Oxygen isotope effects in high-quality thin films of manganites: Quantitative constraints on the physics of manganites

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Oxygen isotope effects on the transport properties have been studied in high-quality epitaxial thin films of La\(_{0.75}\)Ca\(_{0.25}\)MnO\(_3\) and Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\). In the paramagnetic state, the resistivity can be well fitted by \(\rho(T) = (A/\sqrt{T}) \exp(E_\rho/k_B T)\) with the parameters \(A\) and \(E_\rho\) depending strongly on the oxygen isotope mass. The resistivity below 80 K almost perfectly follows \(\rho = \rho_0 + B\omega_s/\sinh^2(\hbar\omega_s/2k_B T)\) with \(\hbar\omega_s/k_B \sim 100\) K. Both \(\rho_0\) and \(B\) increase by about 15(3)% upon replacing \(^{16}\)O by \(^{18}\)O. The results provide quantitative constraints on the basic physics of manganites.

The discovery of “colossal” magnetoresistance (CMR) in thin films of Re\(_{1-x}\)A\(_x\)MnO\(_3\) (Re = a rare-earth element, and A = a divalent element) \(^4\) has stimulated extensive studies of magnetic, structural and transport properties of these materials \(^4\). The physics of manganites has primarily been described by the double-exchange (DE) model \(^3\). However, Millis, Littlewood and Shraiman \(^4\) pointed out that the carrier-spin interaction in the DE model is too weak to lead to the carrier localization in the paramagnetic state, and thus a second mechanism such as small polaronic effects should be involved to explain the observed resistivity data in doped manganites. The central point of the model is that in the paramagnetic state the electron-phonon coupling constant \(\lambda\) is large enough to form small polarons while the growing ferromagnetic order increases the bandwidth and thus decreases \(\lambda\) sufficiently to form a large polaron metallic state. Many recent experiments \(^4\) \(^7\) \(^8\) have provided strong evidence for the existence of small polarons in the paramagnetic state, and qualitatively support these theoretical models \(^4\) \(^7\) \(^8\).

Alexandrov and Bratkovsky \(^6\) have recently argued that the model suggested by Millis et al., cannot quantitatively explain CMR since the characteristic theoretical field (\(\sim 15\) T) for CMR is too high compared with the experimental one (\(\sim 4\) T) \(^4\). They thus proposed an alternative theory for CMR. The basic idea of their model is that the small polarons form localized bond pairs (bipolarons) in the paramagnetic state due to strong electron-phonon coupling while the competing exchange interaction of polaronic carriers with localized spins drives the ferromagnetic transition. The transition is accompanied by a giant increase in the number of small polarons which are mobile carriers and move coherently at low temperatures. This model appears to be able to explain the CMR quantitatively.

In order to discriminate between these different models, we study the oxygen isotope effect on the transport properties of high-quality epitaxial thin films of La\(_{0.75}\)Ca\(_{0.25}\)MnO\(_3\) and Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\). The intrinsic resistivity of these compounds shows a strong dependence on the oxygen isotope mass in both paramagnetic and ferromagnetic states. A quantitative data analysis provides essential constraints on the basic physics of manganites.

FIG. 1. The resistivity of the oxygen-isotope exchanged films of (a) La\(_{0.75}\)Ca\(_{0.25}\)MnO\(_3\); (b) Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\).

The epitaxial thin films of La\(_{0.75}\)Ca\(_{0.25}\)MnO\(_3\) (LCMO) and Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) (NSMO) were grown on \(<100>\) LaAlO\(_3\) single crystal substrates by pulsed laser depo-
sition using a KrF excimer laser [13]. 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 about 1 bar. The $^{18}$O-isotope gas is enriched with 95% $^{18}$O, which can ensure 95% $^{18}$O in the $^{18}$O thin films. The resistivity was measured using the van der Pauw technique, and the contacts were made by silver paste. The measurements were carried out from 5 to 380 K in a Quantum Design measuring system.

Fig. 1 shows the resistivity of the oxygen-isotope exchanged films of (a) LCMO; (b) NSMO over a temperature range 100-300 K. It is striking that, in all the cases, the $^{18}$O samples have lower metal-insulator crossover temperatures and much sharper resistivity drop. The Curie temperature $T_C$ normally coincides with a temperature where $d\ln \rho/dT$ exhibits a maximum. We find that the oxygen isotope shift of $T_C$ is 15.0(6) K for LCMO, and 18.0(6) K for NSMO, in excellent agreement with the results for the bulk samples [16].

In Fig. 2 we plot the low-temperature resistivity of the oxygen-isotope exchanged films of (a) La$_{0.75}$Ca$_{0.25}$MnO$_3$/LAO; (b) Nd$_{0.67}$Sr$_{0.33}$MnO$_3$. The solid lines are fitted curves by Eq. 1.

![Figure 2](image)

FIG. 2. The low-temperature resistivity of the oxygen-isotope exchanged films of (a) La$_{0.75}$Ca$_{0.25}$MnO$_3$/LAO; (b) Nd$_{0.67}$Sr$_{0.33}$MnO$_3$. The solid lines are fitted curves by Eq. 1.

In Fig. 2 we plot the low-temperature resistivity of the oxygen-isotope exchanged films of (a) LCMO; (b) NSMO. In both cases, the residual resistivity $\rho_0$ for the $^{18}$O samples is larger than for the $^{16}$O samples by about 15%. We have repeated the van der Pauw measurements at 5 K for several times with different contact configurations. We checked that the uncertainty of the difference in $\rho_0$ of the two isotope samples is less than 3%. We also found that the isotope effect is reversible upon the isotope back-exchange. It is worth noting that the $\rho_0$ for the $^{18}$O NSMO film is nearly the same as for a single crystalline sample [17]. This indicates that the electrical transport properties observed in our films are intrinsic.

The low temperature resistivity has been explained by small polaron metallic conduction [15], which leads to a formula [15,14]:

$$\rho(T) = \rho_0 + B\omega_s / \sinh^2(\hbar\omega_s/2k_BT),$$  

(1)

where $\omega_s$ is the frequency of the softest optical mode (about 100 K [18]), and $B$ is a constant, being proportional to $m_p/n$ (here $m_p$ is the effective mass of polarons, and $n$ is the mobile carrier concentration). The residual resistivity $\rho_0 \propto m_p/n\tau_0$ [20], where $h/\tau_0$ is the zero temperature scattering rate which is associated with the random potential produced by randomly distributed trivalent and divalent cations [21]. The magnitude of $h/\tau_0$ has been found to be 18(3) meV from optical data of the compounds Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ [17], La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ [24]. Since the Drude weight ($\propto n/m_p$) for Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ [17] is about a factor of 3 smaller than for La$_{0.7}$Ca$_{0.3}$MnO$_3$, nearly the same $h/\tau_0$ observed for both compounds implies that the $h/\tau_0$ is nearly independent of $m_p/n$, and that both $\rho_0$ and $B$ are proportional to $m_p/n$.

The best fit to the data shown in Fig. 2 indeed demonstrates that, in both cases, $\rho_0$ increases by 15(3)% and $B$ by 18(3). The results indicate that there is a substantial oxygen isotope effect on $m_p/n$. Since we have shown that [10,14] the total hole concentrations for two isotope samples should be the same, the observed isotope effect on $m_p/n$ implies that $m_p$ depends strongly on the isotope mass. This strongly suggests that the carriers in the ferromagnetic state are indeed small polarons, in agreement with the theoretical model [7]. We also find that both $\rho_0$ and $B$ for NSMO are about twice as large as those for LCMO, implying that the effective mass of carriers for NSMO is larger by a factor of 2.4 than for LCMO. This is consistent with specific heat data; the electronic specific heat coefficient $\gamma \sim 8$ mJ/moleK$^2$ for La$_{0.8}$Ca$_{0.2}$MnO$_3$ [23], while $\gamma \sim 20$ mJ/moleK$^2$ for Nd$_{0.67}$Sr$_{0.33}$MnO$_3$ [24].

In the paramagnetic state, the dominant conduction mechanism is thermally activated hopping of adiabatic small polarons. The mobility is given by [25]

$$\mu = \frac{ed^2\hbar\omega_o}{h k_BT} \exp(-E_a/k_BT),$$  

(2)

where $d$ is the site to site hopping distance, which is equal to $a/\sqrt{2}$ since the carriers in manganites mainly reside on the oxygen sites [20]. $\omega_o$ is the characteristic frequency of the optical phonons, and $E_a$ is given by [27,28] $E_a = (\eta E_p/2)f(T) - t$, where $E_p$ is the polaron binding energy, $t$ is the “bare” hopping integral, $\eta$ is a constant ($\eta = 1$ for Holstein polarons [25] and $\eta \sim 0.2-0.4$ for Fröhlich polarons [29]), and $f(T) = \tanh(\hbar\omega_o/4k_BT)/(\hbar\omega_o/4k_BT)$. 


If one considers that small polarons can be bound into localized pairs (bipolarons) or to the impurity centers [32], one finds [32] that the mobile carrier density $n = \frac{2(2\pi m_n k_B T/h^2)^{3/2}}{\Delta}$, where $W_p$ is the polaron bandwidth ($m_p = 6h^2/2^2e^2W_p$), $\Delta$ is the bipolaron binding energy or twice the gap between localized impurity levels and the bottom of the polaron band [32]. In fact, the above $n(T)$ expression is the same as that for semiconductors when the chemical potential is pinned to the mobility edge of the NSMO [10]. We can use the values of the parameter $g^* = 6562\pm100$ for the LCMO/NSMO [33]. If we take $\bar{p}_o = 7.2$ meV, which is about half the value observed.

The observed large oxygen isotope effect varying from -2 to 2.

It is clear that the resistivity strongly depends on the paramagnetic state for the $\delta$-O and $\delta$-O films of (a) LCMO; (b) NSMO. For LCMO, the parameter $A$ decreases by 35(5)% and 33(5)% for LCMO and 37(8)% for NSMO.

It is important to clarify whether the small polarons are bound into localized pairs (bipolarons) or just to the impurity centers since the parameter $A$ decreases by 35% for LCMO, and by 33% for the NSMO, in good agreement with the measured values: 35(5)% for LCMO and 37(8)% for NSMO.

In this case, the isotope effect on $E_p$ only arises from the isotope shift of $E_a$, as seen from the relation: $E_p = E_a + \Delta/2$. Since $E_a = (\eta E_p/2)f(T) - W_a/12$, only the quantity $f(T) = (\tanh(h\omega_o/4k_BT))/(h\omega_o/4k_BT)$ may depend on the isotope mass if the temperature is not so high compared with $h\omega_o/k_B$. If we take $\omega_o = 74$ meV, we have $f(T) = 0.855$ and $\delta(T/T_C) = 0.0134$ for $T = 300$ K, where $\delta$ means a change due to the oxygen isotope substitution. Using the relation: $(\eta E_p/2)f(T) - W_a/12 + E_o - \Delta/2$, and $\Delta/2 = E_o = 15$ meV for La$_{0.75}$Ca$_{0.25}$MnO$_3$ [33], we yield $\eta E_p/2 = 0.54$ eV. Then $\delta E_p = \delta E_a = (\eta E_p/2)\delta f(T) = 7.2$ meV, which is about half the value observed.

On the other hand, one can quantitatively explain the isotope dependence of $E_p$ if small polarons form localized bipolarons. In this scenario, $\Delta E = -\delta W_p/2$, so $\Delta \delta = 0.057g^2W_p$. From the deduced values for $g^2$ and $W_p$ above, we calculate that $\delta \Delta = 12.9$ meV for LCMO, and 14.7 meV for NSMO. Then $\delta E_p = \delta E_a + \delta \Delta/2 =$...
13.6 meV for LCMO, and 14.5 meV for NSMO. The calculated values are in excellent agreement with the observed values: 13.2(5) meV for LCMO and 13.5(9) meV for NSMO. In addition, if the small polarons are bound into small bipolarons, there will be a maximum in optical conductivity at the energy $\nu_b = 2g^2\hbar\omega_p + W_p + \Delta$ \[28\]. Substituting $g^2 = 4.61$, $\hbar\omega_p = 74$ meV, $W_p = 49$ meV and $\Delta = 30$ meV for the LCMO $^{16}$O film, we obtain $\nu_b = 0.76$ eV, in excellent agreement with experimental results (i.e., $\nu_b \approx 0.70$ eV for $x = 0.3$, and 0.80 eV for $x = 0.1$)

In summary, the oxygen isotope effects observed in high-quality epitaxial thin films of La$_{0.75}$Ca$_{0.25}$MnO$_3$ and Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ can be quantitatively explained by a scenario \[30\] where the small polarons form localized bound pairs (bipolarons) in the paramagnetic state while the carriers in the ferromagnetic states are small polarons due to the competing exchange interaction of polaronic carriers with localized spins. The electron-phonon coupling strength $g^2$ in the paramagnetic state is about twice of that in the low temperature ferromagnetic state. This is possible because a strong screening effect by mobile charge carriers reduces the electron-phonon interaction in the ferromagnetic state. The present results provide quantitative constraints on the basic physics of manganites.

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[1] 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.amesh, and L. H. Chen, Science 264, 413 (1994).
[2] A. P. Ramirez, J. Phys.: Condens. Matter 9, 8171 (1997).
[3] C. Zener, Phys. Rev. 82, 403 (1951); P. W. Anderson, and H. Hasegawa, Phys. Rev. 100, 675 (1955).
[4] 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, Phys. Rev. Lett. 77, 175 (1996).
[5] H. Röder, J. Zang, and A. R. Bishop, Phys. Rev. Lett. 76, 1356 (1996).
[6] A. Moreo, S. Yunoki, and E. Dagotto, Science 283, 2034 (1994).
[7] A. S. Alexandrov and A. M. Bratkovsky, Phys. Rev. Lett. 82, 141 (1999).
[8] M. Jaime, M. B. Salamon, M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, Phys. Rev. B 54, 11914 (1996).
[9] G. M. Zhao, K. Conder, H. Keller, and K. A. Müller, Nature (London) 381, 676 (1996).
[10] G. M. Zhao, M. B. Hunt and H. Keller, Phys. Rev. Lett. 78, 955 (1997).
[11] G. M. Zhao, K. Ghosh, and R. L. Greene, J. Phys.: Condens. Matter, 10, L737 (1998).
[12] S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier, and J. D. Thompson, Phys. Rev. Lett. 77, 715 (1996).
[13] 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).
[14] C. H. Booth, F. Bridges, G. H. Kwei, J. M. Lawrence, A. L. Cornelius, and J. J. Neumeier, Phys. Rev. Lett. 80, 853 (1998).
[15] W. Prellier, M. Rajeswari, T. Venkatesan and R. L. Greene, App. Phys. Lett. 75, 1146 (1999).
[16] G. M. Zhao, K. Conder, H. Keller, and K. A. Müller, Phys. Rev. B 60, 11 914 (1999).
[17] H. J. Lee, J. H. Jung, Y. S. Lee, J. S. Ahn, T. W. Noh, K. H. Kim, and S. W. Cheong, Phys. Rev. B 60, 5251 (1999).
[18] G. M. Zhao, V. Smolyaninova, W. Prellier, and H. Keller, cond-mat/9912337.
[19] I. G. Lang and Yu. A. Firsov, Sov. Phys. -JETP 16, 1301 (1963); V. N. Bogomolov, E. K. Kudinov, and Yu. A. Firsov, Sov. Phys. - Solid State 9, 2502 (1968).
[20] I. G. Austin and N. F. Mott, Adv. Phys. 18, 41 (1969). [21] W. E. Pickett and D. J. Singh, Phys. Rev. B 55, R8642 (1997); D. A. Papaconstantopoulos and W. E. Pickett, Phys. Rev. B 57, 12751 (1998).
[22] J. R. Simpson, H. D. Drew, V. N. Smolyaninova, R. L. Greene, M. C. Robson, A. Biswas, and M. Rajeswari, cond-mat/9908414.
[23] J. J. Hamilton, E. L. Keatley, H. L. Ju, A. K. Raychauduri, V. N. Smolyaninova, and R. L. Greene, Phys. Rev. B 54, 14926 (1996).
[24] J. E. Gordon, R. A. Fisher, Y. X. Jia, N. E. Phillips, S. F. Reklis, D. A. Wright, and A. Zettl, Phys. Rev. B 59, 127 (1999).
[25] D. Emin and T. Holstein, Ann. Phys. (N.Y.), 53, 439 (1969).
[26] H. L. Ju, H. C. Sohn, and K. M. Krishnan, Phys. Rev. Lett. 79, 3230 (1997).
[27] N. F. Mott and E. A. Davis Electronic Processes in Non-crystalline Materials (Clarendon Press, Oxford, 1979) p. 82.
[28] I. G. Lang and Yu. A. Firsov, Sov. Phys. -JETP 27, 443 (1968).
[29] A. S. Alexandrov and A. M. Bratkovsky, J. Phys.: Condens. Matter, 11, L531 (1999).
[30] A. S. Alexandrov and P. E. Kornilovich, Phys. Rev. Lett. 82, 807 (1999).
[31] M. F. Hundley and J. J. Neumeier, Phys. Rev. B 55, 11 511 (1997).
[32] J. H. Jung, K. H. Kim, T. W. Noh, E. J. Choi, and J. J. Yu, Phys. Rev. B 57, R11 043 (1998).