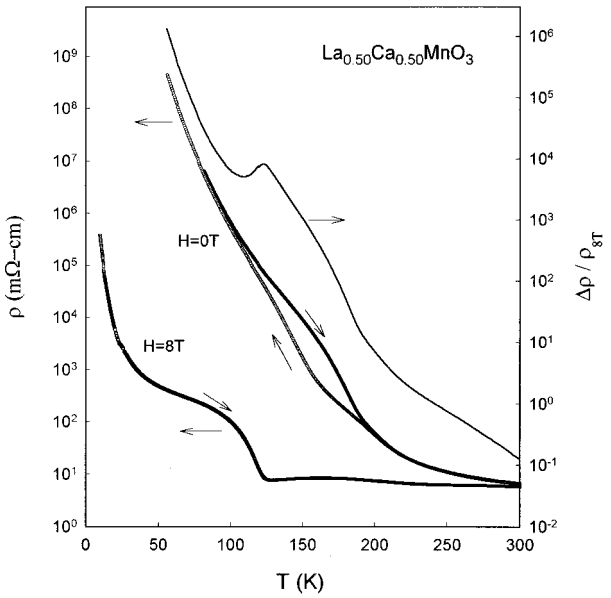

FIG. 1. The temperature (T) dependence of the resistivity, $\rho(T)$, (in log scale) measured in zero and 8 T field for $La_{0.5}Ca_{0.5}MnO_3$. The magnetoresistance ratio defined as $[\rho_0(T)-\rho_{8T}(T)]/\rho_{8T}(T)$ is also shown. The arrows indicate directions of measurement.

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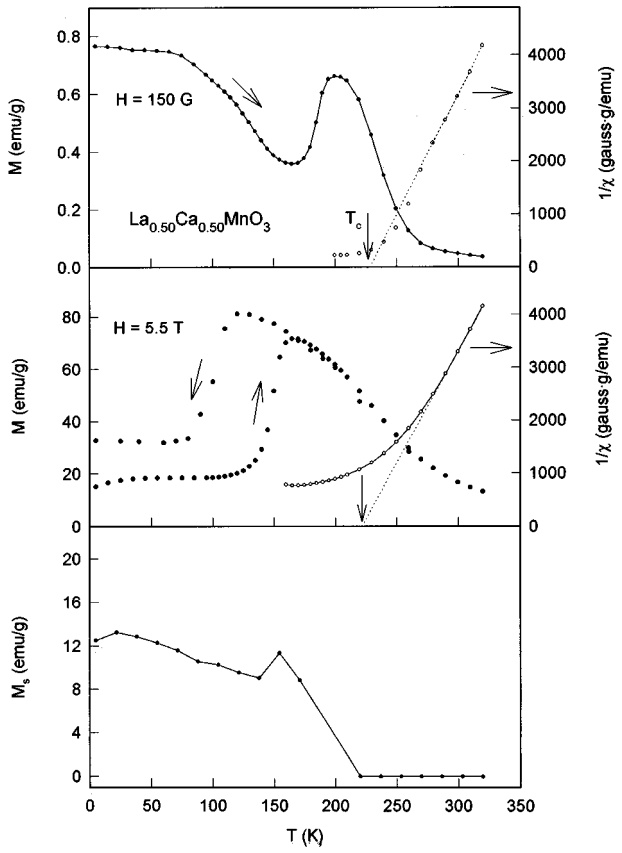

FIG. 2. The T-dependence of magnetization $M(T)$ and inverse susceptibility $\chi^{-1}(T)$ measured at $H=150$ G and 5.5 T. By extrapolating $M(H)$ in the high-H region to $H=0$, we have obtained a small ferromagnetic spontaneous magnetization $M_s(T)$ which is shown in the lower panel.

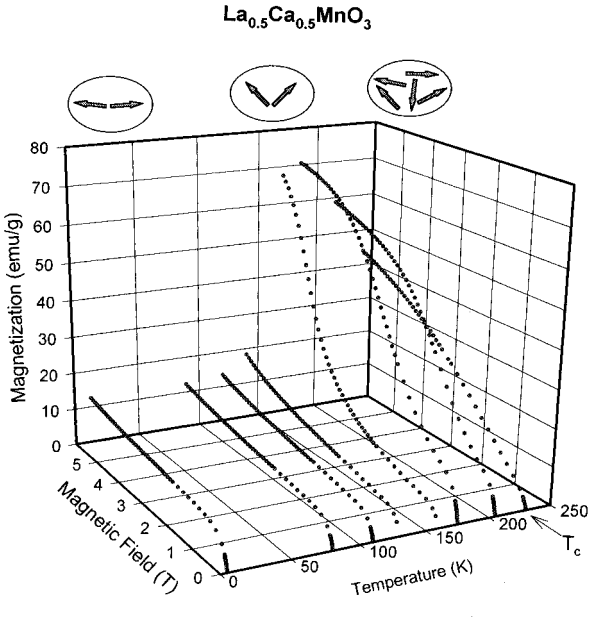

FIG. 3. Magnetization curves $M(H)$ measured at various temperatures. Three magnetic states are shown schematically in various temperature regions: a canted antiferromagnet, a canted ferromagnet, and a paramagnet.

tivity, $\rho(T)$, (in log scale) measured in 0 and 8 T field. The zero field $\rho_0(T)$ reveals a thermal hysteresis between 110 and 190 K in the cooling and warming-up mode. The $\rho_{8T}(T)$ at 8 T was measured only during warming-up. Over the T-range studied, $\rho_0(T)$ experiences a change spanning over eight orders of magnitude. Its T-dependence is semiconductorlike with an activation energy $\Delta(0)\approx 67$ meV. On the other hand, $\rho_{8T}(T)$ is substantially smaller than $\rho_0(T)$ at any given T. Above 120 K, $\rho_{8T}(T)$ is weakly dependent on T, having a value (a few mΩ-cm) typical of a poor metal. Below 120 K, $\rho_{8T}(T)$ experiences a sudden increase and evolves into an activation region with a gap $\Delta(8T)\approx 7.5$ meV, which is about one order of magnitude smaller than $\Delta(0)$. Also shown in Fig. 1 is MR ratio defined as $[\rho_0(T)-\rho_{8T}(T)]/\rho_{8T}(T)$. At $T\approx 60$ K ρ changes over six orders of magnitude between 0 and 8 T, and at $T\approx 125$ K over four orders of magnitude. To our knowledge the CMR effect shown here is the largest reported in $La_{1-x}A_xMnO_3$ and similar systems. It is noted that the maximum CMR in the FM $La_{0.67}Ca_{0.33}MnO_3$ occurs near T_c and vanishes as T approaches zero. However, in $La_{0.5}Ca_{0.5}MnO_3$, CMR seems to increase exponentially with reducing T.

To understand the anomalous magnetotransport, we have measured the magnetic properties of $La_{0.5}Ca_{0.5}MnO_3$. Figure 2 shows the T-dependence of magnetization $M(T)$ and invese susceptibility $\chi^{-1}(T)$ measured in a low field (150 G) and a high field (5.5 T). We have also measured a series of $M(H)$ curves from 0 to 5.5 T and in the T-range between 5 and 230 K. Some representative $M(H)$ curves are shown in Fig. 3. By extrapolating $M(H)$ in the high-H region to $H=0$, we have obtained a small FM spontaneous magnetization $M_s(T)$, which is shown in the lower panel of Fig. 2. Based on Figs. 2 and 3, we describe some of the important features of the magnetic properties.

(1) There exist two magnetic transitions in the T-range studied. The high-T $\chi^{-1}(T)$ provides an extrapolated Curie–Weiss $T_c\approx 225$ K as shown in Fig. 2, indicating a FM transition from a paramagnetic state. Another magnetic transition occurs at a T_d lower than T_c. The transition temperature, T_d, depends on H and on thermal history (zero-field-cooled or field-cooled). The substantial drop of M below T_d is indicative of an FM–AFM transition. The thermal hysteresis in M vs T (see the middle panel of Fig. 2) reveals a first order phase transition.

(2) At a fixed T, the FM–AFM transition can also be induced by an applied H_d (see Fig. 3). At a low T (<100 K), the solid is an AFM up to the maximum 5.5 T of our instrument. At a high T, for example, 150 K, the AFM–FM transition starts at about 4 T. As T approaches T_c, the AFM–FM transition shifts to a lower H, and becomes much smeared. In the zero H field, the solid is probably never a FM even at T near T_c. For example, at $T=205$ K, the $M(H)$ curve is hardly of any FM nature.

(3) Under a high H (e.g., 5.5 T), M approaches ~ 90 emu/g as $T\rightarrow 0$ K. Comparing with the theoretical limit of $M_0=102$ emu/g, one concludes that the canting angle θ_{FM} is about 56° at H=5.5 T in the FM phase [note that $\cos(\theta/2)=M_s^{\mathrm{exp}}/M_0$.] On the other hand, in the AFM phase, the spin orientations are canted too as evidenced from a small FM $M_s(T)$ component shown in the lower panel of Fig. 2. We

estimated that $\theta_{AFM} \approx 165°$. In other words, the AFM–FM transition, that can be either induced by H or by varying T, corresponds to a transition in θ from 165° to 56°.

With the above magnetic properties in mind, we can proceed to explain the magnetotransport data presented in Fig. 1. In zero field, θ remains large between 5 K and T_c. As a consequence, a charge transfer between neighboring sites is difficult, according to the prediction of the double exchange model[9–11] that charge transfer integral t is proportional to $\cos(\theta/2)$. At low T, charges are almost fully localized, which leads a thermally activated $\rho_0(T)$. Neutron diffraction studies[12] on $Pr_{0.5}Sr_{0.5}MnO_3$ have shown that Mn^{3+} and Mn^{2+} sites are spatially ordered at a low T similar to a Wigner lattice.

At a high H (e.g., 8 T), the system is FM above $T \approx 125$ K. In the FM phase, because of a much smaller canting angle, the charge transfer is enhanced substantially, allowing the formation of extended electronic states. The solid then behaves like a metal, albeit a poor one, with a resistivity of a few mΩ-cm. At about 125 K, a FM–AFM transition occurs, causing a charge localization and a thermally activated transport. However, as mentioned earlier, the energy gap at 8 T is much smaller than that at zero field. This is due to the fact that the canting angle in the AFM phase is reduced in the high H region because of the Zeeman energy. A smaller canting angle makes the charge transfer easier. In short, the dramatic CMR effect in the low-T region observed in Fig. 1 is caused by the strongly H dependent energy gap $\Delta(H)$ in the AFM phase. This differs from the CMR mechanism in the FM $La_{0.67}Ca_{0.33}MnO_3$, where the effect of H is to suppress the randomness in spin orientation. The dynamics of the two phenomena, though related, is very different.

Recently Tomioka *et al.*,[5] have studied a single crystal of $Pr_{0.5}Sr_{0.5}MnO_3$ which shows similar magnetic and transport properties to those presented here. The CMR effect they reported, however, is much smaller. Application of a field of 7 T changes ρ by about two orders of magnitude at $T \approx 0$ K. Comparing with the $La_{0.5}Ca_{0.5}MnO_3$ system that has a MR of one-millionfold, the latter seems to develop a much more rigid charge-ordered lattice, yielding a larger energy gap in the AFM phase. The metallic phases of the two systems, on the other hand, do share a similar resistivity (a few mΩ-cm).

In summary, we have obtained record values of CMR in the AFM phase of $La_{0.5}Ca_{0.5}MnO_3$. At $T=125$ K, the CMR is about one million percent. It increases exponentially to 100 million percent at 57 K. The CMR effect at intermediate T's (e.g., 125 K) is associated with a field induced first order FM–AFM phase transition. In the low-T region (<100 K), the AFM phase leads to a charge localization and, possibly, spatially charge ordering. The energy gap in the insulating AFM phase is dependent on H, with a higher H corresponding to a smaller gap. It is this particular nature of the energy gap in the AFM phase that brings about the phenomenal CMR effect.

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