Small-polaron hopping conductivity in bilayer manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$

X. J. Chen, C. L. Zhang, and C. C. Almasan

Department of Physics, Kent State University, Kent, Ohio 44242

J. S. Gardner

NRC-NPMR, Chalk River Laboratory, Chalk River ON KOJ 1PO, Canada

J. L. Sarrao

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We report anisotropic resistivity measurements on a La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ single crystal over a temperature $T$ range from 2 to 400 K and in magnetic fields $H$ up to 14 T. For $T \geq 218$ K, the temperature dependence of the zero-field in-plane $\rho_{ab}(T)$ resistivity obeys the adiabatic small polaron hopping mechanism, while the out-of-plane $\rho_c(T)$ resistivity can be ascribed by an Arrhenius law with the same activation energy. Considering the magnetic character of the polaron and the close correlation between the resistivity and magnetization, we developed a model which allows the determination of $\rho_{ab,c}(H,T)$. The excellent agreement of the calculations with the measurements indicates that small polarons play an essential role in the electrical transport properties in the paramagnetic phase of bilayer manganites.

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Elucidating the nature of the paramagnetic-insulating state is crucial to understanding the correlation between the electrical transport and magnetic properties of 3d transition-metal manganese-oxides. Most previous studies of the manganite perovskites R$_{1−x}$A$_x$MnO$_3$ films (R=rare-earth ion and A=divalent ion) reveal that the high temperature $T$ resistivity follows the adiabatic small polaron transport. The effect of an applied magnetic field $H$ on the resistivity and thermal expansion above the Curie temperature $T_c$ indicates that the polarons have magnetic character. The existence of polarons in the paramagnetic phase of bilayer manganites La$_{2−2x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($x = 0.4$) has been supported by measurements of Raman spectra, x-ray and neutron scattering, optical conductivity spectra, and thermoelectric power. However, there are no magneto-transport measurements which support the presence of polarons in the paramagnetic state of these materials.

Recently, bilayer manganites La$_{2−2x}$Sr$_{1+2x}$Mn$_2$O$_7$ have attracted considerable attention since: (i) the physical properties along the $ab$ plane and $c$ axis are strongly anisotropic, which should yield important insight into the colossal magnetoresistance (CMR) effect, (ii) they can be viewed as an infinite array of ferromagnetic metal (FM)-insulator (I)-FM junctions, (iii) both the in-plane and out-of-plane magnetoresistivities are sensitive to even small magnetic fields pointing to their possible device applications, (iv) they display a rich magnetic phase diagram which depends strongly on the doping level, and (v) they are good candidates for systematic investigations of the electrical resistivity in the paramagnetic regime over a broad $T$ range due to their relative lower $T_c$ compared to the manganite perovskites.

The understanding of electrical transport in the paramagnetic state and in the presence of an applied magnetic field and of the enhanced CMR effect in bilayer manganites is still incomplete and challenging. It has been found that the resistivity is semiconducting-like in the high $T$ paramagnetic state. On cooling, it reaches a maximum followed by a metallic behavior. When an external magnetic field is applied, this metal-insulator transition shifts to higher temperatures, the ferromagnetic transition broadens significantly, and a large reduction of electrical resistivity appears. It is highly desirable to understand the mechanism responsible for this charge dissipation and to develop a quantitative description of these behaviors. This is also essential to the understanding of the microscopic origin for the CMR effect.

In this paper we address the above issues through magnetotransport measurements in a La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ single crystal. Our data show that the adiabatic small polaron hopping dominates the electrical transport of this bilayer manganite. Specifically, all the main characteristics of charge transport, i.e., the $T$ and $H$ dependence of both the in-plane $\rho_{ab}$ and out-of-plane $\rho_c$ resistivities, the resistivity cusp, its shift to higher $T$ with increasing $H$, and the decrease of the resistivity with increasing $H$, are extremely well reproduced by our analysis based on the small polaron hopping, the existence of ferromagnetic clusters in the paramagnetic phase, and the close correlation between the resistivity and magnetization.

Single crystals of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ were melt grown in a floating-zone optical image furnace in flowing oxygen. The crystal used here was cleaved from a boule that was grown at a rate of 4 mm/h and had the lowest impurity phase content. We used a multiterminal lead configuration for the simultaneous measurement of $\rho_{ab}$ and $\rho_c$ on the same single crystal, over temperatures from 2 to 400 K and magnetic fields up to 14 T applied along the $ab$ planes. The electrical current was always applied...
polarons is given by

\[ \rho = CT \exp \left( \frac{E_A}{k_BT} \right). \]  

(1)

Here \( k_B \) is Boltzmann’s constant and \( E_A \) is the activation energy. In the adiabatic limit, the electron motion is assumed to be much faster than the ionic motion of the lattice. In the approximation that all correlations except on-site Coulomb repulsion are ignored, one can express the prefactor \( C \) as:

\[ C = \frac{k_B \Omega}{x(1-x)e^{2a^2\nu}}. \]  

(2)

Above \( \Omega \) is the unit-cell volume, \( x \) is the fraction concentration of occupied sites, \( a \) is the site to site hopping distance, and \( \nu \) is the frequency of the longitudinal optical phonons.

To examine the polaronic nature of the high-temperature resistivity of \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7 \), we plot in Fig. 2, \( \ln(\rho_{ab}/T) \) vs \( 1000/T \) for \( T \geq 140 \text{ K} \) and in zero field. The adiabatic polaron model of Eq. (1) gives a convincing fit to the in-plane resistivity data for \( T \geq 218 \text{ K} \), with a zero-field activation energy \( E_A^0 = 93.8 \text{ meV} \) and a prefactor \( C = 2.0 \times 10^{-6} \text{ \Omega cm/K} \). The fact that Eq. (1) is valid for \( T > \Theta_D/2 \) indicates that the Debye temperature \( \Theta_D \approx 430 \text{ K} \) in the present bilayer compound. Indeed, recent specific heat measurements have shown \( \Theta_D = 425 \text{ K} \) in this compound.\(^{17}\) The experimentally determined \( E_A^0 \) of 93.8 meV from the above resistivity data is much larger the activation energy \( E_S \) of 18 meV from thermoelectric power measurements.\(^{19}\) This large difference comes from the thermally activated nature of the hopping transport at high temperatures and is a characteristic signature of polaronic transport.

Based on the experimentally determined prefactor \( C \) along with the doping level \( x = 0.4 \) and the lattice parameters \( a = 3.87 \times 10^{-8} \text{ cm} \) and \( c = 2.0 \times 10^{-7} \text{ cm} \) taken from neutron diffraction measurements,\(^{19}\) we estimated a characteristic frequency \( \nu = 2.24 \times 10^{14} \text{ Hz} \) for \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7 \) by using Eq. (2). This value is in good agreement with the frequencies of phonon peaks in optical conductivity spectra,\(^{17,19}\) which provides strong evidence in favor of small polaronic transport in the \( ab \) plane of bilayer manganites.

Figure 1 shows \( \rho_{ab}(T) \) and \( \rho_c(T) \) measured in zero field and in several magnetic fields up to 14 T. The trends followed by these data are in good agreement with previous reports,\(^{10}\) though our single crystal has lower resistivities.

The metal-insulator transition temperature \( T_{MI} = 130 \text{ K} \) is found to be slightly higher than \( T_c = 125 \text{ K}. \)\(^{12}\) We also found \( T_{MI} \approx T_{MI} \) in the magnetic fields studied. Both \( \rho_{ab} \) and \( \rho_c \) decrease with increasing \( H \), the cusp becomes less pronounced, and \( T_{MI} \) shifts to higher temperatures. Recently, we found that both \( \rho_{ab} \) and \( \rho_c \) follow a \( T^{9/2} \) dependence in the metallic regime (50 K ≤ \( T \) ≤ 110 K) and both the in-plane \( \sigma_{ab} \) and out-of-plane \( \sigma_c \) conductivities obey a \( T^{1/2} \) dependence at even lower \( T \) (\( T < 50 \text{ K} \)), which are consistent with the two-magnon scattering and weak localization effect, respectively.\(^{12}\) The resistivity as a result of hopping of adiabatic small polarons is given by:

\[ \rho = CT \exp \left( \frac{E_A}{k_BT} \right). \]

(1)
Figure 2 shows also the plot of the resistive anisotropy \( \rho_{cf}/\rho_{ab} \) vs 1000/T for La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) for \( T \geq 140 \) K and zero field. Note that, for \( 150 \leq T \leq 400 \) K in zero field, there is the following relationship between resistivities: \( \gamma \equiv \rho_{cf}/\rho_{ab} = A + B/T \), with \( A = -14.8 \) and \( B = 2.63 \times 10^4 \) K. Since \( \rho_{ab}(T) \) is well described by Eq. (1) for \( T \geq 218 \) K, it follows that \( \rho_{c}(T) \) is described by an Arrhenius-type behavior with the same activation energy \( E_A \) as \( \rho_{ab}(T) \), if the preexponential factor \( \gamma \) is taken into account. Hence,

\[
\rho_c = C \gamma T \exp \left( \frac{E_A}{k_B T} \right) .
\]

In the presence of a magnetic field, the activation energy in Eqs. (1) and (3) has to be replaced by

\[
E_A = E_A^0 (1 - \cos \theta_{ij}) ,
\]

where \( \theta_{ij} \) is the angle between the spins of two Mn ion cores between which the \( e_g \) electron hops. If the azimuthal angle \( \phi_i \) is randomly distributed and if \( \theta_i \), the angle the spins make with the applied field, is uncorrelated, then, by averaging over \( \phi_i \), it can be shown that \( \langle \cos \theta_{ij} \rangle = \cos \theta_{ij} \). The local magnetization \( M \) can also be expressed as a function of \( \theta_i \), i.e., \( M = M_s \langle \cos \theta_i \rangle \), where \( M_s \) is the saturation magnetization. Then, Eq. (4) becomes

\[
E_A = E_A^0 \left[ 1 - \left( \frac{M}{M_s} \right)^2 \right] .
\]

This equation shows that the magnetic field affects the activation energy through the magnetization. At present, there is not an agreement on the theories proposed responsible for the magnetic properties of manganites. It has been shown \(^{20,21,22}\) that the Brillouin function \( B_s(\lambda) \) approximately provides a quantitative description of the reduced magnetization \( M/M_s \) observed experimentally. It is therefore reasonable to take \( M/M_s \approx B_s(\lambda) \) with

\[
B_s(\lambda) = \frac{2S + 1}{2S} \coth \left( \frac{2S + 1}{2S} \lambda \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} \lambda \right) .
\]

Here \( S \) is the average spin and the exchange coefficient and varies with doping as \( S = 3/2 + (1 - x)/2 \). An empirical model \(^{22}\) is used to sort out the magnetic field and temperature dependence of magnetization via the self-consistent equation

\[
\lambda = \frac{\mu H}{k_B T} + 3 \frac{S}{S + 1} \frac{T_c}{T} \frac{M}{M_s} ,
\]

where the effective magnetic moment \( \mu/\mu_B = qS \) with \( \mu_B \) being the Bohr magneton and \( q \) being the gyromagnetic ratio.

We note that, when using the mean-field expression for \( M/M_s \) to analyze their measured magnetization data of pseudocubic manganese-oxide perovskites, Sun et al. \(^{23}\) found that \( \mu/\mu_B = gS \) should be replaced by \( \mu/\mu_B = DgS \), where \( D \) is the mean number of spins per cluster. The ferromagnetic character in the paramagnetic phase of La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) has already been revealed by magnetization measurements \(^{12,24}\) and other experiments. \(^{25}\) Moreover, it was suggested \(^{13}\) that the size of the ferromagnetic clusters correlates with the magnetic correlation length \( \xi \), which increases slightly with decreasing temperature from the high-temperature paramagnetic side and suddenly diverges at \( T_c \). \(^{26}\) Thus the temperature

**FIG. 3:** Temperature \( T \) dependence of (a) the activation energy \( E_A \) and calculated (solid lines) and measured (open circles) (b) normalized in-plane resistivity \( \rho_{ab} \) and (c) normalized out-of-plane resistivity \( \rho_c \) in a La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) single crystal for various magnetic fields \( H \). Inset: Value of mean number of spins per cluster \( D \) vs \( T \).
dependence of $D$ should reflect this behavior. We determined $D(T)$ values from the isothermal resistivity curves. The temperature dependence of $D(T)$ can be expressed as $D = 2.7 + 2^{-3/2} \text{csch}^{3/2}(T - T_c)/320$, which is shown in the inset of Fig. 3(a).

We calculated the $T$ and $H$ dependences of $E_A$ and $\rho_{ab,c}$ from Eqs. (5)-(7) and from Eq. (1). $\rho_c(H,T)$ was then determined from the experimentally measured anisotropy $\gamma(H,T)$. These results for magnetic fields of 1, 3, 6, 10, and 14 T are shown in Figs. 3(a)–3(c) along with the experimental data of resistivities for comparison. In these calculations, we took $g = 2, S = 1.8$ (valid for $x = 0.4$), $T_c = 125 \text{ K}, E_A^3 = 93.8 \text{ meV}$, and $C = 2.0 \times 10^{-6} \Omega \text{ cm/K}$. There is a good agreement between the calculated and experimental results in the paramagnetic state.

As Fig. 3(a) shows, $E_A$ decreases slowly with decreasing $T$ and suddenly drops near $T_{MI}$. This characteristic behavior is responsible for the resistivity cusp shown in Figs. 3(b) and 3(c). With increasing magnetic field, $E_A$ is suppressed and its onset shifts systematically to high temperatures. This is the origin of the decrease of the resistivity as well as the shift of the resistivity cusp to higher $T$ with increasing $H$.

In summary, the small polaron model and the existence of the ferromagnetic clusters in the paramagnetic phase reproduce extremely well the $T$ and $H$ dependence of $\rho_{ab,c}$ for bilayer manganite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Moreover, the present model also accounts for the resistivity cusp, its shift to higher $T$ with increasing $H$, and the decrease of the resistivity with increasing $H$. Hence, this work provides direct evidence of the presence of adiabatic small polarons in bilayer manganites and their essential role in both the electrical transport and the CMR effect.

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