Anomalously Large Gap Anisotropy in the *a-b* Plane of $Bi_2Sr_2CaCu_2O_{8+\delta}$

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Superconducting gap anisotropy at least an order of magnitude larger than that of the conventional superconductors has been observed in the *a-b* plane of $Bi_2Sr_2CaCu_2O_{8+\delta}$ in angle-resolved photoemission spectroscopy. For samples with T_c of 88 K, the gap size reaches a maximum of approximately 20 meV along the Cu-O bond direction, and a minimum of much smaller or vanishing magnitude 45° away. The experimental data are discussed within the context of various theoretical models. In particular, a detailed comparison with what is expected from a superconductor with a $d_{x^2-y^2}$ order parameter is carried out, yielding a consistent picture.

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A key to understanding the mechanism of high-T_c superconductivity is the symmetry of the superconducting order parameter. The conventional BCS theory has an *s*-wave order parameter, reflecting the spherically symmetric nature of the pair wave function. For the high-T_c cuprates, theoretical analysis of the crucial CuO_2 plane with consideration of the strong on-site Coulomb interaction leads to other symmetries of the order parameter [1-10]. In particular, pairing theories based on the Hubbard model or its derivatives lead to a *d*-wave order parameter or a mixed symmetry order parameter with a strong *d*-wave component [1-10]. Very recently, stimulated by the NMR data, this issue of the order parameter has once again attracted great attention in the field [7,8].

Angle-resolved photoemission (ARPES) from $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) has played an important role in helping us understand the cuprate superconductors. For Bi2212, ARPES is sensitive to both the normal-state Fermi surface and the superconducting gap [11-15]. In fact, its ability to measure the superconducting gap as a function of crystal momentum is currently a unique capability,.providing an opportunity to probe the symmetry of the order parameter. Although the superconducting gap as revealed by ARPES only reflects the magnitude of the order parameter, it still provides important constraints for theoretical models. In the past, conflicting results have been published [16,17]. An earlier study showed that the superconducting gap did not vary in **k** space, and therefore provided support for an *s*-wave order parameter [16]. Recently, we reported preliminary results showing sizable superconducting gap anisotropy in the *a-b* plane [15,17], in contrast to the earlier report.

In this paper, we report more comprehensive data from our recent study of Bi2212 showing a gap anisotropy in the *a-b* plane that is at least an order of magnitude larger than that of the conventional superconductors. In addition, we have observed spectra that are indicative of a node in the gap within the experimental limitation. We also discuss in detail the difficulties in the data acquisition and interpretation as a result of finite energy resolution, limited sample lifetime, and other material problems. Next, we address the ARPES results in the context of various theoretical models. In particular, we have compared our data with what is expected from the $d_{x^2-y^2}$ order parameter $\Delta(\mathbf{k}) \sim \cos k_x a - \cos k_y a$, yielding a very consistent picture.

The qualitative picture of the strong gap anisotropy in **k** space has been reproduced in many samples during six different experimental runs using the two chambers. For data in this paper, sample 1 ($T_c \sim 78$ K) was measured in a VSW system using a He discharge lamp under conditions similar to those reported before [15,17]. Samples 2 and 3 ($T_c \sim 88$ K) were measured in another VSW chamber at the beam line 5 of SSRL. The combined energy resolution of the analyzer and the monochromator is about 30 meV. Unless otherwise stated, the samples were cleaved and measured at 35 K. All samples reported in this paper have a superconducting transition width of 2 K or smaller as determined by Meissner shielding. The samples were introduced into the photoemission chamber through a load lock without baking. This procedure is necessary to ensure the sharp superconducing transition, as verified by T_c determinations of several samples before and after the ARPES experiments. The nominal chamber pressure during the measurement was 1×10^{-10} torr.

Figure 1 presents normal (open squares) and superconducting state (solid circles) ARPES spectra from sample 1. The **k**-space locations were chosen so that the normal-state peak is at the Fermi level, and the midpoint of the leading edge in the normal state coincides with the Fermi level at both points *A* and *B*. Very clear spectral changes are observed at *A* as the sample is cooled below T_c. The leading edge of the superconducting spectrum is pulled back to higher binding energy, reflecting the open-

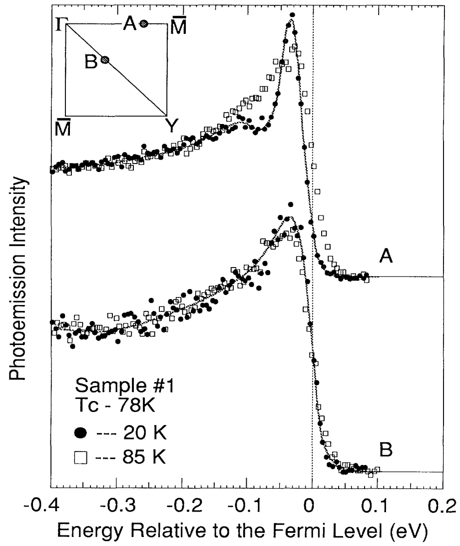

FIG. 1. High resolution photoemission spectra from sample 1 recorded at **k**-space locations A and B, as illustrated in the inset. The spectra at B were measured before those at A. The spectral changes above and below T_c are caused by the opening of the superconducting gap. The change at A is quite visible, yielding a larger gap. The change at B is hardly visible, suggesting a very small or null gap.

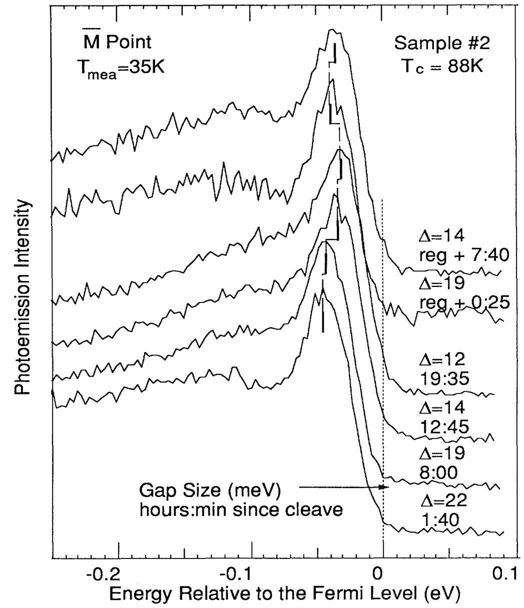

FIG. 2. Spectra from sample 2 recorded at $\overline{M}$ at different times after the sample was cleaved and kept at low temperature. As the sample ages, the superconducting gap becomes smaller. The numbers marked are the gap size and its aging time after the cleave. A decrease of the intensity of the -80 meV dip is clearly visible. The clean sample surface can be regenerated by warming up the sample to room temperature, and then cooling down again.

ing of the superconducting energy gap. At the same time, a "pileup" and a "dip" near -80 meV appear in the data [15,18]. At B, only minor changes with temperature are observed, indicating that the gap is undetectable within experimental uncertainty. This striking difference at the two **k**-space locations indicates that the superconducting gap is very anisotropic.

To quantify the gap anisotropy is an important but difficult task. There are four aspects to the experimental difficulties. First, there is our finite energy resolution which limits the precision and the accuracy of our measurements. Next, energy calibration fluctuations of the spectrometer mainly caused by a drift in the electronics add uncertainty to the Fermi energy location. For data in this paper, the uncertainty is about 1 meV for sample 1, and 2–3 meV for samples 2 and 3. Third, the sample surface flatness and the finite angular resolution limit the momentum resolution of our experiment. The surface flatness is sample dependent, causing a scatter in the experimental data. This remains a technical problem despite our best efforts at selecting the best possible crystals and refining the cleaving technique. Our characterizations show that the surfaces of samples 1 and 3 are flatter than sample 2. Finally, there is the time dependence of the data which will be illustrated in Fig. 2. ARPES is a surface-sensitive technique so that the spectra may change as the sample surface ages.

Figure 2 shows spectra from sample 2 at the $\overline{M}$ point recorded at different times after the sample was cleaved. With time, the superconducting quasiparticle peak shifts to lower binding energy, indicating that the superconducting gap becomes smaller. At the same time, the dip structure at -80 meV also becomes smaller. Importantly, the clean sample surface can be regenerated by warming the sample up to room temperature. The spectrum marked with "reg+0:25" was taken 25 min after the surface had been regenerated and cooled down again. Both the larger superconducting gap size and the -80 meV dip are reproduced in the data. This provides additional support for the suggestion that the dip is an intrinsic superconducting property [15,18]. The ability to regenerate the samples strongly suggests that the changes are due to physisorption of the residual gases onto the sample surface at low temperature.

The theoretical difficulty in quantifying the gap anisotropy is mainly caused by the fact that we do not have an adequate theory to describe the angle-resolved photoemission line shape of either the normal or the superconducting state. For simplicity in determining the gap size without any specific fittings, we chose to call the gap the energy position of the midpoint of the leading edge of the superconducting state spectrum. With this criterion, the spectrum at point A in Fig. 1 has a gap of 12 meV ($2\Delta/k_BT_c=3.6$) and the spectrum at point B gives a gap of 0 to 0.5 meV. In the limit of perfect angular resolution, this method requires that the normal-state band ($\varepsilon_{\mathbf{k}}$) be at the Fermi level. With finite angular resolution, the uncertainty in the gap size caused by the normal-state band being slightly off $\varepsilon_{\mathbf{k}}=0$ is reduced. The qualitative picture of the observed gap anisotropy is not sensitive to the experimental difficulty in determining the exact **k**-space location for $\varepsilon_{\mathbf{k}}=0$ because the gap values found in a small **k**-space region are similar (as can be seen in Fig. 3). We only carried out the gap measurements in **k**-space regions where we see normal-state bands at E_F within our experimental error (shaded area). The normal-state electronic structure information near E_F, depicted by the shaded area in Fig. 3, is a summary of extensive experimental measurements that will be published in the future [19]. The experimental results are consistent with an earlier study where only the data along Γ-Y line were reported [11]. Furthermore, a very flat band at E_F is observed for a large **k**-space region near $\bar{M}$, which is similar to results from YBCO at comparable **k**-space locations [21].

Figure 3 displays the measured **k** dependence of the gap from three samples. In order to account for the time effects, the spectra from the different samples were taken using different time sequences. We limit ourselves to spectra recorded within 12 h after the sample was cleaved. Each spectrum is labeled with a letter, with the order of measurements corresponding to the alphabetic progression. The **k**-space location of the measurement is shown in panel (a), and the magnitude of the gap for each measurement is displayed on the vertical axes of the graphs in panel (b). The horizontal axis of panel (b) is $0.5|\cos k_x a - \cos k_y a|$, allowing a direct comparison with the d-wave theory, as will be discussed later. This function is zero along the Γ-Y line and increases monotonically away from the line and approaches its maximum at $\bar{M}$. Despite the potential problem with time effects, the data in Fig. 3 clearly suggest that the gap is smallest along the Γ-Y direction in the Brillouin zone, and it gets bigger as one moves away from the Γ-Y line. This is true for all samples, and is independent of the measuring time sequence. The magnitude of the measured gap anisotropy is very large, ranging roughly between a factor of 2 and 10, depending upon the sample. This is 1 to 2 orders of magnitude larger than what has been observed in conventional superconductors [22].

Although the qualitative trend of gap variation in **k** space is very reproducible, the gap size shows some scatter along the Γ-Y line. In Fig. 3(b), samples 1 and 3 show a very small gap along Γ-Y (where $|\cos k_x a - \cos k_y a|=0$), while sample 2 shows a significantly larger gap in this region. A hint for the explanation of the scatter in the data can be found in the time dependence of the spectra from sample 3 taken along the Γ-Y direction and the sample quality as indicated by the laser reflection. The earliest spectrum from sample 3 was taken 1.5 h after the cleave and showed a small (1.5 meV) gap. Approximately 7 h later, the gap at that point was observed to grow to 6.5 meV, after which time it again

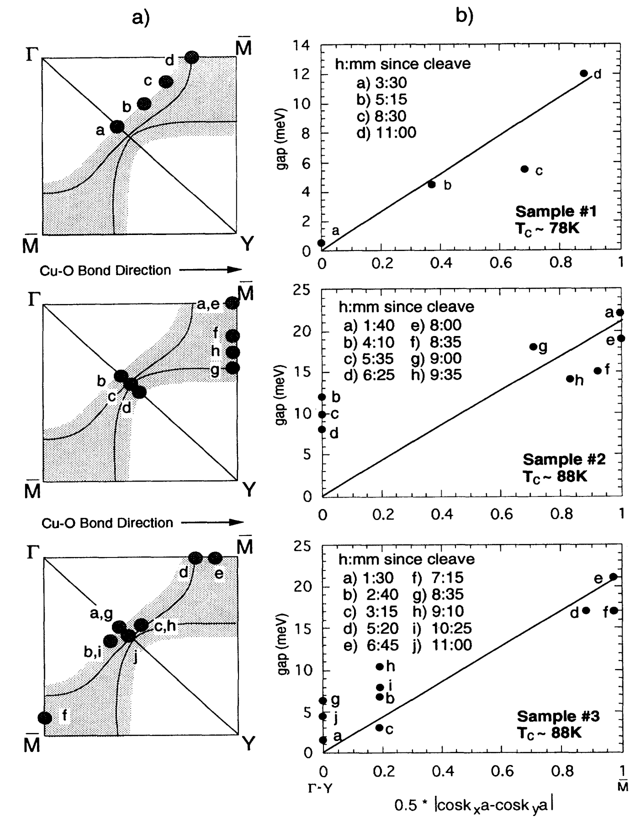

FIG. 3. (a) The Brillouin zone locations where the gap is measured. The shaded areas are **k**-space locations where we found bands very close to E_F. The solid lines represent the Fermi surface due to the two CuO_2 planes only [20]. (b) Gap size vs $0.5|\cos k_x a - \cos k_y a|$. The straight lines are predictions of the $d_{x^2-y^2}$ order parameter. Sample 1 has higher oxygen content and lower T_c. This could account for the smaller Δ near $\bar{M}$.

shrank to near zero after the sample surface was regenerated. The direction of this time dependence is, interestingly, *opposite* to that observed in the region around $\bar{M}$ where the gap is large. We can make sense of all this data by the following hypothesis. The intrinsic gap along Γ-Y is very small (or zero). Both sample 2 and the "aged" spectra of sample 3 had significantly poorer **k** resolution (the physisorbed layer of gas causing the extra scattering for the "aged" sample), producing a spectrum with a significant (but still small) gap by averaging in region of **k** space which had a nonzero gap. No other argument that we are aware of can account for the time and sample dependence of the data as well. This analysis is consistent with the fact that samples 1 and 3 have sharper laser reflections. Given the analysis, we believe that our body of data is consistent with a very small or zero gap along Γ-Y. In fact, it is fair to state that the spectra at B in Fig. 1 suggest that the superconducting gap along Γ-Y is zero within our experimental uncertainty.

The observed superconducting gap variation can be explained by considering only the Cu-O states. Although there is some hybridization of Bi-O states near E_F around $\overline{M}$ [14], one would not expect a larger gap from the Bi-O states since the superconducting properties originate in the CuO_2 layers. In addition, we see a similar gap anisotropy in samples with different oxygen content, which we know the Bi-O states are very sensitive to [14]. For example, compared to samples 2 and 3, sample 1 has a higher oxygen content and somewhat lower T_c, resulting in a large reduction in the gap value at $\overline{M}$; however, the general trend of the gap variation is the same.

Several theoretical models can qualitatively explain the observed gap anisotropy. First, the mechanism of superconductivity based on interlayer coupling attributes the small or vanishing gap along the Γ-Y direction to the vanishing coupling matrix element between the two CuO_2 planes [23]. Second, the mechanism based on the van Hove scenario may be able to attribute the larger gap along Γ-$\overline{M}$ as having been stabilized by the van Hove singularity [24,25]. Finally, any theoretical model with the $d_{x^2-y^2}$ order parameter can also explain our data. We will concentrate on the last scenario because the first two have not been fully developed to give a more detailed comparison with our experiment at this stage. The $d_{x^2-y^2}$ order parameter $\Delta(k) \sim \cos k_x a - \cos k_y a$ will yield a gap that is proportional to $|\cos k_x a - \cos k_y a|$, as shown by the straight lines in Fig. 3(b). The experimental data agree with the d-wave picture well. The fact that the scatter in the measured gap size is larger along Γ-Y than along Γ-$\overline{M}$ is also consistent with the d-wave scenario because $|\cos k_x a - \cos k_y a|$ is most sensitive to the k averaging along the Γ-Y direction. Furthermore, the data in Fig. 1 and the discussion of Fig. 3 are suggestive of the expected d-wave node within the experimental uncertainty. In the same context, we have also considered order parameters with other symmetries such as extended s-wave or $s+id$. Our data are qualitatively incompatible with the extended s-wave scenario, having the gap proportional to $|\cos k_x a + \cos k_y a|$. The present state of the data does not allow us to distinguish pure $d_{x^2-y^2}$ symmetry from a mixed symmetry of $s+id$ because we cannot definitely establish the existence of the node line. However, since the overall agreement of the data to the form $|\cos k_x a - \cos k_y a|$ is good, the data suggest a strong $d_{x^2-y^2}$ component even if a node does not exist.

The above interpretation of our data is another piece of circumstantial evidence for d-wave superconductivity. On the one hand, it is consistent with the d-wave interpretation of the observed anisotropy in the NMR relaxation rate between copper and oxygen [7,8]. On the other hand, it is not consistent with the temperature dependence of the penetration depth of $Nd_{1.85}Ce_{0.15}CuO_4$ [26].

To conclude, we have observed a superconducting gap anisotropy in the a-b plane of Bi2212 that is at least an order of magnitude larger than that of the conventional superconductors. All aspects of the data (the anomalously large gap anisotropy, the specific $\mathbf{k}$ dependence of the anisotropy, and the possible presence of the node along Γ-Y) can be well understood if we assume Bi2212 is a superconductor with the $d_{x^2-y^2}$ order parameter.

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