SUPERCONDUCTORS

Unusual oxygen isotope effects in cuprates?

Arising from: G.-H. Gweon *et al.* *Nature* 430, 187–190 (2004)

The possibility that a pairing boson might act as the ‘glue’ to bind electrons into a Cooper pair in superconductors with a high critical temperature (T_c) is being actively pursued in condensed-matter physics. Gweon *et al.*¹ claim that there is a large and unusual oxygen-isotope effect on the electronic structure, indicating that phonons have a special importance in high-temperature superconductors. However, we are unable to detect this unusual oxygen-isotope effect in new data collected under almost identical material and experimental conditions. Our findings point towards a more conventional influence of phonons in these materials.

In the high-temperature superconductors, oxygen-isotope exchange has been found to have a very small effect on the T_c , particularly for optimally doped (highest- T_c) samples². It was therefore unexpected when Gweon *et al.* reported a large isotope effect on the electronic structure in optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ using angle-resolved photoemission spectroscopy (ARPES)¹. This isotope effect was seen mainly at a broad, high-energy hump feature and was unusually large (10–40 meV shift), by contrast with the expected isotopic phonon shifts of the order of 3 meV. It was argued by many that this is experimental evidence that the coupling between the lattice and electrons plays a particularly significant role.

Figure 1a shows our energy–momentum (E – k) dispersion relations for both ^{16}O and ^{18}O taken along the ‘nodal’ direction of the Brillouin zone. The results show an insignificant shift for the deeper states of -0.9 ± 0.4 meV, by contrast with Fig. 1b of Gweon *et al.*¹, which shows a 15-meV shift of more deeply lying states. We

found that precise rotational alignment of the samples was crucial to obtain repeatable energy positions, especially in the high-energy regime discussed here. The negligible energy shift was confirmed by using three different facilities, samples with multiple doping levels, including the optimal doping described in ref. 1, and with various photon energies, including the same energy used by Gweon *et al.*¹ (33 eV), and a low photon energy (7.0 eV) that gives extreme resolution, as well as increased bulk sensitivity.

Gweon *et al.*¹ show an even larger effect (up to 40 meV) at the ‘antinodal’ portions of the Brillouin zone (towards the $(0, \pi)$ and $(0, -\pi)$ points) — comparable data are shown here in Fig. 1b. We studied ten cuts that had a similar geometry to the key cut 7 of Gweon *et al.*¹, with half of the cuts at positive k_y (momentum along the y direction) values and the others at negative k_y . Having data on both sides of the $(0, 0)$ point allowed the correction of any very slight (0.1 degrees) sample misalignments, which is crucial for removing systematic alignment errors that could cause apparent energy shifts. Figure 1b (right) shows the dispersion of the bottom of the band (determined in each cut as in Fig. 2d of Gweon *et al.*¹) along the $(0, -\pi) \rightarrow (0, \pi)$ symmetry line. The ten sets in Fig. 1b have an average isotope shift of the band bottom of 2 ± 3 meV, which is inconsistent with the 10–40 meV level found by Gweon *et al.*¹.

Our result is not inconsistent with the tunnelling result of a conventional phononic isotope shift on the scale of about 3 meV (refs 3,4) that was performed on the same samples and which conceivably could be seen near the kink energy in future ultra-resolution ARPES.

Although we do not observe the unusual large-scale isotope effect reported by Gweon *et al.*¹, our result does not invalidate electron–phonon coupling as a potential pairing mechanism for high-temperature superconductivity. Rather, it implies that if electron–phonon coupling is responsible, it must do it in a more subtle, roundabout way.

Methods. Our data were measured with 33-eV photons at BL12 of the Advanced Light Source, Berkeley, USA, by use of a high-precision 6-axis sample manipulator. Single crystals of $\text{Bi}_{1.9}\text{Sr}_{2.1}\text{CaCu}_2\text{O}_{8+\delta}$ were annealed in either $^{18}\text{O}_2$ or $^{16}\text{O}_2$ gas under the same thermal conditions: 800 °C at 1 atmosphere for 168 h, followed by 700 °C at 0.2 bar for 24 h. The T_c values of the samples decreased from 92 K to 91 K on isotope substitution. Raman spectra showed a clear shift of the B_{1g} vibration modes, confirming that isotope substitution was nearly complete at 80% or more.

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Figure 1 | Comparison of nodal and antinodal energy (E) and momentum (k) dispersions as a function of oxygen-isotope exchange. All data are from optimally doped ($T_c = 92$ K, unexchanged) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ crystals taken with 33 eV photons at 15 K. Blue line and symbols, ^{16}O data; red line and symbols, ^{18}O data. No large-scale shift of the spectra with isotope exchange is evident. **a**, Nodal dispersion (red diagonal line in **b**, inset) obtained by fitting momentum-distribution curves, in which k_F is the Fermi momentum. **b** (left), Energy-distribution curve from each isotope at the k -point indicated (arrowhead); right, dispersion of the band bottom from energy-distribution peaks along the $(0, -\pi) \rightarrow (0, \pi)$ symmetry line (horizontal lines in the Fermi surface inset).