Enhancement of oxygen isotope effect due to out-of-plane disorder in $Bi_2Sr_2Ln_{0.4}CuO_{6+\delta}$ superconductors

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The disorder dependence of the oxygen isotope effect in optimally doped $Bi_2Sr_{1.6}Ln_{0.4}CuO_{6+\delta}$ superconductors which is introduced into cation sites in the planes adjacent to CuO_2 planes is studied. The degree of out-of-plane disorder is controlled by substituting Ln ions with different ionic radii from La to Gd. This type of disorder does not explicitly alter the nodal electronic structure or the underlying Fermi surface but markedly enhances the oxygen isotope exponent at the superconducting transition temperature (α_{T_c}). The enhancement in α_{T_c} is well explained by the pair-breaking model, suggesting the growth of a pseudogap state around the antinodal region due to the out-of-plane disorder.

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When some charge carriers are doped into CuO_2 planes in cuprates to realize the high-temperature superconductivity (HTS), disorder or chemical inhomogeneity also is inevitably introduced into the building blocks between CuO_2 planes.[1,2] It has been reported that in bismuth-based HTS cuprates, disorder introduced by chemical substitution into cation sites in planes adjacent to CuO_2 planes, conventionally referred as "out-of-plane disorder," strongly affects their superconducting transition temperature (T_c).[3,4] This suggests that the out-of-plane disorder is a potentially important factor concerning the superconducting properties of HTS.

Isotope-effect studies provide crucial evidence of phonon-mediated pairing in conventional superconductivity. In HTS, the isotope exponent in T_c, defined as $\alpha_{T_c} \equiv -d\ln(T_c)/d\ln(M)$, where M is the isotopic mass, increases considerably as the doping level is reduced from the optimum region, whereas it remains nearly unchanged in the overdoped region.[5,6] The universal and anomalous dependence of α_{T_c} on doping has been considered to be a key phenomenon suggesting the role of phonons in the pairing mechanism.[7] Moreover, Chen *et al.*[8] demonstrated that α_{T_c} decreases as the number of CuO_2 layers increases in a manner inversely correlated with T_c in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ ($n=1$, 2, and 3). However, in the previous studies of the oxygen isotope effect in HTS mentioned above, little attention has been paid to the behavior of out-of-plane disorder in α_{T_c}, which has been considered to be a secondary effect on superconducting properties.

In this Brief Report, we report the correlation between α_{T_c} and the out-of-plane disorder in optimally doped $Bi_2Sr_{1.6}Ln_{0.4}CuO_{6+\delta}$ (Ln-Bi2201) superconductors. The out-of-plane disorder is introduced into cation sites in planes adjacent to CuO_2 planes and controlled by substituting Ln ions with different ionic radii from La to Gd. Our results suggest a close relation between the out-of-plane disorder and α_{T_c}.

High-quality $Bi_2Sr_{1.6}Ln_{0.4}O_{6+\delta}$ (Ln-Bi2201) single crystals were prepared with the traveling-solvent floating-zone technique.[3] Although all the samples were prepared to have nominally the same doping level by fixing the Ln content, it was shown that there is some inhomogeneity in their chemical composition in the same crystal rod.[9] This suggests that the actual doping level might be different from the nominal one. In order to solve the problems concerning such inhomogeneity in chemical composition and estimate subtle oxygen isotope shift reliably, T_c for ^{16}O and ^{18}O substituted pairs was estimated using the same sample. Oxygen isotope substitution was performed by annealing (R-Dec Co. Ltd., ASF-11T). To ensure uniform oxygen distribution and the same oxygen content, the as-grown samples were annealed at 700 °C for 96 h in air. Then, the samples were reannealed at 700 °C for 168 h in $^{16}O_2$ gas at 0.2 bars and quenched to room temperature. T_c was determined from the magnetic susceptibility χ by using a Quantum Design superconducting quantum interference device magnetometer. All the samples were measured at an applied field of 1 Oe with $H\|c$. The samples were further annealed under the same conditions, this time in $^{18}O_2$ gas, and their T_c was estimated. Although the thermal histories for the ^{16}O and ^{18}O substituted pairs differ, we confirmed that T_c and the doping level are not affected by the difference in annealing history between the two isotopes, as shown in the area of the underlying Fermi surface (Fig. 2) determined by angle-resolved photoemission spectroscopy (ARPES). The ARPES data were collected at BL-9A of the Hiroshima Synchrotron Radiation Center with a Scienta R4000 electron analyzer. Clean and flat surface of the samples was obtained by cleaving *in situ* in ultrahigh vacuum better than 4×10^{-11} Torr.

To confirm the oxygen isotope substitution, Raman spec-

tra were measured at room temperature. The experimental setup is described elsewhere.[10] Raman frequency changes in oxygen vibrational modes ($\omega > 250$ cm^{-1}) due to isotope substitution are shown in Fig. 1(a). The Raman peaks at approximately 460 and 625 cm^{-1} can be assigned to the O_{Bi} A_{1g} and O_{Sr} A_{1g} modes, respectively.[11] On the basis of the softening of the oxygen vibration modes, the oxygen isotope substitution rates of the SrO and BiO planes were estimated to be higher than 80%.

Figure 1(c) shows the momentum-space mapping of the spectral weight of La-Bi2201, which is integrated within a window of $E_F \pm 10$ meV. The ARPES spectra were taken with a photon energy of 22.7 eV and in the superconducting state at 10 K. Open circles indicate the Fermi momentum (k_F) as determined from the peak positions of the momentum-distribution curves (MDCs). Superstructures due to the Bi-O modulation are denoted as SS. Solid and broken curves show the main and the SS bands, respectively, as determined with a tight-binding fit.[12]

The intensity plot of the ARPES data as a function of binding energy and momentum along the nodal direction is shown in Fig. 1(d). Band dispersions indicated by closed circles are determined from the MDC peak positions. The ARPES spectra were taken at a photon energy of 7.8 eV with a high energy resolution ($\Delta E = 4$ meV). As indicated by the arrow, the band dispersion along the nodal direction shows a sudden change (a kink) in the electron dispersion at a binding energy of approximately 65 meV, which might be caused by the effects of electron-boson interaction.[14,15] A subtle but distinct oxygen isotope shift of the nodal kink (about 3 meV) is revealed in real parts of the self-energy of La-Bi2201 [Fig. 1(e)], providing direct evidence of electron-phonon coupling, as shown in Bi2212.[16] Recent ARPES studies and theoretical calculations suggest that the in-plane "half-breathing" phonon mode in the CuO_2 planes is responsible for the nodal kink.[16–18] Judging from the observed oxygen isotope shift of the nodal kink, the oxygen isotope substitution level for the CuO_2 plane was also estimated to be more than 80%. The observed underlying Fermi surface and band dispersion along the nodal direction are in agreement with the results of previous studies using optimally doped samples.[13,19,20] Note that the nodal dispersions are not affected by the out-of-plane disorder as shown in Fig. 1(b).

To confirm the uncertainty in the doping level, we estimated the area of the underlying Fermi surfaces of all Ln-Bi2201 samples for both ^{16}O and ^{18}O as shown in Fig. 2. The ARPES spectra were taken with a photon energy of 18.5 eV and the mapping images were integrated within a window of $E_F \pm 10$ meV. Open blue (or black) and red (or gray) circles indicate the k_F positions of the normal and the oxygen isotope substituted Ln-Bi2201 samples. The main and SS bands estimated using the same tight-binding parameter t'/t are shown by solid and broken curves, respectively. Although the underlying Fermi surfaces become obscure as the degree of out-of-plane disorder increases,[21] neither the area nor the shape of the underlying Fermi surface is changed by the disorder. This implies that doping level does not depend on the species of the substituted Ln in Bi2201 and that the doping levels for the two isotopes are the same up to levels below 6% (a doping level uncertainty $\Delta x = 0.01$, which does

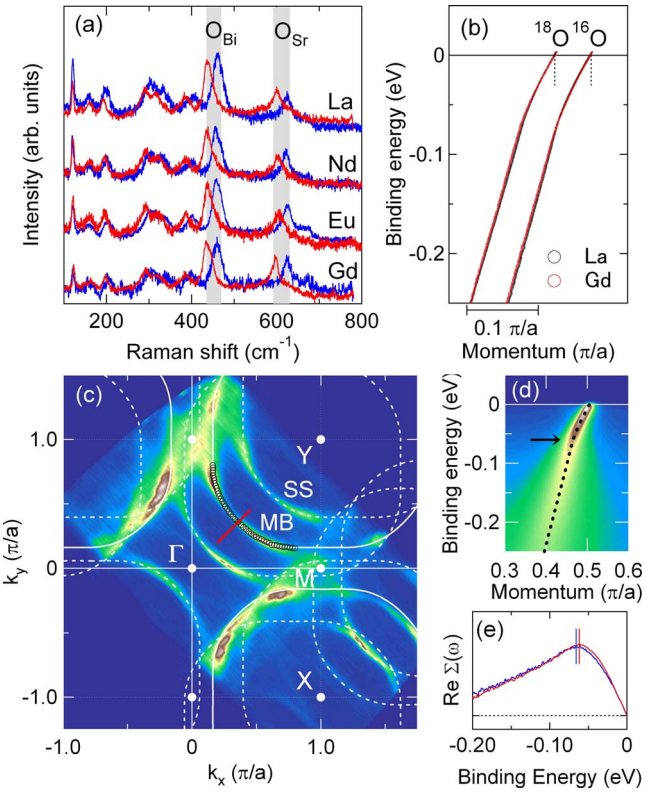

FIG. 1. (Color online) (a) Raman spectra of ^{16}O (blue or black) and ^{18}O (red or gray) Ln-Bi2201 samples. (b) Energy-momentum dispersions along the nodal direction both for ^{16}O (left) and ^{18}O (right) from the least-disordered La-Bi2201 (blue or black) and most-disordered Gd-Bi2201 (red or gray). (c) Momentum-space mapping of the spectral weight of La-Bi2201. (d) Intensity plot of ARPES data as a function of the binding energy and momentum along the nodal direction. (e) Real parts of the self-energy of La-Bi2201 for both ^{16}O (blue or black line) and ^{18}O (red or gray line).

not affect the T_c of the optimally doped samples used here). Note that the size of the "clamshell" around the Γ point, which is made of secondary SS bands, decreases as the degree of the out-of-plane disorder increases. This suggests that SS periodicity changes as a function of Ln.

In Fig. 3(a), we show curves of the field-cooled (Meissner) dc magnetic susceptibility versus temperature for each of the ^{16}O- and ^{18}O-substituted Ln-Bi2201 samples. The T_c for the ^{16}O- and ^{18}O-substituted La-Bi2201 substituted pairs was 32.83 and 32.04 K, respectively, with a transition width of less than 1 K. As shown in the inset, T_c decreases monotonically as the degree of out-of-plane disorder increases, yielding 30.07 and 29.36 K for Nd-Bi2201, 16.90 and 16.18 K for Eu-Bi2201, and 12.27 and 11.31 K for Gd-Bi2201. A subtle but clear decrease in T_c by oxygen isotope substitution (ΔT_c) is revealed for all the Ln-Bi2201 samples. As shown by the circles in the inset, the ΔT_c for the Lanthanides between La and Eu is almost the same

$$(\Delta T_c^{La} = 0.80 \pm 0.09 \text{ K}, \quad \Delta T_c^{Nd} = 0.71 \pm 0.05 \text{ K},$$
$$\Delta T_c^{Eu} = 0.72 \pm 0.17 \text{ K});$$

the ΔT_c for Gd is slightly higher ($\Delta T_c^{Gd} = 0.97 \pm 0.11$ K). The

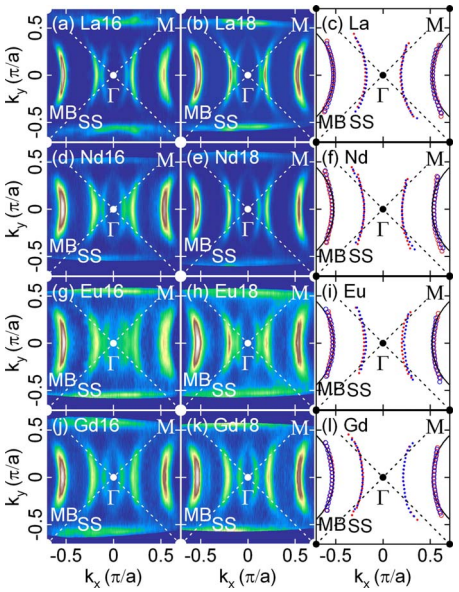

FIG. 2. (Color online) [(a) and (b)] Momentum-space mapping of spectral weight of the normal La-Bi2201 (La16) and the oxygen-isotope-substituted La-Bi2201 (La18), respectively. Note that the respective directions of k_x and k_y correspond to those of Γ-Y and Γ-X. (c) Fermi surfaces extracted by the MDC method with La16 and La18 shown in blue (or black) and red (or gray), respectively. [(d)–(f), (g-i), and (j-l)] Same as in panels, with the exception that Ln is substituted with Nd, Eu, and Gd, respectively.

degree of out-of-plane disorder was scaled by the statistical variance in the distribution of A-site ionic radii, $\sigma^2 \equiv \langle r^2 \rangle - \langle r \rangle^2$, where $\langle\ \rangle$ denotes the site average at the Sr and Ln sites.[1] Figure 3(b) shows the dependence of α_{T_c} on the out-of-plane disorder, where T_c is normalized by T_{c0} (40 K) in the absence of out-of-plane disorder, which is obtained by extrapolating the present results toward $\sigma^2=0$. Since doping level is fixed, it is possible to unambiguously conclude that α_{T_c} is considerably affected by the out-of-plane disorder.

Figure 3(b) clearly shows a drastic increase in α_{T_c} following the increase in degree of out-of-plane disorder. Based on the pair-breaking model proposed by Tallon *et al.*,[22,23] we discuss the disorder dependence of α_{T_c}. The changes in T_c in the presence of a pair breaker, which has been modeled for disorder in two-dimensional superconductors,[24] is given by

$$\ln(T_c/T_{c0}) = \psi\left(\frac{1}{2}\right) - \psi\left[\frac{1}{2} + \frac{2.14(2\alpha/\Delta_{00})}{4\pi(T_c/T_{c0})}\right], \qquad (1)$$

where ψ is the digamma function and $\Delta_{00}=1.213\Delta_{\mathrm{BCS}}$.[25,26] The universal function relation between the pair-breaking parameter and the reduced T_c is shown by the solid curve in Fig. 3(c). Since the pseudogap state competes with superconductivity by diminishing the spectral weight in antinodal regions,[19,20] it is likely that the size of the pseudogap E_{PG} is scaled to the pair-breaking strength α. As in the pseudogap model proposed by Williams *et al.*,[5] two scenarios are considered in order to account for the observed disorder dependence of α_{T_c}: (i) the isotope effect in the superconducting gap energy, $\alpha_{\Delta_{00}} \equiv -d \ln \Delta_{00}/d \ln M$, is finite, while that in the pseudogap, $\alpha_{E_{PG}} \equiv -d \ln E_{PG}/d \ln M$, is zero,[5] and (ii) $\alpha_{\Delta_{00}}=0$, while $\alpha_{E_{PG}} \neq 0$.[27] The gap histogram of optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ derived by scanning tunneling spectroscopy (STS), which can be attributed to the origin of pseudogap rather than to the origin of superconductivity,[28,29] shows no oxygen isotope effect,[30] suggesting $\alpha_{E_{PG}}=0$. Therefore, we will discuss the disorder dependence of α_{T_c} on the basis of the former pseudogap model, that is, $\alpha_{\Delta_{00}} \neq 0$ and $\alpha_{E_{PG}}=0$.

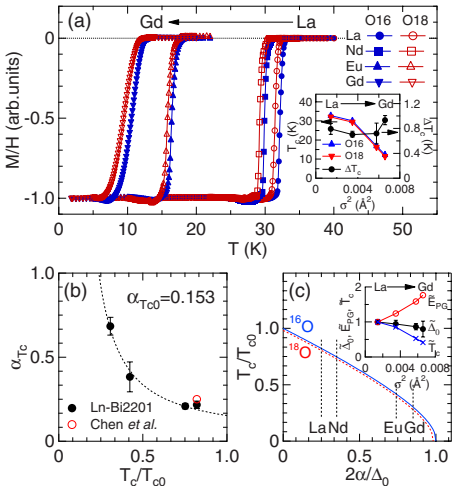

FIG. 3. (Color online) (a) Temperature dependence of the magnetic susceptibility normalized to the value at 5 K for ^{16}O [blue (solid) marks] and ^{18}O [red (open) marks] pairs in disorder-controlled Ln-B2201, where Ln=La, Nd, Eu, and Gd. Disorder dependence of T_c and the decrease in T_c caused by oxygen isotope substitution (ΔT_c) are shown in the inset. (b) Disorder dependence of α_{T_c}. Open (red) circle shows the results for nearly optimally doped $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\delta}$ by Chen *et al.* (Ref. 8). (c) Universal function relation between the pair-breaking parameter and the reduced T_c for ^{16}O (solid curve) and ^{18}O (broken curve). Disorder dependence of $\widetilde{\Delta_0}$ [black (closed) circles], $\widetilde{E}_{PG}$ [red (open) circles], and $\widetilde{T_c}$ [blue crosses], which are normalized by those of La-Bi2201, are shown in the inset. Superconducting gaps at the absolute zero point, $\Delta_0(0)$, are estimated from those at the finite temperature reported in previous ARPES studies (Refs. 21 and 36) on the basis of $\Delta_0(T)=\Delta_0(0)\tanh(\sqrt{\gamma}\sqrt{1-T/T_c}/\tanh(\sqrt{\gamma})$, where $\gamma=3.5$. The pseudogaps are estimated from the superconducting gaps by Harada *et al.* (Ref. 35).

The universal function relation for ^{18}O can be shown as a broken curve in Fig. 3(c) if T_{c0} and Δ_{00} for ^{16}O are used. Here, we have regarded $\alpha_{T_{c0}}$ as a fitting parameter for reproducing the observed α_{T_c}. Then, the broken curve in Fig. 3(b) shows the expected α_{T_c} when $\alpha_{T_{c0}}=0.153$. It is shown that the observed increase in α_{T_c} due to the out-of-plane disorder is well explained by the pair-breaking model. Note that the estimated $\alpha_{T_{c0}}$ of the single-layer Bi2201 in this study is considerably larger than those of multilayer cuprates as shown in previous reports [i.e., 0.06,[5] 0.04,[6] and 0.023 (Ref. 31)]. This indicates that the pseudogap or the pair-breaking potential in single-layer cuprates with no out-of-plane disorder is expected to be larger than that in multilayer cuprates, which is consistent with previous STS reports.[29] A recent

STS study showed that increasing the degree of out-of-plane disorder of Ln-Bi2201 results in the enlargement of the pseudogap region with suppressed coherent peaks.[32] Subsequent ARPES studies also confirmed that the out-of-plane disorder stabilizes the antinodal pseudogap.[21,33,34] Moreover, the systematic evolution of the pseudogap in Ln-Bi2201 with disorder has been reported as shown in the inset of Fig. 3(c).[35] Assuming that E_{PG}^{0} is the expected pseudogap size in the absence of out-of-plane disorder, the difference between the reported pseudogaps and E_{PG}^{0} are proportional to the corresponding pair-breaking parameter as shown by the vertical broken lines in Fig. 3(c). In contrast to the case of the pseudogap state, the superconducting gap around the nodal region is insensitive to the out-of-plane disorder, as shown by the closed circles in the inset of Fig. 3(c),[21,36] indicating $\alpha_{\Delta_{00}}$ is almost constant and independent of the disorder. This might support the validity of the pair-breaking model used here. Interestingly, a recent ARPES study of Bi2201 showed a similar result, that is, the pseudogap monotonically increases as the doping level decreases. However, the size of the superconducting gap is almost the same in the optimally doped and underdoped samples.[19,20] Similarly, a recent STM/S study of Bi2212 shows that the gap increases monotonically as the doping level decreases while the low-energy kink inside the gap is almost constant between the optimally doped region and the underdoped region.[28] Therefore, the behavior of α_{T_c} due to the disorder and the doping level can be comprehensively understood by the modulation of the pair-breaking potential.

In summary, we reported the correlation between the oxygen isotope effect and the out-of-plane disorder. It was shown that this type of disorder does not alter the nodal electronic structure although it markedly increases α_{T_c}, which is well explained by the pair-braking model through the change in the antinodal electronic structure related to the pseudogap state. We conclude that the oxygen isotope exponent in HTS cuprates is determined by the energetic competition between the superconducting gap and the pseudogap.

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