Variable-range-hopping conductivity of the half-doped bilayer manganite LaSr$_2$Mn$_2$O$_7$

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We report measurements of the in-plane ($\rho_{ab}$) and out-of-plane ($\rho_c$) resistivities on a single crystal of the half-doped bilayer manganite LaSr$_2$Mn$_2$O$_7$. In the temperature $T$ range 220 to 300 K, the resistive anisotropy $\rho_c/\rho_{ab} = A + B/T$ (A and B constants), which provides evidence for the variable-range-hopping conduction in the presence of a Coulomb gap. This hopping mechanism also accounts for the quadratic magnetic field $H$ and $\sin^2\varphi$ dependences of the negative magnetoresistivity $\ln[\rho(T,H,\varphi)/\rho(T,H=0)]$ ($i=ab,c$), where $\varphi$ is the in-plane angle between the magnetic field and the current.

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Since the discovery of colossal magnetoresistance in manganese oxides, much effort has been devoted to understanding their magnetic and transport properties. It has been shown that the temperature $T$ dependence of the electronic conductivity in the paramagnetic phase is well described by Mott variable-range hopping (VRH),

$$\sigma = \sigma_0 \exp \left[ -\frac{4\nu_e \alpha^2}{k_B N(E)} \right]^p,$$

(1)

Here, $p = 1/(d+1)$, with $d$ being the dimensionality, $\sigma_0$ is a constant which depends on the assumptions made about the electron-phonon interaction, $\nu_e$ is a dimensionless constant, $\alpha$ is the reciprocal of the localization length $\xi$, and $N(E)$ is the density of states at the Fermi level. However, Eq. (1) usually yields a small value for the localization length ($\xi < 0.2$ nm) of the cubic manganites when $N(E)$ is deduced from the electronic heat-capacity coefficient $\gamma$. Since $\xi$ is expected to be of the order of the Mn-Mn distance, such a small $\xi$ is incompatible with conventional VRH and has an unphysical meaning.

In order to address this inconsistency, Viret, Ranno, and Coey developed a VRH model based on the idea of magnetic localization. Although the estimated value of $\xi$ is physically plausible in this case, it strongly depends on the splitting energy $U_m$ between spin-up and spin-down $e_g$ bands. At present, it is highly desirable to perform accurate measurements of $U_m$ for manganese oxides.

The derivation of dc conductivity, as given by Eq. (1), is based upon the assumption that the density of states near the Fermi level is constant. Efros and Shklovskii developed a VRH theory which takes into account the electron-electron Coulomb interaction, which reduces the density of states near the Fermi level. It was suggested that the Coulomb interaction may have an important effect on the hopping conduction of electrons in manganese oxides. Hence, the theory of weak localization and VRH in the presence of a Coulomb gap, as developed by Shklovskii and Efros (SE), could account for the temperature dependence of conductivity in manganites. Specifically, for half-doped manganites, the Coulomb interaction is believed to be not only the source of charge ordering, but also the convincing candidate for the anisotropy in the orbital-ordered states. Therefore, half-doped manganites can be model systems for clarifying whether the SE-VRH conduction mechanism dominates the electrical transport in their paramagnetic state.

In this paper, we present in-plane ($\rho_{ab}$) and out-of-plane ($\rho_c$) resistivity measurements of a half-doped LaSr$_2$Mn$_2$O$_7$ single crystal as a function of temperature, magnetic field $H$, and the in-plane angle $\varphi$ between the magnetic field and the electrical current. Both resistivities follow a VRH behavior for 220 $K < T < 300$ K well. However, as shown before for the cuprates, the temperature dependence of the resistive anisotropy $\rho_c/\rho_{ab}$ in the VRH regime is a much more effective indicator of the type of hopping than the traditional method based on Eq. (1). Here, we show that $\rho_c/\rho_{ab} = A + B/T$ for 220 $K < T < 300$ K, which unambiguously indicates VRH in the presence of a Coulomb gap. This hopping mechanism also accounts for the $H$ and $\varphi$ dependences of magnetoresistivities $\ln[\rho(T,H,\varphi)/\rho(T,H=0)]$ ($i=ab,c$). We also demonstrate that the negative magnetoresistivity in the VRH regime is a result of the increase of the localization length, hence, the decrease of resistivity when a magnetic field is applied.

Measurements of $\rho_{ab,c}(T,H,\varphi)$ of a single crystal of LaSr$_2$Mn$_2$O$_7$ were performed using a multiterminal lead configuration, over a temperature range from 2 to 300 K and in magnetic fields up to 14 T. The crystal was cleaved from a boule prepared by the optical floating-zone method, as reported elsewhere. A total of eight low-resistance electrodes were applied on the top and bottom faces of the crystal. The electrical current was always applied along one of the crystal faces, while the top and bottom face voltages were measured simultaneously. The rotation of the sample was performed along the $c$ direction, keeping the applied magnetic field within the MnO$_2$ planes. Angle $\varphi$ is defined to be $0^\circ$ ($90^\circ$) when the magnetic field is parallel (perpendicular) to the current. The $dc$ magnetization measurements were carried out using a superconducting quantum interference device magnetometer.

The temperature dependences of the zero-field resistivities $\rho_{ab}$ and $\rho_c$, and of the zero-field-cooled and field-cooled magnetization $M$, measured in an applied magnetic field of 50 Oe with $H||c$, are shown in Fig. 1(a) and 1(b), respectively. These plots display several features which correlate
with the charge-ordering and antiferromagnetic transitions in this half-doped compound. A steep increase of resistivity as well as a hysteresis in magnetization is observed just below 220 K, signaling the presence of a charge and orbital ordered phase. Ordering of the $d_{3x^2-2r^2}$ orbitals of the Mn$^{3+}$ ions, resulting from a cooperative Jahn-Teller distortion, accompanied by a real-space ordering in the Mn$^{3+}$/Mn$^{4+}$ distribution for $T_0$, has been confirmed by electron, neutron, and x-ray diffractions.14–19 A maximum near 180 K, visible in all the resistivity and magnetization curves, coincides with the onset of antiferromagnetism, while a broad minimum around 100 K corresponds to the transition to a canted spin state. These temperature values are consistent with the neutron-diffraction data.14,17

In the half-doped manganites, the Coulomb interaction modifies the density of states at the Fermi level and would affect the charge transport. According to the SE-VRH theory, the temperature dependence of the resistivity in the VRH regime is given by:

$$\rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{1/2},$$  \hspace{1cm} (2)

where $\rho_0$ is a constant and $T_0 = 2.8e^2/(4\pi k_B \varepsilon_0 \xi)$. Here, considering the high density of electrons in manganites, we take the background dielectric constant $\kappa = 1$, like in the jullium model for simple metals.

Figure 2(a) shows semilog plots of zero field $\rho_{ab,c}$ versus $T^{-1/2}$. Clearly, both resistivities exhibit VRH in the paramagnetic state (temperature range 220 to 300 K) above the charge-ordering transition temperature. However, over such a narrow $T$ range, one cannot reliably distinguish between a two-dimensional (2D) Mott VRH [$p = 1/3$ in Eq. (1)] and a SE-VRH ($p = 1/2$). Moreover, parameter $T_0$, determined by fitting the data in Fig. 2(a) with Eq. (2), is larger for $\rho_c$ than for $\rho_{ab}$ by approximately a factor of 2. As shown below, this is the result of ignoring the temperature dependence of the pre-exponential factor. In fact, $T_0$ turns out to be the same for $\rho_{ab}$ and $\rho_c$, in agreement with the theory of anisotropic hopping.

A plot of the resistive anisotropy $\rho_c/\rho_{ab}$ versus $1000/T$ for LaSr$_2$Mn$_2$O$_7$, displayed in Fig. 2(b), clearly shows that in the temperature regime where both resistivities follow the VRH model, there is the following relationship between resistivities:

$$\rho_c = \left( A + \frac{B}{T} \right) \rho_{ab},$$  \hspace{1cm} (3)

with $A = -28.78$ and $B = 4.64 \times 10^4$ K. It has been shown that the resistive anisotropy of an anisotropic material is given by.12

FIG. 1. Temperature dependence of (a) in-plane ($\rho_{ab}$) and out-of-plane ($\rho_c$) resistivities measured in zero field and (b) magnetization $M$ measured both in increasing the temperature after cooling the sample in zero field to 2 K (ZFC measurement), and in decreasing the temperature in the presence of an applied magnetic field (FC measurement) of LaSr$_2$Mn$_2$O$_7$.

FIG. 2. (a) Semilog plot of the zero-field resistivities $\rho_i$ ($i = ab,c$) versus $T^{-1/2}$. The straight lines are guides to the eye. (b) Resistive anisotropy $\rho_c/\rho_{ab}$ vs 1000/T. The straight line is a linear fit of the data with Eq. (3). Inset: Hopping processes in the Mn-O bilayer and the zigzag path in the $c$ direction.
\[ \rho_{c} = \frac{1}{2} \left( \langle R^2 \rangle_{P_{ab}(R)} \right) \approx \frac{1}{2} \left( \langle R^2 \rangle_{P_{ab}(R)} \right) \frac{L^2}{L^2} \rho_{ab}, \]  

where \( R \) is the in-plane hopping distance, \( L \) is the distance between adjacent bilayers, \( P_{ab} \) is the hopping probability between two states on the same bilayer separated by a distance \( R \), and \( P_{c} \) is the hopping probability between two states located on adjacent bilayers and separated by a variable lateral distance \( R \). Also, since the resistivity data follow the SE-VRH mechanism well, up to the highest measured temperature of 300 K, we take \( T \approx 300 \) K as the crossover temperature from NNH to SE-VRH for \( T \approx 300 \) K. With the experimentally determined \( T_{0} = 0.71 \) eV, we obtain \( \Delta = k_{B} \sqrt{T_{0} T} = 0.136 \) eV. We next determine \( U \) from \( U = e^{2}/(4 \pi e_{0} R_{0}) \), where the background dielectric constant is again taken to be \( \kappa = 1 \). The \( T \)-independent average distance \( \bar{R} \) between hopping sites can be determined from the simple formula \( n^{-1} = (4 \pi/3)(\bar{R}/2)^{3} \), where \( n \) is the carrier density given by \( n = 1/eR_{H} \), with \( R_{H} \) being the Hall coefficient. Taking \( R_{H} = 4.0 \times 10^{-14} \) cm\(^{3}\)/C for half-doped manganites, we obtain \( \bar{R}_{0} = 1.07 \times 10^{-8} \) m. The substitution of this estimated \( \bar{R} \) into the equation for \( U \) yields \( U = 0.134 \) eV, in excellent agreement with \( U = 0.136 \) eV, determined above. This result further confirms that SE-VRH model provides a consistent description of the charge transport for \( 220 \approx T \approx 300 \) K.

Next, we show that the negative magnetoresistivity \( \ln[\rho(T,H)/\rho(T,0)] \) \((i = ab, c)\) and its magnetic-field dependence observed in LaSr\(_{2}\)Mn\(_{2}\)O\(_{7}\) for \( 220 \approx T \approx 300 \) K can also be understood based on the SE-VRH model. In Altshuler, Aronov, and Khmelnitskii (AAK) localization theory, the effect of an applied magnetic field is to increase the localization length \( \xi \), which decreases the resistivity and gives rise to negative magnetoresistivity. AAK obtained the following expression for the negative magnetoresistivity in the SE-VRH regime:

\[ \ln[\rho(T,H)/\rho(T,0)] = -C \left( \frac{ea^{2}H}{\hbar c} \right)^{1/2} \ln \rho(T)/\rho_{0}, \]

where \( C \) is a positive constant and \( \nu \) is the critical index for the localization radius and conductivity in the scaling theory of the metal-insulator transition. They predicted \( \nu \approx 1/4 \) and 1 for weak and strong magnetic fields, respectively.

The magnetic-field dependence of \( \ln[\rho(T,H)/\rho(T,0)] \) for \( T \approx 220 \) K is shown in Fig. 3. The magnetoresistivities are, indeed, negative and follow a \( H^2 \) dependence in magnetic fields up to 14 T. This implies that \( \nu \approx 1/4 \) in Eq. (5). Therefore, the magnetic-field dependence of the magnetoresistivity data of LaSr\(_{2}\)Mn\(_{2}\)O\(_{7}\) is consistent with the AAK theoretical prediction of the SE-VRH for weak magnetic fields.

We also measured the temperature dependence of the resistivities at various magnetic fields. \( T_{0} \) and \( \rho_{0} \) are then determined by fitting the \( \rho_{ab} \) versus \( T \) curves in the temperature range 220 to 300 K with Eq. (2). Figure 4 shows the magnetic-field dependence of \( T_{0} \) and \( \rho_{0} \). Notice that the effect of an applied magnetic field is to decrease \( T_{0} \) and to increase \( \rho_{0} \). The former is quadratic in field; i.e., \( T_{0}(H) = T_{0}(1 - \beta H^2) \), with \( T_{0} = 0.71 \) eV and the fitting coefficient \( \beta = 4.00 \times 10^{-3} \) T\(^{-2}\). Prefactor \( \rho_{0} \) is well described by \( \rho_{0}(H) = \rho_{0}(H = 0) \exp(nH^2) \), with \( n = 6.36 \times 10^{-5} \) cm\(^{-1}\) and \( \eta = 1.21 \times 10^{-2} \) T\(^{-2}\). Therefore, the negative magnetoresistivity of this bilayer manganite is a result of the decrease of \( T_{0} \) and the increase of prefactor \( \rho_{0} \) of the SE-VRH resistivity when a magnetic field is applied. Noting that \( T_{0} \approx 1/\xi \), the application of a magnetic field, indeed, gives rise to an increase in \( \xi \). Since \( \rho_{0} \) is an increasing function of magnetic...
field, the AAK localization theory\textsuperscript{25} implies $\rho_0 \propto \xi$. This behavior can be understood within the Landauer expression\textsuperscript{26} $\rho = (2h/e^2) \xi$ by neglecting the inelastic scattering in the zero-temperature limit.

The anisotropy of magnetoresistivity in the heavily doped semiconductors has provided compelling evidence for the localization theory responsible for the negative magnetoresistivity.\textsuperscript{25,27} The anisotropy of both magnetoresistivities of LaSr$_2$Mn$_2$O$_7$ is shown in Fig. 5, which is a plot of magnetoresistivities at $T = 220$ K and in a magnetic field of 14 T. The lines are fits of the data with Eq. (6).

$$\ln \frac{\rho(T,H,\varphi)}{\rho(T,0)} = \ln \frac{\rho(T,H,0)}{\rho(T,0)} (1 + P \sin^2 \varphi)^{1/4},$$

with $\nu = 1/4$ and the only fitting parameter $P = 4.27 \times 10^{-3}$ and $2.43 \times 10^{-3}$ for the in-plane and the out-of-plane resistivity, respectively. Assuming that the current is applied along the crystallographic direction $a$, $D \parallel = 2E_F \tau 3(m^*_{a}/m_{a})$ and $D \perp = 2E_F \tau 3(m^*_{a}/m_{a})$. Since the relaxation time $\tau$ of an electron is isotropic and the components of the effective-mass tensor are almost equal along the $a$ and $b$ directions, one would expect a small difference between $D \parallel$ and $D \perp$. Thus, the small anisotropic magnetoresistivity, i.e., small $P$ value, is the result of a small difference between the in-plane diffusion coefficients.

In conclusion, we report the in-plane and the out-of-plane magnetoresistivity measurements performed on LaSr$_2$Mn$_2$O$_7$, a half-doped bilayer manganite. The resistivity clearly follows a variable-range-hopping behavior for 220 K $\leq T \leq 300$ K. However, due to this narrow-$T$ region, one cannot conclusively determine the type of hopping conduction from the resistivity data. Nevertheless, the $T$ dependence of the resistive anisotropy ($\rho_{\perp}/\rho_{ab} = A + B/T$) indicates that the hopping conduction in this $T$ range is of SE type, i.e., takes place in the presence of a Coulomb gap. The determined localization length $\xi = 56.8$ Å, average hopping energy $\Delta = 0.136$ eV, and energy of the Coulomb interaction $U = 0.134$ eV have physically reasonable values. In magnetic fields up to 14 T, magnetoresistivity $\ln[\rho(T,H,\varphi)/\rho(T,0)] (i = a,b,c)$ vs angle $\varphi$ between the applied magnetic field and the current of LaSr$_2$Mn$_2$O$_7$ measured at $T = 220$ K and in $H = 14$ T. The lines are guides to the eye.

FIG. 3. Magnetoresistivities $\ln\rho(T,H)/\rho(T,H=0)$ ($i = ab,c$) vs $H^2$ of LaSr$_2$Mn$_2$O$_7$ for various temperatures in the variable-range-hopping regime. The straight lines are guides to the eye.

FIG. 4. Magnetic field $H$ dependence of parameters $T_0$ and $\rho_0$ in Eq. (2), obtained by fitting in-plane resistivity data measured for 220 K $\leq T \leq 300$ K and at various magnetic fields of LaSr$_2$Mn$_2$O$_7$. The anisotropy of magnetoresistivity varies as $\sin^2 \varphi$ when the magnetic field is rotated in the MnO$_2$ plane, with a maximum value when $H \parallel I$ and a minimum one when $H \parallel I$. These data are well fitted with

FIG. 5. Magnetoresistivities $\ln\rho(T,H,\varphi)/\rho(T,H=0)$ ($i = ab,c$) vs angle $\varphi$ between the applied magnetic field and the current of LaSr$_2$Mn$_2$O$_7$ measured at $T = 220$ K and in $H = 14$ T. The lines are guides to the eye.
is negative and its magnitude increases proportional to $H^2$ and $\sin^2 \varphi$. These results provide convincing evidence of the SE-type variable-range-hopping conductivity in half-doped manganites.

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