Angle-resolved photoemission spectroscopy study of HgBa$_2$CuO$_{4+\delta}$
Angle-resolved photoemission spectroscopy study of HgBa₂CuO₄⁺δ

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HgBa₂CuO₄⁺δ (Hg1201) has been shown to be a model cuprate for scattering, optical, and transport experiments, but angle-resolved photoemission spectroscopy (ARPES) data are still lacking owing to the absence of a charge-neutral cleavage plane. We report on progress in achieving the experimental conditions for which quasi-particles can be observed in the near-nodal region of the Fermi surface. The d-wave superconducting gap in near-optimally-doped Hg1201 is found to have a maximum of 39 meV. At low temperature, a kink is detected in the nodal dispersion at approximately 51 meV below the Fermi level, an energy that is different from other cuprates with comparable Tc. The superconducting gap, Fermi surface, and nodal band renormalization measured here provide a crucial momentum-space complement to other experimental probes.

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I. INTRODUCTION

Hg1201 is a cuprate whose structural simplicity and low residual resistivity makes it an ideal compound for many experiments including charge transport [1,2], Raman scattering [3–5], NMR [6–8], thermodynamics [9–12], and neutron [13–18] and x-ray scattering [19,20]. It has a simple tetragonal single-layer crystal structure (P4/mmm), and oxygen dopants reside in the Hg layer, relatively far from the CuO2 planes, minimizing disorder effects [21,22]. In fact, Hg1201 is a model cuprate for gaining quantitative information from transport and optical measurements [1,2,22–26]. Additionally, quantum oscillations have recently been reported in underdoped Hg1201, attesting to a long mean free path and confirming the universality of small Fermi pockets in the field-induced resistive state [26]. The highest superconducting Tc was reported in a related triple-layer compound [27], so in addition to offering general insight on the cuprates, the study of Hg1201 may provide a perspective on how to maximize Tc [28].

However, there have not yet been peer reviewed angle-resolved photoemission spectroscopy (ARPES) studies of Hg1201 in the literature. The reason for this is that the cleaved surfaces are not ideal, which makes it difficult to obtain useful spectra. Here, we present the progress we have made in obtaining the optimal experimental conditions to study Hg1201 with ARPES, which allowed us to quantitatively measure the near-nodal electronic structure of this material. We find that data quality strongly hinges on selecting the proper experimental conditions. With the experiment optimized to achieve the sharpest near-nodal spectra, we are able to estimate the Luttinger volume, measure the d-wave superconducting gap near the node, and observe a nodal renormalization feature near 51 meV. 

II. EXPERIMENTAL CONDITIONS

The schematic crystal structure of Hg1201 is shown in Fig. 1(a). It can be seen that the structure lacks a natural cleavage plane, as there is nowhere to slice the unit cell in a fashion that would yield identical atomic planes on both sides of the cleave, and that it lacks a neutral cleavage plane, as each layer in the unit cell is charged. Additionally, in the Hg1201 crystal structure, adjacent layers have opposite charges [Fig. 1(b)], so any pure termination would produce a polar catastrophe [29] (electric potential increasing to infinity), which must be mitigated either by self-doping or by a mixed termination. Scanning surface microscopies of Hg1201 have indicated that the topography of cleaved surfaces consists of 4-nm step edges with flat terraces extending hundreds of nanometers [30]. Core level x-ray photoelectron spectroscopy (XPS) suggests that the surface termination is near the Hg layer because the Hg:Cu and Hg:Ba intensity ratios normalized by the XPS sensitivity to those elements were larger than expected from the chemical formula [31].

Single crystals were grown by the two-step flux method by which a maximum Tc onset of 97 K (Tc midpoint: 95 K) can be achieved [32]. Annealing conditions are described in Ref. [22]. In preparing Hg1201 samples for ARPES experiments, care was taken to ensure electrical conductance between the sample and the sample post. Samples were glued onto the copper...
sample post using EPO-TEK H21D silver epoxy (Epoxy technology Inc). While this silver epoxy provides adequate conduction between the copper post and most compounds, Hg1201 samples were not found to be properly grounded to the post after this step. This may be due to the epoxy reacting with the Hg1201 surface. Thus the silver epoxy provides only mechanical adhesion in our experiments. For conduction, silver paint (Dupont 4299N) was applied to the side of the sample and the copper post and cured at room temperature. Conduction between the top of the sample and the copper post was confirmed. Care was also taken to maximize the probability of a good cleaved surface. A precut was made on the side of the sample using a surgical razor blade, parallel to the \(a-b\) face. This was to ensure cleaving at a designated location, rather than at inclusions and imperfections as would be the tendency without a precut [22]. This is one of the essential steps that enabled successful ARPES measurements.

We studied nearly-optimally doped Hg1201 (\(T_c = 95\) K, determined at the transition midpoint). Data were taken at SSRL at 10 K with a Scienta R4000 analyzer and 10 meV energy resolution. Samples were cleaved \textit{in situ} at a pressure better than \(5 \times 10^{-11}\) Torr.

Experiments were attempted with a 7 eV laser, near 55 eV at beamline 10.0.1 of the Advanced Light Source (ALS), and near 19 eV at beamline 5-4 at Stanford Synchrotron Radiation Lightsource (SSRL). The latter experimental condition was found to yield the best spectra, and the quality of the measured spectra depended sensitively on the experimental conditions. Figure 1(d) shows energy distribution curves (EDCs) at the Fermi crossing momentum, \(k_F\), at the node taken with several photon energies between 18.6 and 19.6 eV. The amplitude of the quasiparticle peak relative to the background varies rapidly with the choice of photon energy, even within this narrow range. Quasiparticle peaks were clearly observed for 19–19.4 eV photon energy and very weak for 18.6, 18.8, and 19.6 eV photon energies. The nodal quasiparticle peak was found to be most pronounced for 19.4 eV photon energy and \(\Gamma-M\) cut geometry. For this cut geometry, the polarization of the beam at SSRL is 45° from the Cu-O bond direction. Note that because Hg1201 is tetragonal, the \(M\) point is the Brillouin zone corner, and \(\Gamma-M\) cuts are along the (0,0)-(\(\pi,\pi\)) line.

### III. MOMENTUM DEPENDENCE

Using the optimal experimental configuration, electron states near the node are accessible, but the spectral intensity is very small at the antinode, likely because of extrinsic reasons. Fig. 2 shows momentum dependence of spectra. The band is most pronounced near the node in this experimental configuration, and spectral intensity diminishes away from the node. By \(\theta = 21^\circ\), quasiparticles are no longer observed. EDCs at \(k_F\) are shown in Fig. 2(h). All spectra have a strong energy-dependent background, shown in Fig. 2(g), which is identical for all cuts. Previous studies have suggested that this ARPES background can be attributed to photoelectrons which scattered inside the sample and lost their momentum information prior to being photoemitted [33]. In Hg1201, an additional contribution to the background may come from photoelectrons scattering from surface step edges. Subtracting this background EDC highlights the quasiparticle peaks, as shown in Fig. 2(i). We caution that this procedure is most reliable at lower binding energy where the background EDC is farthest from the quasiparticle dispersion. Similar methods have been used to discern spectral features buried beneath a large background in other cuprates [34].

The apparent decrease of cross-section away from the node is likely not intrinsic, as most cuprates with comparable \(T_c\) show antinodal quasiparticles at optimal doping with proper experimental conditions [35–37]. Matrix element effects are generally one reason spectral intensity may be unobservable. In ARPES experiments, the measured spectral intensity is modulated by a dipole matrix element term \(|M|^2 = |\langle \Psi_f | \mathbf{A} \cdot \mathbf{p} | \Psi_i \rangle|^2\), where \(\mathbf{A}\) is the photon vector potential, \(\mathbf{p}\) is the electron momentum, and \(\Psi_f (\Psi_i)\) are wave functions of the final (initial) electron states. Changes in the photon energy or polarization can affect the intensity of a band measured by ARPES and also which orbitals are highlighted [38,39].
FIG. 2. (Color online) (a)–(f) Image plots of near-nodal cuts. All images have the same linear color scale. Color scale and Fermi surface angle $\theta$ are defined below (f). Color scale is in arbitrary units. Data taken with 19 eV photons, cuts parallel to $\Gamma-M$, and $T = 10$ K. Red vertical line in (b) marks Fermi momentum ($k_F$) and black dashed line marks momentum of background EDC. (g) Background EDCs, taken at momentum indicated in (b), (h) EDC at $k_F$, (i) EDC at $k_F$ with background EDC subtracted.

cuts along high-symmetry directions in the Brillouin zone, certain light polarization can suppress a band in the ARPES spectrum based on the band’s orbital character. Final-state effects can completely suppress a band in the ARPES spectrum if there are no final states to excite into with the chosen photon energy. Further exploration is needed to find an experimental relation that provide the best fit to dispersions from first-principles calculations [40]: $(t, t', t'', t''') = (0.46, -0.105, 0.08, -0.02)$.

The chemical potential was adjusted to compare to the Fermi-crossings data (red and blue symbols in Fig. 3). For experiment A, the Fermi surface encloses an area of 1.47 Å$^{-2}$, which amounts to a hole doping of 11.9 ± 1.2%, using $1 + p = 2A_{FS}/A_{BZ}$, where $A_{FS}$ ($A_{BZ}$) is the area of the Fermi surface (Brillouin zone). Experiment B yielded a hole doping of 11.6 ± 0.7%. A lattice constant of 3.876 Å was used [41]. The nominal doping of the material is in the range 13–16%. If $T_{c,max}$ for this compound is taken to be 95 K ($T_c$ midpoint), the doping is 16% via a commonly used empirical relation [42], and if the $T_{c,max}$ is taken to be 97 K ($T_c$ onset), the doping is 14.4%. Additionally, data from powder samples yield $T_{c,max} = 98$ K, and thermopower measurements on these samples suggest that a $T_c$ of 95 K corresponds to 12.7% hole doping [43]. Thus the experimentally measured Fermi surface area is within 1% of the lower end of the nominal range.

We note that the correspondence between nominal doping and Fermi surface area is much better than in as-cleaved YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO), another cuprate that lacks a neutral cleavage plane. In YBCO, a polar catastrophe is avoided by self-doping of the surface layer such as as-cleaved surfaces...
are very overdoped \( p \approx 0.3 \) [44], and surface preparation techniques such as \textit{in situ} surface dosing with potassium is required to produce optimally doped and underdoped YBCO surfaces for ARPES study. The measured FS area in Hg1201 indicates that self-doping of the surface layer is less of an issue, which makes Hg1201 a promising cuprate for comparing ARPES data to established bulk probes without the need for complex surface preparation.

Several caveats should be considered when interpreting the Fermi surface area in Fig. 3. First, there is uncertainty due to the lack of observed Fermi crossings in the antinodal region. The exact shape of the Fermi surface is not known because the antinodal segments have not been accessed experimentally. Second, the lack of a natural cleavage plane may cause the hole concentration on the surface to be different from the bulk. It should also be noted that the agreement between Fermi surface area and nominal doping reported in the literature is mixed. In La\(_{2-x}\)Sr\(_x\)CuO\(_4\) (LSCO), the measured Fermi-surface area follows Luttinger’s theorem, while in Ca\(_{2-x}\)Na\(_x\)CuO\(_2\)Cl\(_2\) (Na-CCCOC) and Bi\(_2\)Sr\(_2\)CuO\(_{6+\delta}\) (Bi2201), it increases more rapidly with nominal doping [45,46]. A future ARPES study of the Fermi surface doping dependence in Hg1201 can be expected to clarify the interpretation of the Fermi surface area observed in this experiment.

IV. NODAL DISPERSION ANALYSIS

Figure 5 shows momentum distribution curves (MDCs) taken at the node. Selected MDCs are shown in panel (a), and they have certain peculiarities which were observed in every experiment on Hg1201. First, the MDCs near \( E_F \) deviate from a Lorentzian line shape, with extra weight in the tails, such that the peak amplitude and width cannot be simultaneously captured. At higher binding energy, the MDCs become increasingly asymmetric, with extra weight on the side of the peak further from the \( \Gamma \) point. Every sample studied with a favorable experimental configuration, we were able to measure the momentum dependence of the superconducting gap in Hg1201 using ARPES, as shown in Fig. 4. Background EDCs were subtracted in order to emphasize the quasiparticle contribution for accurate extraction of the gap. \( E_F \) was determined from a polycrystalline gold sample that was electrically connected to the Hg1201 sample. Spectra were symmetrized and EDCs at \( k_F \) were fit to a minimal model convolved with the energy resolution of the experiment [47]. Fitted gaps are plotted as a function of the simple \( d \)-wave form. \( \frac{1}{2} |\cos(k_x) - \cos(k_y)| = 1 \).
showed the same asymmetry. The MDC asymmetry might reflect interesting physics, such as a momentum-dependent self-energy due to correlation effects [52]. However, given the lack of a neutral cleavage plane, surface electric fields might be responsible [53]. Because of this asymmetric MDC line shape, using the usual fitting procedure of a Lorentzian peak plus a constant background does not yield the correct peak position at higher binding energy when asymmetry is strong [Fig. 5(b)]. Using a linear background for each MDC better reproduces the peak position [Fig. 5(c)].

Figure 6(b) shows MDC-derived dispersions at the node using both a constant (red) and constant-linear (blue) background. Both methods indicate dispersion anomalies near 50 and 200 meV, and they yield comparable low-energy dispersions (<50 meV). The former kink is ubiquitous in cuprates, but the latter is slightly unusual because the high-energy anomaly is generally observed at higher binding energy in hole-doped cuprates [54]. The lower energy kink will be the focus of the remainder of the discussion. Using a constant background yields steeper dispersions at a higher binding energy, which is not physically correct because this fit does not capture the maximum of each MDC. The Fermi velocity ($v_F$) is found to be similar to other cuprates [55], disregarding a potential contribution from the very low energy kink ($\omega < 10$ meV), which is not accessible in this experiment [56]. The velocity at higher energy ($v_{HE}$, 80–180 meV) is strongly dependent on the fitting scheme, with a constant background giving a slope that is 25% larger. This discrepancy can lead to an overestimation of the mass renormalization at the ≈51 meV kink. A linear background yields $v_F(0-40$ meV) = 2.008 ± 0.002 eV Å and $v_{HE}(80-180$ meV) = 3.956 ± 0.064 eV Å giving a mass enhancement factor $1 + \lambda \approx v_{HE}/v_F = 1.97 \pm 0.09$.

Many-body interactions in materials are captured in the self-energy, $\Sigma(\omega) = \text{Re}\Sigma(\omega) + i\text{Im}\Sigma(\omega)$, where $\text{Re}\Sigma(\omega)$ and $\text{Im}\Sigma(\omega)$ describe interaction-induced corrections to the band dispersion and quasiparticle lifetime, respectively. Both quantities are available from ARPES data [57,58], and because $\text{Re}\Sigma(\omega)$ and $\text{Im}\Sigma(\omega)$ are Kramers-Kronig related, many-body effects show features in both quantities. Most analyses, including this one, assume that $\Sigma$ is independent of $k$ normal to the Fermi surface. Figure 6(c) shows the real part of the self-energy, $\text{Re}\Sigma$, at the node, approximated by subtracting an assumed linear bare band [blue dashed line in Fig. 6(b)] from the measured MDC dispersion (blue solid line). This quantity is peaked at 51 meV. The imaginary part of the self-energy, $\text{Im}\Sigma$, is approximated by the MDC FWHM multiplied by the slope of the assumed bare band. $\text{Im}\Sigma$ shows an inflection point at a similar energy, affirming data quality and confirming a genuine many-body effect (electron-boson coupling) at that energy. There is a small upturn in $\text{Im}\Sigma$ near $E_F$, but this is within the error bars, and likely not significant. We observed some sample-to-sample variation in the kink energy, with another good cleave showing a kink energy as high as 58 meV.

Interestingly, analysis of optical conductivity data in Hg1201 yielded a bosonic “glue” energy between 50 and 60 meV, consistent with the energy of this kink [59]. In Figs. 6(e) and 6(f), comparisons are made to Bi2212 with a similar $T_c$ (UD92, $\rho = 0.14$). In Bi2212, the kink energy is larger in Bi2212, with $\text{Re}\Sigma$ peaking at 66 meV. Figure 4 indicates that the superconducting gap in Hg1201 is comparable to that in Bi2212, which suggests that bosonic modes of different energy are responsible for the kinks in the two compounds. For further comparison, optimally doped Bi2212 ($T_c = 33$ K, $\Delta = 15$ meV) has multiple distinct contributions to the nodal kink, and the most prominent features appear at 70 and 41 meV [60].

The origin of the 50–80 meV nodal kink in the cuprates is still a topic of debate with some explanations favoring a phononic origin [61,62] and others favoring a magnetic origin [63,64]. We will consider the former first. For optical phonons, the kink will appear at an energy $\Omega + \Delta$, where $\Omega$ is the phonon energy and $\Delta$ is the antinodal gap, because the electron-phonon coupling vertex is generally nonzero for momentum transfer $q = k_{\text{antinode}} - k_{\text{node}}$ [62,65]. Thus, given a 39 meV extrapolated antinodal superconducting gap, the kink observed in Hg1201 between 50–58 meV implies an optical phonon between 11–19 meV. Reference [19] shows in-plane optical phonon branches dispersing between 8 and 14 meV together with an enhanced calculated phonon density of states at similar energy. Additionally, Raman spectroscopy reports Raman-active phonons at 9 meV (Ba, $E_g$ symmetry) and near 20 meV (apical oxygen, $E_{1g}$; Ba, $A_{1g}$) [66,67]. These are potential candidates for the nodal kink in Hg1201, though we note that strong coupling to low-energy optical phonons is not supported by ARPES data on other cuprates. In Bi2212, the nodal kink near 70 meV, is often attributed to an oxygen $B_{1g}$ mode at $\approx 35$ meV. The energy of this mode is inconsistent with the difference between the kink energy and gap energy in Hg1201, and additionally, single-layer cuprates are not expected to show electron-phonon coupling to first order for this mode [68]. In Hg1201, the lack of a neutral cleavage plane and potential resultant surface electric fields may present
FIG. 6. (Color online) (a) and (b) Nodal MDC analysis using constant (red) and linear (blue) background. (a) Image plot with MDC peak position from both fitting schemes. Background EDC has been subtracted from entire image. (b) MDC peak position dispersions, offset horizontally for clarity. Arrows mark key dispersion anomalies. Inset shows geometry for nodal cuts. (c) Real part of self-energy, Re$\Sigma$, derived using the bare band indicated in (b), as discussed in text. Linear-background fitting [Fig. 5(c)] was used. Arrow marks the peak position. (b) Imaginary part of self-energy, Im$\Sigma$. (Inset) Derivative Im$\Sigma$ (smoothed) with respect to energy. Arrow marks the extremum. (e) and (f) Re$\Sigma$ and Im$\Sigma$ for Bi2212 with $T_c = 92$ K and $p = 0.14$. Arrows mark the peak of Re$\Sigma$ and inflection of FWHM. Bi2212 data were taken at 10 K and 3 meV energy resolution using 7 eV photons and a SES2002 analyzer.

More recently, neutron scattering experiments have found magnetic scattering centered at $q = (0.5, 0.5)$ and peaked at 51 meV in underdoped Hg1201 [69]. If electrons couple strongly to this excitation, it is another candidate for the origin of the kink observed in ARPES. Further investigation of the doping, temperature, and momentum-dependence is needed to clarify the origin of the nodal kink seen in Hg1201.

V. CONCLUSIONS

Despite its lack of a natural cleavage plane, Hg1201 is a crucial compound to explore with ARPES because of its structural simplicity and the wealth of high-quality data obtained with other probes. The present work describes our...
experimental progress and measurement of basic electronic properties available in ARPES: superconducting gap, nodal kink energy, and band renormalization.

Future studies may be aided by a more controlled method to cleave the samples [70,71], by better control of the surface termination, and by finding experimental conditions for which the antinode has adequate cross section. The use of higher photon energy (hν > 100 eV) may be a promising route toward the latter goal [72]. Ultimately, studies of Hg1201 may be very fruitful in addressing the question of “what causes a high Tc?” via comparisons to other single-layer cuprates. A great body of ARPES work exists for LSCO and Bi2201, the “low-Tc” single-layer cuprates [45,57,73–75]. In contrast, there have been fewer ARPES studies on Tl2Ba2CuO6+δ (Tl2201) [37,76,77] and none on Hg1201 prior to the present work. Through comprehensive studies of Hg1201 and Tl2201, new and nontrivial features might be found in the electronic structure that distinguish the low-Tc compounds from the high-Tc ones.

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