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# Isotope effects and possible pairing mechanism in optimally doped cuprate superconductors

Guo-meng Zhao,[1,2] Vidula Kirtikar,[2] and Donald E. Morris[2]
[1]*Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland*
[2]*Morris Research, Inc., 44 Marguerito Road, Berkeley, California 96707*

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We have studied the oxygen-isotope effects on $T_c$ and in-plane penetration depth $\lambda_{ab}(0)$ in an optimally doped three-layer cuprate $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y}$ ($T_c \sim 107$ K). We find a small oxygen-isotope effect on $T_c$ ($\alpha_O = 0.019$), and a substantial effect on $\lambda_{ab}(0)$ [$\Delta\lambda_{ab}(0)/\lambda_{ab}(0) = 2.5 \pm 0.5\%$]. The present results along with the previously observed isotope effects in single-layer and double-layer cuprates indicate that the isotope exponent $\alpha_O$ in optimally doped cuprates is small while the isotope effect on the in-plane effective supercarrier mass is substantial and nearly independent of the number of the $CuO_2$ layers. A plausible pairing mechanism is proposed to explain the isotope effects, high-$T_c$ superconductivity, and tunneling spectra in a consistent way.

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The pairing mechanism responsible for high-$T_c$ superconductivity is still controversial. In conventional superconductors, a strong effect of changing ion mass $M$ on the transition temperature $T_c$ implies that lattice vibrations (phonons) play an important role in the microscopic mechanism of superconductivity. An isotope exponent $\alpha(= -d \ln T_c / d \ln M)$ of about 0.5 is consistent with the phonon-mediated BCS theory. A nearly zero oxygen-isotope effect ($\alpha_O \simeq 0.03$) was earlier observed in a double-layer cuprate superconductor $YBa_2Cu_3O_{7-y}$ which is optimally doped ($T_c \sim 92$ K).[1,2] Such a small isotope effect might suggest that phonons should not be important to the pairing mechanism. On the other hand, large oxygen-isotope shifts were later observed in several underdoped cuprate superconductors.[3–9] Further, three indirect experiments have consistently demonstrated that the difference in the hole densities of the $^{16}O$ and $^{18}O$ samples is smaller than 0.0002 per Cu site.[7–9] Moreover, a quantitative data analysis on the isotope-exchanged $YBa_2Cu_3O_{6.94}$ (Ref. 10) suggested that there is a negligible oxygen-isotope effect on the supercarrier density $n_s$.

Since muon-spin rotation experiments[11] showed that $T_c$ is approximately proportional to $n_s/m^{**}_{ab}$ in deeply underdoped cuprates (where $m^{**}_{ab}$ is the in-plane effective supercarrier mass), a large oxygen-isotope shift of $T_c$ observed in this doping regime should arise from a large oxygen-isotope effect on $m^{**}_{ab}$. Indeed, several independent experiments[7–9,12] have consistently demonstrated that both the average supercarrier mass $m^{**}$ and the in-plane supercarrier mass $m^{**}_{ab}$ strongly depend on the oxygen isotope mass in underdoped cuprates. Such an unconventional isotope effect suggests that there exist polaronic charge carriers, which are condensed into supercarriers in the superconducting state. This appears to give support to a theory of (bi)polaronic superconductivity.[13] On the other hand, within this theory, it is difficult to explain a small isotope shift of $T_c$ and a large reduced energy gap [i.e., $2\Delta(0)/k_B T_c > 6$] observed in optimally doped cuprates where the single-particle excitation gap vanishes above $T_c$.[14] Therefore, an alternative theoretical approach is required to explain superconductivity in optimally doped and overdoped cuprates. A possibly correct pairing mechanism should be able to consistently explain a small isotope shift of $T_c$, a substantial isotope effect on the supercarrier mass,[8,10] and a large reduced energy gap.

Here we report the observation of the oxygen-isotope effects on $T_c$ and in-plane penetration depth $\lambda_{ab}(0)$ in a three-layer cuprate $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y}$ ($T_c \sim 107$ K). We find a small oxygen-isotope effect on $T_c$ and a substantial effect on $\lambda_{ab}(0)$. We propose a possible theoretical model which is able to consistently explain these isotope effects and the large reduced energy gap.

Samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y}$ were prepared from high purity $Bi_2O_3$, PbO, $SrCO_3$, $CaCO_3$, and CuO. The samples were ground, pelletized and fired at 865/855/845 °C for 37/40/44 h in air with two intermediate grindings. Two samples were prepared under nearly the same heat treatment. To ensure that the samples have small grain size and enough porosity, they were reground thoroughly, pelletized, and annealed in flowing oxygen at 600 °C for 10 h.

Two pelletized samples were broken into halves (producing two sample pairs), and the halves were subject to the $^{16}O$ and $^{18}O$ isotope diffusion, which was conducted in two parallel quartz tubes separated by about 2 cm.[5,10,7] The diffusion was carried out for 68 h at 600 °C and oxygen pressure of 0.8 bar for sample pair I, and for 40 h at 650 °C and oxygen pressure of 1 bar for sample pair II. The cooling rate was 30 °C/h. The oxygen isotope enrichments were determined from the weight changes of both $^{16}O$ and $^{18}O$ samples. The $^{18}O$ samples had $85 \pm 5\%$ $^{18}O$ and $15 \pm 5\%$ $^{16}O$.

The susceptibility was measured with a quantum design superconducting quantum interference device (SQUID) magnetometer. The field-cooled, measured-on-warming susceptibility was measured in a field of 15 Oe for sample pair I, and 10 Oe for sample pair II. The temperature measurements were performed with a platinum resistance thermometer (Lakeshore PT-111) placed in direct contact with the sample and driven by a microprocessor controlled ac bridge in the SQUID magnetometer. The resolution is 2.5 mK and reproducibility is 10 mK at 77 K after cycling to room temperature.[5,10]

In Fig. 1, we show the susceptibility near $T_c$ for the $^{16}O$ and $^{18}O$ samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y}$: (a) pair I; (b) pair II. In all the cases, the $T_c$ for the $^{18}O$ samples is 0.22

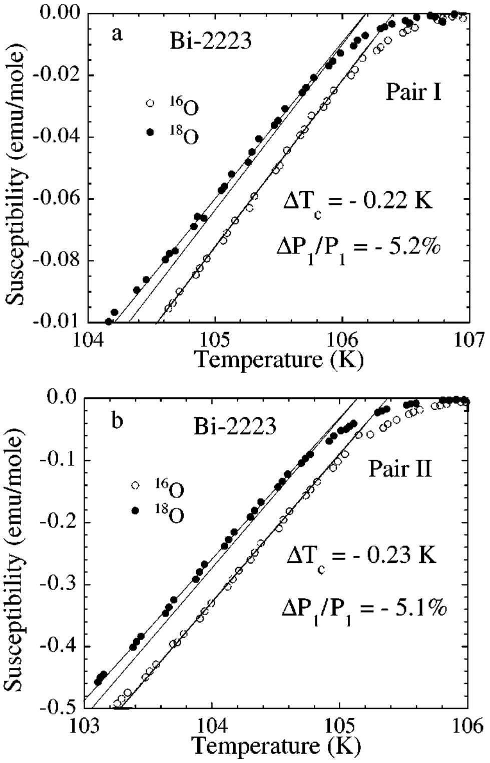

FIG. 1. The susceptibility near $T_c$ for the $^{16}$O and $^{18}$O samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y}$ (Bi-2223): (a) pair I; (b) pair II.

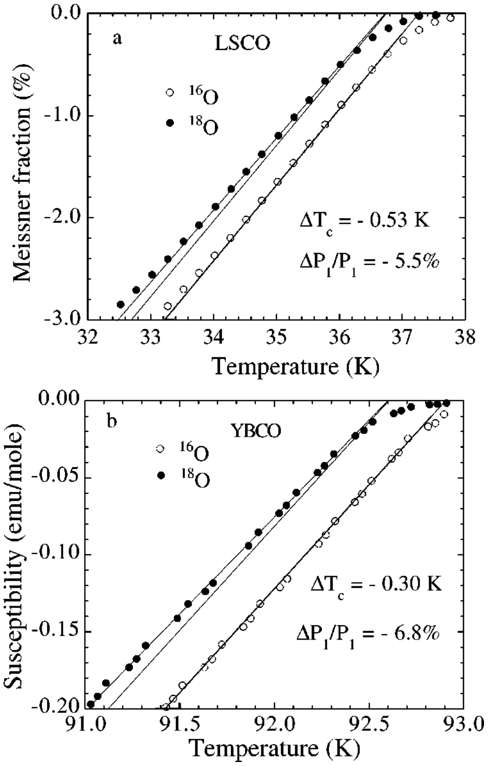

FIG. 2. The susceptibility data near $T_c$ for the $^{16}$O and $^{18}$O samples of (a) $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) and (b) $YBa_2Cu_3O_{6.94}$ (YBCO) (after Refs. 8 and 10).

$\pm 0.01$ K lower than for the $^{16}$O samples. Extrapolating to 100% exchange, we calculate the isotope exponent $\alpha_O = -d\ln T_c/d\ln M_O = 0.019\pm 001$. We also note that there is a well-defined linear portion on the transition curve ~1 K below the diamagnetic onset temperature. It is evident that the slope of the linear portion (denoted by $P_1$) for the $^{18}$O samples is 5.0±1.0 % smaller than for the $^{16}$O samples, that is, $\Delta P_1/P_1 = -5.0\pm 1.0\,\%$.

For comparison, the results for single-layer $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) and double-layer $YBa_2Cu_3O_{6.94}$ (YBCO) compounds are reproduced in Fig. 2. It is clear that $\Delta P_1/P_1 = -5.5\pm 1.0\%$ for LSCO and $-6.8\pm 1.0\,\%$ for YBCO. Comparing Fig. 2 with Fig. 1, one can see that the isotope effect on $P_1$ is nearly the same for all three compounds within the experimental uncertainty. It is also interesting to note that the isotope effect on $T_c$ decreases monotonically with increasing $T_c$.

The observed oxygen-isotope effect on the slope $P_1$ is caused by the dependence of the penetration depth on the oxygen mass. For nearly isotropic materials with $\lambda_{ab}(0) \sim \lambda_c(0) \sim \lambda(0)$, it was shown that:[10] $\Delta P_1/P_1 = -\Delta T_c/T_c - 2\Delta\lambda(0)/\lambda(0)$. For highly anisotropic materials such as cuprates, a relation $\lambda_c(T) \gg \lambda_{ab}(T) > R$ (where $R$ is the maximum particle size) holds near $T_c$ so that the diamagnetic signal is proportional to $1/\lambda_{ab}^2(T)$.[15] Then one readily finds that

$$\Delta P_1/P_1 \simeq -\Delta T_c/T_c - 2\Delta\lambda_{ab}(0)/\lambda_{ab}(0). \qquad (1)$$

From Fig. 1 and Fig. 2, we obtain $\Delta\lambda_{ab}(0)/\lambda_{ab}(0) = 3.2 \pm 0.7\,\%$ using Eq. (1). This is in remarkably good agreement with the recent muon spin rotation experiments on the oxygen-isotope exchanged $YBa_2Cu_3O_{6.96}$, which show that $\Delta\lambda_{ab}(0)/\lambda_{ab}(0) = 2.5\pm 0.5\,\%$.[16]

Since both $n$ and $n_s$ are independent of the isotope mass as discussed above, the observed oxygen-isotope effect on the in-plane penetration depth is caused by the isotope dependence of $m_{ab}^{**}$. The substantial isotope effect on $m_{ab}^{**}$ may suggest that charge carriers in the optimally doped cuprates remain polaronic nature, and that those polaronic carriers are condensed into supercarriers in the superconducting state.

Now a question arises: why is the isotope effect on $m_{ab}^{**}$ substantial while the isotope shift of $T_c$ is very small in these optimally doped cuprates? In order to answer this question, we should first find out which phonon modes are strongly coupled to doped holes in these materials. Inelastic neutron scattering experiments[17,18] show that the Cu-O bond stretching modes in the $CuO_2$ planes are strongly coupled to the doped holes. The average frequency of this mode is about 75 meV in $La_{1.85}Sr_{0.15}CuO_4$,[17] and about 60 meV in $YBa_2Cu_3O_{6.92}$.[18] Such a strong electron-phonon coupling should be also manifested in tunneling spectra, as is the case in conventional superconductors. Although it is difficult to obtain reliable tunneling spectra for cuprates due to a short coherent length, there are two high-quality tunneling spectra for slightly overdoped YBCO (Ref. 19) and $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO).[20]

In Fig. 3, we show normalized conductance data for scanning tunneling microscopy (STM) on a slightly overdoped

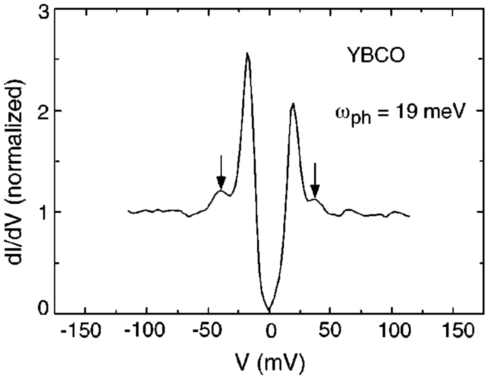

FIG. 3. The normalized conductance data for a scanning tunneling microscopy (STM) tunnel junction on a slightly overdoped $YBa_2Cu_3O_{7-y}$ (YBCO) crystal with a Pt-Ir tip at 4.2 K (after Ref. 19).

YBCO crystal with a Pt-Ir tip at 4.2 K.[19] The crystal has $T_c \simeq 90$ K with $\sim 1$ K transition width.[19] Since the presence of oxygen vacancies in the CuO chains can lead to residual density of states and to zero-bias conductance in the superconducting state, a negligible zero-bias conductance in the spectrum suggests that the spectrum represents the intrinsic density of states contributed only from the $CuO_2$ planes. It is striking that the strong coupling features similar to that in conventional superconductors can be clearly seen in the spectrum (as indicated by the arrows). The strong-coupling features correspond to a strong coupling between charge carriers and the phonon mode with $\omega_{ph} = 19$ meV. The phonon density of states in an optimally doped YBCO also reveals a large peak at about 20 meV.[21]

In Fig. 4, we plot the electron-phonon spectral density $\alpha^2F(\omega)$ for an optimally doped BSCCO crystal, which was extracted from a superconductor-insulator-superconductor (SIS) break-junction spectrum.[20] A strong coupling feature at an energy of about 20 meV is clearly seen. This feature also corresponds to the large peak in the phonon density of states at about 20 meV (see open circles). In addition to a strong coupling feature at 20 meV, there is another strong coupling feature at about 73 meV, which corresponds to the phonon energy of the Cu-O bond stretching mode discussed above. Therefore, these tunneling spectra (Figs. 3 and 4) consistently suggest that both the low-energy phonon mode at about 20 meV and the high-energy phonon mode at about 73 meV are strongly coupled to conduction electrons in these double-layer compounds.

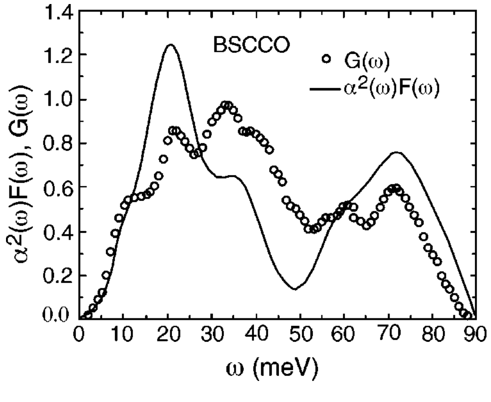

FIG. 4. The electron-phonon spectral density $\alpha^2F(\omega)$ for an optimally doped $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO) crystal, which was deduced from an SIS break-junction spectrum (Ref. 20).

A theoretical approach to a strong electron-phonon coupling system depends not only on the adiabatic ratio $\omega/E_F$ but also on the coupling strengths with different phonon modes. When the Fermi energy $E_F$ is smaller than these strong-coupling phonon energies, the phonon-induced effective interaction between carriers is nonretarded so that the real-space pairing (e.g., intersite bipolaron formation) becomes possible.[13,22] This should be the case for the doping level $x \leqslant 0.10$ in $La_{1-x}Sr_xCuO_4$.[9] In contrast, $E_F$ in doped oxygen-hole bands may lie in between 20 and 73 meV in the optimally doped and overdoped regimes, so that the pairing interaction becomes retarded for the low-energy phonons, and remains nonretarded for the high-energy phonons. The retarded electron-phonon coupling for the low-energy phonons could be treated within the Migdal approximation, while the nonretarded electron-phonon coupling for the high-energy phonons should be modeled separately within the polaron theory. This theoretical approach has been successfully applied to fullerenes.[23] The strong coupling between doped holes and the high-energy phonons leads to a polaronic mass enhancement and to an attractive nonretarded potential between doped holes. Effectively, the polaronic holes could then form *k*-space Cooper pairs by interacting with the low-energy phonons. The problem could thus be solved within Eliashberg equations with an effective electron-phonon spectral density for the low-energy phonons and a negative Coulomb pseudopotential produced by the high-energy phonons and other high-energy bosonic excitations of purely electronic origin (e.g., spin fluctuations, excitons, and plasmons). Within this simplified approach, the effective electron-phonon coupling constant $\lambda_{ep}$ for the low-energy phonons is enhanced by a factor of $f_p = \exp(g^2)$. Here $g^2 = A/\omega_H$, $A$ is a constant, and $\omega_H$ is the frequency of the high-energy phonon mode. The effective Coulomb pseudopotential $\mu^*$ is negative and also proportional to $f_p$.

For slightly overdoped BSCCO, $g^2$ can be evaluated from the midinfrared optical conductivity which exhibits a maximum at $E_m \simeq 0.12$ eV.[26] With $E_m = 0.12$ eV, $\hbar\omega_H = 75$ meV, we find $g^2 = E_m/(2\hbar\omega_H) = 0.8$, leading to $f_p = 2.2$. From the spectral density shown in Fig. 4, we can extract the effective electron-phonon coupling constant $\lambda_{ep}$ for the low-energy phonon mode, that is, $\lambda_{ep} \simeq 2.6$. If there were no polaronic mass enhancement due to the high-energy phonons, the coupling constant contributed from the low-energy phonons would be about 1.2. With $\mu^* = 0.1$ and $\lambda_{ep} = 1.2$, we calculate $T_c = 18$ K according to a $T_c$ formula

$$k_BT_c = 0.25\hbar\sqrt{\langle\omega^2\rangle}[\exp(2/\lambda_{eff}) - 1]^{-1/2}, \tag{2}$$

where

$$\lambda_{eff} = (\lambda_{ep} - \mu^*)/[1 + 2\mu^* + \lambda_{ep}\mu^* t(\lambda_{ep})]. \tag{3}$$

The function $t(\lambda_{ep})$ is plotted in Fig. 2 of Ref. 27. In the present case, $\hbar\sqrt{\langle\omega^2\rangle}$ is contributed only from the low-energy phonons and equal to 20 meV. Therefore, without the high-energy phonons, $T_c$ would not be higher than 20 K. The high-energy phonons not only enhance $\lambda_{ep}$ by a factor of 2.2, but also reduce $\mu^*$ substantially.[23] It has recently been shown that $\mu^*$ in cuprates becomes negative (i.e., $\mu^* \simeq -0.05$) due to the presence of low-energy electronic collective modes (acoustic plasmons) in layered conductors.[24] Since the high-energy phonon mode reduces $\mu^*$ further, it is likely that the value of $\mu^*$ should be in the range of $-0.1$ to $-0.2$. If we take $\mu^* = -0.15$, $\lambda_{ep} = 2.6$ (see above), we can get $T_c = 95$ K. This leads to $k_B T_c/(\hbar\sqrt{\langle\omega^2\rangle}) = 0.41$, and $2\Delta(0)/k_B T_c \simeq 7$ according to the known relation between $k_B T_c/(\hbar\sqrt{\langle\omega^2\rangle})$ and $2\Delta(0)/k_B T_c$.[25] The calculated reduced energy gap is in good agreement with experiment. We would like to mention that the present calculation is valid for an isotropic *s*-wave gap, which should be the case for the polaronic oxygen-hole bands near $(0,\pm\pi)$ and $(\pm\pi,0)$ regions. In addition to the polaronic oxygen holes, there are electronlike free carriers which could condense into supercarriers through interband scattering. The pairing symmetry of the two-carrier system may be an extended *s*-wave with eight line nodes.[28]

Now we can calculate the total isotope exponent $\alpha$ using Eqs. (2) and (3), and the relations $\lambda_{ep} \propto f_p$, $\mu^* \propto f_p$, $t(\lambda_{ep}) \simeq 1.8/\lambda_{ep}$. The calculated total isotope exponent is $\alpha \simeq 0$. The nearly zero isotope exponent is due to the fact that the isotope dependencies of $\lambda_{ep}$ and $\mu^*$ (arising from the polaronic effect) cancel out the isotope effect on the prefactor of Eq. (2). Moreover, the formation of polaronic Cooper pairs naturally explains the sizable isotope effect on the supercarrier mass.

In summary, we report the observation of the oxygen-isotope effects in the three-layer cuprate $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y}$. The present results along with the previously observed isotope effects in single-layer and double-layer cuprate superconductors indicate that the isotope effect on $T_c$ in optimally doped cuprates is small while the isotope effect on the effective supercarrier mass is substantial. These isotope effects and tunneling spectra observed in optimally doped cuprates can be consistently explained within a scenario where polaronic oxygen holes are bound into Cooper pairs.

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