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# Strong oxygen-isotope effect on the intrinsic resistivity in the ferromagnetic state of manganites

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Oxygen-isotope effects on the intrinsic resistivity have been studied in high-quality epitaxial thin films of $La_{0.75}Ca_{0.25}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$. We found that the residual resistivity $\rho_o$ increases by about 15(3)% upon replacing $^{16}O$ by $^{18}O$. Furthermore, the temperature dependent part of the resistivity at low temperatures consists of an $AT^{4.5}$ term contributed from two-magnon scattering, and a $B\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$ term which arises from scattering by a soft optical phonon mode. The absolute magnitudes of the coefficient $A$ and the phonon energy $\hbar\omega_s$ for both isotope samples are in quantitative agreement with theoretical predictions.

The magnetic properties of the manganite perovskites $R_{1-x}A_xMnO_3$ ($R$=a rare-earth element, and $A$=a divalent element) have attracted renewed interest because of the observation of colossal magnetoresistance (CMR) in thin films of these materials.[1] Despite tremendous experimental efforts,[2] the basic physics and the microscopic mechanism for the colossal magnetoresistance in these materials remain controversial.[3–5] In particular, the very nature of the charge carriers and the electrical transport mechanism in the low-temperature metallic state have not been fully understood.

At low temperatures, a dominant $T^2$ contribution in resistivity is generally observed, and has been ascribed to electron-electron scattering.[6] In contrast, Jaime *et al.*[7] have shown that the resistivity is essentially temperature independent below 20 K and exhibits a strong $T^2$ dependence above 50 K. They proposed single magnon scattering with a cutoff at long wavelengths to explain their data. In their scenario,[7] they considered a case where the manganese $e_g$ minority (spin-up) band lies slightly above the Fermi level (in the majority spin-down band) with a small energy gap of about 1 meV. This appears to be in contradiction with the optical data[8] which show that the minimum band gap between the $e_g$ minority and majority bands is even larger than 0.5 eV and that the size of the gap strongly depends on the chemical pressure. Alternatively, Zhao *et al.*[9] have recently shown that the temperature dependent part of the resistivity at low temperatures is mainly due to scattering by a soft optical phonon mode.

Various CMR theories[3–5] predict different natures of charge carriers in the ferromagnetic state. In a theory of Alexandrov and Bratkovsky,[5] polarons are considered as the carriers even in the low-temperature metallic state, while others[3,4] believe that polaronic effects might not be important at low temperatures. The clarification of the nature of charge carriers in the ferromagnetic state can discriminate those theoretical models. One of the effective and clear ways to address this issue is to study the isotope effect on the effective carrier mass.

It is well known that the renormalized effective mass of carriers is independent of the ion mass $M$ in ordinary metals where the Migdal adiabatic approximation is believed to be valid. However, if the interactions between electrons and nuclear ions are strong enough for electrons to form po-

larons, their effective mass $m_p^*$ will depend on $M$. This is because the polaron mass $m_p^*=m\exp(\gamma E_p/\omega)$,[10,11] where $m$ is the band mass in the absence of the electron-phonon interaction, $\gamma$ is a constant ($<1$), $E_p$ is the polaron binding energy which is independent of $M$ in the harmonic approximation, and $\omega$ is a characteristic optical phonon frequency which depends on the masses of ions. Hence, there is a large isotope effect on the polaronic carrier mass, in contrast to the zero isotope effect in ordinary metals.

Here we report studies of the oxygen-isotope effect on the intrinsic low-temperature resistivity in high-quality epitaxial thin films of $La_{0.75}Ca_{0.25}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$. The residual resistivity of these compounds shows a strong dependence on the oxygen-isotope mass. Our quantitative data analyses may suggest that the nature of the charge carriers in the ferromagnetic state of doped manganites should be polaronic.

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 $\langle 100 \rangle$ $LaAlO_3$ single crystal substrates by pulsed laser deposition using a KrF excimer laser.[12] 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 $^{18}O$-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 in a Quantum Design measuring system.

Figure 1 shows the resistivity of the oxygen-isotope exchanged films of $La_{0.75}Ca_{0.25}MnO_3$ (LCMO) and $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO) over 100–300 K. It is apparent that 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 14.0(6) K for LCMO and 17.5(6) K for NSMO, in excellent agreement with the results for the bulk samples.[13]

In Fig. 2 we plot the low-temperature resistivity of the oxygen-isotope exchanged films of (a) LCMO and (b)
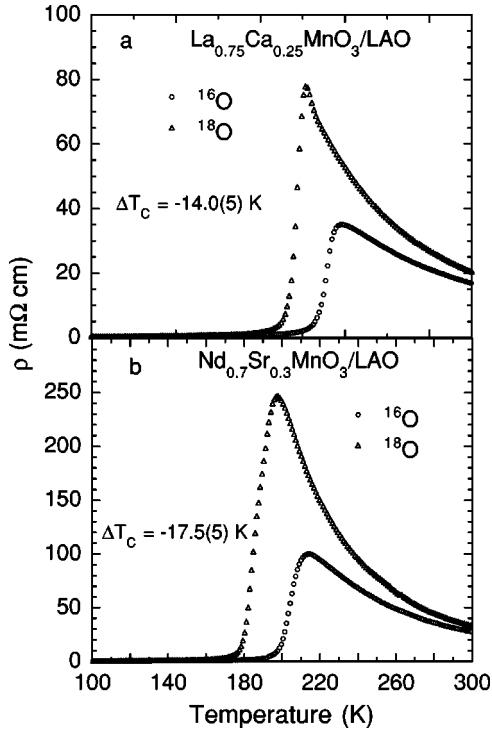
FIG. 1. The resistivity of the oxygen-isotope exchanged films of (a) $La_{0.75}Ca_{0.25}MnO_3$ and (b) $Nd_{0.7}Sr_{0.3}MnO_3$.



FIG. 2. The low-temperature resistivity of the oxygen-isotope exchanged films of (a) $La_{0.75}Ca_{0.25}MnO_3$ and (b) $Nd_{0.7}Sr_{0.3}MnO_3$.

NSMO. In both cases, the residual resistivity $\rho_o$ 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 several times with different contact configurations. We checked that the uncertainty of the difference in $\rho_o$ of the two isotope samples is less than 3%. We also found that the isotope effect is reversible upon isotope back exchange. It is worth noting that the $\rho_o$ for our LCMO $^{16}O$ film is similar to that for a single crystal with a similar $T_C$,[14] while the $\rho_o$ for our NSMO $^{16}O$ film is about 40% higher than those for single crystals.[14,15] This indicates that the electrical transport observed in our LCMO films is intrinsic. On the other hand, a larger $\rho_o$ and a small upturn in the low-temperature resistivity of our NSMO films are most likely to arise from carrier localization when the low-temperature resistivity is larger than a critical value of about 300 $\mu\Omega$cm.[15] The larger $\rho_o$ in our NSMO films might be caused by a contamination of impurities (e.g., Al) that may diffuse from the LAO substrate during the high-temperature annealing. We should mention that the intrinsic resistivity cannot be obtained from ceramic samples where the boundary resistivity is dominant. Thus one cannot use ceramic samples to study the isotope effect on the intrinsic resistivity. Moreover, the van der Pauw technique is particularly good to precisely measure the resistivity difference between the oxygen-isotope exchanged films which have the same thickness. Thus the data shown in Fig. 2 represent the precise measurements on the intrinsic resistivity of the isotope substituted samples.

It is known that the residual resistivity $\rho_o \propto m^*/n\tau_o$. Here $\hbar/\tau_o$ is the scattering rate which is associated with the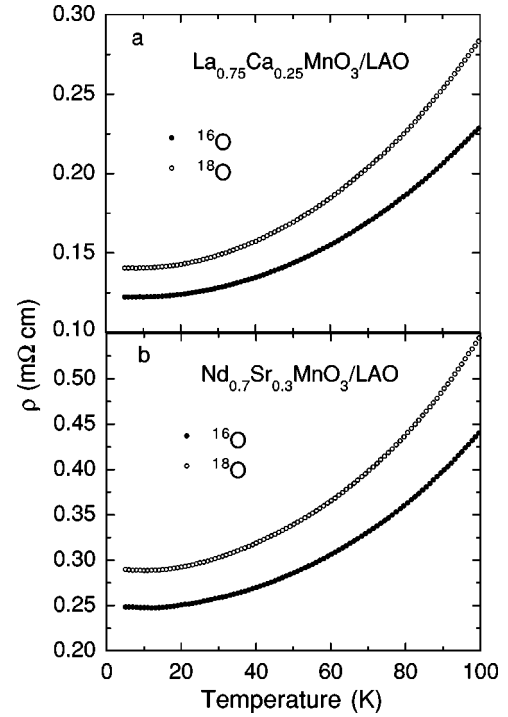 random potential produced by randomly distributed trivalent and divalent cations,[16] and/or with impurities; $m^*$ is the effective mass of carriers at low temperatures, and $n$ is the mobile carrier concentration. If the chemical potential is far above the mobility edge, $\rho_o \propto (m^*)^2$, that is, $\hbar/\tau_o \propto m^*$. This is what one expects from the simple Born approximation. On the other hand, one can show[17] that $\rho_o \propto m^*$ if the chemical potential is slightly above the mobility edge. Since these materials are close to the Mott-Anderson transition, the chemical potential in these materials should not be far away from the mobility edge so that $\rho_o \propto (m^*)^\beta$ with $\beta \simeq 1$. Therefore, the large oxygen-isotope effect on $\rho_o$ implies that the effective mass of the carriers strongly depends on the oxygen mass.

In order to gain further insight, it is important to make more quantitative analyses on the temperature dependence of the resistivity for two isotope samples. If the charge carriers at low temperatures are polaronic, the temperature dependence of the resistivity should agree with polaron metallic conduction. This is indeed the case as recently demonstrated by Zhao *et al.*[9] There are three contributions to the resistivity: the residual resistivity $\rho_o$, the term $AT^{4.5}$ contributed from two-magnon scattering,[18] and the term $B\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$, which arises from polaron coherent motion involving a relaxation due to a soft optical phonon mode that is strongly coupled to the carriers.[9] Here $\omega_s$ is the frequency of a soft optical mode. The temperature dependent part of the resistivity is then given by

$$\rho(T) - \rho_o = AT^{4.5} + B\omega_s/\sinh^2(\hbar\omega_s/2k_BT). \qquad (1)$$

It was shown that the parameter $B$ is proportional to $m^*/n$.[9] This implies that $B$ and $\rho_o$ should have a similar

relative change upon the isotope substitution if $\rho_o \propto m^*$. Although the first term in Eq. (1) was derived for a free carrier system, the theory should be also valid for polaronic carriers which can propagate in the Bloch states at low temperatures like heavy fermions scattered by magnons, phonons, impurity potentials, and themselves.[19] The coefficient $A$ has an analytical expression in the case of a simple parabolic band (occupied by single-spin holes).[18] In terms of the hole density per cell $n$, the average spin stiffness $\bar{D}$, and the effective hopping integral $t^*$, the coefficient $A$ can be written as[18]

$$A = \left(\frac{3a\hbar}{32\pi e^2}\right)(2-n/2)^{-2}(6\pi^2 n)^{5/3}\left(2.52 + 0.0017\frac{\bar{D}}{a^2 t^*}\right)$$
$$\times \left\{\frac{a^2 k_B}{\bar{D}(6\pi^2)^{2/3}(0.5^{2/3}-n^{2/3})}\right\}^{9/2}. \quad (2)$$

Here we have used the relations: $ak_F = (6\pi^2 n)^{1/3}$ (where $\hbar k_F$ is the Fermi momentum, and $a$ is the lattice constant); $E_F = t^*(6\pi^2)^{2/3}(0.5^{2/3}-n^{2/3})$ (where the Fermi energy $E_F$ is measured from the band center); and the effective spin $S^* = 2-n/2$. The value of $t^*$ can be estimated to be about 40 meV from the measured effective plasma frequency $\hbar\Omega_p^* = 1.1$ eV and $n \sim 0.3$ in La$_{0.7}$Ca$_{0.3}$MnO$_3$.[20] Since $\bar{D}$ is about 100 meV Å$^2$ (see below), one expects that the term $0.0017\bar{D}/a^2 t^* \ll 2.52$, and thus can be dropped out in Eq. (2). We should mention that by considering realistic polaronic band structure and the random potentials, Eq. (2) should be modified. However, we believe that $A$ should be still proportional to $(T/\bar{D})^{4.5}$ but with a different numerical coefficient.

From Eq. (2), one can see that there are two parameters $n$ and $\bar{D}$ that determine the magnitude of $A$. In doped manganites, $n$ should be approximately equal to the doping level $x$. The average spin stiffness $\bar{D}$ should be close to the long-wave spin stiffness $D(0)$ if there is negligible magnon softening near the zone boundary. On the other hand, $\bar{D} < D(0)$ if there is a magnon softening near the zone boundary as the case of low-$T_C$ materials.[21] In any cases, one might expect that the average $\bar{D}$ should be proportional to $T_C$ so that $\bar{D}/k_B T_C$ is a universal constant in the manganite system. Since the magnon softening becomes unimportant when the $T_C$ is higher than 350 K,[21] then $\bar{D} \simeq D(0)$ in the compound La$_{0.7}$Sr$_{0.3}$MnO$_3$ with the highest $T_C = 378$ K.[22] Thus, the universal value of $\bar{D}/k_B T_C$ should be close to the value of $D(0)/k_B T_C$ in La$_{0.7}$Sr$_{0.3}$MnO$_3$, which was found to 5.8 $\pm 0.2$ Å$^2$.[22]

Now we fit the $\rho(T)-\rho_o$ data below 100 K by Eq. (1) for the LCMO $^{16}$O and $^{18}$O samples, as shown in Fig. 3. It is striking that the fits to the data of both isotope samples are very good. In order to see more clearly the quality of the fits, we plot in Fig. 4 the relative difference $\Delta\rho/\rho$ between the data and the fitted curves. It is clear that there is a negligible systematic deviation below 100 K. We exclude the data above 100 K in the fitting since $n/m^*$ above 100 K becomes temperature dependent.[20] The fitting parameters $A$, $B$, and $\hbar\omega_s$ are summarized in Table I. Since the fits are excellent,
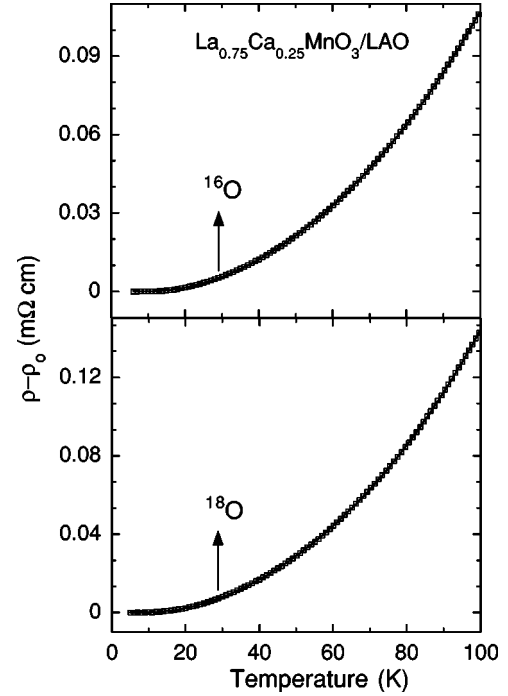


FIG. 3. $\rho(T)-\rho_o$ for the $^{16}$O and $^{18}$O films of La$_{0.75}$Ca$_{0.25}$MnO$_3$. The solid lines are fitted curves by Eq. (1).

the uncertainties in the fitting parameters are very small (see Table I). On the other hand, since there is a small upturn at the low-temperature resistivity of the NSMO films (see Fig. 2 and discussion above), one needs three additional parameters in order to fit the low-temperature upturn. Therefore, we did not attempt to fit the NSMO data with six parameters, but gave the values of the resistivity at 5 K for both isotope samples in Table I.

From Table I, one can see that $\rho_o$ increases by 15(3)%, and $B$ by 17(3)%. This provides additional evidence that $\rho_o \propto m^*$, in agreement with the above argument. Thus the observed large oxygen-isotope effects on both $\rho_o$ and $B$ consistently suggest that the effective mass of carriers should depend strongly on the oxygen-isotope mass. This cannot be explained by any conventional models.
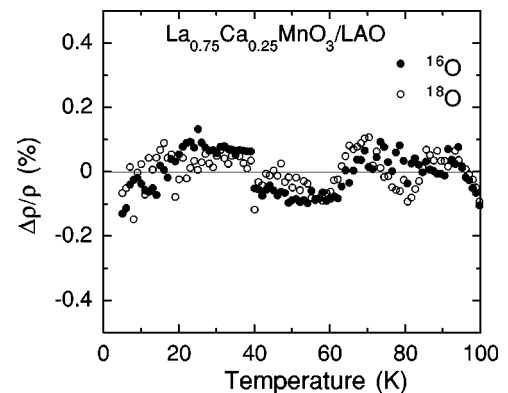


FIG. 4. The relative differences between the resistivity data and the fitted curves for the $^{16}$O and $^{18}$O films of La$_{0.75}$Ca$_{0.25}$MnO$_3$. The systematic deviations are very small.

TABLE I. The summary of the fitting parameters $A$, $B$, and $\hbar\omega_s/k_B$ for the $^{16}O$ and $^{18}O$ films of La$_{0.75}$Ca$_{0.25}$MnO$_3$ (LCMO), and the summary of the $T_C$ and $\rho_o$ values for the LCMO films and the Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ films (NSMO). The uncertainty in $T_C$ is $\pm 0.3$ K. The uncertainty in $\rho_o$ is discussed in the text.

| Compounds | $T_C$ (K) | $\rho_0$ ($\mu\Omega$ cm) | $A$ (m$\Omega$ cm/K$^{4.5}$) | $B$ ($\mu\Omega$ cm/K) | $\hbar\omega_s/k_B$ (K) |
|---|---|---|---|---|---|
| LCMO($^{16}O$) | 231.3 | 122.4 | $1.20(2)\times10^{-11}$ | 0.370(3) | 74.4(2) |
| LCMO($^{18}O$) | 217.3 | 140.5 | $1.89(2)\times10^{-11}$ | 0.434(3) | 66.8(3) |
| NSMO($^{16}O$) | 203.9 | 248.2 | | | |
| NSMO($^{18}O$) | 186.4 | 289.2 | | | |

In addition, $\omega_s$ decreases by about 10(1)% upon replacing $^{16}O$ with $^{18}O$. This may imply that the soft mode might be associated with the motion of the oxygen atoms and has a large anharmonicity. It was shown that the tilt/rotation mode of the oxygen octahedra in cuprates has a strong electron-phonon coupling (quadratic coupling) and a large anharmonicity.[23,24] The large anharmonicity of the mode can possibly lead to a decrease of $\omega_s$ by 12.5% upon replacing $^{16}O$ with $^{18}O$.[23] In a similar perovskite superconductor Ba(Pb$_{0.75}$Bi$_{0.25}$)O$_3$, both neutron and tunneling experiments[25] show that a soft mode with $\hbar\omega_s/k_B = 70$ K is related to rotational vibrations of the oxygen octahedra, and has a strong electron-phonon coupling. Moreover, the frequency of the rotational mode in Ba(Pb$_{0.75}$Bi$_{0.25}$)O$_3$ is nearly the same as that of the soft mode ($\hbar\omega_s/k_B = 74$ K) in the La$_{0.75}$Ca$_{0.25}$MnO$_3$ $^{16}O$ film. Both the frequency of the soft mode and its isotope dependence can be quantitatively explained if the soft mode in the manganites is also associated with the rotational vibrations of the oxygen octahedra.

Now we turn to the discussion on the magnitude of the parameter $A$ and its isotope dependence. From Eq. (2), one can see that $n$ and/or $\bar{D}$ should be isotope dependent in order to explain the large isotope effect on the parameter $A$. As discussed above, the $\bar{D}$ in Eq. (2) should be proportional to $T_C$. Then one can obtain $\bar{D}$ values from the $T_C$ values using $\bar{D}/k_B T_C = 5.8$ Å$^2$ (see the above discussion). Substituting the $\bar{D}$ and $A$ values (see Table I) into Eq. (2), we find $n = 0.235$ for the La$_{0.75}$Ca$_{0.25}$MnO$_3$ $^{16}O$ film, and $n = 0.240$ for the La$_{0.75}$Ca$_{0.25}$MnO$_3$ $^{18}O$ film. The fact that $n \simeq x$ for both isotope samples is consistent with the above interpretation of the isotope dependence of $\rho_o$ being caused only by $m^*$. The $AT^{4.5}$ term in our resistivity data is in quantitative agreement with the two-magnon scattering theory.[18]

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$_3$ suggest that the charge carriers in the ferromagnetic state should be polaronic. Moreover, the temperature dependent part of the resistivity at low temperatures is in quantitative agreement with a transport mechanism where the resistivity is due to two-magnon scattering[18] and to the scattering from a soft optical phonon mode.

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[1] R. von Helmolt *et al.*, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin *et al.*, Science **264**, 413 (1994).

[2] A.P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).

[3] A.J. Millis, P.B. Littlewood, and B.I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); H. Röder, J. Zang, and A.R. Bishop, *ibid.* **76**, 1356 (1996).

[4] A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1994).

[5] A.S. Alexandrov and A.M. Bratkovsky, Phys. Rev. Lett. **82**, 141 (1999).

[6] A. Urushibara *et al.*, Phys. Rev. B **51**, 14 103 (1995).

[7] M. Jaime *et al.*, Phys. Rev. B **58**, R5901 (1998).

[8] A. Machida, Y. Moritomo, and A. Nakamura, Phys. Rev. B **58**, R4281 (1998).

[9] G.M. Zhao *et al.*, Phys. Rev. Lett. **84**, 6086 (2000).

[10] A. S. Alexandrov and N. F. Mott, *Polarons and Bipolarons* (World Scientific, Singapore, 1995); A. S. Alexandrov and P. E. Kornilovitch, Phys. Rev. Lett. **82**, 807 (1999).

[11] G.M. Zhao *et al.*, Nature (London) **381**, 676 (1996).

[12] W. Prellier *et al.*, Appl. Phys. Lett. **75**, 1446 (1999).

[13] G.M. Zhao *et al.*, Phys. Rev. B **60**, 11 914 (1999).

[14] P. Dai *et al.*, Phys. Rev. B **61**, 9553 (2000).

[15] Y. Sawaki *et al.*, Phys. Rev. B **61**, 11 588 (2000).

[16] W.E. Pickett and D.J. Singh, Phys. Rev. B **55**, R8642 (1997); D.A. Papaconstantopoulos and W.E. Pickett, *ibid.* **57**, 12 751 (1998).

[17] A. S. Alexandrov *et al.* (unpublished).

[18] K. Kubo and N.A. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).

[19] I.G. Austin and N.F. Mott, Adv. Phys. **18**, 41 (1969).

[20] J.R. Simpson *et al.*, Phys. Rev. B **60**, R16 263 (1999).

[21] H.Y. Hwang *et al.*, Phys. Rev. Lett. **80**, 1316 (1998).

[22] M.C. Martin *et al.*, Phys. Rev. B **53**, 14 285 (1996).

[23] V.H. Crespi and M.L. Cohen, Phys. Rev. B **48**, 398 (1993).

[24] W.E. Pickett, R.E. Cohen, and H. Krakauer, Phys. Rev. Lett. **67**, 228 (1991).

[25] W. Reichardt, B. Batlogg, and J.P. Remeika, Physica B **135**, 501 (1985).