Large magnetothermopower in $La_{0.67}Ca_{0.33}MnO_3$ films

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We have studied transport properties, including the thermopower and its field dependence, between 5 K and room temperature in films of $La_{0.67}Ca_{0.33}MnO_3$ fabricated by simple metalorganic decomposition technique. A large negative magnetothermopower, $[S(H)-S(0)]/S(0)$, amounting to as much as 38% has been observed in addition to a large negative magnetoresistivity, $[\rho(H)-\rho(0)]/\rho(0)$, with a peak value of 70% in a field of 5 T. $S(H)$ is found to correlate with $\rho(H)$ in the form $S(H)\propto\ln\rho(H)+\text{const}$ while $\rho(H,T)$ scales with magnetization according to $\rho_m\exp[-M(H,T)/M_0]$ below the magnetic transition temperature. Above the transition $\rho(H)\propto\exp[-M^2(H)]$, while $\rho(0)$ displays Arrhenius behavior. All these facts are consistent with a picture of electrical conduction being dominated by magnetic polaron hopping which has its origin in the local magnetic order.

The recent discovery of giant magnetoresistance effects in certain magnetic metallic superlattices[1] has renewed interest in studying magnetotransport in a family of perovskite-like oxides of the form $La_{1-x}M_xMnO_3$ where $M=$Ba,Ca,Sr.[2,3] The parent compound, $LaMnO_3$ (Mn^{3+}; $t_{2g}^3e_g^1$), is an antiferromagnetic insulator characterized by a superexchange coupling between Mn^{3+} sites facilitated by a single e_g electron which is subject to strong correlation effects. Substitution on the La^{3+} site by a $+2$ valent alkaline earth ion results in a mixed valence Mn^{3+}/Mn^{4+} state where Mn^{4+} ionic state lacks the e_g electron. The itinerant hole associated with the Mn^{4+} ion may hop to Mn^{3+} sites but, because of a strong on-site exchange interaction (Hund's rule) with the localized Mn electrons, only hopping between sites with parallel localized spins is favored. This is the essence of the double exchange model which is believed to represent the physical nature of the interaction,[4–6] and the spin-oriented Mn^{3+}/Mn^{4+} pair together with an associated carrier form what is frequently referred to as a magnetic polaron.[7] Upon increasing the number of itinerant holes, i.e., with increasing doping, a point will be reached where the gain in the kinetic energy associated with the hopping of magnetic polarons exceeds the loss of the exchange energy of the localized spins which favors the antiparallel spin configuration. When this happens, for doping exceeding $x=0.2$ and up to $x=0.5$, the material undergoes a transition to the metallic ferromagnetic state.[8,9] For the above family of perovskites the ordering temperature, T_c, falls between 100–350 K.

From the perspective of carrier transport, it is obvious that a close coupling between the charge dynamics and the spin dynamics via the double exchange should give rise to interesting correlations between the transport properties such as resistivity and the magnetization of the material. Furthermore, the sensitivity of the magnetic polarons to the external magnetic field should lead to a rather marked magnetoresistance. Recent experiments support this point of view, and extremely large values of magnetoresistance (colossal magnetoresistance) are observed in the vicinity of the ferromagnetic transition.[2,4,10–12] In this work we are interested in the transport behavior of $La_{0.67}Ca_{0.33}MnO_3$ films prepared by the technique of metalorganic decomposition (MOD) and in broadening the scope of measurements to include the thermopower and its magnetic field dependence.

The MOD technique is a very versatile, simple way of depositing high quality, thick films over large areas.[13,14] Neodecanoate salts of La, Ca, and Mn were first synthesized, dissolved in xylene, and combined in appropriate proportions. The viscosities of these solutions were then adjusted to yield crack-free films with La:Ca:Mn ratio of 0.67:0.33:1. Previous work has shown that lanthanum manganite films of the highest quality are formed on $LaAlO_3$ substrates due to the small ($<2.5\%$) lattice mismatch; we have consequently adopted this approach as well. In the MOD process, sample fabrication is achieved by a spin-on technique in which the substrate is flooded with solution and spun dry, followed by pyrolysis in air at 550 °C for 3 min. The resulting coating is approximately 2000 Å thick. For the transport study described here, films 1.2 μm thick were obtained by repeating the sequence in six successive coats. We have found that the highest quality films with the sharpest magnetic transitions are obtained after rapid thermal annealing in oxygen at 900 °C for 5 min. The thermopower was measured using the steady state method. A thermal gradient was generated by a resistive heater mounted at one end of the film and its magnitude was determined using a chromel-constantan thermocouple. Measurements were done in a cryostat equipped with a superconducting magnet generating fields up to 6 T. The magnetization and the resistivity data were collected using a Quantum Design superconducting quantum interference magnetometer.

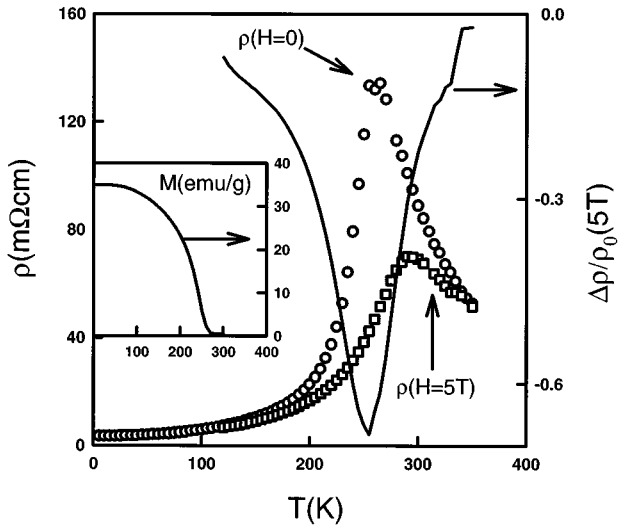

FIG. 1. Temperature dependence of zero field resistivity, $\rho(0)$, (open circles and left axis), resistivity measured at 5 T, $\rho(5T)$, (open squares and left axis), and magnetoresistance, $\Delta\rho/\rho(0)$ at 5 T (solid curve and right axis). The inset shows the temperature dependence of magnetization at $H=0.005$ T.

We first discuss the behavior of the resistivity and the magnetoresistance. The temperature dependence of $\rho(0)$, $\rho(5T)$ and the magnetoresistance (solid curve) defined as $\Delta\rho/\rho(0)=[\rho(0)-\rho(5T)]/\rho(0)$ are plotted in Fig. 1. The inset in Fig. 1 gives the temperature dependence of magnetization determined at $H=0.005$ T. At low temperatures the magnetic moment is large and the resistivity is characterized by strong ferromagnetic coupling between the magnetic ions which prevents formation of magnetic polarons and any significant spin disorder. Consequently, the scattering potential is weak yielding a low resistance state and metallic conduction. The magnetic field has virtually no effect in this low-temperature regime. As the temperature increases above 200 K, the magnetization rapidly decreases and, concurrently, we observe a rapid rise in the resistivity, and the transport behavior becomes field sensitive. At 255 K the resistivity displays a sharp peak and the magnetoresistance shows a deep minimum. This temperature coincides with the magnetic ordering

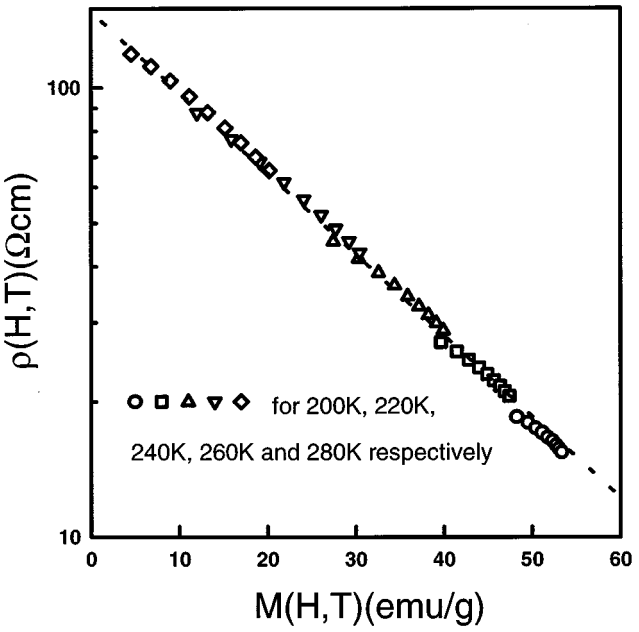

FIG. 2. Magnetoresistance $\rho(H,T)$ on a logarithmic scale vs magnetization at five temperatures from 200 to 280 K in intervals of 20 K. The dashed line is a guide for the eye.

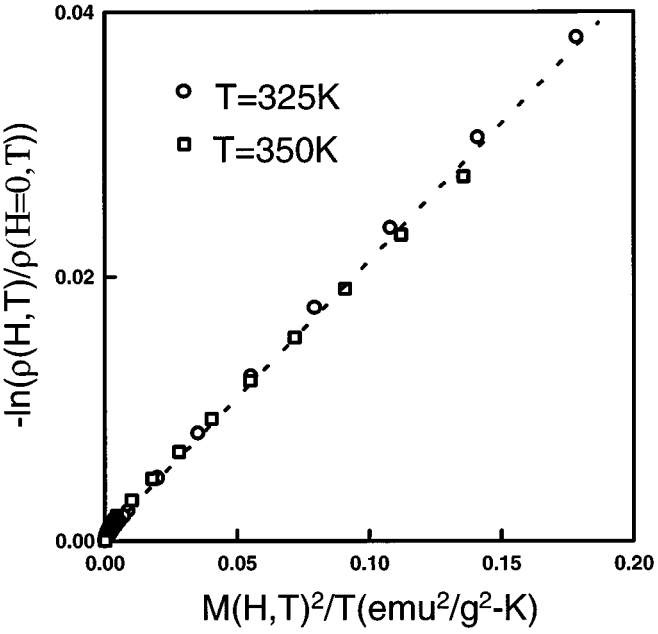

FIG. 3. A plot of $\ln[\rho(H,T)/\rho(H=0,T)]$ vs $M^2(H,T)/T$ at 325 and 350 K. Field ranges from 0 to 5 T.

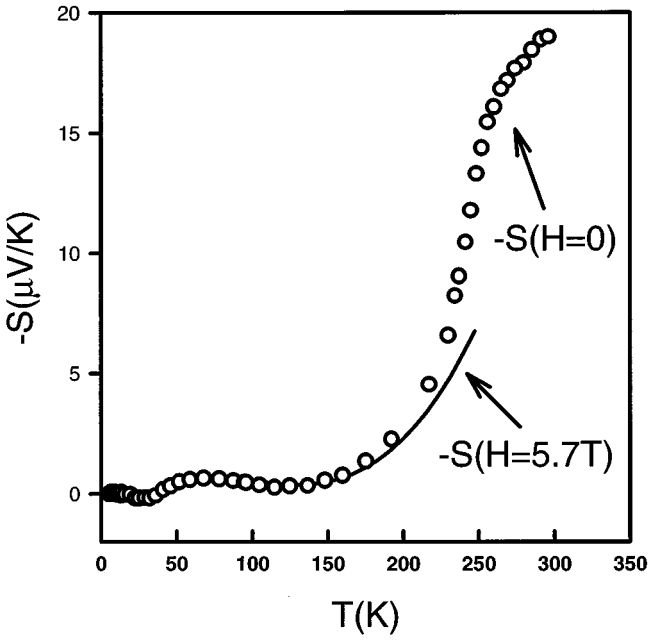

FIG. 4. Temperature dependence of zero field thermopower (open circles), and of the thermopower measured in the field of 5.7 T (solid curve). Note, the negative thermopower is plotted in both cases.

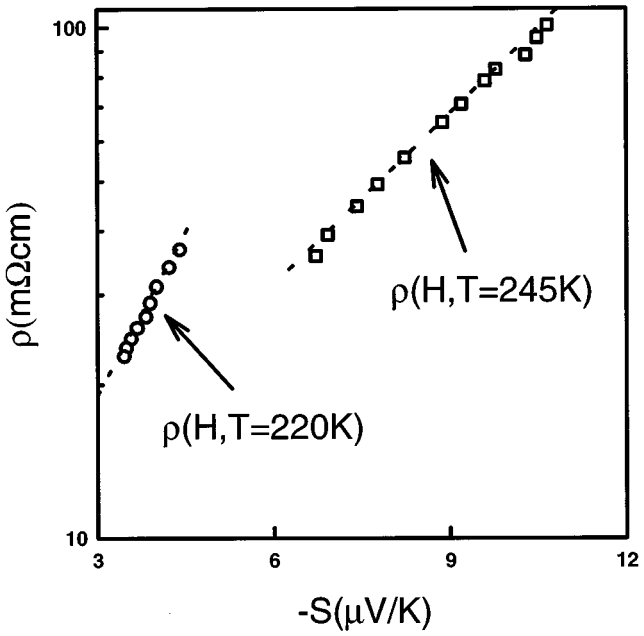

FIG. 5. Magnetoresistance, $\rho(H)$, in logarithmic scale vs magnetothermopower, $-S(H)$, at 220 and 245 K.

temperature determined from the plot of H/M vs M^2. The highly resistive state is the result of spin disorder and formation of magnetic polarons.

In films displaying extremely large values of magnetoresistance (truly colossal magnetoresistance effects)[3] the maximum change in the magnetoresistance was observed at temperatures significantly lower than where the resistivity peaks, i.e., well below the ordering temperature. This and other detailed features of the transport which seem not to conform to predictions based on the influence of magnetic polarons have led to a suggestion[15] that the magnetic polaron picture is incomplete and needs to be supplemented by additional physics, such as a strong electron-phonon coupling originating in the Jahn-Teller splitting of the Mn^{3+} ion.

Due to the instability of magnetic polarons in an external magnetic field, the resistivity peak shifts to higher temperatures and its magnitude drastically diminishes as one applies the magnetic field. The result is a large (negative) magnetoresistance near the ordering temperature which is depicted in Fig. 1 by a solid curve. In spite of an order of magnitude larger thickness and a considerably larger peak resistivity ($\sim$135 mΩ cm vs 17 mΩ cm) of our films, in comparison to the pulsed-laser deposited films described in the recent work of Hundley *et al.*,[11] our films show quite favorable peak magnetoresistance: 70% as against 85% reported in Ref. 11. Above the ordering temperature the resistivity shows an activated behavior, $\rho \propto \rho_0 \exp(\varepsilon/k_B T)$, where $\rho_0 = 2.447$ mΩ cm and the activation energy $\varepsilon = 93$ meV. This activation energy is comparable to 100 meV reported in Ref. 11 and is somewhat smaller than 119 meV for the molecular beam epitaxy grown films[12] of nominally the same cation stoichiometry. A close tie between the transport and magnetism of these films is reflected in correlations between the magnetoresistance $\rho(H,T)$ and magnetization $M(H,T)$ displayed in Fig. 2. Here $\rho(H,T)$ measured at five different temperatures from 200 to 280 K as a function of magnetic field between 1 and 5 T is plotted against $M(H,T)$ at the corresponding temperatures and fields. A clear correlation is seen of the form $\rho(H,T) = \rho_m \exp[-M(H,T)/M_0]$ where $\rho_m = 148.6$ mΩ cm and $M_0 = 24.22$ emu/g. This kind of correlation was noted by Hundley *et al.*[11] and it underscores the influence of local magnetism on the transport properties. The above correlation ceases to exist above about 280 K because the film becomes essentially paramagnetic with no sign of ferromagnetic fluctuations. Our data indicate, see Fig. 3, that well above 280 K the magnetoresistance can be expressed as $\rho(H) = \rho_n \exp[-M^2(H)/k_B T]$ where ρ_n is roughly a constant. When $M \to 0$, the expression reduces to $\rho \propto 1 - M^2$.

We now turn our attention to the thermopower. The absolute value of zero field thermopower, Fig. 4, shows a sharp increase as we approach the transition from below and the thermopower rises from a typically metallic value of a few μV/K below 150 K to values nearly an order of magnitude larger above 250 K. The rapid rise clearly coincides with the behavior of the resistivity, but no peak is observed near the ordering temperature. Rather, the thermopower acquires an almost linear temperature dependence above 250 K. The thermopower was also probed in a field of 5.7 T but only in a limited temperature range up to 250 K. In our cryostat and/or magnet system we have difficulty sustaining high temperatures for an extended period of time without excessive helium boiloff. As was the case of resistivity, magnetic field has virtually no effect on the thermopower at low temperatures. However, for temperatures above 200 K, the thermopower becomes field dependent and at 250 K the magnetothermopower reaches 38%. Undoubtedly, the same physical mechanism responsible for a large magnetoresistance is also responsible for the field dependence of the thermopower. To support this point of view, we plot in Fig. 5 the magnetoresistance versus magnetothermopower at temperatures of 220 and 245 K. The linear correlation between $S(H)$ and $\ln\rho(H)$ is evident. It is interesting to note a small peak in the thermopower in the vicinity of 70 K. We do not know the origin of this anomaly but speculate that it arises either from electron-magnon scattering or, if indeed strong electron-phonon interaction is part of the physical picture,[15] from a phonon drag contribution. Detailed studies, particularly those including dopant concentration dependence and working with films displaying truly colossal values of magnetoresistance should shed light on the source of this thermopower anomaly.

In conclusion, we have studied both magnetothermopower and magnetoresistance on thick films of $La_{0.67}Ca_{0.33}MnO_3$ prepared by a metalorganic decomposition technique. Our results indicate that a strong correlation with the local magnetism of the structure pertains not just to the galvanomagnetic properties but also to the thermomagnetic behavior.

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