Small-polaron hopping conduction in bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$

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We report anisotropic resistivity measurements on a $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal over a temperature T range from 2 to 400 K and in magnetic-fields H up to 14 T. For $T \geqslant 218$ K, the temperature dependence of the zero-field in-plane resistivity $\rho_{ab}(T)$ obeys the adiabatic small polaron hopping mechanism, while the out-of-plane resistivity $\rho_c(T)$ can be ascribed by an Arrhenius law with the same activation energy. Considering the magnetic character of the polarons and the close correlation between 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 understand the correlation between the electrical transport and magnetic properties of $3d$ transition-metal manganese oxides. Most previous studies of the manganite perovskites $R_{1-x}A_xMnO_3$ films (R = rare-earth ion and A = divalent ion) reveal that the high-temperature resistivity follows the adiabatic small polaron transport.[1,2] 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.[3] The existence of polarons in the paramagnetic phase of bilayer manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.4$) has been supported by measurements of Raman spectra,[4] x ray, and neutron scattering,[5] optical conductivity spectra,[6,7] and thermoelectric power.[8] However, there are no magnetotransport measurements that support the presence of polarons in the paramagnetic state of these materials.

Recently, bilayer manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ 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,[9] (iii) both the in-plane and out-of-plane magnetoresistivities are sensitive to even small magnetic fields,[10] pointing to their possible device applications, (iv) they display a rich magnetic phase diagram that depends strongly on the doping level x,[11] and (v) they are good candidates for systematic investigations of the electrical resistivity in the paramagnetic regime over a broad temperature T range due to their relative low 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. 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 $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal. Our data show that 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 in-plane ρ_{ab} and out-of-plane ρ_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 $La_{1.2}Sr_{1.8}Mn_2O_7$ 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.[12] We used a multiterminal lead configuration[13] for the simultaneous measurement of ρ_{ab} and ρ_c on the same single crystal, over a temperature range from 2 to 400 K and magnetic fields up to 14 T applied along the ab planes. The electrical current was always applied along one of the crystal faces, while the top and bottom face voltages were measured simultaneously.

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 fol-

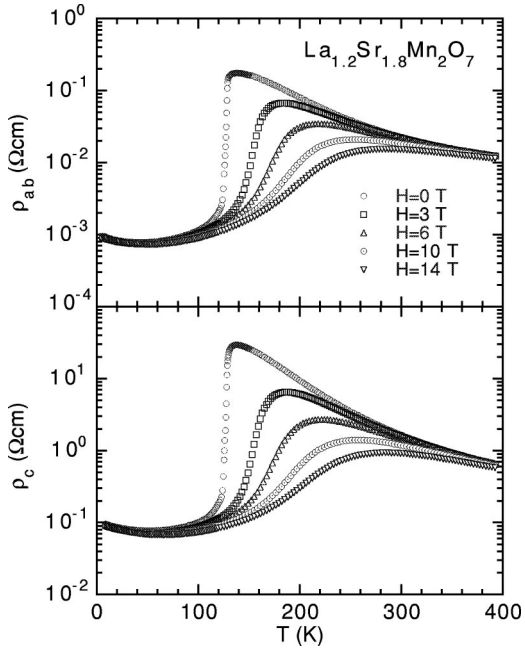

FIG. 1. In-plane ρ_{ab} and out-of-plane ρ_c resistivities as a function of temperature T of a $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal for various magnetic fields.

lowed by these data are in good agreement with previous reports,[10] though our single crystal has lower resistivities. The metal-insulator transition temperature $T_{MI}=130$ K is found to be slightly higher than $T_C=125$ K.[12] We also found that $T_{MI}^{ab}\simeq T_{MI}^{c}$ in the magnetic fields studied. Both ρ_{ab} and ρ_c decrease with increasing H, the cusp becomes less pronounced, and T_{MI} shifts to higher temperatures. Recently, we found that both ρ_{ab} and ρ_c follow a $T^{9/2}$ dependence in the metallic regime ($50\ \text{K}\leqslant T\leqslant 110$ K) and that both in-plane σ_{ab} and out-of-plane σ_c conductivities obey a $T^{1/2}$ dependence at even lower T ($T<50$ K). These results are consistent with two-magnon scattering and weak localization effect, respectively.[14]

The resistivity as a result of hopping of adiabatic small polarons is given by[15]

$$\rho = CT\exp\left(\frac{E_A}{k_BT}\right). \tag{1}$$

Here E_A is the activation energy and k_B is Boltzmann's constant. 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[1,16]

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

Above, Ω is the unit-cell volume, x is the fraction concentration of occupied sites, a is the site to site hopping distance, and ν is the frequency of the longitudinal optical phonons.

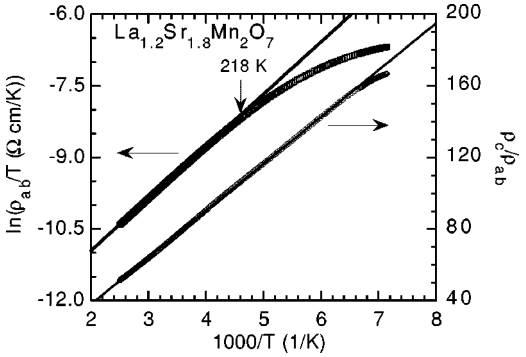

FIG. 2. Plot of $\ln(\rho_{ab}/T)$ and resistive anisotropy ρ_c/ρ_{ab}, measured in zero field, vs $1000/T$ for a $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal.

To examine the polaronic nature of the high-temperature resistivity of $La_{1.2}Sr_{1.8}Mn_2O_7$, we plot zero-field $\ln(\rho_{ab}/T)$ vs $1000/T$ for $T\geqslant 140$ K in Fig. 2. The adiabatic polaron model of Eq. (1) gives a convincing fit to the in-plane resistivity data for $T\geqslant 218$ K, with a zero-field activation energy $E_A^0=93.8$ meV and a prefactor $C=2.0\times10^{-6}\ \Omega$ cm/K. The fact that Eq. (1) is valid for $T>\Theta_D/2$ indicates that the Debye-temperature $\Theta_D\approx 430$ K in the present bilayer compound. Indeed, recent specific-heat measurements have shown that $\Theta_D=425$ K in this compound.[17] We note that the activation energy E_A^0 of 93.8 meV determined from the above resistivity data is much larger than 18 meV determined from thermoelectric power measurements.[18] This large difference indicates that conventional band theory does not occur above T_C and is a characteristic signature of polaronic transport.

We estimate a characteristic frequency $\nu=2.24\times10^{14}$ Hz for $La_{1.2}Sr_{1.8}Mn_2O_7$ by using Eq. (2) with the experimentally determined prefactor C, the doping level $x=0.4$, and the lattice parameters $a=3.87\times10^{-8}$ cm and $c=2.0\times10^{-7}$ cm taken from neutron-diffraction measurements.[19] This value of ν is in good agreement with the phonon peak frequency in optical conductivity spectra,[6,7] providing strong evidence for small polaronic transport in the ab plane of bilayer manganites.

Figure 2 shows also the plot of the resistive anisotropy ρ_c/ρ_{ab} vs $1000/T$ for $La_{1.2}Sr_{1.8}Mn_2O_7$ for $T\geqslant 140$ K and zero field. Note that, for $150\leqslant T\leqslant 400$ K, there is the following relationship between resistivities measured in zero field: $\gamma\equiv\rho_c/\rho_{ab}=A+B/T$, with $A=-14.8$ and $B=2.63\times10^4$ K. Since $\rho_{ab}(T)$ is well described by Eq. (1) for $T\geqslant 218$ 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 γ is taken into account. Hence,

$$\rho_c = C\gamma T\exp\left(\frac{E_A}{k_BT}\right). \tag{3}$$

In the case of magnetic polarons, there is a magnetic exchange contribution to the activation energy. In the presence of a magnetic field, the activation energy in Eqs. (1) and (3) has to be replaced by

$$E_A = E_A^0(1 - \langle \cos\theta_{ij} \rangle), \tag{4}$$

where θ_{ij} is the angle between the spins of the two Mn ion cores between which the e_g electron hops. If the azimuthal angle ϕ_i is randomly distributed and if θ_i, the angle the spins make with the applied field, is uncorrelated, then, by averaging over ϕ_i, it can be shown that $\langle \cos\theta_{ij} \rangle = \langle \cos\theta_i \rangle^2$.[20] The local magnetization M can also be expressed as a function of θ_i, i.e., $M = M_s \langle \cos\theta_i \rangle$, where M_s is the saturation magnetization. Then, Eq. (4) becomes

$$E_A = E_A^0 \left[1 - \left(\frac{M}{M_s} \right)^2 \right]. \tag{5}$$

This equation shows that the magnetic field affects the activation energy through the magnetization. At present, there is no agreement on the proposed theories regarding the magnetic properties of manganites. It has been shown[20–22] that the Brillouin function $B_s(\lambda)$ provides a quantitative description of the reduced magnetization M/M_s observed experimentally. It is, therefore, reasonable to take $M/M_s \simeq B_s(\lambda)$ with

$$B_s(\lambda) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S} \lambda \right) - \frac{1}{2S} \coth\left(\frac{1}{2S} \lambda \right). \tag{6}$$

Here S is the average spin, which varies with doping as $S = 3/2 + (1-x)/2$, and λ is the exchange coefficient. We use an empirical model[22] to determine the magnetic field and temperature dependence of magnetization via the self-consistent equation

$$\lambda = \frac{\mu H}{k_B T} + 3 \frac{S}{S+1} \frac{T_c}{T} \frac{M}{M_s}, \tag{7}$$

where the effective magnetic-moment $\mu/\mu_B = gS$, with μ_B being the Bohr magneton and g 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 $La_{1.2}Sr_{1.8}Mn_2O_7$ has already been revealed by magnetization measurements[12,24] and other experiments.[25] Moreover, it was suggested[3] that the number of spins per cluster correlates with the magnetic correlation length ξ, which increases slightly with decreasing temperature from the high-temperature paramagnetic side and suddenly diverges at T_C.[3,26] Thus, the temperature dependence of D should reflect this behavior. We determined the $D(T)$ values from the isothermal $\rho_{ab}(H)$ curves. The temperature dependence of $D(T)$ can be expressed as $D = 2.7 + 2^{-3/2} csch^{3/2}[(T - T_c)/320]$, which is shown in the inset to Fig. 3(a).

We calculated the T and H dependences of E_A and ρ_{ab} from Eqs. (5)–(7) and Eq. (1), respectively. $\rho_c(T,H)$ was then determined from the experimentally measured anisotropy $\gamma(T,H)$ and the already calculated $\rho_{ab}(T,H)$. 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 the resistivities for comparison. In these calculations, we took $g = 2$, $S = 1.8$ (valid for $x = 0.4$), $T_C = 125$ K, $E_A^0 = 93.8$ meV, and $C = 2.0 \times 10^{-6}$ Ω cm/K. There is an excellent agreement between the calculated and experimental results in the paramagnetic state.

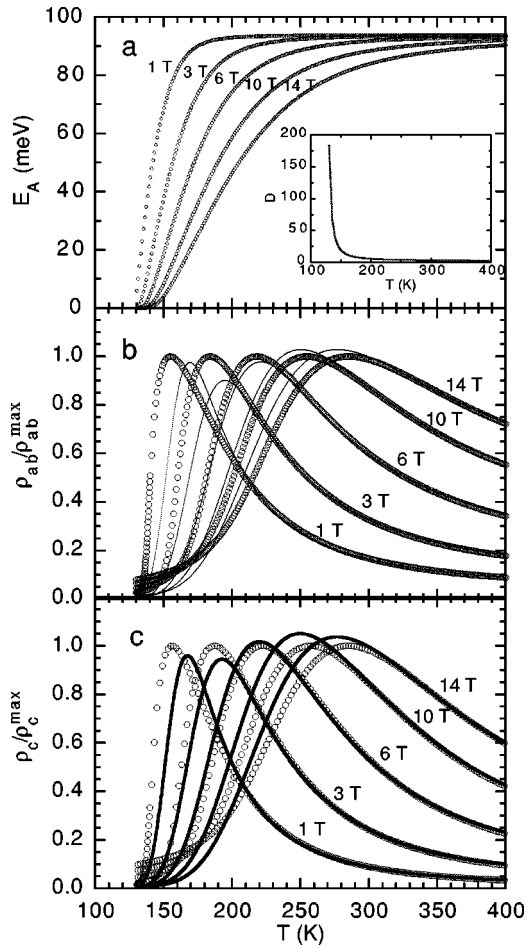

FIG. 3. Temperature T dependence of (a) the activation energy E_A, and calculated (solid lines) and measured (open circles) (b) normalized in-plane resistivity ρ_{ab} and (c) normalized out-of-plane resistivity ρ_c in a $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal for various magnetic-fields H. Inset, plot of mean number of spins per cluster D vs T.

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 ferromagnetic clusters in the paramagnetic phase reproduce extremely well the T and H dependence of $\rho_{ab,c}$ for bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$. 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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[1] D.C. Worledge, G. Jeffrey Snyder, M.R. Beasley, T.H. Geballe, R. Hiskes, and S. DiCarolis, J. Appl. Phys. **80**, 5158 (1996).
[2] J.M. De Teresa, K. Dörr, K.H. Müller, L. Schultz, and R.I. Chakalova, Phys. Rev. B **58**, R5928 (1998).
[3] J.M. De Teresa, M.R. Ibarra, P.A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. García, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).
[4] D.B. Romero, V.B. Podobedov, A. Weber, J.P. Rice, J.F. Mitchell, R.P. Sharma, and H.D. Drew, Phys. Rev. B **58**, R14 737 (1998).
[5] L. Vasiliu-Doloc, S. Rosenkranz, R. Osborn, S.K. Sinha, J.W. Lynn, J. Mesot, O.H. Seeck, G. Preosti, A.J. Fedro, and J.F. Mitchell, Phys. Rev. Lett. **83**, 4393 (1999).
[6] T. Ishikawa, T. Kimura, T. Katsufuji, and Y. Tokura, Phys. Rev. B **57**, R8079 (1998).
[7] H.J. Lee, K.H. Kim, J.H. Jung, T.W. Noh, R. Suryanarayanan, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **62**, 11 320 (2000).
[8] J.-S. Zhou, J.B. Goodenough, and J.F. Mitchell, Phys. Rev. B **58**, R579 (1998).
[9] T. Kimura, A. Asamitsu, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **79**, 3720 (1997).
[10] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).
[11] K. Hirota, Y. Moritomo, H. Fujioka, M. Kubota, H. Yoshizawa, and Y. Endoh, Jpn. J. Phys. **67**, L3380 (1998).
[12] N.O. Moreno, P.G. Pagliuso, C. Rettori, J.S. Gardner, J.L. Sarrao, J.D. Thompson, D.L. Huber, J.F. Mitchell, J.J. Martinez, and S.B. Oseroff, Phys. Rev. B **63**, 174413 (2001).
[13] C.N. Jiang, A.R. Baldwin, G.A. Levin, T. Stein, C.C. Almasan, D.A. Gajewski, S.H. Han, and M.B. Maple, Phys. Rev. B **55**, R3390 (1997).
[14] C.L. Zhang, X.J. Chen, C.C. Almasan, J.S. Gardner, and J.L. Sarrao, Phys. Rev. B **65**, 134439 (2002).
[15] D. Emin and T. Holstein, Ann. Phys. (N.Y.) **53**, 439 (1969).
[16] R. Raffaelle, H.U. Anderson, D.M. Sparlin, and P.E. Parris, Phys. Rev. B **43**, 7991 (1991).
[17] S. B. Oseroff (private communication).
[18] S. Nakamae, D. Colson, A. Forget, I. Legros, J.-F. Marucco, C. Ayache, and M. Ocio, Phys. Rev. B **63**, 092407 (2001).
[19] J.F. Mitchell, D.N. Argyriou, J.D. Jorgensen, D.G. Hinks, C.D. Potter, and S.D. Bader, Phys. Rev. B **55**, 63 (1997).
[20] M. Viret, L. Ranno, and J.M.D. Coey, Phys. Rev. B **55**, 8067 (1997).
[21] See M. Oretzki and P. Gaunt, Can. J. Phys. **48**, 346 (1970); K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972); G. Jakob, W. Westerburg, F. Martin, and H. Adrian, Phys. Rev. B **58**, 14 966 (1998); P. Wagner, I. Gordon, L. Trappeniers, J. Vanacken, F. Herlach, V.V. Moshchalkov, and Y. Bruynseraede, Phys. Rev. Lett. **81**, 3980 (1998).
[22] G.F. Dionne, J. Appl. Phys. **79**, 5172 (1996).
[23] J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, and S.S.P. Parkin, Appl. Phys. Lett. **69**, 1002 (1996).
[24] C.D. Potter, M. Swiatek, S.D. Bader, D.N. Argyriou, J.F. Mitchell, D.J. Miller, D.G. Hinks, and J.D. Jorgensen, Phys. Rev. B **57**, 72 (1998).
[25] T.G. Perring, G. Aeppli, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **78**, 3197 (1997).
[26] S. Rosenkranz, R. Osborn, L. Vasiliu-Doloc, J.W. Lynn, S.K. Sinha, and J.F. Mitchell, cond-mat/9909059 (unpublished).