

Comment on “Evidence for the immobile bipolaron formation in the paramagnetic state of the magnetoresistive manganites”

Aritra Banerjee,^{1,*} S. Bhattacharya,¹ S. Mollah,^{2,3} H. Sakata,⁴ H. D. Yang,² and B. K. Chaudhuri^{1,2,†}

¹*Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700 032, India*

²*Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China*

³*Department of Physics, Aligarh Muslim University, Aligarh-202 002, India*

⁴*Department of Applied Chemistry, School of Engineering, Tokai University, Hiratsuka, Kanagawa 259-1292, Japan*

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Recently, Zhao *et al.* [Phys. Rev. B **62**, R11 949 (2000)] reported that bipolarons are formed in the high-temperature paramagnetic phase (above the metal-insulator transition temperature T_p) in oxygen-isotope-diffused epitaxial thin films of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ and $\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$. But many earlier observations indicated the formation of small polarons in the said temperature range in different manganites. We have confirmed that the transport properties in the high-temperature phase ($T > T_p$) of the above manganites can be well explained by a small-polaron hopping mechanism and the consideration of bipolaron formation is inadequate. We have presented an explanation of the O-isotope effect on the transport properties of the same manganite sample studies by Zhao *et al.*

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The electrical resistivity (ρ) is directly related to the double-exchange (DE) mechanism¹ between the parallel spins of neighboring Mn ions by the arbitration of O ions in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ manganites. However, the conduction mechanism in these mixed valence materials is a complex interplay between magnetic spin, charge ordering, and structural change.² On the other hand, the DE mechanism alone cannot explain the resistivity³ and small polarons play a major role in the conduction mechanism in the high-temperature ($T > T_p$) regime.^{4,5} Hall effect study also indicated small polarons in manganites.⁶ But some of the research groups reported in favor of the formation of large polarons or bipolarons to explain the high-temperature ($T > T_p$) conductivity.⁷ Zhao *et al.*⁸ have studied the oxygen isotope effect on the resistivity of epitaxial thin films of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ (LCMO) and $\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ (NSMO) grown on $\langle 100 \rangle$ LaAlO_3 single-crystal substrates by the laser deposition technique, while the thermoelectric power (TEP) measurements were carried out on isotope-dependent LCMO ceramic pellets. These authors⁸ concluded that small polarons formed localized immobile bound pairs (bipolarons) in the high-temperature ($T > T_p$) paramagnetic (PM) phase. The same authors also argued that the coexistence of small polarons and bipolarons in the PM state might lead to a dynamic phase separation into the insulating antiferromagnetically coupled region where the bipolarons resided and the ferromagnetically coupled region where the small polarons sat. But it is to be pointed out that the use of the bipolaron (BP) model is not possible in the present system. Bipolarons are formed in a system when two different defect centers (site) are responsible for the localization of charge carriers.^{9–11} In turn, this implies the charge carriers to be two electrons in association and the BP hopping model assumes that carrier motion occurs by means of hopping over the potential barrier separating these two defect sites.¹² The Coulombic correlation between these charged defect centers results in a correlation between the barrier height and the intersite separation, and thus the bipolaron hopping model is

intimately linked with the correlated barrier-hopping- (CBH) type mechanism.¹³ From recent work on the $\text{La}_{0.7}\text{Ca}_{(0.3-y)}\text{Na}_y\text{MnO}_3$ ($y = 0.0-0.3$) series of samples⁴ and similar other works on La-Ca-Mn-O,⁵ we find that small-polaron theory can very well explain the conductivity and TEP data in the high-temperature ($T > T_p$) PM phase. Actually the existence of BP's is mainly observed in strongly correlated electron systems of highly disordered materials like semiconducting glasses, chalcogenide glasses, polymers, etc. The CBH mechanism was first used by Pike to explain the frequency-dependent (ac) conduction in scandium oxide.¹³ Later application of the BP hopping model was proposed by Elliot to explain the ac conductivity of chalcogenide glasses.^{11,12} Pramanik *et al.* applied the CBH mechanism in the case of chalcogenide films.¹⁴ Further, recently Brahma *et al.* also used the BP hopping mechanism in polycrystalline-antimony-oxide-doped barium hexaferrites.¹⁵ This is quite justified since in the said system two different groups of ions ($\text{Sb}^{3+}/\text{Sb}^{5+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$) coexist, which are responsible for the creation of two different types of defect centers.¹⁵ But the colossal magnetoresistive (CMR) manganites of present interest are not so much highly disordered material as indicated by small electron-phonon (el-ph) coupling constant compared to the usual amorphous/disordered oxide semiconductors. Again, in the manganite system, lattice distortion arises due to the localization of the e_g electron of Mn^{3+} ions only.¹⁶ Hence one can say that in rare-earth manganites only one type of defect center exists, which does not support the formation of bipolarons. Thus the transport data, particularly in the high-temperature semiconducting regime of the present system of interest, could only be explained by the small-polaron hopping model¹⁶; on the other hand, the bipolaron hopping mechanism is inadequate to apply for the present system.

This is also confirmed from the analysis of the resistivity (ρ) and TEP (S) data of Zhao *et al.*⁸ in the PM phase using the small-polaron transport mechanism. In this Comment, we have replotted the resistivity (ρ) and TEP data (of Ref. 8) and found that the small-polaron hopping model⁹ well ex-

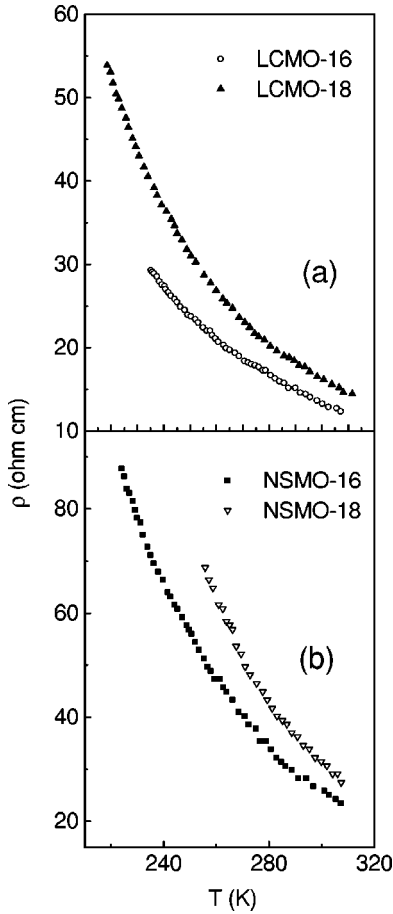


FIG. 1. Temperature-dependent resistivity curves of oxygen isotope exchanged films (Ref. 8) of (a) $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ and (b) $\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$.

plains the transport data of Zhao *et al.* as discussed below. The ^{16}O - and ^{18}O -diffused $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ samples⁸ are referred to as LCMO-16 and LCMO-18, respectively. Similarly, the ^{16}O - and ^{18}O -diffused $\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ samples⁸ are referred to as NSMO-16 and NSMO-18, respectively.

Figure 1 represents the temperature-dependent resistivity (ρ) of the LCMO-16, LCMO-18, NSMO-16, and NSMO-18 samples of Ref. 8. The reported Curie temperatures ($T_c \sim T_p$) of the samples⁸ are given in Table I. It is noteworthy to mention that the curves reported by Zhao *et al.*⁸ showed the thermal variation of resistivity only above the respective Curie temperatures. However, the signature of the small-polaron hopping (SPH) conduction mechanism is observed from the temperature-dependent resistivity data as discussed below. It is perceived that the resistivity data⁸ can be well fitted with the thermally activated small-polaron hopping model,¹⁷ similar to many other samples^{18,19} of the CMR family. According to this model,¹⁷ the expression for conductivity (σ) is given by

$$\sigma_{sp} = \sigma_{0,sp} \exp(-W_M/k_B T), \quad (1)$$

where $\sigma_0 = [v_{ph} N e^2 R^2 C (1-C)] / k_B T \exp(-2R\alpha)$, k_B is the Boltzmann constant, and T is the absolute temperature. N is the number of ion sites per unit volume (calculated from

TABLE I. Some important physical parameters of the samples (Ref. 8) and the best-fit parameters obtained from fitting with Eqs. (1), (4), and (5). Other relevant parameters are obtained from the conductivity data.

Parameters	LCMO-16	LCMO-18	NSMO-16	NSMO-18
T_p (K)	231.5	216.5	204.0	186.0
θ_D (K)	510.2	—	—	—
ν_{ph} (Hz)	1.06×10^{13}	—	—	—
W_M (meV)	72.8	86.0	78.8	92.9
E_s (meV)	13.2	18.7	—	—
W_H (meV)	59.6	67.4	—	—
W_D (meV)	119.2	134.8	—	—
γ_p	2.71	3.06	—	—
$N(E_F)$ ($\text{eV}^{-1} \text{cm}^{-3}$)	6.30×10^{18}	3.27×10^{18}	3.06×10^{18}	1.55×10^{18}
α'	-0.47	-0.63	—	—
ϕ (meV)	21.00	—	—	—
J (meV)	2.98	—	—	—
$W_H/3$ (meV)	19.87	—	—	—

density data), R is the average intersite spacing obtained from the relation $R = (1/N)^{1/3}$, C is the fraction of sites occupied by a polaron, α is the electron wave function decay constant, and ν_{ph} is the optical phonon frequency. W_M is the activation energy given, by the relations²⁰ $W_M = W_H + W_D/2$ for $T > \theta_D/2$ and $W_M = W_D$ for $T > \theta_D/4$ where W_H is the polaron hopping energy given by $W_H = W_M - E_s$ (discussed later), W_D is the disorder energy, and θ_D is the Debye temperature. Resistivity data are replotted as $\ln \sigma$ vs $1/T$ in Fig. 2. It is customary to determine $\theta_D/2$ from the temperature, where deviation from linearity occurs in the high-temperature region of the $\ln \sigma$ vs $1/T$ curve (Fig. 2). Since the complete range of data is not available from Fig. 1 of Ref. 8, no such deviation is observable from the resistivity data. We have taken $\theta_D = 510.2$ K for the LCMO-16 sample (Table I) from our recent work on $\text{La}_{0.7}\text{Ca}_{(0.3-y)}\text{Na}_y\text{MnO}_3$ ($y = 0.0-0.3$) series of samples.⁴ Here we should mention that for most of the CMR materials θ_D lies within 400–500 K. This means that the phonon frequency (ν_{ph}) is almost same ($\sim 10^{13}$ Hz) for all CMR materials. The corresponding value of the disorder energy and phonon frequency (ν_{ph}) is also estimated for this sample from the relation $h\nu_{ph} = k_B \theta_D$ and given in Table I. Almost similar values of the phonon frequency are also obtained from the infrared (IR) spectra of the samples.⁴ The nature of these curves (Fig. 2) confirms the applicability of Mott's small-polaron hopping mechanism (model) (Ref. 17) in the insulating (semiconducting) region (above T_p), predicting a temperature dependence of the activation energy in this region. The estimated values of the activation energy (W_M) for LCMO and NSMO samples studied by Zhao *et al.*⁸ are given in Table I. We also use the same values of the activation energy for fitting the conductivity data.

But in the case of bipolarons, two different defect centers (with energy difference Δ), as mentioned above, are coupled together and the effective potential barrier W over which

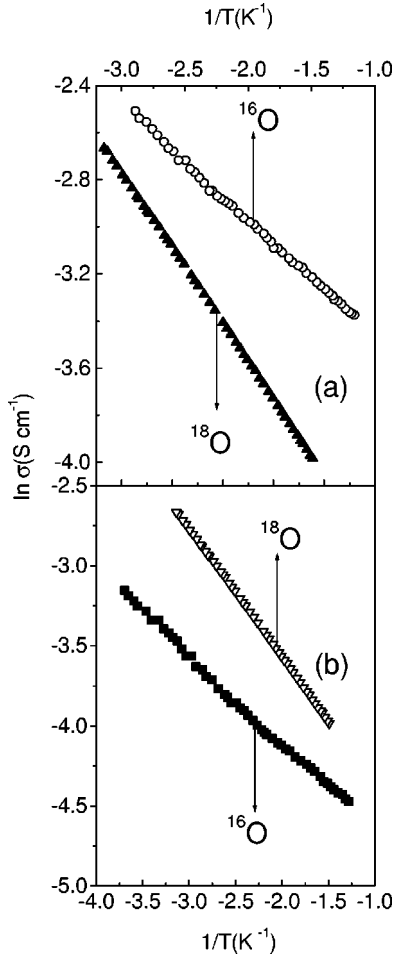


FIG. 2. Variation of $\ln \sigma$ as a function of inverse temperature ($1/T$) of (a) LCMO-16 and LCMO-18 and (b) NSMO-16 and NSMO-18.

carriers must hop is the random variable and variations in the W arise from the variations in the distance R separating the two centers.^{11,13} W_M is the potential energy associated with a defect site, which actually represents the energy needed for a bipolaron to migrate between centers of infinite separations.^{11,13,14} The Coulombic interaction between two neighboring sites lowers the binding energy W_M and the effective barrier height W is then related to the intersite separation R via the equation^{11,13,14}

$$W = W_M - 4e^2/\epsilon R_p, \quad (2)$$

where ϵ is the effective dielectric constant and R_p is the critical percolation radius given by $R_p = (2.7 \times 3/4\pi N)^{1/3}$. Thus the conductivity equation for the bipolaron is given by^{11,13-15}

$$\sigma_{bp} = \sigma_{obp} \exp[-(W_M - 4e^2/\epsilon R_p)/k_B T], \quad (3)$$

where $\sigma_{obp} = N^2(R_p^5 - R_{min}^5)/15$, and R_{min} is the lower bound for the hopping distance and is given by $R_{min} = 2e^2/\pi\epsilon\epsilon_0 W_M$ (ϵ_0 is the free space permittivity). It is clearly observed that σ_{obp} is largely controlled by the barrier height at the critical percolation radius; i.e., the correlation

arising due to Coulombic interactions between two different defect sites plays a major role. Further, the preexponential factors in the two processes, σ_{osp} and σ_{obp} [Eqs. (1) and (3)] are also quite different. So from precisely fitting the experimental resistivity data one can unambiguously indicate the nature of polarons.

It is well known¹⁷ that conductivity data of semiconducting oxide systems in the low-temperature regime (below $\theta_D/2$) follow Mott's variable-range hopping (VRH) model of charge carriers. Recently, working with similar manganite systems, like La-Sr-Mn-Cu-O and La-Ca-Mn-O, different research groups^{21,22} applied the VRH model to fit the conductivity data for the entire high-temperature ($T > T_p$) range. Thus, for the present series of samples,⁸ we have also tried to fit the conductivity data with the VRH model in the given temperature. In the three-dimensional (3D) case, the dc conductivity data according to the VRH model follows the equation¹⁷

$$\sigma = \sigma_0 \exp(-[T_0/T]^{1/4}), \quad (4)$$

where T_0 is a constant $= 16\alpha^3/k_B N(E_F)$ and $N(E_F)$ the density of states (DOS) at the Fermi level. T_0 is obtained from the slope of the $\ln \sigma$ vs $T^{-1/4}$ curve (Fig. 3). The straight line of Fig. 3 gives the best-fit line obtained from fitting the conductivity data with Eq. (4). From the values of T_0 , we have also calculated the DOS at the Fermi level, $N(E_F)$ (Table I), using $\alpha = 2.22 \text{ nm}^{-1}$ (Refs. 23 and 24), estimated earlier for similar CMR oxide samples.

Let us now consider the most important result of temperature-dependent thermoelectric power (S) for two Ca-doped samples, viz., LCMO-16 and LCMO-18, shown in Fig. 4(b). Recently extensive efforts have been made to discuss the polaronic transport in the high-temperature ($T > T_p$) PM phase of the CMR systems.¹⁴ We also notice that like resistivity at high temperature, TEP data can also be fitted very well with Mott's equation¹⁷ of the Seebeck coefficient (S) which has the form

$$S = k_B/e [E_s/k_B T + \alpha']. \quad (5)$$

A similar model was also used by Zhao *et al.*⁸ to fit their TEP data, but they did not estimate α' which gives the condition of small-polaron or bipolaron formation. In Eq. (5), E_s is the activation energy obtained from the TEP data, which is the same as observed by Zhao *et al.*⁸ α' is a constant of proportionality between the heat transfer associated with electron and the kinetic energy of the electron. It has been shown theoretically by Austin and Mott,²⁰ Appel,²⁵ and Mott²⁶ that $\alpha' > 2$ for large polarons, whereas for small-polaron formation $\alpha' < 1$. Qualitatively, one can argue that for narrow-band semiconductors with small-polaron formation, the polaron bandwidth is very much smaller than $k_B T$. Due to localization of electrons, the heat transfer associated with electrons should be small compared with $k_B T$ and as a consequence the constant α' should be less than 1 (Ref. 27).

On the other hand, according to Heikes²⁸ the term α' is of the form $\alpha' = \Delta S'/k_B$, where $\Delta S'$ is the change in the entropy of the ion (lattice) due to the presence of an electron on the transition-metal site.^{20,26,28} This must be due to the

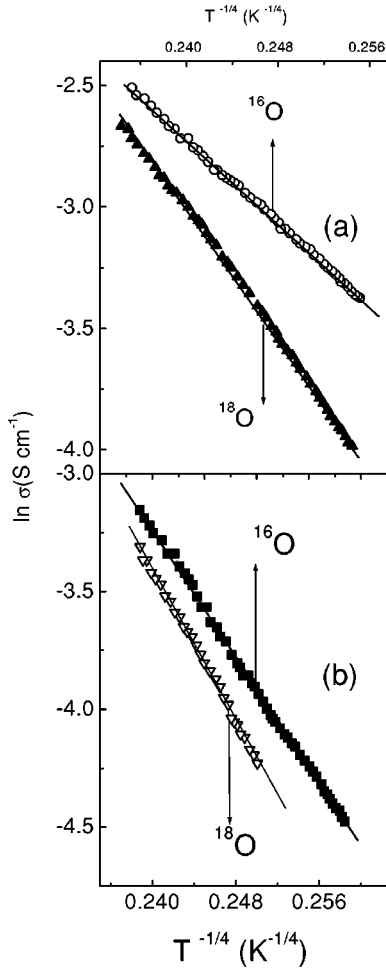


FIG. 3. Plot of $\ln \sigma$ vs $T^{-1/4}$ for the samples of (a) LCMO-16 and LCMO-18 and (b) NSMO-16 and NSMO-18. The solid lines indicate the best fits with Mott's VRH model [Eq. (4)].

change in the vibrational frequency (ω_0) of the surrounding atoms due to the presence of an electron.²⁶ Detail calculation shows that²⁰

$$\Delta S'/k_B = \Delta \omega_0/\omega_0 = 3\lambda W_p/E_a,$$

where $\Delta \omega_0$ is the change in vibrational frequency (w_0), E_a is the energy required to displace an atom, and W_p is polaronic energy ($=2W_H$, where W_H is the polaron hopping energy).^{17,20} Now since $E_a \sim eV$ (Refs. 20 and 26) and $W_H \sim 100$ meV (discussed later), α' should be less than unity for small polarons. The solid line in the S vs $1/T$ plot [Fig. 4(a)] gives the best-fit curve to Eq. (5). From the slope of the curve we obtain E_s , the activation energy from the TEP data for two typical samples studied by Zhao *et al.*⁸ and are given in Table I. The parameter α' , obtained from the fitting of the curves, is shown in Table I. Further, a similar small negative value of α' has also been obtained by other research groups (Ref. 27 and references therein). From the calculated values of α' (Table I), it is seen that $\alpha' < 1$. This again strongly supports the validity of the small-polaron hopping conduction²³ for the system of samples under investigation in contrast to the immobile bipolarons as reported by Zhao

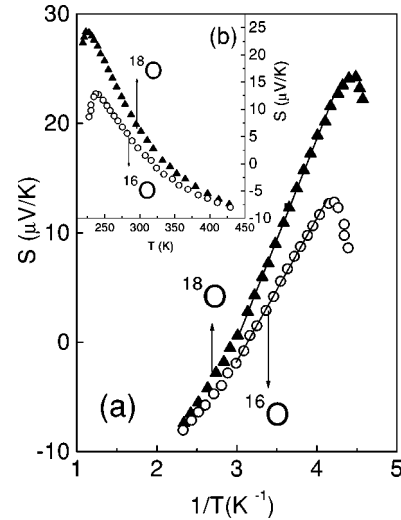


FIG. 4. (a) Variation of thermopower S (Ref. 8) as a function of inverse temperature $1/T$ for LCMO-16 and LCMO-18. The solid lines indicate the best fit with Mott's SPH model of thermoelectric power [Eq. (5)]. (b) Thermal variation of the Seebeck coefficient (S) for the same samples.

*et al.*⁸ The values of E_s obtained from TEP measurements are nearly one order of magnitude smaller than those (W_M , Table I) obtained from the resistivity data. The reason for such a difference, as originally pointed out by Mott and Davis¹⁷ and also recently supported by others,²⁹ is due to the thermally activated nature of hopping transport at high temperature. This large difference is also an indication of the small-polaron hopping mechanism. The estimated value of the hopping energy W_H ($=W_M - E_s$) is presented in Table I.

We have further attempted to estimate the dimension of the polaron. According to Mott and Davis,¹⁷ small polarons should exist if the condition $J < W_H/3$ is satisfied. The value of the polaron bandwidth J is calculated independently from the model proposed by Mott and Davis,¹⁷ viz.,

$$J \sim e^3 [N(E_F)/\epsilon_p^3]^{1/2}. \quad (6)$$

The values of the dielectric constant ϵ_p are calculated from the relation

$$W_H = e^2/4\epsilon_p(1/r_p - 1/R), \quad (7)$$

where the polaronic radius r_p and R , the average intersite spacing, are estimated to have the same value of our recent reported work⁴ on the $\text{La}_{0.7}\text{Ca}_{(0.3-y)}\text{Na}_y\text{MnO}_3$ ($y = 0.0-0.3$) series of samples and the obtained value of ϵ_p is 12.81. Here we should mention that there is some uncertainty in the estimation of ϵ_p indirectly from Eq. (7). We noticed that for the manganite samples ϵ_p varies from 5 to 15, for which J values vary from 2 to 10 meV (approximately). These values of ϵ_p agree with those obtained from IR reflection spectra. However, all these J values satisfy the condition of small-polaron hopping discussed below. Putting the values of $N(E_F)$ and ϵ_p , the independently calculated value of J is 2.98 meV (Table I). Comparing the values of $W_H/3$ and J given in Table I, we found that $J \ll W_H/3$. Hence the hopping is actually due to small polarons, which is also observed

from the TEP data discussed above. Here also we do not find evidence of large polarons as in the case of thermoelectric power data. This signifies that hopping is actually due to small polarons³⁰ in the system studied by Zhao *et al.*⁸

An attempt has also been made to confirm the nature of small-polaron hopping conduction for the present samples⁸ from Holstein's condition.³¹ According to this condition, the polaron bandwidth J should satisfy the inequality^{20,31} $J > \phi$ (for adiabatic hopping conduction) and $J < \phi$ (for the nonadiabatic hopping conduction) where

$$\phi = (2k_B T W_H / \pi)^{1/4} (h \nu_{ph} / \pi)^{1/2}. \quad (8)$$

The value of ϕ calculated from Eq. (8) for LCMO-16 is found to be 21.00 meV (Table I). Comparing these values of J and ϕ (Table I), it is observed that for the LCMO-16 sample, $J < \phi$; i.e., the nonadiabatic hopping condition is strictly satisfied. LCMO-18 and other samples also behave similarly.

We have also made an effort to calculate the small-polaron coupling constant γ_p which is a measure of the el-ph interaction strength for these samples, using the relation²⁰ $\gamma_p = 2W_H / h \nu_{ph}$. The estimated values of γ_p are given in Table I. The values of γ_p are less than the strong electron-phonon coupling limit, for which $\gamma_p > 4$ (Ref. 20). This indicates the freezing (or melting) of the small polarons and

the corresponding increase of electron-electron and spin-spin interactions, leading finally to the metallic state. Dynamic phase separation in the PM state as pointed out by Zhao *et al.*⁸ might appear due to the freezing of small polarons and the formation of both ferromagnetic and antiferromagnetic domains depending on the strength of exchange interaction which increases with the freezing of the small polarons. The estimated γ_p values are of the same order of magnitude reported earlier for similar samples,³² which further supports the theory of lattice distortion and, hence, the formation of small polarons. The γ_p for the ¹⁶O diffused system is smaller than the ¹⁸O-diffused system. This means that the isotope effect plays a dominant role in the electron-phonon interaction. The isotope effect is related to the electron-phonon interaction constant (γ_p), since the polaron effective mass (m_p) is proportional to $\exp(\gamma_p)$.

Finally, from the above discussion, we may conclude that the hopping mechanism in the LCMO-16, LCMO-18, and other samples is actually due to small polarons; consideration of bipolarons as reported by Zhao *et al.*⁸ is inadequate. We further affirm that the isotope effect is actually associated with the polaron effective mass—i.e., the electron-phonon interaction term. The SPH model discussed above is also valid for all other manganites and related materials in the form of both bulk and thin films.

*Present address: Physical Metallurgy Section, Indira Gandhi Center for Atomic Research, Kalpakkam-603 102, India.

[†]Electronic address: sspbkc@mahendra.iacs.res.in

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