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## Variable-range hopping of small polarons in mixed-valence manganites

Young Sun, Xiaojun Xu and Yuheng Zhang

Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China

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**Abstract.** Mixed-valence manganites  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  exhibit complicated transport behaviour resulting from complex interplays among charge, spin and lattice. In the paramagnetic phase, the carriers are trapped in localized states as small polarons due to the incorporation of three different localization features: (i) strong electron–phonon interaction, (ii) the variations in the Coulomb potential due to the presence of  $\text{Ln}^{3+}$  and  $\text{A}^{2+}$  ions in the lattice, (iii) the magnetic localization due to spin disorder on the interatomic scale. When the thermal energy is not enough for small polarons to hop between nearest-neighbour sites, the transport of small polarons could be accomplished by two steps: first, the small polaron is thermally activated into an intermediate state in which the carrier is weakly localized; then it feels the potential fluctuation due to an electrical and magnetic disorder and transports by variable-range hopping. We term this kind of transport process as variable-range hopping of small polarons, and derive the expression of resistivity as  $\rho = BT \exp[E_a/kT + (T_0/T)^{\frac{1}{4}}]$ .

### 1. Introduction

The  $(\text{Ln}_{1-x}\text{A}_x)\text{MnO}_3$  mixed-valence manganites, where Ln is a rare earth ion and A represents a divalent alkaline earth ion such as Ca, Sr, Ba, have attracted considerable attention due to the colossal magnetoresistance (CMR) effect as well as substantial physics content [1]. Because of the incorporation of variable interplays among charge, spin and lattice, these compounds exhibit complex transport behaviour and offer an unusual research opportunity for condensed matter physics. Many recent experimental results, including thermopower measurements [2], microscopic techniques [3] and isotopic effects [4], have provided strong evidence to suggest the presence of small polarons in the paramagnetic phase. Furthermore, a crossover from itinerant large polarons to localized small polarons was proposed to interpret the metal–insulator transition associated with the ferromagnetic–paramagnetic transition [5, 6]. Although it is becoming generally recognized that the presence of small polarons plays a key role in the peculiar transport properties for mixed-valence manganites [7–9], the true nature and the exact transport process of small polarons is still under discussion.

The transport mechanism in the paramagnetic phase for mixed-valence manganites is attractive but still controversial. At present, three models are mainly discussed: (i) the band-gap model,  $\rho = \rho_0 \exp(E_a/kT)$ , (ii) the adiabatic nearest-neighbour hopping model of small polarons,  $\rho = AT \exp(E_a/kT)$ , and (iii) the variable-range hopping (VRH) model,  $\rho = \rho_0 \exp(T_0/T)^{\frac{1}{4}}$ . For each model, some experimental support can be found in the literature. Since small polarons exist in the paramagnetic phase, it seems natural to adopt a small polaron model to describe the resistivity. However, this does not mean that the present adiabatic

nearest-neighbour hopping model of small polarons (Holstein theory) is a sufficient candidate for mixed-valence manganites.

The Holstein theory of small polaron motion [10], which is based on the molecular-crystal model, was originally proposed for an ordered situation in which all the lattice sites are energetically equivalent. In addition, this theory assumes that the coupling strength of electron–lattice interaction is the same for the charge carrier (electron or hole) residing on every lattice site. The expression of resistivity in this theory is calculated in a two-dimensional lattice assuming a dilute, non-interacting gas of polarons, i.e. neglecting the polaron–polaron interaction. However, these preconditions are not satisfied in the mixed-valence manganites due to the severe electrical and magnetic disorder induced by ion doping. Moreover, some authors have also emphasized the importance of polaron–polaron interaction [11] and deduced the non-nearest-neighbour hopping of small polarons from the Hall-effect sign anomaly [12]. The case for mixed-valence manganites is actually that the small polarons live in complex disordered systems so that the transport behaviour is not simply nearest-neighbour hopping. In this paper, referring to previous classical work by several authors [10, 16, 17], we propose a new model of small polaron hopping, termed as the VRH of small polarons, to fulfill the peculiar localization features in mixed-valence manganites.

## 2. Peculiar localization features in mixed-valence manganites

Since the carriers are localized as small polarons in the paramagnetic phase, the localization features in mixed-valence manganites determine not only the true nature of the polarons but also their transport behaviour. Therefore, it is crucial to fully understand the mechanism for carrier localization in these compounds.

Generally, the localization of carriers in mixed-valence manganites has three distinct features.

- (1) Strong electron–phonon coupling. Three different kinds of lattice distortion could contribute to the electron–phonon coupling: (i) Jahn–Teller (J–T) distortion. Because the  $\text{Mn}^{3+}$  ion is J–T type, a local J–T distortion of the oxygen octahedron surrounding the Mn ion can lower the energy of the outermost  $e_g$  electron, (ii) breathing-type distortion due to the presence of formally two different valence states,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  [13], (iii) distortion from the A-site cation size mismatch. In a sum of the above three sources, the electron–phonon coupling in mixed-valence manganites can be very strong, consequently, the carriers may be localized in the form of small polarons when the bare bandwidth is narrow enough. Extensive studies have shown that this electron–phonon interaction is strong enough to localize the carriers as small polarons, and it should be the main localization feature in mixed-valence manganites [13].
- (2) The variations in the Coulomb potential due to the presence of trivalent  $\text{Ln}^{3+}$  and divalent  $\text{A}^{2+}$  ions in the lattice, which might be comparable to the one-electron bandwidth, leading to Anderson localization [14].
- (3) The magnetic localization due to spin disorder on the interatomic scale ( $\sim 1$  nm) in the paramagnetic phase. The carriers can be trapped in locally ferromagnetic regions when the overall ferromagnetic order is not perfectly collinear above  $T_c$  [14, 15].

Additionally, for polycrystalline samples, the grain boundaries also act as potential barriers and contribute to the localization of carriers. Corresponding to the above localization features, there are two distinctive localization lengths. For feature (1), the carriers are localized as small polarons with a scale of about Mn–O bond length  $\sim 2$  Å [5]. For features (2) and (3), the localization is relatively weaker so that the carriers may be localized within a wavepacket

covering several lattice parameters and their combination will lead to the formation of a mobility edge [14, 16].

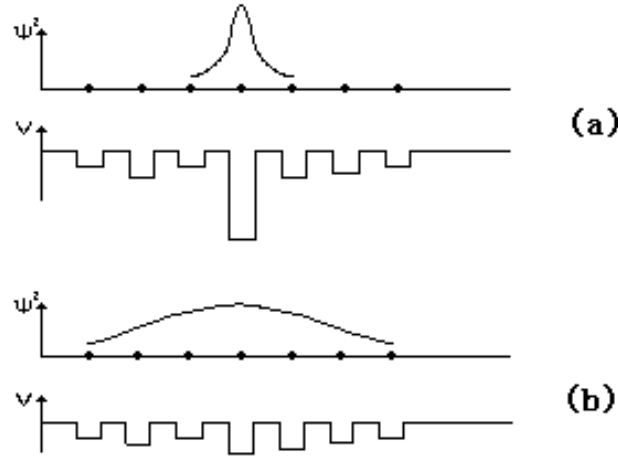
In the absence of feature (1) (or if it is weak), i.e. features (2) and (3) are the dominating localization mechanisms, the carriers are no longer localized as small polarons but as ‘large-spin polarons’, and the conduction is expected through VRH. This view was proposed and discussed by Coey *et al* [14]. However, the localization lengths  $1/\alpha$  estimated by Coey *et al* are much smaller than expected. This problem implies that the electron–phonon coupling should not be considered as a minor localization factor. Below, we demonstrate that the transport process could be a novel form of VRH (VRH of small polarons) if one considers both the strong electron–phonon coupling and the disorder and magnetic localization in mixed-valence manganites.

### 3. VRH of small polarons

Originally, the VRH theory was developed to explain electrical transport in doped semiconductors, where electrons with wavefunctions  $\psi = \psi_0 \exp(-\alpha r)$  are localized by potential fluctuations associated with the dopant [16, 17].  $1/\alpha$  is the localization length. Electrons can hop from site to site with phonon assistance. When the thermal energy is not great enough to allow electrons to hop to their nearest neighbours, it is more favourable for the electrons to hop further to find a site with a smaller potential difference. Thus, variable-range hopping occurs. But, if the electrons are deeply trapped as small polarons, the thermal energy is not sufficient for an electron to overcome the deep potential well and hop out of its site, while it is more likely to be activated into an intermediate state first, which is still a localized state but with higher energy. Then, the thermal energy is enough for the electron to hop out from the intermediate state to either nearest-neighbour sites or further sites. For the former case, i.e. hopping to nearest-neighbour sites, it can be considered as multi-phonon assisted nearest-neighbour hopping. For the latter case, the hopping is non-nearest-neighbour, which may be termed as variable-range hopping of small polarons because the carrier, in both the initial and the final state, is localized as small polarons. We think it could be the dominating transport mechanism in the paramagnetic phase of mixed-valence manganites, at least for some chemical compositions and certain temperature ranges, because of their peculiar localization features.

In this model, the transport of a small polaron in mixed-valence manganites is accomplished by two steps. First, the self-trapped small polaron is thermally activated into an intermediate state; then it experiences the random potential fluctuation due to localization features (2) and (3), and hops to a proper site with a small energy difference. Figure 1 illustrates the electron localization and wavepacket in the initial and intermediate states, respectively. It is well known that the case of the small polaron is realized when the electronic bandwidth  $2J$  is small compared to the binding energy of the small polaron. The role of the first step is just to reduce the small polaron binding energy, which is mainly caused by electron–phonon coupling, so that the small polaron upgrades into an extended wavepacket, regarded as ‘large spin polarons’ by Coey *et al*. Then, the electrons hop or tunnel across the surface barriers between one wavepacket and the next. It is apparent that this process involves multi-phonons.

Now, we derive the expression of resistivity for the variable-range hopping model of small polarons. In the initial state, the electron is well localized with the wavefunction  $\psi = \psi_0 \exp(-\alpha_0 r)$ . The localization length  $1/\alpha_0$  is less than the lattice parameter  $a$ . The probability for the electron to be activated into an intermediate state is  $P = \nu_0 \exp(-E_1/kT)$ , where  $\nu_0$  is the characteristic frequency of phonons and  $E_1$  is the energy difference between the initial and intermediate states. The electron in the intermediate state is weakly localized so



**Figure 1.** Illustration of the localization of electron wavepacket in (a) the initial state and (b) the intermediate state, for mixed-valence manganites.

that the wavefunction becomes  $\psi = \psi_0 \exp(-\alpha r)$ ,  $1/\alpha > 1/\alpha_0$ . Then, the hopping rate for the electron to a site at a distance  $R$  is  $\gamma = \gamma_0 \exp(-2\alpha R - \Delta E/kT)$ , where  $\gamma_0$  is a constant,  $R$  is the distance between the end and original sites and  $\Delta E$  is the potential energy difference between the final and intermediate states. As Mott discussed [16, 17], there is competition between the potential energy difference and the distance an electron can hop. This is reflected by the relation

$$\frac{4\pi}{3}R^3 \int_{\mu}^{\mu+\Delta E} N(E)d(E) = 1 \quad (1)$$

which represents the condition that on average one pair of sites with an energy difference in the interval 0 to  $\Delta E$  is present in the volume  $(4\pi/3)R^3$ . Assuming that the density of states  $N(E)$  depends only weakly on  $E$  near the Fermi level, one may express  $\Delta E$  by  $R$ ,  $\Delta E = [(\frac{4}{3}\pi R^3 N(E))]^{-1}$ . Therefore, by maximizing the exponential in the expression of  $\gamma$ , one finds  $R = [9/8\pi\alpha N(E)kT]^{1/4}$ . Substituting this value in  $\gamma$ , we eventually get,

$$\gamma = \gamma_0 \exp\{-2.06[\alpha^3/N(E)kT]^{1/4}\} \equiv \gamma_0 \exp[-(T_0/T)^{1/4}] \quad (2)$$

where  $kT_0 = 18\alpha^3/N(E)$ . Thus, the total hopping rate from the initial to the final state reads:

$$\Gamma = P \times \gamma = v_0 \exp(-E_1/kT) \times \gamma_0 \exp[-(T_0/T)^{1/4}]. \quad (3)$$

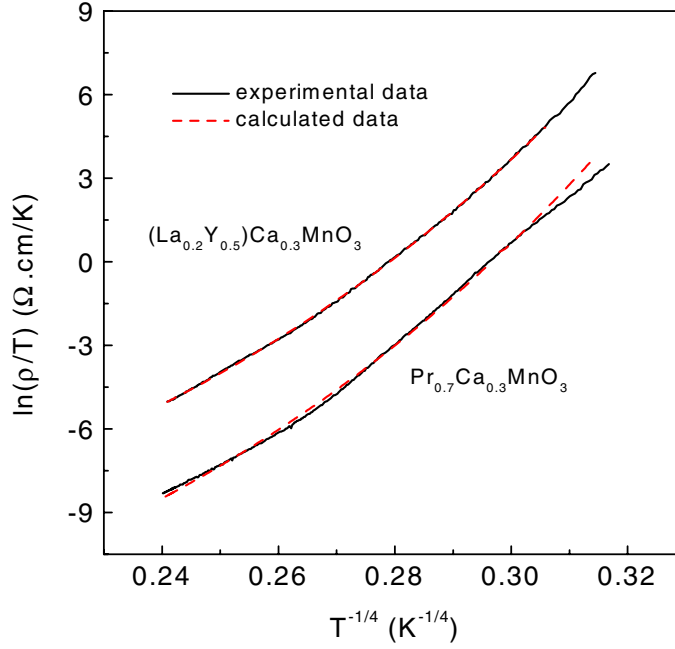
Hence, the expression for the resistivity ( $\rho \propto kT/q^2\Gamma$ ) is

$$\rho = BT \exp[E_1/kT + (T_0/T)^{1/4}]. \quad (4)$$

To examine this model, we apply it to the resistivity data of some typical mixed-valence manganites. In figure 2, we depict the fitting results for two representative manganites. The obtained fitting parameters are summarized in table 1. By taking the electronic density of states from low-temperature heat capacity measurements by Coey *et al*,  $N(E_F) \approx 4 \times 10^{28} \text{ m}^{-3} \text{ eV}^{-1}$ , we deduced the localization lengths  $1/\alpha$  in the intermediate state (see table 1).

**Table 1.** Parameters from the variable-range hopping model of small polaron for some mixed-valence manganites.

Samples	$E_1$ (meV)	$T_0$ (K)	$1/\alpha$ (Å)	$T^*$ (K)
$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$	76	$7.16 \times 10^3$	9.0	143
$\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$	78	$2.07 \times 10^4$	6.3	420
$\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	95	$1.46 \times 10^4$	7.1	300
$\text{Nd}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$	82	$3.74 \times 10^6$	1.1	$7.8 \times 10^4$
$(\text{La}_{0.75}\text{Gd}_{0.25})_{0.67}\text{Ca}_{0.33}\text{MnO}_3$	115	$1.26 \times 10^4$	7.4	260
$(\text{La}_{0.2}\text{Y}_{0.5})\text{Ca}_{0.3}\text{MnO}_3$	67	$2.14 \times 10^4$	6.2	440
$\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$	78	$2.29 \times 10^4$	—	—

**Figure 2.**  $\ln(\rho/T)$  Vs  $T^{-1/4}$  for two representative mixed-valence manganites. The solid lines are the experimental result. The dashed lines are the fitting curves by our model.

These values are compatible with variable-range hopping associated with Anderson localization. For further identification, we also estimated the maximum temperature  $T^*$  which VRH holds, by using the well known condition that the minimum hopping distance should be larger than the localization length in the intermediate state,  $R_m = [9/8\pi\alpha N(E)kT]^{1/4} \geq 1/\alpha$ . For  $\text{R}_{0.7}\text{A}_{0.3}\text{MnO}_3$  composition, the estimated value of  $T^*$  is about 480 K when the localization length is 6 Å, and 143 K when the localization length is 9 Å. Since the effective temperature range of the variable-range hopping of small polarons should be below  $T^*$ , these results indicate that our model is more applicable for those manganites with a low Curie temperature rather than those with a high Curie temperature. Moreover, we noticed that our model is reasonable for the La-site doped (such as by Gd or Y) manganites in which the degree of disorder is enhanced and consequently makes variable range hopping of small polarons more likely. From the above examinations, we can conclude that the variable-range hopping model of small polarons is reasonable for some mixed-valence manganites within certain temperature ranges.

#### 4. Conclusions

In conclusion, the peculiar localization features in mixed-valence manganites are discussed in detail. With this discussion, we suggest that the transport of small polarons in the paramagnetic phase could be accomplished by two steps. First, the small polaron is thermally activated into an intermediate state; then it feels the random potential fluctuation due to either electrical or magnetic disorder, and hops to a proper site with a small energy difference. We term this kind of transport of small polarons as variable-range hopping of small polarons. The deduced localization lengths in the intermediate state for some typical manganites are reasonable, and consequently implies the validity of our model for some mixed-valence manganites.

#### 5. Acknowledgments

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