Mechanism of Hopping Transport in Disordered Mott Insulators

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By using a combination of detailed experimental studies and simple theoretical arguments, we identify a novel mechanism characterizing the hopping transport in the Mott insulating phase of Ca2−xSrxRuO4 near the metal-insulator transition. The hopping exponent α shows a systematic evolution from a value of α = 1/2 deeper in the insulator to the conventional Mott value α = 1/3 closer to the transition. This behavior, which we argue to be a universal feature of disordered Mott systems close to the metal-insulator transition, is shown to reflect the gradual emergence of disorder-induced localized electronic states populating the Mott-Hubbard gap.

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The interplay of electron correlation and disorder near metal-insulator (MI) transitions represents one of the most fundamental, yet least understood, problems in contemporary condensed matter physics. For example, recent studies on manganites have revealed the emergence of coexisting clusters near the MI transition, which plays a crucial role in the mechanism for colossal magnetoresistance [1]. Similar inhomogeneities have been observed in underdoped high-Tc cuprates, where spin glass and stripe formation feature disorder effects near the MI transition [2]. Despite extensive experimental efforts [1–3], however, the effects of the intrinsic randomness on the doping/substitution in Mott transition systems remain largely an open problem, especially regarding the process of closing the Mott-Hubbard gap.

Among the Mott transition systems, the single layered ruthenate Ca2−xSrxRuO4 provides a rare case of the MI transition that is highly susceptible to chemical pressure because of strong lattice-orbital coupling [4–6]. While one end member, Sr2RuO4, is a spin-triplet superconductor [7], complete substitution of Ca ion changes the superconductor into the Mott insulator Ca2RuO4 by introducing distortions to RuO6 octahedra [8–11]. The lattice deformation in both pure and Sr substituted Ca2RuO4 stabilizes the insulating state by inducing orbital polarization (orbital order) that creates a half-filled configuration near εF [12–16]. In addition, the results by both Raman and optical conductivity measurements indicate that the superexchange coupling J and the effective bandwidth (≈√J) in the insulating region are relatively insensitive to Sr content [13,17]. Instead, the Sr substitution mainly controls the orbital polarization; the strong orbital polarization becomes gradually relaxed with substitution, but suddenly vanishes at the MI transition to stabilize the metallic state [12–16].

This system is particularly suitable for the study of disorder effects in closing of the Mott-Hubbard gap because the isovalent Sr substitution provides statistical randomness without altering the key parameters: the net carrier density and the effective bandwidth. Furthermore, the variation in other parameters that usually complicates the analysis (crystal structure, phonon dispersions, etc.) should be small since a moderate substitution of Sr (<10%) is sufficient to suppress the Mott insulating state.

This Letter presents the study of the effects of intrinsic randomness due to Sr substitution on the MI transition in Ca2−xSrxRuO4. In this system, a well-defined Mott insulator appears at low Ts by the first-order MI transition in 0 ≤ x < 0.2. In the insulating phase, a systematic change in the transport and thermodynamic properties is observed, which elucidates the evolution of strongly localized states in closing the Mott-Hubbard gap. Furthermore, these localized states most likely reflect the tendency to spontaneously form inhomogeneities due to nanoscale phase separation in the vicinity of the Mott transition [1,2]. Our analysis reveals that this situation gives rise to a novel mechanism for hopping transport, unique to insulating phases of strongly correlated systems with moderate disorder.

Experiment. Single crystals of Ca2−xSrxRuO4 were prepared using a floating zone method [18]. X-ray powder diffraction show single phase samples without chemical segregation. Thus, Ca-Sr mixture provides a statistical disorder that prohibits classical percolation effects. Resistivity was measured by a standard four-probe dc technique. Magnetization was measured with a commercial SQUID magnetometer. Specific heat was measured by a thermal relaxation method.

Figure 1(a) presents the T-dependence of the in-plane resistivity ρ∥(T) measured on cooling. While Ca2RuO4 is a Mott insulator at low T and exhibits a MI transition above 300 K [8–11], slight Sr substitution dramatically decreases the MI transition temperature TM−1 to below 300 K. The transition is clearly seen by an abrupt increase of ρ∥ by a factor of 104. This change at TM−1 involves large thermal hysteresis, indicating that the MI transition
is first-order. This is due to the first-order structural transition that occurs simultaneously with the MI transition [5]. Reflecting the quasi-2D electronic structure, the anisotropy \( \rho_{ab}(T)/\rho_{ab}(T) \) in the insulating phase reaches the value of the order of \( 10^3 \) to \( 10^4 \) (not shown). As illustrated in Fig. 1(a) and 1(b), \( \rho_{ab} \) in the metallic phase and \( T_{M-1} \) both rapidly decrease with \( x \), and the system becomes fully metallic at \( x = 0.2 \).

In the insulating phase, an antiferromagnetic (AF) ordering appears as in \( \text{Ca}_2\text{RuO}_4 \). Figure 2 shows the \( T \) dependence of the in-plane component of the susceptibility \( \chi(T) \) measured in a field-cooled sequence. The distinct increase in \( \chi(T) \) at low \( T \) arises from canted AF, as clarified by neutron diffraction measurements [5]. The AF transitions are different in nature in the following two regions: in \( 0 \leq x < 0.1 \), the AF ordering occurs at \( T < T_{M-1} \) without any hysteresis, while in \( 0.1 \leq x \leq 0.15 \), it coincides with the MI transition. In fact, for \( x = 0.06 \) and 0.09, the MI transition is reflected in the susceptibility hysteresis in the paramagnetic state (see the inset I of Fig. 2). The decrease of the paramagnetic \( \chi \) at \( T_{M-1} \) is attributable to the disappearance of Pauli component in the insulating phase. However, at \( x = 0.15 \), a large hysteresis is observed at \( T_{AF} \), indicating that both MI and AF transitions at \( x = 0.15 \) occurs concomitantly with the first-order structural transition.

Here, we note two important facts that confirm the Mott insulating ground state in \( 0 \leq x < 0.2 \). First, the AF ordering occurs only in the insulating phase. Second, \( \rho(T) \) does not show any anomaly at \( T_{AF} \) for \( x = 0.06 \) and 0.09. These facts agree well with the significant feature of Mott insulators: the separation between charge and spin degrees of freedom due to a large charge (Mott-Hubbard) gap compared to low energy spin excitations.

**Observation of hopping transport.** In order to elucidate the electronic state in the insulating phase, we analyze \( \rho_{ab}(T) \) shown in Fig. 1(a). The result of \( \text{Ca}_2\text{RuO}_4 \) (\( x = 0 \)) fits well to activation-type insulating behavior

\[
\rho_{ab}(T) = A \exp(E_G/2k_BT)
\]

below \( 250 \) K to the lowest \( T \) measured, giving \( E_G \approx 4500 \) K, consistent with the gap observed by the optical conductivity measurements [14,19]. Since \( \text{Ca}_2\text{RuO}_4 \) is a Mott insulator, \( E_G \) should give the gap size between the upper and lower Hubbard bands (UHB and LHB).

Variable-range hopping (VRH) conduction

\[
\rho_{ab}(T) = A \exp(T_0/T)^\alpha
\]

with \( \alpha = 1/2 \) also describes the \( T \) dependence over almost the same \( T \) region in agreement with Ref. [10]. VRH is usually observed in systems with strongly localized states near \( \varepsilon_F \). However, fitting of the resistivity in a limited region alone does not give conclusive evidence for the presence of localized electronic states. In the case of \( \text{Ca}_2\text{RuO}_4 \), we measured the specific heat \( C_p(T) \) and found the electronic specific heat coefficient \( \gamma \) to be \( 0 \pm 0.5 \) mJ/molK², as shown in the inset II of Fig. 2. Most likely there are no localized states near \( \varepsilon_F \) and activation-type behavior is the consistent interpretation of the low \( T \) transport in \( \text{Ca}_2\text{RuO}_4 \).

To obtain the systematic estimate of \( E_G \), we also try to fit the \( \rho(T) \) curve for each \( x \) to Eq. (1). However, the well fitted region becomes rapidly narrower with \( x \), indicating that the Sr substituted region does not obey activated behavior. In contrast, as in Fig. 3(a), the VRH widely describes the insulating behavior. Equation (2) with \( \alpha = 1/2 \) describes \( \rho_{ab}(T) \) for \( x = 0.06 \) and 0.09 over a respectable temperature range: 236 K–150 K (\( x = 0 \)), 155 K–46 K (0.06), 152 K–14.0 K (0.09), and 21 K–7.3 K (0.15). It should be noted that \( \rho_{ab}(T) \) obeys VRH with \( \alpha = 1/2 \) over a decade of \( T \) for \( x = 0.09 \) and over a comparable range for \( x = 0.06 \). The \( x \) dependence of the fitting pa-
obtained with a smaller value of the exponent $\gamma$. This fit gives $\rho_\text{ab}(T)$ not to follow Eq. (2) well with $x = 0.15$ and the upper axis $T > 10^3 \text{K}$. Inset I: $T_0$ obtained by fitting of $\rho(T)$ to Eq. (2) with $\alpha = 1/2$ for $\text{Ca}_2\text{SrRuO}_4$ (solid circle) as a function of $x$ (lower axis), and for theory (open circle) as a function of $W$ (upper axis). Inset II: Model band structure used in our calculation. As the disorder increases ($\text{WaN} 0.02 \text{eV} \rightarrow 0.16 \text{eV}$), the band-tails gradually fill in the Mott gap, producing a soft gap similar to that predicted by Efros and Shklovskii, but on a much larger energy scale.

For the highest Sr concentration $x = 0.15$, $\rho_\text{ab}(T)$ does not follow Eq. (2) well with $\alpha = 1/2$, but better fits are obtained with a smaller value of the exponent $\alpha = 1/3$ over a decade of $T$ (5 K–65 K), as shown in Fig. 3(a). The fit gives $T_0 = 8.8 \times 10^3 \text{K}$. This value of the hopping exponent $\alpha$ is consistent with two-dimensional (2D) transport, within the Mott VRH picture [20]. Because our system has essentially a quasi 2D electronic structure with large anisotropy $\rho_\text{c}/\rho_\text{ab} = 10^3$ in the insulating phase, 2D hopping seems a natural choice.

**Origin of hopping transport.** Generally, in the process of carrier doping in conventional semiconductors such as Si and Ge, the evolution of the transport behavior from simple activation to Efros-Shklovskii (ES) VRH (Eq. (2) with $\alpha = 1/2$) and finally to Mott VRH has been observed, as the localized states fill in the band gap [21]. The Mott VRH, observed at $x = 0.15$ for a decade of $T$, usually appears when the system has a localized band with a nearly constant density of states (DOS) $\nu(e)$ around $E_F$. The low temperature $C_\text{p}/T$ for $x = 0.15$ is well described by $\gamma + \beta T^2$ with the same Debye temperature $\Theta_D = 410 \text{K}$ as $\text{Ca}_2\text{RuO}_4$ (411 K) and $\text{Sr}_2\text{RuO}_4$ (410 K) (inset II of Fig. 2). The electronic contribution $\gamma$ is about $1.5 \pm 0.5 \text{mJ/molK}^2$. The extra entropy release of $0.36 \text{J/mol K}$ due to the increase in $C_\text{p}/T$ below 14 K is much smaller than $R\ln3 = 9.13 \text{J/mol K}$ expected for $S = 1$ moment at each Ru site, and is attributable to the freezing of the uncorrelated spins induced by disorder. Therefore, the $\gamma$ value above should give an appropriate estimate of $\nu(e_F)$ at $T > 14 \text{K}$. For 2D Mott VRH, the localization length $\xi$ can be estimated using the formula $k_B T_0 \approx 8.6/\nu(e_F) \xi^2 d$, where $d$ is interlayer spacing. Our results yield a reasonable value of $\xi = 25 \text{Å}$, that is several times the Ru-Ru interatomic spacing (~3.8 Å).

In contrast, ES VRH usually appears when the long-range Coulomb interaction between localized electrons is important, forming the so-called Coulomb gap (CG) with $\nu(e) \propto |e - e_F|$ in 2D [21]. This leads to VRH with $\alpha = 1/2$ and $k_B T_0 \approx e^2/\kappa \xi$, where $\kappa$ is a dielectric constant. However, $T_0$ observed in our system (inset I of Fig. 3(b)) is too large for long-range Coulomb interaction. In fact, assuming $\kappa = 100$ as in $\text{Ca}_2\text{RuO}_4$ [10], we obtain $\xi$ of the order of 0.03 Å for $x = 0.06$, which is not physically meaningful. Correspondingly, the energy scale of fitting regions ($T \approx 150 \text{K}$) is also much too high in comparison with the ordinary size of CG (10–100 K) [21]. It is therefore unlikely that the emergence of the Coulomb gap is the physical origin of the apparent ES-like behavior.

What could then lie at the origin of the observed VRH with $\alpha = 1/2$? To answer this question, we note that the gap-type structure in the DOS is essential for the exponent $\alpha = 1/2$. The standard Mott VRH picture assumes an energy-independent DOS, leading to a small hopping exponent $\alpha = 1/3$ in 2D, while the formation of the CG gives a strongly energy-dependent DOS, which in turn produces a larger hopping exponent $\alpha = 1/2$. However, we have seen that the CG is too small to account for our observations. Instead, given the large energy scale of both the fitting region and $T_0$, the energy gap has to be $0.1 \rightarrow 1 \text{eV}$, which actually fits well in the range of the Mott gap. Since the insulating phase of our system is a Mott insulator, we propose that the disorder-modified Mott gap lies at the origin of the VRH with $\alpha = 1/2$, as a new mechanism distinct from the ES scenario.

Materials near a first-order transition separating two competing ground states are generally fragile against phase separation; moderate randomness can create coexisting clusters of competing ordered states [1]. In our case, the first-order MI transition separates the Mott insulating phase and the paramagnetic metallic phase. The statistical distribution of Ca-Sr inevitably creates (although small) the locally Sr-rich region with a broader local bandwidth. This statistical distribution of the local bandwidth should create extended tails of both UHB and LHB at their edges, which are easily localized. As the system approaches the metallic phase, the band-tails extend...
deeper into the Fermi level region by enhancing their DOS. Finally, for large enough $x$(Sr), these tails are expected to overlap and produce strongly localized states near $e_F$. As the intrinsic disorder steadily increases, we thus expect the behavior to gradually cross over from activated, to ES-like VRH, and finally to Mott-like VRH. This is exactly what is observed in our experiment.

Theory: To put these physical ideas on a more rigorous basis, we now present a simple theoretical model for hopping transport in disordered Mott insulators. First, we generalize the arguments of Mott [20] and Efros-Shklovskii [21] to a situation where the DOS has an arbitrary energy dependence. According to these approaches, the transition probability is

$$\sigma = \sigma_o \exp\left(-2R/\xi - \epsilon_o(R)/k_B T\right).$$  \hspace{1cm} (3)

where $\sigma_o$ is an “attempt frequency,” $R$ is the distance between the two sites, $\epsilon_o(R)$ is their energy difference, and $\xi$ is the localization length. The further the sites are from each other, the smaller the wave function overlap between the two states. However, sites with small energy difference are typically more distant from each other. The lowest energy $\epsilon_o(R)$ of the accessible state within a radius $R$ from a given site is implicitly given (in 2D) by the solution of

$$1 = \pi R^2 H[\epsilon_o(R)],$$  \hspace{1cm} (4)

where $H(\epsilon) = \int_0^\epsilon \nu(\epsilon')d\epsilon'$. At any given temperature, the most probable hopping distance $R$ is determined by minimizing the exponent of Eq. (3), giving

$$\frac{1}{\xi} = \frac{[\pi H(\epsilon_o)]^{3/2}}{\pi \nu(\epsilon_o) k_B T}.$$  \hspace{1cm} (5)

The solution of these equations determines $R(T)$ and thus $\epsilon_o(T)$, which should be substituted in Eq. (3) to obtain the desired $T$-dependent resistivity $\rho(T) \sim 1/\sigma$. For the special cases of constant or linear forms for $\nu(\epsilon)$, these equations can be solved analytically, reproducing the respective Mott ($\alpha = 1/3$) or ES ($\alpha = 1/2$) hopping laws. In our case, $\nu(\epsilon)$ assumes a more complex form, and a numerical solution is necessary. Given our fortuitous situation where the Sr substitution does not make significant change in net carrier density nor effective bandwidth, we chose a simple model for $\nu(\epsilon)$. Specifically, we take the UHB and LHB to have constant DOS and bandwidth of 1 eV, with a gap of 0.4 eV, and $\xi = 28$ Å, which corresponds to our material. The effect of disorder is described by introducing Gaussian band-tails of width $W$, which tend to gradually fill in the gap, as shown in the inset II of Fig. 3(b). We examine the evolution of $\rho(T)$ and the fitting parameter $T_0$ to VRH with the exponent $\alpha = 1/2$, as a function of $W$. The theoretical results are presented in Fig. 3(b) for $\rho(T)$ in the same fashion as in Fig. 3(a), and in the inset I of Fig. 3(b) for $T_0(W)$. The theory is able to reproduce all the qualitative and even some quantitative aspect of the experimental data for both $\rho(T)$ and $T_0$, giving strong support to the proposed physical picture.

In summary, detailed analysis of the Mott insulating phase in Ca$_2$-xSr$_x$RuO$_4$ reveals that the Sr substitution to Ca$_2$RuO$_4$ changes transport from the activation-type to the variable-range-hopping. The moderate randomness intrinsic to the Sr substitution leads to the formation of strongly localized states around the closing of the Mott-Hubbard gap. As a result, hopping transport emerges of the form similar to that predicted by Efros and Shklovskii but with a distinctly different physical origin and on a distinctly different energy scale.

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