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 (ρ_{ab}) and out-of-plane (ρ_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 $\ln[\rho_i(T,H,\varphi)/\rho_i(T,H=0)]$ ($i=ab,c$), where φ is the in-plane angle between the magnetic field and the current.

Since the discovery of colossal magnetoresistance in manganese oxides, much effort has been devoted to understanding their magnetic and electrical transport properties. It has been shown[1–3] that the temperature T dependence of the electrical conductivity in the paramagnetic phase is well described by Mott variable-range hopping (VRH),[4,5] that is,

$$\sigma=\sigma_0\exp\left[-\left(\frac{4\nu_c\alpha^d}{k_BN(E)T}\right)^p\right].$$ (1)

Here, $p=1/(d+1)$, with d being the dimensionality, σ_0 is a constant which depends on the assumptions made about the electron-phonon interaction, ν_c is a dimensionless constant, α is the reciprocal of the localization length ξ, 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 γ.[1] Since ξ is expected to be of the order of the Mn-Mn distance, such a small ξ is incompatible with conventional VRH and has an unphysical meaning.

In order to address this inconsistency, Viret, Ranno, and Coey[3] developed a VRH model based on the idea of magnetic localization. Although the estimated value of ξ 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.[6,7] It was suggested that the Coulomb interaction may have an important effect on the hopping conduction of electrons in manganese oxides.[8,9] 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,[10] but also the convincing candidate for the anisotropy in the orbital-ordered states.[11] 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 (ρ_{ab}) and out-of-plane (ρ_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 φ between the magnetic field and the electrical current. Both resistivities follow a VRH behavior for 220 K$\leq T\leq$300 K well. However, as shown before for the cuprates, the temperature dependence of the resistive anisotropy ρ_c/ρ_{ab} in the VRH regime is a much more effective indicator of the type of hopping than the traditional method based on Eq. (1).[12] Here, we show that $\rho_c/\rho_{ab}=A+B/T$ for 220 K$\leq T\leq$300 K, which unambiguously indicates VRH in the presence of a Coulomb gap. This hopping mechanism also accounts for the H and φ dependences of magnetoresistivities $\ln[\rho_i(T,H,\varphi)/\rho_i(T,H=0)]$ ($i=ab,c$). 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,[13] 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.[14] A total of eight low-resistance electrodes were applied on the top and bottom faces of the crystal, using thermally treated silver paint. 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 φ is defined to be 0° (90°) 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 ρ_{ab} and ρ_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
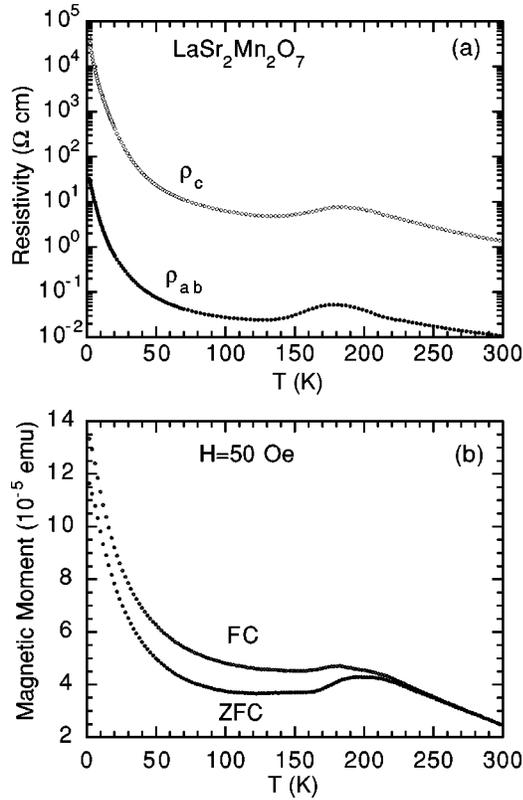
FIG. 1. Temperature dependence of (a) in-plane (ρ_{ab}) and out-of-plane (ρ_c) resistivities measured in zero field and (b) magnetization M measured both in increasing the temperature after cooling the sample in zero field to 2 K (ZFC measurement), and in decreasing the temperature in the presence of an applied magnetic field (FC measurement) of LaSr$_2$Mn$_2$O$_7$.
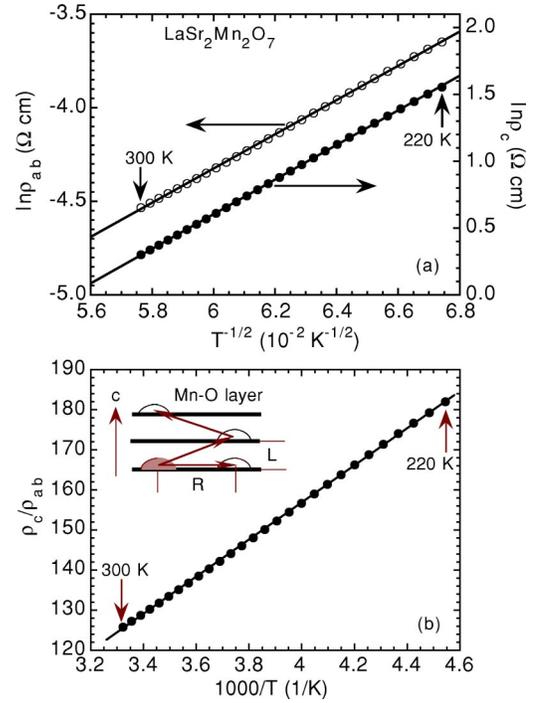

FIG. 2. (a) Semilog plot of the zero-field resistivities ρ_i ($i = ab,c$) vs $T^{-1/2}$. The straight lines are guides to the eye. (b) Resistive anisotropy ρ_c/ρ_{ab} vs 1000/T. The straight line is a linear fit of the data with Eq. (3). Inset: Hopping processes in the Mn-O bilayer and the zigzag path in the c direction.

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 $d_{3x^2-r^2}/d_{3y^2-r^2}$ 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 $T<220$ K 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[20] and would affect the charge transport. According to the SE-VRH theory,[7] the temperature dependence of the resistivity in the VRH regime is given by:

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

where ρ_0 is a constant and $T_0 = 2.8e^2/(4\pi k_B \epsilon_0 \xi)$. 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.[9]

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 ρ_c than for ρ_{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 ρ_{ab} and ρ_c, in agreement with the theory of anisotropic hopping.[7]

A plot of the resistive anisotropy ρ_c/ρ_{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:

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

with $A=-28.78$ and $B=4.64\times10^4$ K. It has been shown that the resistive anisotropy of an anisotropic material is given by:[12]

$$\frac{\rho_c}{\rho_{ab}} = \frac{1}{2}\frac{\langle R^2 P_{ab}(R)\rangle}{L^2\langle P_c(R)\rangle} \approx \frac{1}{2}\frac{\langle R^2\rangle\langle P_{ab}(R)\rangle}{L^2\langle P_c(R)\rangle}, \qquad (4)$$

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 and *fixed* transverse distance L [see inset to Fig. 2(b)]. Equation (4) reflects the experimental relationship given by Eq. (3) if $P_{ab}(R)\propto P_c(R)$. Then, $\rho_c/\rho_{ab}\propto\langle R^2\rangle/L^2$. This implies that the experimentally observed T^{-1} dependence of the anisotropy, given by Eq. (3), is a result of increasing mean-square in-plane hopping distance with decreasing temperature as $\langle R^2\rangle\propto A+BT^{-1}$ and T independent out-of-plane step L. In the SE-VRH model, the Coulomb interaction leads to an increase of the average in-plane hopping distance with decreasing temperature as $\langle R\rangle = (\xi/4)(T_0/T)^{1/2}$.[21] Thus, the T dependence of the anisotropy, given by Eq. (3) unambiguously points toward SE-VRH as the hopping conduction mechanism for 220 K$\lesssim T \lesssim$ 300 K.

On the other hand, in the case of the 2D Mott-VRH conduction, the average in-plane hopping length $\langle R\rangle \propto\xi(T_0/T)^{1/3}$,[7] which gives $\rho_c/\rho_{ab}\propto\langle R^2\rangle/L^2\propto T^{-2/3}$. Such a resistive anisotropy has been found in the insulating PrBa$_2$Cu$_3$O$_{7-\delta}$,[12] but not in the present bilayer manganite. Therefore, although the resistivity data of the present bilayer manganite can be fitted with Eq. (1) with $p=1/3$ almost as well as with $p=1/2$ (SE-VRH), the T dependence of the resistive anisotropy excludes the Mott-VRH conduction and conclusively points toward SE-VRH conduction.

Equation (3) also indicates that when one takes into account the pre-exponential factor $A+BT^{-1}$ in $\rho_c(T)$, both resistivities have the *same* exponential factor $\exp[(T_0/T)^{1/2}]$. Using this experimentally determined T_0 of 0.71 eV, we get a localization length $\xi_{ab}=56.8$ Å. This value is about 15 times larger than the Mn-Mn separation of 3.87 Å in this half-doped bilayer manganite.[14,17] Thus, the localization length obtained, based on SE-VRH conduction, is physically reasonable. Also, as discussed above, $\xi_c\equiv L\approx 4$ Å. This indicates that the charge transport in this manganite is 2D in nature, with the in-plane localization length one order of magnitude larger than the out-of-plane one. As a note, VRH theory in the presence of a Coulomb gap leads to the same temperature dependence of the resistivity [Eq. (2)] for both the 2D and the 3D cases.

For the SE-VRH model to be valid, the average hopping energy Δ should be equal to energy U of the Coulomb interaction between the sites. Δ and U can be estimated from the experimental data as follows. The transition from nearest-neighbor hopping (NNH) to SE-VRH takes place at a critical temperature T_V at which the NNH energy E_A [$\rho(T)=\rho_0\exp(E_A/k_BT)$] becomes equal to the average SE-VRH energy Δ; i.e., $\Delta\equiv E_A=k_BT(T_0/T)^{1/2}|_{T=T_V}$. The high-temperature electrical transport of bilayer manganites is usually described by nearest-neighbor thermally-activated hopping.[22,23] Also, since the resistivity data follow the SE-

VRH mechanism well, up to the highest measured temperature of 300 K, we take $T_V=300$ K as the crossover temperature from NNH for $T>300$ K to SE-VRH for $T<300$ K. With the experimentally determined $T_0=0.71$ eV, we obtain $\Delta=k_B\sqrt{T_0T_V}=0.136$ eV. We next determine U from $U\approx e^2/(4\pi\epsilon_0\overline{R_0})$, where the background dielectric constant is again taken to be $\kappa=1$. The T-independent average distance $\overline{R}_0$ between hopping sites can be determined from the simple formula $n^{-1}=(4\pi/3)(\overline{R}_0/2)^3$, where n is the carrier density given by $n=1/eR_H$, with R_H being the Hall coefficient. Taking $R_H=4.0\times10^{-4}$ cm^3/C for half-doped manganites,[24] we obtain $\overline{R}_0=1.07\times10^{-8}$ m. The substitution of this estimated $\overline{R}_0$ into the equation for U yields $U=0.134$ eV, in excellent agreement with $\Delta=0.136$ eV, determined above. This result further confirms that SE-VRH model provides a consistent description of the charge transport for $220\lesssim T\lesssim 300$ K.

Next, we show that the negative magnetoresistivity $\ln[\rho_i(T,H)/\rho_i(T,0)]$ ($i=ab,c$) and its magnetic-field dependence observed in LaSr$_2$Mn$_2$O$_7$ for 220 K$\leqslant T\leqslant$ 300 K can also be understood based on the SE-VRH model. In Altshuler, Aronov, and Khmelnitskii (AAK) localization theory,[25] the effect of an applied magnetic field is to increase the localization length ξ, which decreases the resistivity and gives rise to negative magnetoresistivity. AAK obtained the following expression for the negative magnetoresistivity in the SE-VRH regime:[25]

$$\ln\frac{\rho(T,H)}{\rho(T,0)} = -C\left(\frac{ea^2H}{\hbar c}\right)^{1/2\nu}\ln\frac{\rho(T)}{\rho_0}, \qquad (5)$$

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

The magnetic-field dependence of $\ln[\rho_i(T,H)/\rho_i(T,0)]$ ($i=ab,c$) for $T\geqslant 220$ 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 $\nu=1/4$ 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 ρ_0 are then determined by fitting the ρ_{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 ρ_0. Notice that the effect of an applied magnetic field is to decrease T_0 and to increase ρ_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 $\beta=4.00\times10^{-3}$ T^{-2}. Prefactor ρ_0 is well described by $\rho_0(H)=\rho_0\exp(\eta H^2)$, with $\rho_0=6.36\times10^{-5}\Omega$ cm and $\eta=1.21\times10^{-2}$ T^{-2}. Therefore, the negative magnetoresistivity of this bilayer manganite is a result of the decrease of T_0 and the increase of prefactor ρ_0 of the SE-VRH resistivity when a magnetic field is applied. Noting that $T_0\propto1/\xi$, the application of a magnetic field, indeed, gives rise to an increase in ξ. Since ρ_0 is an increasing function of magnetic
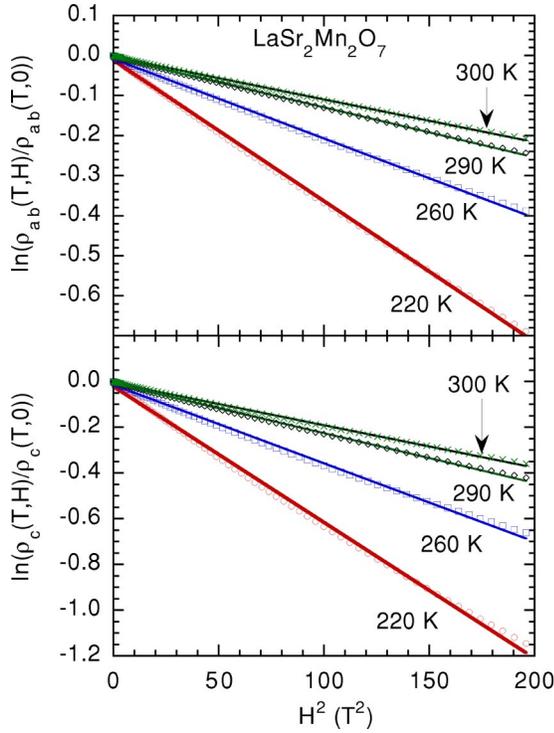
FIG. 3. Magnetoresistivities $\ln \rho_i(T,H)/\rho_i(T,H=0)$ $(i=ab,c)$ vs H^2 of LaSr$_2$Mn$_2$O$_7$ for various temperatures in the variable-range-hopping regime. The straight lines are guides to the eye.

field, the AAK localization theory[25] implies $\rho_0 \propto \xi$. This behavior can be understood within the Landauer expression[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.[25,27] The anisotropy of both magnetoresistivities of LaSr$_2$Mn$_2$O$_7$ is shown in Fig. 5, which is a plot of the in-plane and out-of-plane magnetoresistivities, measured at 220 K in a magnetic field of 14 T, versus the angle between the magnetic field and the current. Both magnetoresistivities vary as $\sin^2\varphi$ when the magnetic field is rotated in the MnO$_2$ plane, with a maximum value when $H\perp I$ and a minimum one when $H\|I$. These data are well fitted with
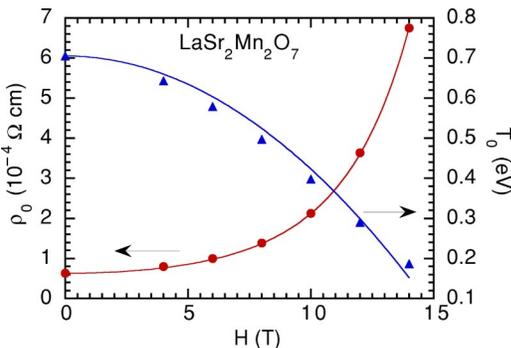

FIG. 4. Magnetic field H dependence of parameters T_0 and ρ_0 in Eq. (2), obtained by fitting in-plane resistivity data measured for 220 K $\leq T \leq$ 300 K and at various magnetic fields of LaSr$_2$Mn$_2$O$_7$.
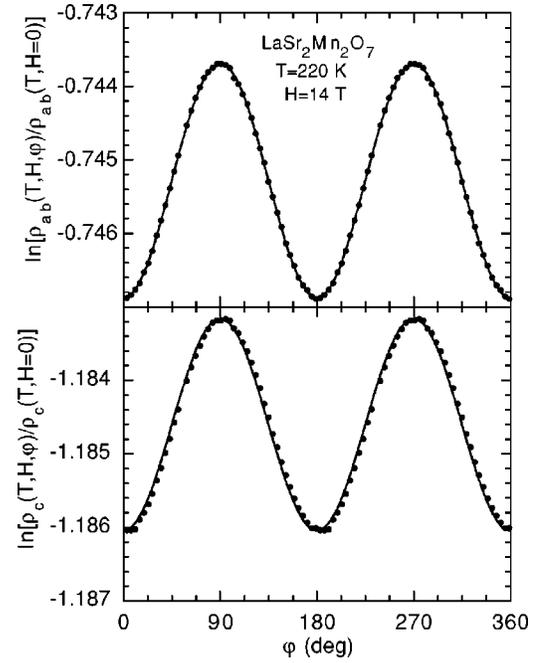

FIG. 5. Magnetoresistivities $\ln \rho_i(T,H,\varphi)/\rho_i(T,H=0)$ $(i=ab,c)$ vs angle φ between the applied magnetic field and the current of LaSr$_2$Mn$_2$O$_7$ measured at $T=220$ K and in $H=14$ T. The lines are fits of the data with Eq. (6).

$$\ln\frac{\rho(T,H,\varphi)}{\rho(T,0)} = \ln\frac{\rho(T,H,0)}{\rho(T,0)}(1+P\sin^2\varphi)^{1/4\nu}, \quad (6)$$

with $\nu=1/4$ and the only fitting parameter $P=4.27\times10^{-3}$ and 2.43×10^{-3} for the in-plane and the out-of-plane resistivity, respectively. Equation (6) is consistent with the prediction of the localization theory in the SE-VRH regime for weak magnetic fields $(\nu=1/4)$, in which $P=(D_\|-D_\perp)/D_\perp$, with $D_\|$ and $D_\perp$ being the diffusion coefficients parallel and perpendicular to the current, respectively.[25] Assuming that the current is applied along the crystallographic direction a, $D_\|=2E_F\tau/3(m_a^3/m_b^2)$ and $D_\perp=2E_F\tau/3m_b$.[27] Since the relaxation time τ 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 $D_\|$ 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 $(\rho_c/\rho_{ab}=A+B/T)$ 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 $\ln[\rho_i(T,H,\varphi)/\rho_i(T,0)]$ $(i$

$=ab,c$) 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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