Ubiquitous antinodal quasiparticles and deviation from simple $d$-wave form in underdoped Bi-2212

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The momentum dependence of the superconducting gap in the cuprates has been debated, with most experiments reporting a deviation from a simple $d_{x^2-y^2}$ form in the underdoped regime and a few experiments claiming that a simple $d_{x^2-y^2}$ form persists down to the lowest dopings. We affirm that the superconducting gap function in sufficiently underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) deviates from a simple $d$-wave form near the antinode. This is observed in samples where doping is controlled only by oxygen annealing, in contrast to claims that this effect is only seen in cation-substituted samples. Moreover, a quasiparticle peak is present at the antinode down to $p=0.08$, refuting claims that a deviation from a simple $d$-wave form is a data analysis artifact stemming from difficulty in assessing a gap in the absence of a quasiparticle.

Angle-resolved photoemission spectroscopy (ARPES) can measure the spectral gap in the superconducting state to great precision, but yet there are still disputes about the details of the momentum dependence. In underdoped Bi-2212, there is wide agreement that the superconducting gap function follows a simple $d$-wave form, expressed at 0.5 times the Fermi momentum, $k_F$, or $\cos(2\theta)$ in $k$-space. We use the former convention in this paper. In the underdoped regime, there are experiments that find that the gap function deviates from a simple $d$-wave form with the antinodal region exhibiting a larger gap than implied by the simple $d$-wave trend in the near nodal region. This is reported in Bi-2212, (Bi,Pb)$_2$(Sr,La)$_2$CuO$_{8+\delta}$ (Bi-2012) La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ (LSCO), and Bi$_2$2223 which is more underdoped than the other plane and YBa$_2$Cu$_{3+y}$O$_y$ (YBCO). Recently, Zhao et al have reported that the reported deviation from a simple $d$-wave form in Bi-2212 is an artifact of cation substitution which is used to achieve stable underdoping. They claim that cation substitution (Dy or Y) on the Ca site suppresses the antinodal quasiparticle, and when antinodal quasiparticles are present, the gap function always follows a simple $d$-wave form. They also claim that without cation substitution, the gap function always follows a simple $d$-wave form.

In the ARPES literature, a deviation of the superconducting gap function from a simple $d$-wave form is often taken as evidence that the pseudogap coexists with superconductivity below $T_c$, which implies that it is a distinct phase. However, the purpose of this paper is not to discuss the relationship between the pseudogap and superconductivity. Rather, we simply aim to clarify the experimental facts. We show data demonstrating a deviation from a simple $d$-wave form in a sample which was underdoped only by oxygen annealing. Then, we demonstrate that antinodal quasiparticles are clearly observed in samples with various compositions down to a $T_c$ of 50K ($p=0.08$), and that the gap function deviates from a simple $d$-wave form in underdoped samples with a $T_c$ of 75K or smaller. We explore various reasons for the discrepancy between our result and that of Zhao et al including matrix elements and resolution.

ARPES experiments were performed at Stanford Synchrotron Radiation Lightsource (SSRL). Samples were cleaved in situ at the measurement temperature ($T<T_c$) at a pressure better than $5\times10^{-11}$ Torr. The Fermi energy, $E_F$, was determined from the Fermi edge of polycrystalline gold which is electrically connected to the sample. Table I shows the composition and experimental configuration for all of the samples presented in this paper. Most samples were measured with a SCIENTA R4000 analyzer (angular resolution $\approx 0.1^\circ$), except for UD50 which was measured with a SCIENTA SES-200 analyzer (angular resolution $\approx 0.3^\circ$). Energy resolutions are also listed in Table I.

Fig. 1 shows energy distribution curves (EDCs) at the Fermi momentum, $k_F$, for UD75, as well as gaps derived from those data. Notably, the $T_c$ of this sample was achieved only by oxygen annealing, and no cation substitution. Quasiparticles (QPs) are observed over the entire Fermi surface (FS), from the node to the antinode. Symmetrization, given by $I(k_F,\omega)+I(k_F,-\omega)$, is used to remove the Fermi-Dirac cutoff, assuming particle-hole symmetry, which should be valid assumption in the superconducting state. The gap at each momentum is determined in two ways in Fig. 1(d): by fitting symmetrized EDCs to a minimal model and from the peak positions of symmetrized EDCs. Both yield results within error bars of one another. The momentum dependence of the superconducting gap is illustrated by plotting as a function of the simple $d$-wave form, expressed as $0.5|\cos(k_x)-\cos(k_y)|$. This expression is equal to zero at the node (along the $0,0$ to $\pi,\pi$ line) and close to one at the antinode (where the FS meets the Brillouin zone boundary). A superconducting gap is said to follow a simple $d$-wave form if all data points fall on a straight
TABLE I. Summary of samples discussed in this work with their composition and experimental setup. ΓY refers to cuts taken parallel to the (0,0)-(π,π) line and ΓM refers to cuts taken parallel to (π,0)-(π,π). UD(OD) refers to underdoped (overdoped) samples and the number which follows gives the $T_c$.

| Sample | Composition | Photon energy | Cut geometry | Resolution | Temperature |
|--------|-------------|---------------|--------------|------------|-------------|
| UD50   | Bi$_2$Sr$_2$(Ca,Y)Cu$_2$O$_{8+δ}$ | 19eV | ΓY (2nd BZ) | 14 meV | 10K |
| UD55   | Bi$_2$Sr$_2$(Ca,Dy)Cu$_2$O$_{8+δ}$ | 18.4, 19, 21, 22.7 eV | ΓM | 8 meV | 9K |
| UD65   | Bi$_2$+xSr$_2−x$CaCu$_2$O$_{8+δ}$ | 22.7 | ΓM | 8 meV | 12K |
| UD75   | Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ | 22.7eV | ΓM | 7 meV | 10K |
| UD92   | Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ | 22.7eV | ΓM | 7 meV | 10K |

FIG. 1. Antinodal EDCs and deviation from simple $d$-wave form in sample whose doping is controlled only by oxygen annealing without any cation substitution. (a) Raw EDCs at $k_F$ for UD75 from near the node (1, top) to the antinode (bottom) (b) Symmetrized EDCs at $k_F$, same cuts as (a). (c) Gap as a function of the simple $d$-wave form, represented by $0.5*|\cos(k_x) − \cos(k_y)|$. Gap defined from symmetrized EDCs in two ways: 1) fitting to assumed model (green) and 2) from energy of EDC peak (cyan). Dashed lines are linear fits to the first 5 data points. (d) Gap as a function of Fermi surface angle, $θ$, defined in inset. Dashed lines are fits of first 5 data points to $\Delta(θ) = \Delta_0 \cos(2θ)$ and color definitions are same as panel (c). Inset: Fermi crossings for EDCs in (a)-(b) and gap fits in (c)-(d). Dashed lines represent cut geometry of experiment. (e) EDC width as a function of simple $d$-wave form, determined by two different methods: (1)the $Γ_1$ parameter in the Norman model which defines the EDC width (orange) and (2) Lorentzian FWHM when a portion of the EDC is fit to a Lorentzian plus linear background (green). (f) Both EDC peak width fitting methods, shown for cut 5.

line when plotted in terms of $0.5*|\cos(k_x) − \cos(k_y)|$. By this criterion, the gap function in Fig. (d) does not follow a simple $d$-wave form over the entire FS. In the near-nodal region, the gap function does follow a simple $d$-wave form, and the linear fit to the first 5 data points is shown by dashed lines for both methods of determining gaps. In the antinodal region, measured gaps are larger than the trend implied by the dotted lines, indicating a deviation of the gap function from a simple $d$-wave form. Another expression for the simple $d$-wave form is $\cos(2θ)$, and gaps are plotted in terms of the FS angle, $θ$ in Fig. (d). Again, fitting the five data points closest to the node to a simple $d$-wave form yields a trend from which the antinodal points deviate. These data refute the claim in Ref. 3 that a deviation from a simple $d$-wave form is only observed in cation substituted samples. To emphasize the robustness of antinodal quasiparticles, the EDC width is plotted as a function of $0.5*|\cos(k_x) − \cos(k_y)|$ in Fig. (e). Two methods of quantifying the EDC width are shown. The simplest method is to assume a Lorentzian peak on a background which varies linearly with binding energy. The second method is from the so called single-particle scattering rate, $Γ_1$, from the same phenomenological model from which the gap was fit in panels (c)-(d). The EDC width derived by both methods varies approximately by a factor of two around the Fermi surface, demonstrating that the EDC width does not diverge in the antinodal region.
FIG. 2. Ubiquitous QPs all around the FS for various compositions and corresponding gap functions (a)-(c) EDCs at $k_F$ from the node (top) to the antinode (bottom) for UD50, UD65, and UD92. Corresponding fitted gaps are plotted in (d)-(f). Dashed lines in (d)-(f) represent simple $d$-wave form.

This verifies that the criterion used to assess the gap is the same in the near-nodal and near-antinodal regions. Notably, the EDC width in the antinodal region is smaller than the gap energy. We note that the increase in EDC width near the node arises from momentum resolution which can broaden lineshapes in energy for a dispersive band.

Fig. 2 shows EDCs around the Fermi surface for several samples of varying compositions together with their fitted gaps. In the most underdoped sample, UD50, doping is achieved by substituting Y on the Ca site. The second most underdoped sample, UD65, an excess of Bi achieves lower $T_c$. UD92 represents the as-grown doping of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8+\delta$. In Fig. 2, the two most underdoped samples clearly show QPs all around the Fermi surface together with a deviation of the gap function from a simple $d$-wave form. This together with an identical result for UD75 in Fig. 2 demonstrates that the conclusion of a universal simple $d$-wave form of the superconducting gap in Ref. 3 is simply not correct. We note that in the inner-plane of a trilayer cuprate, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi-2223), a deviation of the gap function from a simple $d$-wave form is also accompanied by quasiparticles.$^{22}$ As an aside, recent high-resolution experiments showed subtle deviations from a simple $d$-wave form in UD92 in the portion of the FS intermediate between the node and antinode, and this behavior persisted up to $p=0.19$.11

The ARPES results shown in Figs. 1 and 2 are in agreement with other spectroscopies, including Raman and scanning tunneling spectroscopy (STS) which show different energy scales in the near-nodal and near-antinodal regions of momentum space implying a deviation from a simple $d$-wave form.$^{12–14}$ This is illustrated with STS data in Fig. 3 showing spectra for a UD58 sample. Spectra averaged over a large field of view clearly show two energy scales, marked with black and red arrows. If the gap function followed a simple $d$-wave form, STS would only show one energy scale, and this is indeed what is observed in overdoped samples.$^{12}$ In the $d$-wave superconducting state, energies close to zero bias voltage correspond to momenta near the node, so the lower energy scale (black arrow) corresponds to the near-nodal gap and the higher energy scale (red arrow) corresponds to the antinodal gap. At higher bias voltage, STS shows local inhomogeneity on several-nanometer length scales$^{15,16}$, but crucially, the two distinct energy scales are clearly visible in local spectra as well as the spectrum averaged over a large field of view. The averages spectrum is most relevant for comparisons to ARPES where the beam spot size is usually larger than 100 $\mu$m. STS data suggest that a deviation from a simple $d$-wave form is a generic feature of underdoped cuprates, rather than an anomaly observed by a single experimental technique.

What might be the cause of the differing conclusions from our data and from Ref. 3? A key point which must be clarified is that the absence of a quasiparticle is not as conclusive as the presence of a quasiparticle. In particular, matrix element effects arising from a poor choice of experimental configuration (polarization,
EDCs at \( k_F \) at the antinode (bonding band) for UD55. Curves for different incident photon energies are offset vertically for clarity.

Another difference between experiments is that the ones highlighted in this manuscript were typically performed with energy resolutions of better than 10 meV, while those of Zhao et al were performed with energy resolutions of 15-20 meV. A poorer resolution can affect the EDC peak position, particularly in the near-nodal region where bands are more dispersive and gaps are smaller. This can diminish the visibility of details of the momentum dependence of the gap, such as a deviation from a simple \( d \)-wave form, in the superconducting state which are clearly visible in experiments performed with better resolution. Simulations of energy and momentum resolution effects are shown in the Supplementary Materials.

The work in Ref. [3] brought up an important question about the effects of chemistry on the momentum-resolved electronic structure of cuprates, and it is crucial that future ARPES experiments address this with adequate rigor. This is an important avenue for understanding the mechanism of high temperature superconductivity: in single-layer cuprates, \( T_c,\text{max} \) varies by more than a factor of two depending on the composition of the charge reservoir layers between the \( \text{CuO}_2 \) planes and the types of disorder which are present. ARPES has addressed this issue in single-layer \( \text{Bi}_2\text{Sr}_1\text{La}_{0.4}\text{CuO}_y \) (\( L = \text{La}, \text{Nd}, \text{Eu}, \text{Gd} \)), and Gd doping has been shown to lower \( T_c \) substantially, accompanied by a loss of antinodal coherence and an enhanced antinodal gap. Eu doping also suppresses \( T_c \), and has been shown to increase \( T_c \). In Bi-2212, crystal-growth studies have shown that Sr-site disorder, particularly, excess Bi on the Sr site, suppresses \( T_c \), although not as acutely as in Bi-2201. Bi-2212 samples with a stoichiometric composition have a maximum \( T_c \) of 94K, but typical samples have an excess of Bi, which brings the maximum \( T_c \) down to 89-92K. By doping 8% Y on the Ca site, it is possible to raise the maximum \( T_c \) of Bi-2212 to 96K, by stabilizing growth of samples with stoichiometric Bi and Sr concentrations. The fact that cation substitution is required to maximize the \( T_c \) of Bi-2212 refutes claims that cation substituted samples are more disordered. However, the effect this has on ARPES observables—gaps, dispersions, and spectral weight—has not been explored systematically. This is crucial for interpreting ARPES data going forward. However, this should not be confused by the claims of Ref. [3] that attribute the shape of the gap function to chemistry effects. Data collected from similar samples as in Ref. [3] with better resolution and optimized matrix element detected clear QP peak, questioning the claim that the QP are suppressed in deeply underdoped samples due to this chemistry effect. Additionally, similar results are observed in other cuprates by a number of research groups. The work presented in this manuscript reaffirms the intrinsic nature of a gap function that deviates from simple \( d \)-wave form in underdoped cuprates, suggesting a pseudogap origin of this observation.

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