Oxygen isotope effect in $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n=1,2,3$) single crystals

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We report measurements of the oxygen isotope effect in $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n=1,2,3$) single crystals. For optimally doped materials the isotope exponent is found to decrease with increasing the number of $\text{CuO}_2$ layers in a manner of inversely correlating with the superconducting transition temperature in this homologous family. This behavior is in contrast to the general belief that the isotope effect can be negligible for the optimally doped cuprates. Our results highlight the important role played by phonons and interlayer coupling in the high-temperature superconductivity.

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The coupling mechanism which causes high-temperature superconductivity in cuprates remains a challenging issue in condensed matter physics. Although it is generally believed that antiferromagnetism is important for superconductivity, there has been growing experimental evidence1−4 for the role of phonons in the electronic state. Isotope effects provide a good indication for electron-phonon interaction. Gweon et al.3 reported a large isotope effect on the electronic structure involving shifts of the band bottom as large as $10−40$ meV in optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ($\text{Bi}_2212$) using angle-resolved photoemission spectroscopy (ARPES), indicating that the coupling between the lattice and electrons plays an important role. Douglas et al.,4 in contrast found no large isotope effect in the same material, but concluded that their measurements are not inconsistent with a conventional isotope shift of the order of $3$ meV. Based on $d^2\Pi/dV^2$ imaging measurements using scanning tunneling microscopy (STM), Lee et al.,5 obtained a bosonic mode of $\text{Bi}_2212$ irrespective of doping level with energy of $52$ meV which was identified as a lattice mode from the observed $6\%$ energy shift upon substitution for $^{18}\text{O}$ by $^{16}\text{O}$. The fact that their samples are poorly characterized because the superconducting transition temperature $T_c$ is $76$ K for the $^{16}\text{O}$ sample and $88$ K for the $^{18}\text{O}$ sample, far beyond the expected change solely through the isotope exchange, leaves a possibility for other interpretations. On the other hand, an inelastic neutron-scattering experiment6 showed a negligible shift of the magnetic resonance energy in $\text{YBa}_2\text{Cu}_3\text{O}_{6.88}$ upon oxygen isotope substitution ($^{18}\text{O}→^{16}\text{O}$), thus placing a severe limit on the role of electron-phonon coupling in cuprate superconductors.

The isotope effect on $T_c$ as a direct experimental probe in revealing electron-phonon coupling supported phonon-mediated pairing in conventional superconductors. Such studies7 in cuprate superconductors, particularly in $\text{YBa}_2\text{Cu}_3\text{O}_{7−\delta}$ and $\text{La}_{2−x}\text{Sr}_x\text{CuO}_4$, have established that $T_c$ exhibits a weak shift upon isotope substitution at optimal doping where $T_c$ is maximal. Recent experiments8,9 suggested a sharp transition in quasiparticle dynamics precisely at optimal doping. Neutron diffraction data10 also showed a sharp change of the in-plane Cu–O bond distribution at optimal doping, underscoring a strong electron-phonon coupling. It is apparently crucial to investigate superconducting properties at this magic doping level. The striking feature of cuprate superconductors is the appearance of the $\text{CuO}_2$ plane. Even at optimal doping, $T_c$ initially increases with increasing the number of $\text{CuO}_2$ layers within a unit cell in a homologous layered system. It is still unknown how the $\text{CuO}_2$-layer number affects the isotope effect in a homologous series. Although mercury- and thallium-based families have relatively high $T_c$’s, the oxygen-isotope studies in both systems are very difficult due to the complexity of the self-doping effect involving the partial substitution of copper for mercury11 or thallium.12 Among the various layered families discovered so far, the bismuth-based series then becomes the only promotional candidate for such a purpose. Unlike other families, all members of the bismuth-based family have high-quality single crystals available. Moreover, most systematic data of ARPES1−3 and STM5 were collected in bismuth-based single crystals, allowing direct comparison for clarifying the phonon contribution to superconductivity.

In this work we report measurements of the oxygen isotope effect in $\text{Bi}_2\text{Sr}_2\text{Ca}_{n−1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n=1,2,3$) single crystals. We find that the optimally doped monolayer material has a sizeable oxygen isotope exponent $\alpha$. However, $\alpha$ decreases monotonically with the number of $\text{CuO}_2$ layers in a way opposite to $T_c$ in this homologous family at optimal doping. This behavior directly points to the importance of electron-phonon interactions as well as the interlayer coupling effect in layered cuprates.

Single crystals of $\text{Bi}_2\text{Sr}_2\text{La}_{0.3}\text{Cu}_0\text{O}_{6+\delta}$ ($\text{Bi2201}$), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ($\text{Bi2212}$), and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{10+\delta}$ ($\text{Bi2223}$) were grown by the traveling-solvent floating-zone method with very slow growth rates and steep temperature gradients, as described in detail elsewhere.13−15 Plate-shaped crystals were cleaved from crystal ingots. The purity and crystallinity of the samples were checked out by x-ray diffraction (Fig. 1). The fact that only sharp $(00l)$ reflection peaks can be observed in each pattern confirms the high crystalline quality and phase purity of these samples. The three Bi-based cuprates used for oxygen isotope studies have simi-
The structures of the tetragonal $I4/mmm$ space group ($a = b = 5.4$ Å). Their unit cells differ only in the number ($n = 1$) of CuO$_2$-Ca-CuO$_2$ slabs packed along the $c$ axis with lattice parameters of 24.33(7), 30.80(6), and 37.07(7) Å for the monolayer, bilayer, and trilayer Bi-based cuprates, respectively.

The $c$-axis length in Bi-based cuprates has been found to be a sensitive measure of oxygen doping level. The $c$-axis length monotonically decreases with increasing $\delta$ in these materials. For the monolayer and bilayer cuprates, $T_c$ increases with decreasing $c$-axis length, reaching its maximum, and then decreases with decreasing $c$-axis length, reflecting the bell-shaped doping dependence of $T_c$. In the case of Bi2223, $T_c$ first increases with decreasing $c$-axis length similar to other members of this family. However, once the maximum value is achieved, $T_c$ remains fixed irrespective of the further decrease of the $c$-axis length. Measurements of optical and transport properties clearly show that the carrier has been doped continuously even in the constant $T_c$ region. Our measured $c$-axis lattice parameters for Bi2201 and Bi2223 indicate that these materials are in reality optimally doped, although the maximum $T_c$'s are scattered for both materials in the literature. The Bi2212 sample was found to be nearly optimally doped but in the underdoped regime based on its $c$-axis length. Using the correlation between $\delta$ and $c$-axis length difference, we may estimate the oxygen content $\delta \sim 0.12$ for our present Bi2212 sample. The oxygen content $\delta$ of the present Bi2201 samples was estimated to be 0.36 as described previously, and the value of $\delta$ for Bi2223 is believed to be $\sim 0.28$.

For the oxygen isotope substitution, we chose each pair of Bi-based cuprate single crystals. The selected samples were annealed in isotonically enriched oxygen under identical conditions following a similar procedure described in Ref. 18. Each sample of crystals of Bi-based cuprates was cut into halves. A pair of them was sealed in separated quartz tubes. One tube was charged with high-purity $^{16}$O gas while the other was charged with 99% $^{18}$O enriched oxygen. All exchange procedures were performed simultaneously in two adjacent quartz tubes at 650 °C and 1 bar oxygen pressure for 96 h to ensure the same content. Then both tubes were slowly cooled to room temperature at a rate of 20 °C/h in order to oxidize them completely. The annealing was repeated with a fresh charge of $^{18}$O. Estimates based on the mass change upon isotope replacement indicate that the $^{18}$O contents were 80(5)% in the exchanged samples.

The isotope exchange process was examined by very accurate ellipsometric measurements performed at the U4IR beamline of the National Synchrotron Light Source at Brookhaven National Laboratory detailed in Ref. 19. Figure 2 shows the real parts of the $c$-axis optical conductivity $\sigma_1(\omega)$ and the dielectric function $\varepsilon_1(\omega)$ for the Bi2212 single crystals for $^{16}$O and $^{18}$O substitution measured at 150 K and in the energy range from about 100 to 700 cm$^{-1}$. Six main peaks with energies of 97, 168, 210, 304, 358, and 583 cm$^{-1}$ are observed in the $^{16}$O standard sample. The peak assignments are as follows: The two low-frequency modes at 97 and 168 cm$^{-1}$ arise from motion of the heavy Bi atoms and the Cu ions, respectively. The $A_{2u}$ mode at 210 cm$^{-1}$ is due to the vibrations of Ca and O(1) atoms in the Cu-O planes, and from the O(3) atoms in the Bi-O planes to the $c$ axis oscillations. The three high-energy vibrations are predominantly oxygen related. The mode at 304 cm$^{-1}$ is basically due to O(3) and O(1) vibrations, with a predominant contribution from the O(3) atoms. The Cu–O bond-bending character mode at 358 cm$^{-1}$ involves significant contribution from the O(1) atoms. The highest frequency mode at 583 cm$^{-1}$ is mainly from the vibrations of O(2) apical atoms in the Sr-O planes. These phonon modes are clearly identified especially due to the resonance features in $\varepsilon_1(\omega)$ as shown in Fig. 2(b).

Upon $^{18}$O substitution, the two low-frequency modes at 97 and 168 cm$^{-1}$ show no shift at all, thus confirming their heavy metal ion feature. With $^{18}$O exchange the four $A_{2u}$ phonons at 210, 304, 358, and 583 cm$^{-1}$ soften in frequency by 4.1, 4.4, 5.3, and 5.5%, respectively, yielding an average isotope exchange ratio consistent with the estimate from
mass change. The relatively large frequency shifts of the 358 and 583 cm$^{-1}$ modes suggest that the O(1) site in the Cu-O planes and the apical O(2) site are nearly fully occupied by $^{18}$O. The observed sizeable redshift of the 210 cm$^{-1}$ mode upon $^{18}$O substitution further indicates that this mode indeed contains appreciable contribution from the O(1) and O(3) atoms. It is also interesting to note that there are two more small peaks at 465 and 630 cm$^{-1}$ in the $^{18}$O exchanged sample these two peaks all move to low frequency by 4.7% again consistent with 80% $^{18}$O exchange.

Superconducting transition temperatures were determined by magnetic susceptibility $\chi$ in a Quantum Design superconducting quantum interference device magnetometer. All samples were measured in an applied field of 10 Oe with $H$//c. To compare the temperature dependence of the isotope pairs, the data points are normalized by taking $\chi$ at each value of temperature and dividing by $\chi$ at 5 K. In Fig. 3, we show the normalized zero-field-cooled susceptibility versus temperature curves for the $^{16}$O and $^{18}$O exchanged samples. $T_c$ was taken as the temperature where the linearily extrapolated transition slope intersects the zero line, which has been generally used in isotope-effect studies. We find a lower $T_c$ for all the $^{18}$O exchanged samples. Oxygen isotope shift of $\Delta T_c$ was obtained to be $-0.79(10)$, $-1.19(15)$, and $-0.27(15)$ K for the Bi2201, Bi2212, and Bi2223, respectively.

Using the definition of the isotope exponent $\alpha = (\Delta T_c / T_c) / (\Delta M / M)$ with $M$ being the oxygen isotopic mass, we have $\alpha = 0.25(4)$ for Bi2201, 0.14(3) for Bi2212, and 0.02(1) for Bi2223. The present $\alpha$ of Bi2201 is the first determined for the isotope effect in this material, and its value lies in the $\alpha$ range for other optimally doped low-$T_c$ monolayer compounds. This observation indicates that the optimally doped monolayer cuprates indeed possess a non-negligible isotope effect. The trilayer Bi2223 has a very small but positive oxygen isotope effect. This finding concludes the early controversy regarding whether the oxygen isotope effect in this material is negative. Importantly, the samples used in our experiments are single crystals and lead-free. Lead-containing powder samples were used in previous experiments. In the case of Bi2212, Gweon et al. noticed that an $^{16}$O $\rightarrow$ $^{18}$O substitution leads to $T_c$ shifting from 92 to 91 K. Taking the exchange rate of their $^{18}$O sample of 75%, one would have $\alpha = 0.12$ for the optimally doped Bi2212, which is close to but smaller than our result for the nearly optimally doped sample on the overdoped side. Previous isotope studies on the overdoped side give $\alpha = 0.05 \pm 0.01$ and 0.03 for samples having $T_c = 84.7$ K (Ref. 18) and 75.5 K, respectively. One then readily gets the information on how $\alpha$ evolves around optimal doping in Bi2212: $\alpha$ slightly decreases with doping, reaching a minimum on the overdoped side, and then increases for heavily overdoped materials. In Fig. 4, we plot the CuO$_2$ layer dependence of $\alpha$ for the optimally doped Bi-based materials. It is quite clear that the oxygen isotope exponent $\alpha$ systematically decreases with the increase of the number of CuO$_2$ layers, which is the central message provided in the present work.

The sizable $\alpha$ of the monolayer Bi2201 indicates that phonons are directly or indirectly involved in determining superconducting state. Just like the $T_c$ behavior, $\alpha$ also has a systematic CuO$_2$ layer dependence in the Bi-based cuprates. Therefore the same physical parameter(s) should control the Cu-O layer effect on both the $T_c$ and $\alpha$. Keeping in mind that the trilayer material has the highest $T_c$ in this homologous series but it has very small isotope effect. Clearly, the argument that a mechanism other than an electron-phonon interaction dominates the superconductivity based only on a small $\alpha$ in a cuprate with a relatively high $T_c$ is inappropriate. The observed CuO$_2$-layer dependence of the isotope effect indicates that the interlayer coupling between the adjacent CuO$_2$ planes is necessary for superconductivity in layered cuprates. For the monolayer materials having lower
$T_c$'s, the interlayer coupling plays a less important role and $T_c$ can be mainly controlled by the phonon coupling, yielding a larger size of isotope exponent. With increasing the number of CuO$_2$ layers in a unit cell, the interlayer coupling begins to play an important role in enhancing $T_c$ and the isotope effect is expected to be small.\textsuperscript{26}

In summary, our experimental finding of the non-negligible oxygen isotope effect in optimally doped Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_2$O$_{2n+4+\delta}$ ($n=1,2,3$) highlights the role of phonons played in the high-$T_c$ superconductivity. Most important is the systematic reduction of the isotope exponent with the number of CuO$_2$ layers in a way opposite to $T_c$ in this homologous family. Our results also suggest that the interlayer coupling effect should be included in any quantitative analysis of layered cuprates.

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