PHYSICAL REVIEW B VOLUME 55, NUMBER 5 1 FEBRUARY 1997-I

Superconducting-gap anisotropy in $YBa_2Cu_3O_{7-\delta}$: Photoemission results on untwinned crystals

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(Received 9 April 1996)

Polarization-dependent angle-resolved photoemission studies of untwinned single crystals of $YBa_2Cu_3O_{6.95}$ (Y123) reveal modifications of the near-Fermi-edge spectral weight which are indicative of an anisotropic superconducting gap. The measured magnitude of the leading edge shift increases monotonically from the $\Gamma-S$ line toward the zone boundary, reaching a maximum value of approximately 25 meV, similar to the behavior seen in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212). Within experimental uncertainty, we find variation which is consistent with that expected for a $d_{x^2-y^2}$ order parameter, providing additional evidence in support of the d-wave pairing hypothesis. [S0163-1829(97)10205-3]

Determination of the symmetry of the superconducting order parameter in the cuprates is believed to be a key to understanding the underlying mechanism of superconductivity. Observation of a highly anisotropic gap in photoemission from Bi2212 has fueled much recent discussion on this topic, generally centered on the question of d-wave vs anisotropic, or extended, s-wave symmetries.[1–4] Symmetries of the former type arise from theories which emphasize the strongly correlated nature of the Cu-O planes, such as the Hubbard and t-J models or from antiferromagnetic fluctuations, while the latter can arise from modifications of conventional BCS theory.[5–8] Recently several elegant experiments on Y123 have provided strong evidence for a phase change under 90° rotation, consistent with the d-wave hypothesis.[9] Angle-resolved photoemission, although only sensitive to the magnitude of the order parameter, is nevertheless able to place strong upper bounds on the maximum gap magnitude at the node line, and has the unique capability of directly measuring the **k** dependence of this quantity. Unfortunately, previous attempts to measure the gap in materials other than Bi2212 have failed. In particular, a gap has never been reproducibly observed by photoemission in Y123 This absence is particularly puzzling in light of numerous results obtained with other experimental techniques, and has been attributed to generic ‘‘surface effects.’’

In this report we present results from an extensive study of untwinned single crystals of Y123. We observe shifts in the photoemission spectra consistent with the presence of an anisotropic superconducting gap with magnitude and **k** dependence in good agreement with observations on Bi2212. We discuss the significance of this finding within the context of the current debate on order-parameter symmetry, and compare our results with the predictions of a simple d-wave model.

Data in this paper were acquired on four separate cleaves of extremely high-quality untwinned single crystals of Y123 (typical transition widths <0.25 K). Plane polarized synchrotron radiation of $h\nu=28$ eV was provided by the undulator beamline V at SSRL. Photoemission spectra were measured using a goniometer-mounted hemispherical analyzer of 50 mm mean radius, providing a combined instrumental energy resolution (monochromator and analyzer) of ≈ 50 meV, somewhat poorer than previous studies on Bi2212 due to the higher photon energy, and an angular resolution of $\pm 1°$. All samples were cleaved parallel to the a-b plane and kept at or below 20 K in order to prevent the surface degradation which is observed in this material for temperatures above ≈ 50 K.[10,11] Chamber base pressure was better than 5×10^{-11} torr at all times during data acquisition. Samples were oriented *ex situ* using Laue diffraction with an accuracy of $\approx \pm 1°$, and mounted with the b axis at a 45° angle to the photon polarization. The combination of high photon flux and excellent vacuum enabled us to acquire spectra throughout the entire Brillouin zone in three distinct orientations, which provided the insight necessary for a more complete understanding of this complex system. Most of these results will be presented separately;[11] here we focus specifically on those aspects relevant to the superconducting gap.

In Fig. 1 we present photoemission spectra from sample X III taken along six distinct cuts through the two-

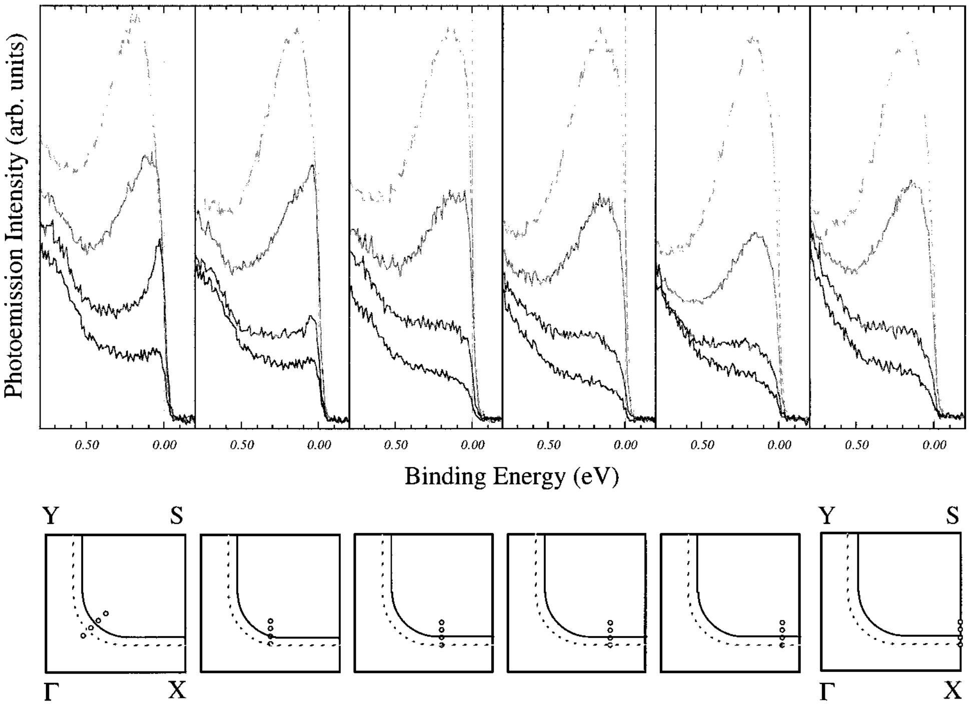

FIG. 1. Photoemission spectra along various cuts through the Brillouin zone, clearly revealing a Fermi-surface crossing. The lower portion schematically illustrates the points in **k** space corresponding to each spectrum. A possible second Fermi-surface sheet is indicated by the hatched line.

dimensional (2D) Brillouin zone (BZ), normalized to the weight above E_f arising from higher-order photons. Each panel clearly reveals a Fermi surface (FS) crossing, with a schematic representation of the points in the BZ corresponding to the spectra shown beneath. A crossing is identified by an abrupt loss of intensity in the quasiparticle feature as it moves above E_f. The importance of accurately determining the precise **k**-space location of the crossing has been extensively discussed in the context of gap studies on Bi2212.[2] We identify the crossing using two criteria: (i) the point where the integrated intensity in the quasiparticle is reduced by half, and (ii) the point where the midpoint of the leading edge near E_f reaches the farthest forward (i.e., the lowest binding energy).

Figure 2 compares the leading-edge regions of spectra taken at the FS crossing points; only four of the six crossings are shown for reasons of clarity. The Fermi-edge spectrum from our Au reference sample is indicated by the thick line. A monotonic shift of the leading edge is seen as we move along the FS from $\Gamma-S$ toward $X-S$, with the clear appearance of a gap in the spectra near X. While this behavior is similar to the gap phenomena seen in Bi2212, there are a number of important differences. In particular, we fail to observe the sharp peak which appears prominently near M (equivalent to X in Y123) in the superconducting state. Also, spectra along $\Gamma-S$ exhibit qualitatively different crossing behavior when compared with those along $X-S$, with the former showing a pronounced sharpening, while the latter diminish in intensity without significant changes in the line shape. Finally the leading edges of the spectra nearest the $\Gamma-S$ line appear to lie significantly above the Fermi level as determined by our reference sample. This effect is also seen in Bi2212, but it is markedly more pronounced in our Y123 data. We believe that these observations are closely related, and may be understood by considering the interplay between the underlying spectral function and the finite instrument resolution.

Our inability to compare spectra above and below T_c in Y123 makes careful analysis of line shapes crucial. Simple numerical simulations of photoemission spectra can provide insight into the behavior seen in Fig. 2, the details of which are presented in a forthcoming publication.[11] Relying on the spectral function interpretation of the photoemission process, we can model a quasiparticle dispersing through E_f with a simple Lorentzian peak, cut by a Fermi function and convolved with a Gaussian corresponding to the experimental

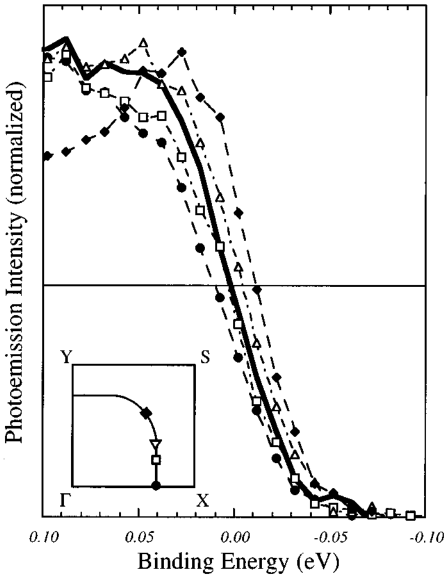

FIG. 2. The near E_f region of spectra at the Fermi surface crossing are superimposed, revealing the presence of a monotonic shift of the leading edge to higher binding energies from the $\Gamma-S$ crossing to the $X-S$ crossing. A reference spectrum for a Au sample is shown by a thick line for comparison. Spectra are normalized for purposes of visualization.

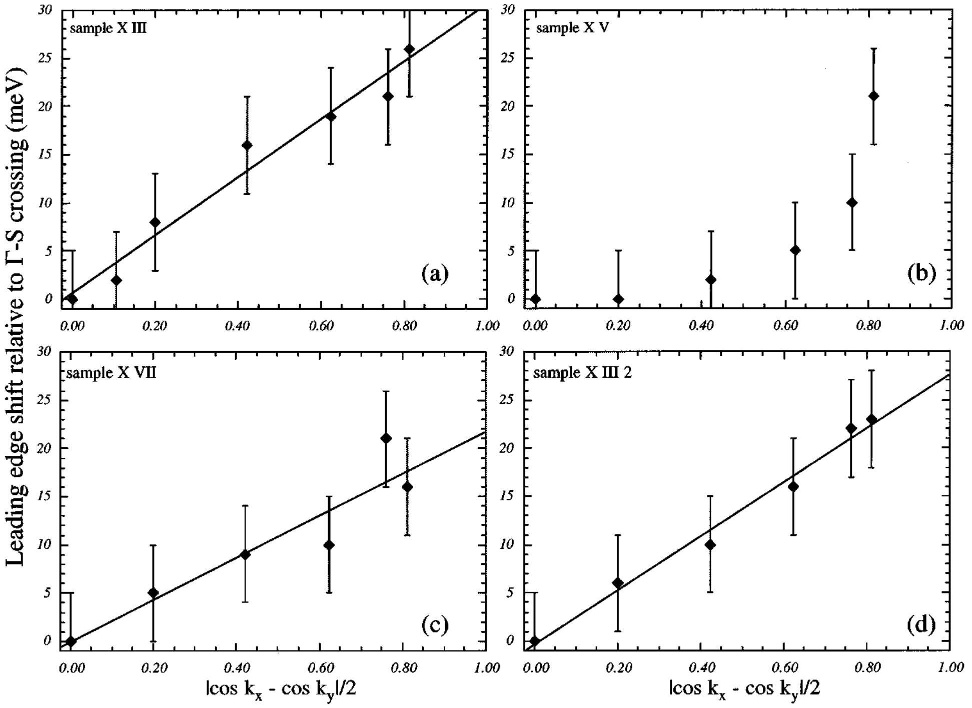

FIG. 3. Measured shifts (meV) in the leading edges of the photoemission spectra for four samples, taken at crossings along the Fermi surface, plotted relative to the quantity $|\cos k_x - \cos k_y|/2$. Samples X III, X VII, and X III 2 exhibit strong linear correlations, consistent with an order parameter having $d_{x^2-y^2}$ symmetry. The extended region of zero shift in sample X V may be indicative of ''dirty'' *d*-wave behavior, as discussed in the text.

energy resolution. In order for a spectrum to exhibit a large shift of the leading edge above E_f, it is necessary for the underlying quasiparticle to be narrow and lie near the Fermi level, in which case the instrumental broadening will lead to a forward shift on the order of the Gaussian standard deviation. From the figure, we see a shift of approximately 15 meV, which is of the magnitude expected given our experimental resolution. This implies that the peak at the $\Gamma - S$ crossing must have a small or zero gap. It is also important to note that the appearance of a gap in our photoemission spectra, as indicated by a shift of the leading edge below the Fermi level of the Au reference, cannot be explained without invoking a real gap.

Very little is known about the intrinsic form of the spectral function in these materials, making quantitative analysis of the photoemission spectra difficult. Rather than subjectively identifying the leading-edge shift by visually determining the midpoint, we have chosen a simple fitting procedure to ensure consistency between different samples and regions of **k** space. We do not ascribe any physical significance to this procedure; it is simply a means of quantitatively estimating the leading-edge shift; we find that it also provides values for the shift which are generally in good agreement with the traditional, subjective method.

The absence of a sharp peak at the $X - S$ crossing is a source of concern, particularly since it is such a prominent feature in the superconducting state of Bi2212. However, the presence of a gap of unknown origin in the excitation spectrum is clearly indicated by the data, and has been reproduced on four separate samples. Unlike Bi2212 in which the bands near $(\pi,0)$ are quite flat and remain near the Fermi level over an extended region of **k** space, we observe significant dispersion (≈ 0.5 eV) near the Fermi-surface crossing along $X - S$, although an additional flatter band may also be seen near the X point. This large dispersion, in conjunction with decreased momentum resolution at the higher photon energies used on Y123, can lead to broadening of the spectra. We can make a simple quantitative estimate of the momentum related broadening by comparing our angular resolution of approximately 10% of the $\Gamma - X$ distance with the observed dispersion to find a total contribution of ≈ 150 meV, significantly larger than the experimental energy resolution. In addition, we have found some evidence to substantiate the local-density approximation prediction of two distinct plane derived Fermi-surface sheets. The presence of such a bifurcation could lead to a strong overlap of two quasiparticle features in the photoemission spectra, obscuring any sharp features. With these caveats in mind, we believe that it is most reasonable to attribute the leading-edge shifts in our data to modifications due to the presence of a superconducting gap. This interpretation leads to a self-consistent picture which agrees with photoemission measurements of the superconducting gap on Bi2212 and with other experimental results on Y123. In this picture, the shifts of the leading-edge along the Fermi surface will reflect, to first order, relative variation in the magnitude of the superconducting gap at different points along the FS.

We present the measured leading edge shifts, as determined by our fitting procedure, in Fig. 3 and Table I. Due to our experimental uncertainty in determining the absolute magnitude of the gap along $\Gamma - S$, we measure all shifts relative to the position of the leading edge at this crossing. The error bars in the figure represent the uncertainty in determination of the shift due to line shape issues discussed above; errors due to uncertainty in the fitting parameters or in the reference E_f position are substantially smaller. Comparison of the relative shift with the characteristic **k**-space dependence of a d-wave order parameter, $|\cos k_x - \cos k_y|/2$, reveals clear linear dependence for three of the four samples (X III, X VII, and X III 2), while the data from sample X V shows an extended node region, with the gap rapidly growing only near the zone boundary. This behavior may be representative

TABLE I. Superconducting gap: leading edge shifts relative to $\Gamma - S$ crossing.

$\vert \cos k_x - \cos k_y \vert$	Δ (meV):	X III	X V	X VII	X III 2
0.81		26	21	16	23
0.76		21	10	21	22
0.62		19	5	10	16
0.42		16	2	9	10
0.20		8	0	5	6
0.11		2			
0.00		0	0	0	0
$2\Delta_0/kT_c$		7.6		5.4	7.0

of a ''dirty'' d-wave material, and is consistent with our observations that the quasiparticle feature was substantially less distinct and the cleave visually inferior to those in other samples. Extrapolation of the linear region to the zone boundary provides values for $2\Delta_0/kT$ in the range of 5.4–7.6. Recent microwave penetration depth measurements on similar samples have revealed critical behavior belonging to the 3D XY universality class, which implies a single, complex superconducting order parameter such as pure s- or d-wave,[12] while strong evidence for a change of phase on crossing the $(0,0)-(\pi,\pi)$ line has been found in Y123 in both Josephson tunnelling and scanning superconducting quantum interference device magnetometer measurements.[9] In conjunction with these experiments it is difficult to interpret our data as being consistent with a non-d-wave order-parameter symmetry.

The failure of previous studies to observe a superconducting gap in Y123 (see Ref. 13 for a review of earlier work), despite six years of effort, requires some explanation. Two critical elements of our experiment differ from these attempts, enabling us to observe the presence of leading-edge shifts. First, we use *untwinned* samples, in which the Cu-O chain axes are uniformly oriented. Because twinning mixes the normally inequivalent X and Y points, significant mixing of the spectral function occurs throughout the Brillouin zone. Second, we consider the photoemission spectra in three distinct sample orientations relative to the plane of photon polarization, which enables us to identify a previously unseen dispersive feature which is strongly enhanced in only one geometry. Also, the large dispersion of this band makes sample alignment critical, unlike the case of Bi2212. It is also important to note that, as in previous studies, we do not observe gaplike shifts in the leading edges of spectra taken near the X/Y points; our measurements correspond to the innermost Fermi-surface sheet centered on the S point. This absence of a gap remains a puzzle, perhaps related to the strong hybridization of chain and antibonding plane states in conjunction with electronic structure effects from the chain-terminated surface.

To summarize, we observe the presence of leading-edge shifts in photoemission spectra of untwinned Y123 which are consistent with the presence of a highly anisotropic superconducting gap. We are unable to conclusively associate these with the onset of the superconducting transition due to the surface instability of this material above T_c, but believe that our interpretation is the simplest self-consistent explanation. We also find that their **k** dependence exhibits the expected behavior for a pure d-wave order parameter, although we are unable to exclude the possibility of symmetries such as $d+id$ or highly anisotropic s wave with a gap magnitude mimicking the d-wave form. These results underscore the complexity of this system, and we hope that they will stimulate further interest in gap measurements on Y123.

The data in this study were obtained at the Stanford Synchrotron Radiation Laboratory (SSRL) which is operated by the DOE Office of Basic Energy Sciences, Division of Chemical Sciences. The Office's Division of Materials Science has provided support for this research. The Stanford work was also supported through the NSF Grant No. DMR-9311566, and the Center for Materials Research. D.A.B., R.L., and W.N.H. acknowledge the support of the Natural Science and Engineering Research Council of Canada, and the Canadian Institute for Advanced Research. M.C.S. would like to acknowledge the support of the Fannie and John Hertz Foundation.

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