

## Evidence for the immobile bipolaron formation in the paramagnetic state of the magnetoresistive manganites

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Recent research suggests that the charge carriers in the paramagnetic state of the magnetoresistive manganites are small polarons. Here we report studies of the oxygen-isotope effects on the intrinsic resistivity and thermoelectric power in several ferromagnetic manganites. The precise measurements of these isotope effects allow us to make a quantitative data analysis. Our results do not support a simple small-polaron model, but rather provide compelling evidence for the presence of small immobile bipolarons, i.e., pairs of small polarons.

The discovery of “colossal” magnetoresistance (CMR) in thin films of  $R_{1-x}A_x\text{MnO}_3$  ( $R$  = a rare-earth element, and  $A$  = a divalent element)<sup>1</sup> has stimulated extensive studies of magnetic, structural, and transport properties of these materials.<sup>2</sup> The physics of manganites has primarily been described by the double-exchange (DE) model.<sup>3</sup> Recently, several theoretical investigations<sup>4–6</sup> indicated that, in addition to the DE interaction, a second mechanism such as the formation of small polarons in the paramagnetic (PM) state should be involved in explaining the basic physics of doped manganites. On the other hand, Alexandrov and Bratkovsky<sup>7</sup> showed that, in order to explain CMR quantitatively, one needs to consider the formation of small bipolarons (pairs of small polarons) in the PM state.

Experimental evidence for small polaronic charge carriers in the PM state was provided by transport measurements.<sup>8</sup> It was found that the activation energy  $E_p$  deduced from the conductivity data is one order of magnitude larger than the activation energy  $E_s$  obtained from the thermoelectric power data. Such a large difference in the activation energies is the hallmark of the small-polaron hopping conduction. The giant oxygen-isotope shifts of the ferromagnetic transition temperature  $T_C$  give clear evidence for the presence of polaronic charge carriers in this system.<sup>9,10</sup> Moreover, the fast and local techniques have directly shown that the doped charge carriers are accompanied by local Jahn-Teller distortions.<sup>11–14</sup> However, all these experiments cannot make a distinction between small polarons and small bipolarons since both are dressed by local lattice distortions. Small bipolarons are normally much heavier than small polarons, and should be localized in the presence of small random potentials. In order to discriminate between polarons and bipolarons and to place constraints on the CMR theories, we studied the oxygen-isotope effects on the intrinsic resistivity in the high-quality epitaxial thin films of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . We also measured the thermoelectric power for the oxygen-isotope exchanged ceramic samples of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . The data cannot be explained by a simple small-polaron model, but are in quantitative agreement with a model where the formation of small immobile bipolarons is essential.

Epitaxial thin films of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  (LCMO) and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (NSMO) were grown on  $\langle 100 \rangle$   $\text{LaAlO}_3$  single-crystal substrates by pulsed laser deposition using a KrF excimer laser.<sup>15</sup> The film thickness was about 190 nm for NSMO and 150 nm for LCMO. Two halves were cut from the same piece of a film for oxygen-isotope diffusion. The diffusion for LCMO/NSMO was carried out for 10 h at about 940/900 °C and oxygen pressure of 1 bar. The  $^{18}\text{O}$ -isotope gas is enriched with 95%  $^{18}\text{O}$ , which can ensure 95%  $^{18}\text{O}$  in the  $^{18}\text{O}$  thin films. The ceramic  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  were the same as those reported in Ref. 16. The resistivity was measured using the van der Pauw technique, and the contacts were made by silver paste. The measurements were carried out in a Quantum Design measuring system. The thermoelectric power was measured using an apparatus modeled after a seesaw technique.<sup>17</sup> The absolute uncertainty is less than 0.25  $\mu\text{V/K}$  and the systematic error is  $\pm 0.1 \mu\text{V/K}$ .

Figure 1 shows the resistivity of the oxygen-isotope exchanged films of LCMO and NSMO above  $1.1T_C$ . The  $T_C$  values for these films are summarized in Table I. The oxygen-isotope shift of  $T_C$  for the LCMO films is 15.0(6) K, in excellent agreement with the results for the bulk samples.<sup>16</sup> From the figure, one can see that there is a large difference in the intrinsic resistivity between the two isotope samples. Such a large isotope effect is reversible upon the oxygen isotope back exchange. We should mention that the intrinsic resistivity of the compounds can be only obtained in high-quality thin films and single crystals. Our LCMO films even have lower residual resistivity  $\rho_0$  than the corresponding single crystals,<sup>18</sup> indicating a high quality of the films. We also checked that the resistivity for a ceramic sample of  $\text{La}_{0.66}\text{Ba}_{0.34}\text{MnO}_3$  is very different from that for the corresponding single crystal; the activation energy  $E_p$  for the former is about three times larger than for the latter. The temperature dependence of the resistivity obtained in the ceramic samples does not represent the intrinsic behavior of the bulk, and thus one cannot use ceramic samples to study the isotope effect on the intrinsic resistivity. Moreover, the van

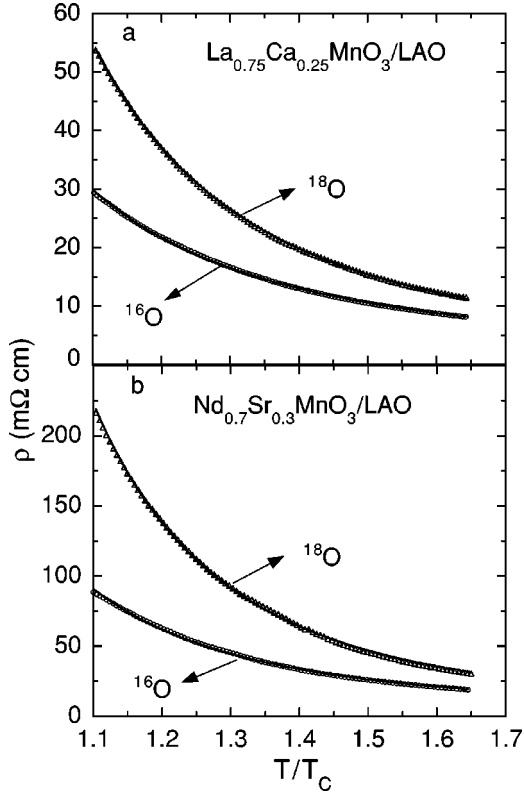


FIG. 1. The resistivity of the oxygen-isotope exchanged films of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . The maximum temperature of the data points for the  $^{16}\text{O}$  film of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  is 380 K. The solid lines are the fitted curves by Eq. (2). As in Ref. 8, we excluded the data points below  $1.1T_C$  for the fitting.

der Pauw technique is particularly good to precisely measure the resistivity difference between oxygen-isotope exchanged films whose thicknesses are identical. Thus the data shown in Fig. 1 represent precise measurements on the intrinsic resistivity of two isotope samples.

Now we try to understand the origin of such an isotope effect. It is known that the resistivity can be generally expressed as  $\rho = 1/\sigma = 1/ne\mu$ , where  $n$  is the mobile carrier concentration and  $\mu$  is the mobility of the carriers. For adiabatic small-polaron hopping, the mobility is given by<sup>19</sup>

$$\mu = \frac{ed^2}{h} \frac{\hbar\omega_o}{k_B T} \exp(-E_a/k_B T). \quad (1)$$

Here  $d$  is the site to site hopping distance, which is equal to  $a/\sqrt{2}$  in manganites since the doped holes in this system

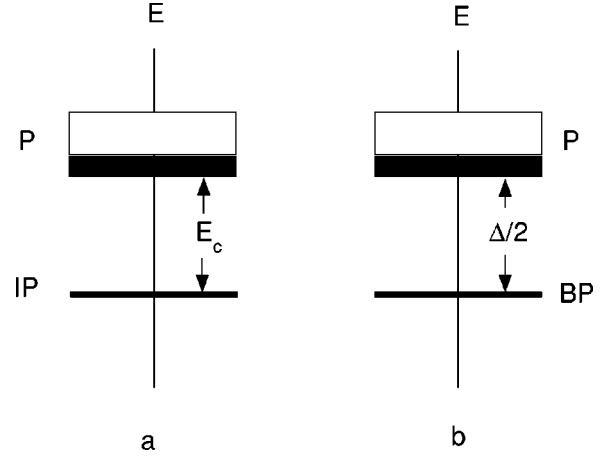


FIG. 2. A schematic diagram of the polaron band and polaron trapping into impurity (IP) states (a) (Ref. 21), or into localized bipolaron (BP) states (b) (Ref. 7). The bipolaron binding energy  $\Delta$  is isotope-mass dependent (Ref. 22), while  $E_c$  is independent of the isotope mass  $M$  (Ref. 21).

mainly reside on the oxygen sites;<sup>20</sup>  $\omega_o$  is the characteristic optical phonon frequency;  $E_a = (\eta E_p/2)f(T) - t$ ;  $f(T) = [\tanh(\hbar\omega_o/4k_B T)]/(\hbar\omega_o/4k_B T)$  for  $T > \hbar\omega_o/4k_B \approx 200$  K;<sup>21</sup>  $E_p$  is the polaron binding energy;  $t$  is the ‘‘bare’’ hopping integral;  $\eta \leq 1$ .<sup>19,22</sup> In the harmonic approximation,  $E_p$  is independent of the isotope mass  $M$ .

The mobile polaron density  $n$  can be calculated for the two possible cases shown in Fig. 2. If we assume a simple parabolic band, then  $n = 2(k_B T/1.05a^2 W_p)^{3/2} \exp(-E_s/k_B T)$  for  $T \ll W_p/k_B$ .<sup>7,21</sup> Here  $W_p$  is the polaron bandwidth;  $E_s = E_c$  if polarons are trapped into impurity (IP) states,<sup>21</sup> while  $E_s = \Delta/2$  if polarons are bound into localized bipolaron (BP) states.<sup>7</sup> The bipolaron binding energy  $\Delta = 2(1 - \Gamma)E_p - V_c - W_p$ , where  $V_c$  is the Coulombic repulsion between bound polarons and  $\Gamma$  is a constant ( $< 1$ ).<sup>22</sup> In fact, the above  $n(T)$  expression is the same as that for semiconductors when the chemical potential is pinned to the impurity levels. Using the above  $n(T)$  expression and Eq. (1), we finally have

$$\rho = \frac{C}{\sqrt{T}} \exp(E_p/k_B T), \quad (2)$$

where  $E_p = E_a + E_s$ , and  $C = (ah/e^2 \sqrt{k_B}) (1.05 W_p)^{1.5} / \hbar\omega_o$ . The quantity  $C$  should strongly depend on the isotope mass  $M$  and decrease with increasing  $M$ . This is because  $W_p$  decreases strongly with increasing  $M$  according to  $W_p$

TABLE I. Summary of the fitting and measured parameters for the  $^{16}\text{O}$  and  $^{18}\text{O}$  films of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  (LCMO) and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (NSMO). The errors of the parameters come from the fitting and from the van der Pauw measurement. The absolute uncertainty of the thickness of the films was not included in the error calculations since it only influences the absolute values of the resistivity.

Compounds	LCMO( $^{16}\text{O}$ )	LCMO( $^{18}\text{O}$ )	NSMO( $^{16}\text{O}$ )	NSMO( $^{18}\text{O}$ )
$T_C$ (K)	231.5(3)	216.5(3)	204(1)	186(1)
$C$ ( $\text{m}\Omega \text{ cm K}^{0.5}$ )	17.3(5)	12.9(3)	23.2(8)	16.2(7)
$E_p$ (meV)	72.8(2)	86.0(1)	78.8(4)	92.9(4)
$E_s$ (meV)	13.2(3)	18.7(3)		
$W_p$ (meV)	49.0(9)	38.8(7)	60(2)	45(2)

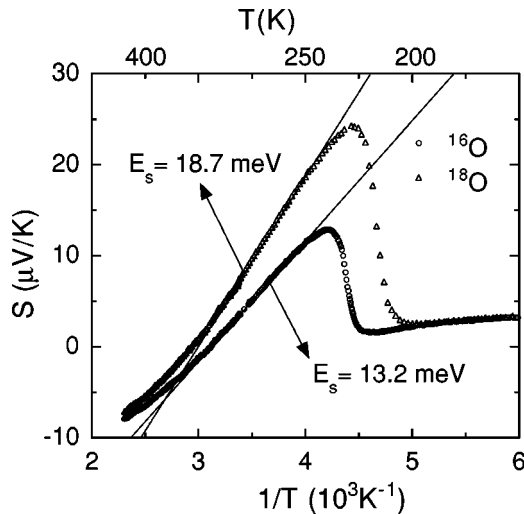


FIG. 3. The thermoelectric power  $S(T)$  of the oxygen-isotope exchanged ceramic samples of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ .

$\propto \exp(-\Gamma E_p/\hbar\omega_o) = \exp(-g^2)$ .<sup>22,23</sup> We would like to mention that Eq. (2) is valid only if  $T \ll W_p/k_B$ . For  $T \gg W_p/k_B$ , the prefactor in Eq. (2) should be proportional to  $T/\omega_o$ .<sup>8</sup>

The thermoelectric power is given by<sup>21</sup>

$$S = E_s/eT + S_o, \quad (3)$$

where  $S_o$  is a constant depending on the kinetic energy of the polarons and on the polaron density.<sup>21</sup> One should note that Eq. (3) is valid only if there is one type of carriers (e.g., holes).

One can make a distinction between the two cases shown in Fig. 2. If small polarons are bound to impurity centers, there will be no isotope effect on  $E_s$  since  $E_c$  is independent of  $M$ .<sup>21</sup> On the other hand, if small polarons are bound to localized bipolaron states, both  $E_p$  and  $E_s$  in Eq. (2) and Eq. (3) will depend on  $M$  due to the fact that  $\Delta$  is  $M$  dependent. In general, the isotope shift of  $E_p$  will be larger than the isotope shift of  $E_s$ . This is because  $E_a = (\eta E_p/2)f(T) - t$ , and  $f(T) = [\tanh(\hbar\omega_o/4k_B T)]/(\hbar\omega_o/4k_B T)$ , which may depend on  $M$  if the temperature is not so high compared with  $\hbar\omega_o/k_B$ .

We now fit our data by Eq. (2) (see solid lines in Fig. 1). It is apparent that the fits are quite good for both isotope samples. The fitting parameters are summarized in Table I. From Table I, one can see that, upon replacing  $^{16}\text{O}$  with  $^{18}\text{O}$ , the parameter  $C$  for LCMO/NSMO decreases by 35(5)/40(7)%, while  $E_p$  increases by 13.2(3)/14.2(8) meV. The huge oxygen-isotope effect on the parameter  $C$  is consistent with Eq. (2).

We can obtain the isotope shift of  $E_s$  by measuring the thermoelectric power for two isotope samples according to Eq. (3). In Fig. 3, we plot the thermoelectric power  $S$  as a

function of  $1/T$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . Both  $T_C$ 's and the isotope shift of the ceramic samples<sup>16</sup> are the same as those in the corresponding thin films. Since the grain-boundary effect on  $S$  is negligible, the thermoelectric power obtained in ceramic samples should be intrinsic. From the slopes of the straight lines in Fig. 3, we find  $E_s = 13.2 \pm 0.3$  meV for the  $^{16}\text{O}$  sample and  $18.7 \pm 0.3$  meV for the  $^{18}\text{O}$ . The isotope shift is  $\delta E_s = 5.5 \pm 0.6$  meV, which is about half the isotope shift of  $E_p$ . The observed oxygen-isotope effects on both  $E_p$  and  $E_s$  do not support a simple small-polaron model,<sup>21</sup> but provide evidence that small polarons are bound into localized bipolaron states.

We can use the values of the parameter  $C$  to calculate the polaron bandwidth  $W_p$  according to the relation:  $C = (ah/e^2\sqrt{k_B})(1.05W_p)^{1.5}/\hbar\omega_o$ . The calculated  $W_p$  values are listed in Table I. In the calculation, we have taken  $\hbar\omega_o = 74$  meV for the  $^{16}\text{O}$  samples,<sup>22</sup> and assumed  $\hbar\omega_o$  for the  $^{18}\text{O}$  samples is 5.7% lower than for the  $^{16}\text{O}$  samples. From the  $W_p$  values (see Table I), one can see that for our data  $T < W_p/k_B$ , which justifies the use of Eq. (2). We would like to point out that larger  $W_p$  values for the NSMO films might be an artifact since the residual resistivity of our NSMO films are more than 40% larger than that of the best single crystal.<sup>24</sup>

Furthermore, one can quantitatively explain the isotope dependence of  $E_s$  if small polarons form localized bipolarons. In this scenario,<sup>22</sup>  $\delta\Delta = -\delta W_p$ . From Table I,  $\delta W_p = -11.2 \pm 1.6$  meV for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . So  $\delta E_s = \delta\Delta/2 = 5.6 \pm 0.8$  meV for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ , in quantitative agreement with the value ( $5.5 \pm 0.6$  meV) deduced from the thermoelectric power data.

In summary, we have observed large oxygen isotope effects on the intrinsic resistivity in high-quality epitaxial thin films of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , and on the thermoelectric power in the ceramic samples of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . The data can be quantitatively explained by a scenario<sup>7</sup> where the small polarons form localized bound pairs (bipolarons) in the paramagnetic state. The coexistence of small polarons and bipolarons in the PM state may lead to a dynamic phase separation into the insulating antiferromagnetically coupled region where the bipolarons reside, and into the ferromagnetically coupled region where the polarons sit. This simple picture can naturally explain the observation of the ferromagnetic clusters in the PM state.<sup>25</sup> Although we cannot completely rule out the possibility that the other models might also be able to explain the present isotope effects, we would like to point out that the agreement between theory and experiment should be quantitative.

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<sup>1</sup>R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen,

Science **264**, 413 (1994).

<sup>2</sup>A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).

<sup>3</sup>C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955).

<sup>4</sup>A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev.

- Lett. **74**, 5144 (1995); A. J. Millis, B. I. Shraiman, and R. Müller, *ibid.* **77**, 175 (1996).
- <sup>5</sup>H. Röder, J. Zang, and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996).
- <sup>6</sup>A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1994).
- <sup>7</sup>A. S. Alexandrov and A. M. Bratkovsky, Phys. Rev. Lett. **82**, 141 (1999); J. Phys.: Condens. Matter **11**, 1989 (1999).
- <sup>8</sup>M. Jaime, M. B. Salamon, M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, Phys. Rev. B **54**, 11 914 (1996).
- <sup>9</sup>G. M. Zhao, K. Conder, H. Keller, and K. A. Müller, Nature (London) **381**, 676 (1996).
- <sup>10</sup>G. M. Zhao, M. B. Hunt, and H. Keller, Phys. Rev. Lett. **78**, 955 (1997).
- <sup>11</sup>S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier, and J. D. Thompson, Phys. Rev. Lett. **77**, 715 (1996).
- <sup>12</sup>C. H. Booth, F. Bridges, G. H. Kwei, J. M. Lawrence, A. L. Cornelius, and J. J. Neumeier, Phys. Rev. Lett. **80**, 853 (1998).
- <sup>13</sup>D. Louca, T. Egami, E. L. Brosha, H. Röder, and A. R. Bishop, Phys. Rev. B **56**, R8475 (1997).
- <sup>14</sup>A. Lanzara, N. L. Saini, M. Brunelli, F. Natali, A. Bianconi, P. G. Radaelli, and S. W. Cheong, Phys. Rev. Lett. **81**, 878 (1998).
- <sup>15</sup>W. Prellier, M. Rajeswari, T. Venkatesan, and R. L. Greene, Appl. Phys. Lett. **75**, 1146 (1999).
- <sup>16</sup>G. M. Zhao, K. Conder, H. Keller, and K. A. Müller, Phys. Rev. B **60**, 11 914 (1999).
- <sup>17</sup>R. Resel, E. Gratz, A. T. Burkov, T. Nakama, M. Higa, and K. Yagasaki, Rev. Sci. Instrum. **67**, 1970 (1996).
- <sup>18</sup>G. M. Zhao, V. Smolyaninova, W. Prellier, and H. Keller, Phys. Rev. Lett. **84**, 6086 (2000).
- <sup>19</sup>D. Emin and T. Holstein, Ann. Phys. (N.Y.) **53**, 439 (1969).
- <sup>20</sup>H. L. Ju, H. C. Sohn, and K. M. Krishnan, Phys. Rev. Lett. **79**, 3230 (1997).
- <sup>21</sup>I. G. Austin and N. F. Mott, Adv. Phys. **18**, 41 (1969).
- <sup>22</sup>A. S. Alexandrov and A. M. Bratkovsky, J. Phys.: Condens. Matter **11**, L531 (1999).
- <sup>23</sup>A. S. Alexandrov and P. E. Kornilovitch, Phys. Rev. Lett. **82**, 807 (1999).
- <sup>24</sup>Y. Sawaki, K. Takenaka, A. Osuka, R. Shiozaki, and S. Sugai, Phys. Rev. B **61**, 11 588 (2000).
- <sup>25</sup>J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).