

## Gap anisotropy in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ by ultrahigh-resolution angle-resolved photoemission

Hong Ding, J. C. Campuzano, and K. Gofron

*Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439  
and Department of Physics, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607*

C. Gu, R. Liu, B. W. Veal, and G. Jennings

*Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439*

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Ultrahigh-resolution ( $\Delta E$  up to 10 meV) angle-resolved photoemission spectroscopy on single crystals of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212) show a highly anisotropic superconducting energy gap: the gap is minimized, with a value close to zero, along the  $\Gamma$ - $X$  and  $\Gamma$ - $Y$  symmetry directions, while a large gap ( $\Delta = 22$  meV) is observed along the  $\Gamma$ - $\bar{M}$  (Cu-O bond) direction. However, the observation of gap anisotropy may depend on sample conditions; in a few cases the gap becomes more isotropic. A dip in the spectral weight at 65 meV below the Fermi energy is clearly observed only in samples with an anisotropic gap.

The discovery of high-temperature superconductors with many unusual properties has simulated various theoretical proposals for the high- $T_c$  mechanism. The symmetry of the superconducting energy gap within the Cu-O plane has become one of key issues in understanding the superconducting mechanism. In the BCS theory with an isotropic interaction  $V$ , essentially isotropic phonons lead to an isotropic  $s$ -wave order parameter. However, some nonphonon pairing mechanisms, including the antiferromagnetic-spin-fluctuations-induced interaction,<sup>1-4</sup> imply a  $d_{x^2-y^2}$  symmetry. In addition, an interlayer tunneling mechanism proposed by Chakravarty *et al.*<sup>5</sup> exhibits an anisotropic  $s$ -wave gap. Thus, the experimental determination of the symmetry of the order parameter plays an important role constraining theoretical models. Consequently, several experimental methods, such as measurements of nuclear magnetic resonance, microwave penetration depth, Josephson tunneling, Raman and neutron scattering, etc.,<sup>6</sup> have been used in an attempt to reveal the symmetry of the pairing order parameter. But so far, rather conflicting results have been obtained, even using a same experimental technique. Most techniques cannot measure the momentum dependence of the superconducting gap. Angle-resolved photoemission spectroscopy, however, has the unique capability of directly probing the momentum dependence of the gap, which makes it an excellent candidate to study the symmetry of the superconducting order parameter. So far there have been some photoemission reports on this issue. The first report<sup>7,8</sup> indicated an essentially isotropic superconducting gap in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212). However, a more recent study<sup>9</sup> on this material found an anisotropic gap structure that is different from the conventional  $s$ -wave isotropic gap.

In an attempt to clarify this issue, we conducted an angle-resolved photoemission study, with energy resolution much improved relative to previous studies, on Bi-2212 single crystals. This study constitutes a reexamination of Bi-2212 samples that are comparable to samples (i.e., from the same batch) previously investigated by Olson and co-workers.<sup>7,8</sup> Repeated angle-resolved photoemission spectroscopy (ARPES) measurements were made with particular attention directed to the possible occurrence of gap anisotropy. We

report the observation of significant gap anisotropy within the  $a$ - $b$  plane on most of the samples studied, confirming the recent reports of Shen *et al.*<sup>9</sup> However, the detection of gap anisotropy appears to depend on a number of factors, possibly including surface smoothness, intergrowth structures, sample crystallinity, and defects. Gap anisotropy was not observed in all measurements. We believe that experimental complications affecting measurements of gap anisotropy would generally tend to make the gap appear more isotropic; thus, we regard the appearance of observable gap anisotropy as significant, and not likely to be an experimental artifact. In our measurements, a dip in the spectral weight at 65 meV ( $\sim 3\Delta$ ) below the Fermi energy is clearly observed only in samples with an anisotropic gap.<sup>10,11</sup> (Note that the dip feature, like gap anisotropy, was not observed in all reported Bi-2212 measurements; both features are sample dependent. The measurements by Olson and co-workers<sup>7,8</sup> did not show gap anisotropy nor the presence of a dip in the spectral function.) However, we do not find a clear correlation between these spectral characteristics (gap anisotropy, spectral function dip) and the widths of the superconducting transition temperature. This may be because transition widths are determined by composition inhomogeneities throughout the bulk whereas ARPES is obtained from a very thin, near surface region that might have a more homogeneous composition and sharper superconducting transition.

Single crystals of Bi-2212 were fabricated at Argonne National Laboratory. As-grown samples were then extensively annealed in an 8% atmosphere oxygen. The samples typically have 85-K superconducting transition onsets and transition widths 1–7 K. ARPES measurements were carried out at the Synchrotron Radiation Center in Stoughton, Wisconsin using the Four Meter Normal Incidence Monochromator. The total-energy resolution (photons and electrons) ranged from 10 to 15 meV as determined by the 10–90% transition width of a Pt Fermi edge at 13 K. The analyzer angle resolution is  $2^\circ$  (total acceptance angle). Crystal orientation was determined first by Laue backscattering prior to mounting in the vacuum chamber. The crystals were cleaved *in situ* in a vacuum of  $4 \times 10^{-11}$  Torr at 13 K. After cleaving, the

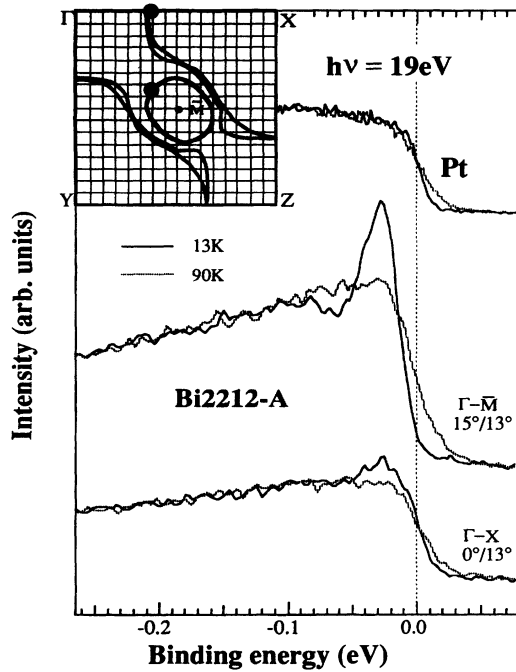


FIG. 1. EDC's for superconducting and normal states from sample *A* taken with 19 eV photon energy at Fermi-surface crossing points along  $\Gamma$ - $\bar{M}$  and  $\Gamma$ - $X$  directions. The positions of measurement points in the Brillouin zone are shown in the inset. Note that the corresponding Pt EDC's are also shown in the figure for a better comparison.

sample alignment was further checked by monitoring the symmetry of the ARPES spectra. The Fermi energy was determined by measuring a clean Pt foil electrically connected to the samples. The photon and instrument energy stability was periodically monitored by repeated measurement of the Pt Fermi edge reference during the experiment. The uncertainty of the Fermi energy is less than 2 meV. The spectra were normalized to the synchrotron beam current.

Figure 1 shows energy distribution curves (EDC's) obtained at a photon energy of 19 eV from a sample coded *A*, whose *b* axis is parallel to the polarization plane of the photons. The solid and dotted lines are spectra taken at 13 K and 90 K, respectively. At 90 K, which is comfortably above the  $T_c$ , all valence band features show a metallic Fermi edge which is aligned with that from the Pt reference. As temperature was reduced to 13 K, which is well below  $T_c$ , the spectra taken along the  $\Gamma$ - $\bar{M}$  (Cu-O bond) direction shows significant changes due to superconductivity: the leading edge is pulled back to higher binding energy, and a large condensation peak appears at approximately 35 meV. However, along the  $\Gamma$ - $X$  symmetry direction, there is little change in the spectra. Using a fitting program developed in our laboratory<sup>12</sup> we are able to determine the gap size to be 22 meV ( $2\Delta/k_B T_c = 6.0$ ) along the  $\Gamma$ - $\bar{M}$  direction. From Fig. 1, we also notice that the dip, which recently attracted attention,<sup>10,11</sup> is clearly revealed in the superconducting state spectrum near  $\bar{M}$ . Its position can be accurately determined to be  $65 \pm 2$  meV below the Fermi energy.

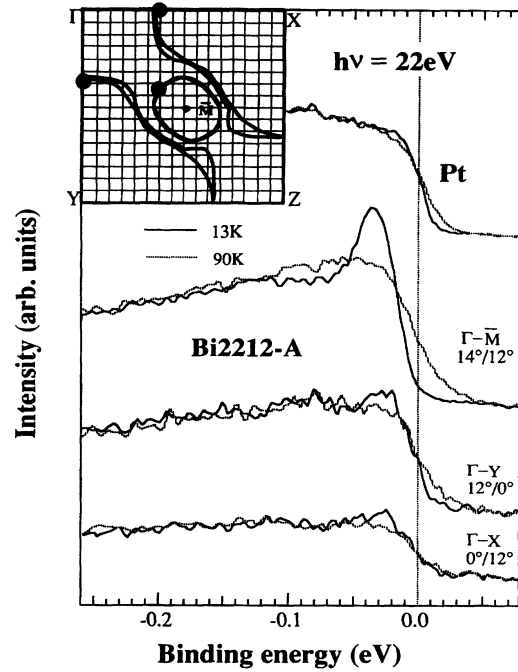


FIG. 2. EDC's for superconducting and normal states from sample *A* taken with 22 eV photon energy. Note that the gap is zero along the  $\Gamma$ - $Y$  direction as well as along the  $\Gamma$ - $X$  direction.

For 19 eV photon energy the intensity near the Fermi energy is very weak along the  $\Gamma$ - $Y$  direction, possibly due to final-state effects, preventing a clear determination of the gap. However, at a photon energy of 22 eV, the intensity near the Fermi level along  $\Gamma$ - $Y$  becomes much stronger. Measured EDC's are shown in Fig. 2. These results show that, for  $h\nu = 22$  eV, the gap is nearly zero (within measurement precision) along both  $\Gamma$ - $X$  and  $\Gamma$ - $Y$  while a large gap is observed along  $\Gamma$ - $\bar{M}$ .

Previous photoemission reports on gap structure along  $\Gamma$ - $X$ ( $Y$ ) have been controversial. Olson *et al.*<sup>8</sup> reported an 18-meV gap opening along  $\Gamma$ - $X$ , and the same value near  $\bar{M}$ . Shen and co-workers<sup>13</sup> observed a smaller, but perceptible gap opening (6–15 meV) along  $\Gamma$ - $X$  in their early report. However, in their subsequent measurement,<sup>9</sup> they observed a significant gap anisotropy between  $\Gamma$ - $\bar{M}$  and  $\Gamma$ - $Y$ . Shen and co-workers did not address the size of the gap along  $\Gamma$ - $X$ . Such ambiguity has not been clarified at the present time. In our experiments, we have observed significant gap anisotropy for several samples, but on occasion, an apparently more isotropic gap was observed. One example is shown in Fig. 3, from a sample coded *B*. This crystal was taken from the same batch as sample *A*. The sample was mounted with the *a* axis parallel to the photon beam polarization. The gaps opening along  $\Gamma$ - $\bar{M}$  and along  $\Gamma$ - $X$  are almost the same and are very similar to the measurements along  $\Gamma$ - $\bar{M}$  shown in Fig. 2. Also note that there is no clearly discernible "dip" in the spectral weight for the EDC's shown in Fig. 3.

X-ray-diffraction and electron-diffraction x-ray fluorescence (EDX) measurements were conducted on these two samples after photoemission spectra were acquired. The results showed little difference in lattice constants, crystal do-

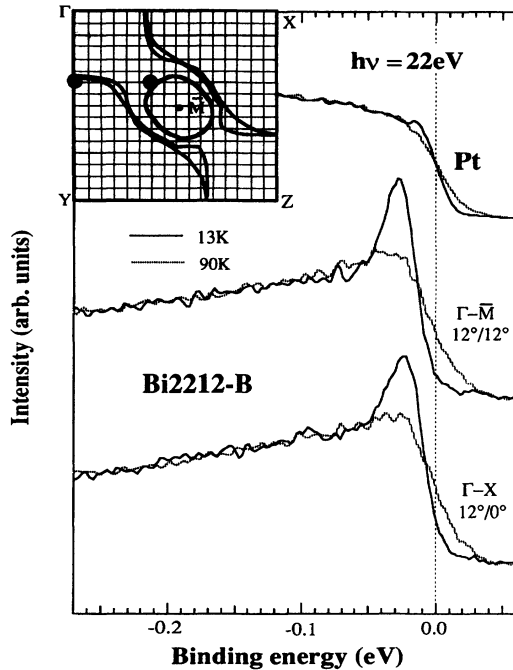


FIG. 3. EDC's for superconducting and normal states from sample *B*. The photon energy used is 22 eV. Unlike the case of sample *A*, there is a clear gap apparently opening along the  $\Gamma$ - $X$  direction which makes the gap apparently more isotropic.

main size and chemical composition for the two samples. Moreover, when sample *B* was cleaved and remeasured, an anisotropic gap similar to the one in sample *A* (Fig. 2) was observed. It appears that the properties of the cleaved sample surface have a strong influence on the gap anisotropy. The anisotropy might be strongly affected by impurities or defects on the cleaved surface.<sup>9</sup> These imperfections could result from impurities, chemical inhomogeneities, cation site interchanges, intergrowths, oxygen inhomogeneities, or the presence of growth domains with varying degrees of misorientation.

Besides the two cases mentioned above, we have occasionally observed that in some samples there is a small gap (less than 5 meV) along the  $\Gamma$ - $X$  direction, while the gap size remains close to zero along the  $\Gamma$ - $Y$  direction. This may result from the incommensurate modulation along the  $b$  axis in Bi-2212 crystals. The wiggling bonds along the  $b$  axis may effectively smear momentum resolution along the  $\Gamma$ - $Y$  direction. While such a momentum averaging effect does not affect the no-gap conclusion along the  $\Gamma$ - $Y$  direction, it may cause some admixture of states near  $\bar{M}$  into the spectra measured along the  $\Gamma$ - $X$  direction, causing an apparent small gap opening in the data. Such a momentum averaging effect may be sample or cleave dependent.

The observed gap anisotropy is consistent with  $d_{x^2-y^2}$ -wave symmetry, which in turn predicts a gap anisotropy  $\Delta(x) = \Delta_0(\cos k_x a - \cos k_y b)$ , where  $\Delta_0$  is the maximum value of the gap, and  $k_x, k_y$  are along the Cu-O planar bond

directions, which coincide with the  $\Gamma$ - $\bar{M}$  direction in Bi-2212. The signature of this  $d$ -wave gap are the nodes in  $\mathbf{K}$ -space. The observation of a negligible gap along  $\Gamma$ - $X$  and  $\Gamma$ - $Y$  might be a manifestation of such nodes. On the other hand, the observation of an isotropic gap in some cleaves might indicate that impurities or defects near sample surfaces influence the gap anisotropy. Shen *et al.* have observed that, when samples are aged *in situ*, the gap tends to become more isotropic.<sup>9</sup> They attribute this effect to surface scattering resulting from adsorbed gases.

As recently pointed out by Norman,<sup>14</sup> such impurity effects, if they result from enhanced scattering, can be better explained within the framework of anisotropic  $s$ -wave pairing. In  $d$ -wave pairing, impurity scattering destroys the gap rather than rendering it isotropic, whereas in anisotropic  $s$ -wave pairing impurities tend to drive the gap toward its average value. However, the detailed dependence of gap anisotropy on impurities and defects in Bi-2212 remains unclear; further experiments are necessary to settle this issue. Also, the observation that the dip at  $E = 3\Delta$  disappears in isotropic samples is most significant. For example, Coffey and Coffey<sup>15</sup> propose that the dip is a consequence of an anisotropic gap. As for the interlayer tunneling theory proposed by Chakravarty *et al.*, an anisotropic  $s$ -wave gap is given by  $\Delta(k) = \Delta_0 + T_j(K)/2$ , where  $\Delta_0$  is the isotropic gap (but not of BCS origin; a typical value of 3 meV was given in their paper).<sup>5</sup> Since this value is close to our measurement uncertainty (about 2 meV) we cannot exclude the possibility applicability of this anisotropic  $s$ -wave description. However, if we accept the presumption that those samples which show the greatest anisotropy are most representative of the bulk superconducting material, then we must conclude that the minimum  $\Delta_0$ , is very small, i.e.,  $\sim 2$  meV or smaller.

In summary, we have observed a superconducting gap anisotropy in several single crystals of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  by ultrahigh-energy-resolution angle-resolved photoemission spectroscopy. The gap minimum, with a value close to zero, occurs along the  $\Gamma$ - $X$  and  $\Gamma$ - $Y$  symmetry directions, while a large gap ( $\Delta = 22$  meV) is observed along the  $\Gamma$ - $\bar{M}$  (Cu-O bond) direction. However, some samples show a nearly isotropic gap, which is comparable in magnitude to the maximum gap (Cu-O bond direction) that is observed in the anisotropic samples. Since sample imperfections and experimental limitations could produce apparent gap structure along  $\Gamma$ - $X$ ( $Y$ ), we believe that the anisotropic behavior is likely to be more characteristic of the bulk superconducting material. A dip in the spectral weight at 65 meV below the Fermi energy is clearly observed only in samples with an anisotropic gap. This might be an additional indicator of sample quality.

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- <sup>1</sup>D. Monthoux and D. Pines, *Phys. Rev. Lett.* **69**, 961 (1992).
- <sup>2</sup>G. Kotliar and J. Liu, *Phys. Rev. B* **38**, 5142 (1988).
- <sup>3</sup>S. R. White, D. J. Scalapino, R. Suger, N. E. Bickers, and R. Scalettar, *Phys. Rev. B* **39**, 839 (1989).
- <sup>4</sup>P. A. Lee and N. Nagaosa, *Phys. Rev. B* **46**, 5621 (1992).
- <sup>5</sup>S. Chakravarty, A. Sudbo, P. W. Anderson, and S. Strong, *Science* **261**, 337 (1993).
- <sup>6</sup>B. G. Levi, *Phys. Today* **46**(5), 17 (1993).
- <sup>7</sup>C. G. Olson, R. Liu, A.-B. Yang, D. W. Lynch, A. J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, *Science* **245**, 731 (1989).
- <sup>8</sup>C. G. Olson, R. Liu, D. W. Lynch, A. J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, *Solid State Commn.* **76**, 411 (1990).
- <sup>9</sup>Z.-X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, T. Loeser, and C. H. Park, *Phys. Rev. Lett.* **70**, 1553 (1993).
- <sup>10</sup>Y. Hwu, L. Lozzi, M. Marsi, S. La Rosa, M. Winokur, P. Davis, M. Onellion, H. Berger, F. Gozzo, F. Levy, and G. Margaritondo, *Phys. Rev. Lett.* **67**, 2573 (1991).
- <sup>11</sup>D. S. Dessau, B. O. Wells, Z.-X. Shen, W. E. Spicer, A. J. Arko, R. S. List, D. B. Mitzi, and A. Kapitulnik, *Phys. Rev. Lett.* **66**, 2160 (1991).
- <sup>12</sup>J. C. Campuzano, G. Jennings, A. J. Arko, R. S. List, B. W. Veal, and R. Benedek, *J. Phys. Chem. Solids* **52**, 1411 (1991).
- <sup>13</sup>D. S. Dessau, Z.-X. Shen, B. O. Wells, and W. E. Spicer, *J. Phys. Chem. Solids* **52**, 1401 (1991).
- <sup>14</sup>M. R. Norman (unpublished).
- <sup>15</sup>D. Coffey and L. Coffey, *Phys. Rev. Lett.* **70**, 1529 (1993).