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Evidence for k-dependent, in-plane anisotropy of the superconducting gap in $Bi_2Sr_2CaCu_2O_{8+\delta}$

B. O. Wells, Z. X. Shen, D. S. Dessau, and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

D. B. Mitzi,* L. Lombardo, and A. Kapitulnik
Department of Applied Physics, Stanford University, Stanford, California 94305

A. J. Arko
Los Alamos National Laboratory, Los Alamos, New Mexico 87545
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We find the superconducting gap in $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals is anisotropic in **k** space by roughly a factor of 2 using angle-resolved photoemission spectroscopy. Matching the **k**-space symmetry of the gap values provides a stringent constraint on theories of the mechanism of high-temperature superconductivity. A review of the literature shows that many puzzling results can be explained by anisotropic gaps in the high-T_c cuprates.

In conventional superconductors there has been little interest in the **k** space anisotropy of the superconducting gap. This was probably due to the lack of pressing theoretical questions after BCS theory was established and to the difficulty in directly measuring such anisotropic effects. Traditionally, the more direct measurements of superconducting gaps have been made by techniques such as tunneling, infrared measurements, and Raman spectroscopy. None of these techniques provide an easy way to measure the **k** dependence of the gap function. Other techniques, such as ultrasonic attenuation, [1] have provided good **k** information but do not provide a direct measurement of the gap. We have used angle-resolved photoemission spectroscopy to provide a direct, **k** dependent measurement of the gap in the high-T_c cuprate superconductors. We present data in this paper that shows the gap is anisotropic in the **a-b** plane for $Bi_2Sr_2CaCu_2O_{8+\delta}$. The discovery of high-$T_c$ superconductivity has stimulated the development of many different new theories. We suggest that these results will help distinguish among these competing ideas by determining the symmetry of the order parameter. In addition, the results of many experiments have made it clear that the gap in the cuprate superconductors must be anisotropic, we can now directly show that this is the case and provide detailed **k** information about this anisotropy.

EXPERIMENTAL DETAILS

Single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ were grown by the directional solidification technique. The oxygen content of these crystals are readily varied by annealing in different partial pressures of oxygen to achieve transition temperatures from $T_c = 91-78$ K. The samples had sharp Meissner transitions not exceeding 2 K. Details of the sample preparation process and characterization are available elsewhere.[2,3] The crystals were cleaved in a vacuum of 1×10^{-10} Torr at approximately 20 K. The photoemission spectra shown here were recorded by a Vacuum Science Workshop (VSW) hemispherical analyzer in two different modes, one with an acceptance angle of $\pm4°$ and the other with angular acceptance of $\pm1°$. Light was provided by a He discharge lamp at 21.2 eV. The total system energy resolution was 40 meV for the $\pm4°$ data and 35 meV for the $\pm1°$ data as determined by the 10–90 % transition of a Au Fermi edge measured at 20 K, which was also used to frequently monitor the Fermi energy. During data collection we noticed occasional aging problems of the sample where the gap features degrade over time. We have taken care to ensure that these results are reliable.

QUALITATIVE RESULTS

The top panel in Fig. 1 shows the changes observed in the photoemission spectra above and below T_c for two different electron emission angles, or **k** positions, near the band crossing along Γ-$\bar{M}$. As the material goes superconducting, spectral weight is lost near the Fermi energy and there is a pile-up of intensity at about -40 meV. Also, the cold spectrum shows a characteristic dip at about -100 meV that has been thoroughly discussed earlier.[4] It is instructive to attempt to analyze the data first with no fitting procedures and directly compare the data from different parts of the Brillouin zone. The bottom panel of Fig. 1 shows the two cold spectra from the top panel to compare edge positions. The spectra have been normalized so that the height of the edge is the same. For spectra that involve a sharp edge with a Gaussian broadening function, making the heights of the edge the same will allow a comparison of the edge position regardless of the intensity of the peak. The fact that the edges are at the same energy even though the band has dispersed indicates that the position of the edge is a good measure of gap size regardless of small shifts in normal-state band energy, even though this is not consistent with the BCS development for specific **k** points.

The two panels of Fig. 2 compare the edge position for

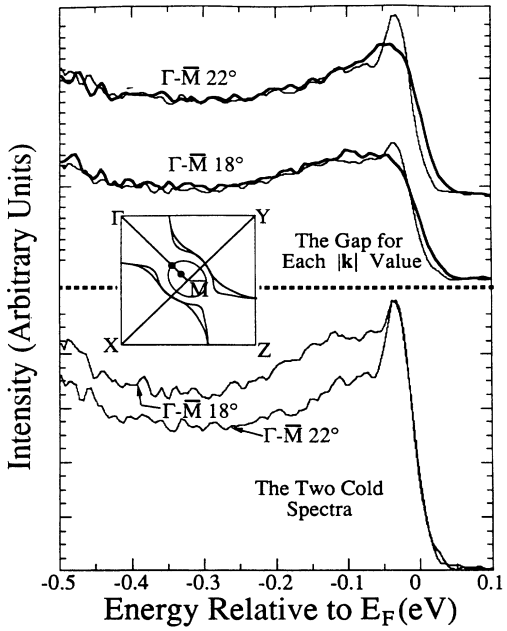

FIG. 1. The high resolution photoemission data taken at two different points along the Γ-$\bar{M}$ direction. The top panel shows the effect of the gap at each point by superimposing the warm ($T=85$ K/ thick line) and cold ($T=20$ K/ thin line) spectra for a $T_c=78$ K sample. The bottom panel directly compares the two cold spectra showing that the leading edges align. The inset is the calculated Fermi surface of Ref. 11 with dots to indicate the points in the Brillouin zone where the data was taken. Note the Fermi surface shown is as calculated and not necessarily completely accurate for this sample.

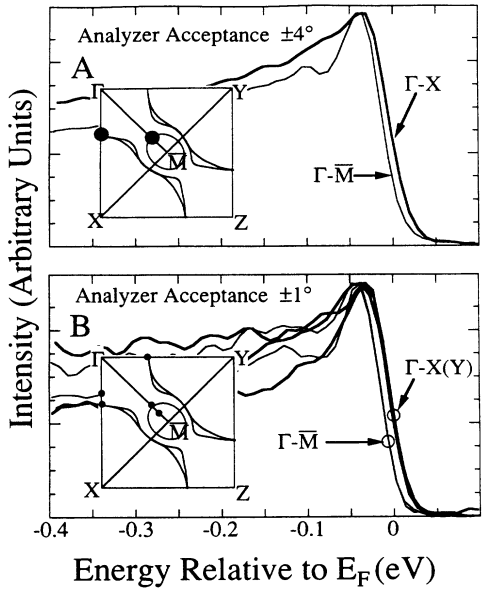

FIG. 2. High resolution photoemission data at **k** locations along the Brillouin zone edge (heavy line in both planes) and the zone diagonal (light line) for a 78-K sample. Panel A compares the edge positions for an analyzer acceptance of ±4°. Panel B shows spectra taken at two angles near the crossing point along Γ-X along with one along Γ-Y vs two angles near the crossing point along Γ-$\bar{M}$, all with an angular acceptance of ±1°. All data taken at $T=20$ K. The inset is the calculated Fermi surface of Ref. 11 with dots to indicate the points in the Brillouin zone where the data was taken.

k values along the two different high symmetry directions. Panel A shows data taken with poor angular resolution (±4°) but very good statistics that compares Γ-$\bar{M}$ and Γ-X data for a $T_c=78$ K sample. Several curves taken with better angular resolution (±1°) on a similar sample are displayed in panel B in order to indicate the level of reproducibility in the data. Among the curves in panel B are two spectra taken at different angles near the band-crossing point along Γ-X that align with one along Γ-Y, and these three are compared to two spectra taken along the Γ-$\bar{M}$ direction. In all cases the leading edge of the spectra for the Γ-$\bar{M}$ data is clearly shifted further away from the Fermi edge than it is for the Γ-$X(Y)$ spectra. This indicates that a larger gap exists for the states along Γ-$\bar{M}$. These two sets of data are taken in different experimental geometries and both clearly show evidence that the gap seen has a different size for the two directions. The same trend is seen in the data for the samples annealed to have a higher T_c (91 K) with a slightly larger shift between the data taken in the two different directions. All of the angle-resolved photoemission data we have taken is consistent, with an average shift between the edges of 11 meV for the $T_c=91$ K samples and 7.5 meV for the $T_c=78$ K samples. These results are not the same as those reported earlier by Olson *et al.*[5] Olson reported the same size gap for several positions in the Brillouin zone including both along Γ-$\bar{M}$ and Γ-X. We believe that our results are intrinsic to the $Bi_2Sr_2CaCu_2O_{8+\delta}$ material for several reasons. First, we have found consistent results on more than a dozen samples in experiments performed with different equipment

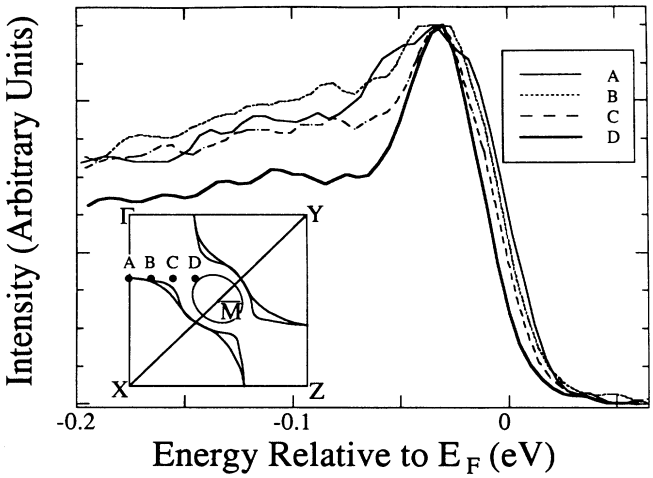

FIG. 3. High resolution photoemission spectra of the gap region taken at positions in between the high symmetry directions shown in Fig. 2. The data were taken at 20 K and an angular resolution of ±1°. The inset is the calculated Fermi surface of Ref. 11 with dots to indicate the points in the Brillouin zone where the data was taken. Note the Fermi surface shown is as calculated and not necessarily completely accurate for this sample.

and with different experimental geometries. These results are correct for our crystals. Further, the crystals themselves are high quality, they have sharp transitions with large Meissner fractions, and have been characterized in many ways.[2,3]

The data presented to this point leave two possibilities. One is that there are two gaps, perhaps each gap associated with a different band. The second is that an anisotropic gap exists which varies smoothly in **k** space. There are many results in the literature, as will be discussed below, which may be consistent with either scenario. To distinguish between the two scenarios we have measured the gap at angles in between the two high symmetry directions. In Fig. 3 we present gap data taken in between the high symmetry directions. The energy axis is blown up in order to focus on the position of the leading edges of the spectra. The edge shifts monotonically from the smallest gap along the Γ-X line to the largest gap along Γ-$\bar{M}$. We expect that the results should be identical between Γ-Y and Γ-$\bar{M}$ since the rest of our data seem to reflect fourfold symmetry. Clearly the gap is a smoothly varying function of position in **k** space and there are not two constant gaps that exist for different bands.

QUANTITATIVE ANALYSIS

Once we have established a qualitative picture of the anisotropy of the gap it is desirable to quantify the gap sizes measured. There are many difficulties in establishing definite numbers for the gap size as measured by photoemission. If the experimental resolution were better we could directly read off a gap size from the data as can often be done from tunneling dI/dV measurements on traditional superconductors. Since this is not possible for photoemission data, other authors have fit their data to a simple BCS expression.[6,7] Finding a correct fitting procedure is difficult. First, even for the normal state there is no accepted theory. A paper by Liu *et al.* shows the

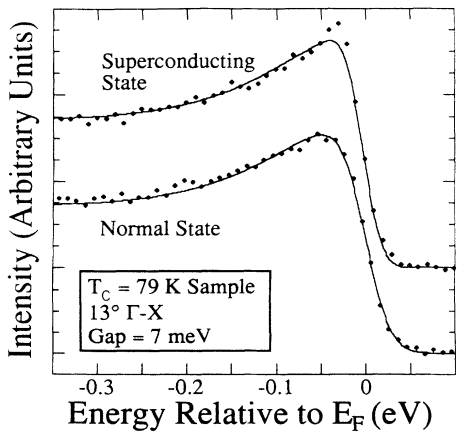

FIG. 4. The BCS fit to our data used to determine values for the gap, Δ, for spectra taken at the band crossing point along the Γ-X direction on a $T_c = 78$ K sample. The solid line is the fit and the dots the data. The zero intensity line for the superconducting state spectrum is offset for clarity. The superconducting state data was taken at $T = 20$ K and the normal state data at $T = 90$ K. For details see the text.

TABLE I. Proposed gap values. Values obtained for the gap in millielectron volts and the corresponding $2\Delta/k_B T_c$ for each high symmetry direction in the plane and for samples with low ($T_c = 91$ K) and high ($T_c = 78$ K) oxygen content.

k-space direction:	Sample type $T_c = 91$ K meV	$2\Delta/kT_c$	$T_c = 78$ K meV	$2\Delta/kT_c$
Γ-$\bar{M}$	26	6.6	16	4.8
Γ-X	15	3.8	8	2.4

difficulties is making an accurate fit with physically relevant parameters using available theories.[8] The superconducting state spectra are more difficult. There are many new theories of high temperature superconductivity most of which are not developed to the point of producing a gap line-shape function. Within BCS theory there are still problems. Our data seems to be better fit with the simple **k** averaged function than with a **k** resolved expression. Presumably our data has sufficient **k** averaging from the finite acceptance angle of the analyzer and inelastic scattering to destroy the ability to consider the data as arising from δ functions at specific points in **k** space. For example, Fig. 1 shows that the superconducting edges align in energy despite small changes in normal-state band energy $\varepsilon_{\mathbf{k}}$, although BCS predicts that the superconducting-state energy positions go as $E_{\mathbf{k}} = \sqrt{\varepsilon_{\mathbf{k}}^2 - \Delta^2}$. Also where the gap is large, strong coupling corrections should be incorporated into the analysis. Motivated by the 100-meV binding energy dip, Arnold *et al.*[9] have inverted some of our data using Eliashburg strong coupling equations and find gap values consistent with those reported here. However, this is also an angle integrated theory. We have chosen to follow the fitting procedure of Olson *et al.*[6] to systematize our results since it is simple and is a well-known result. This procedure involves fitting the normal state spectra with a Lorentzian normal state peak and multiplying this expression by the angle-integrated BCS expression to fit the superconducting state spectrum. We depart from the method of Ref. 6 in that we chose the condition for best fit to be when the leading edge (emission onset) of the calculated and measured superconducting spectra most closely matched. We can fit most of the data with a precision of ± 2 meV.

Figure 4 shows one of our fits along the Γ-X direction. The fit matches the data well except that the pile-up peak in the superconducting state is not large enough. We can usually fit the pile-up peak in the Γ-$\bar{M}$ data but cannot reproduce the dip feature. Table I lists the gap values we obtained on different samples at different **k** locations. The fitted values for the gap show a large anisotropy in the plane in both types of samples with the gap roughly twice as large along Γ-$\bar{M}$ as Γ-X. The gap is consistently much smaller in the $T_c = 78$ K sample (12 atmosphere O_2 annealed) than in the $T_c = 91$ K sample (H_2 in Ar annealed sample). We note that $2\Delta/k_B T_c$ is not a constant for these fitted gap values. It is surprising to see such a large change in $2\Delta/k_B T_c$ for a relatively small change in T_c.

DISCUSSION

The qualitative picture that emerges for $Bi_2Sr_2CaCu_2O_{8+\delta}$ is of a large gap where there is Fermi surface along the Γ-$\bar{M}$ direction, a much smaller gap along the Γ-X direction, with the gap size varying smoothly between the two directions. We should be able to understand these results in terms of the symmetry of the superconducting order parameter, the square of which gives the magnitude of the gap. ARPES is a natural measurement to find how the gap varies in **k** space, i.e., the symmetry of the gap. The overall symmetry that we observe is similar to that expected for d-wave symmetry. The largest gap is along Γ-$\bar{M}$, along the Cu—O bonds. The smallest gap is along Γ-X, diagonal to the Cu—O bonds. However, d wave symmetry implies that the gap should go to zero along Γ-X. We see the smallest gap along Γ-X but no node. This may not rule out a d-wave order parameter. Since our experiments do integrate over a finite range of **k** space, it is likely that even if a gap node exists along the diagonal, we would still see an apparent small gap. The finite resolution of the photoemission experiment makes it difficult to determine whether the spectra represent a superposition of states, some of which have no gap. However, our initial modeling indicates that the gap we do see is larger than we should see if a node does exist. Another possibility is that the order parameter has a mixed symmetry such as $s+\imath d$.[10] This sort of order parameter should give a gap that generally has the symmetry of d wave but would not have a node. Our data seems to point to an $s+\imath d$ order parameter but ARPES may not be the best experiment to establish whether a node exists.

There are some details which may complicate the interpretation of the results presented in this paper. It has been suggested in the literature that a surface effect may cause an enhancement of the gap near the surface of a superconductor with a short coherence length.[11] This sort of argument is not consistent with finding a smoothly varying gap function in a layered, strongly two-dimensional material. A further complication arises from the nature of the band structure in $Bi_2Sr_2CaCu_2O_{8+\delta}$. The exact Fermi surface for $Bi_2Sr_2CaCu_2O_{8+\delta}$ is a matter of controversy, but LDA calculations indicate it may include a Bi-O electron pocket as well as the usual Cu-O plane related piece.[12] In particular, we do know that the Γ-$\bar{M}$ states have a large contribution from Bi-O (Ref. 13) while the Γ-X states are more purely Cu-O in origin. It is surprising that the states with Bi-O character have a larger gap than the more Cu-O states, considering the overwhelming evidence that the Cu-O planes are the critical regions for high-T_c superconductivity. However, once again the smoothly varying gap size with **k** indicates that the anisotropic gap is probably not the effect of two different bands, although may be related to different amounts of hybridization. Our latest results indicate that in fact all of the measurements in Fig. 3 come from the same band. Details of our latest band mapping will be published in a later paper. Examining experiments using other methods to measure the gap should add insight as to whether an anisotropic gap is an intrinsic feature of cuprate superconductors or just an artifact of photoemission or the $Bi_2Sr_2CaCu_2O_{8+\delta}$ material.

Until now there has been no single, conclusive experiment that has shown an in-plane anisotropic gap. Taken as a whole however, there is substantial evidence from previous experiments that there are multiple gaps in the superconducting cuprates. An indication that there may be multiple gaps is that reported gap values range from about $2\Delta/k_BT_c=2-8$. Nuclear magnetic resonance (NMR) experiments measuring the spin relaxation rate on the high-T_c superconductors show no coherence peak at T_c,[14] and seem to indicate that the low-temperature inverse relaxation rate falls off as a power law.[15,16] Both are indications of nodes in the gap and definitely indicate an anisotropic gap. Other strong evidence that there is an anisotropic gap in one particular sample comes from Raman spectroscopy. Raman studies have shown an indication of an anisotropic gap in $YBa_2Cu_3O_7$, $YBa_2Cu_4O_8$, and $Bi_2Sr_2CaCu_2O_{8+\delta}$.[17–19] Different gaps are detected depending on the polarization of the incident light. This is interpreted as gaps of different sizes in states with different symmetries rather than according to their **k** space locations as in our work. There is also indication in the Raman that there are regions of zero gap in the superconductors,[19] possibly reflecting a node in the gap function. Raman spectroscopy is not nearly as surface sensitive as photoemission, so surface effects are not likely to be the cause of the observed gap anisotropy in both cases. NQR measurements have also found multiple gaps in a single $YBa_2Cu_3O_7$ sample.[20] Most tunneling data gives gap sizes on the order of our larger values. It has been speculated that the line shapes observed in tunneling indicate the presence of multiple gaps.[21] Since tunneling is not **k** specific, the gap anisotropy that we observe should appear in tunneling as a superposition of gaps. The behavior of the gap inferred from penetration depth measurements in $YBa_2Cu_3O_7$ can be fit by assuming multiple gaps or an anisotropic gap is present.[22] In general the large zero bias current that is usually observed in tunneling on cuprate superconductors and the structure in the conductance within the gap may both be indications that a gap node exists. Thus in the literature to date there are several indications of multiple gaps in both $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $YBa_2Cu_3O_7$, indicating that an anisotropic gap may be a general bulk feature of the cuprate superconductors.

It is important to point out that along the zone diagonal, Γ-$\bar{M}$, we see both a larger gap and the appearance of a large dip at higher binding energies around -90 meV, while in the Γ-X direction, the region of smaller gap, the spectra look more conventional, although there may be more spectral weight in the pile-up than is lost from the gap.[4,5] We suggest that the presence of a large anisotropy in the gap as well as the **k**-dependent anomalies in the spectral line shape near the gap may prove important in distinguishing between different theories. While there has been extensive theoretical discussion of the symmetry of the gap in the high-T_c cuprates,[23–28] we hope this experimental result will stimulate further work matching theory to the experimental information described here,

including the presence of the dip in the region of large gap.

Our experimental observations have shown that the gap in 2:2:1:2 as measured by angle resolved photoemission is anisotropic within the *a-b* plane. These results show the overall behavior expected for a *d*-wave order parameter although no gap node is detected. Perhaps this is an indication of a superposition of symmetries such as in an $s+\imath d$ model for the order parameter. Quantitative analysis of the gaps observed in photoemission is difficult as we have pointed out. Our best efforts at quantifying our results indicate an anisotropy of $\Delta_{max}/\Delta_{min}=2$, with values for the large and small gaps that are consistent with other results in the literature. While there is evidence that the region with the largest gap has substantially more Bi-O character than the region with the smallest gap, we do not know how or if this affects the observed anisotropy of the gap.

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*Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598.

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