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Photoemission study of single-crystal $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$

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We performed exploratory angle-integrated and angle-resolved photoemission-spectroscopy measurements on Pr-stabilized single crystals of $Bi_2Sr_2CuO_6$ ($T_c \sim 10$ K). Fermi-level crossings along principal directions match some crossings predicted by tight-binding calculations. These crossings differ from both the Fermi-surface mapping and the local-density-approximation-derived Fermi surfaces on the much studied $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ ($T_c \sim 75$–96 K). We observe optical-polarization effects in the angle-resolved spectra, which is consistent with the states near E_F being derived from the orbitals containing $d_{x^2-y^2}$ symmetry. The density-of-states contribution from the Pr $4f$ states derived by resonant-photoemission spectroscopy suggests that the Pr $4f$ states do not hybridize strongly and lie away from the Fermi level, thus not affecting the superconductivity of the Bi-Sr-Ca-Cu-O system.

I. INTRODUCTION

Since 1986, when Bednorz and Muller discovered high-T_c superconductivity in the cuprates,[1] there has been an enormous amount of activity trying to understand their properties. The traditional BCS theory of superconductivity assumes that the electrons in the normal state can be described by the Fermi-liquid concept. The cuprate superconductors, however, are highly correlated. This casts doubts as to whether these cuprates are Fermi liquids.

A thorough understanding of the electronic structure would aid in developing an understanding of the normal state properties and, eventually, a theory of superconductivity in this class of materials. Photoemission spectroscopy, which directly measures the microscopic electronic structure, has played a key role in advancing our understanding of these novel superconductors. Angle-resolved photoemission, in particular, allows one to map the Fermi surface as well as to map the bands close to the Fermi level.[2–6] The comparison of the experimentally measured Fermi surface, band dispersion, as well as photoemission spectral line shape with various theories provides an important test for the validity of the Fermi-liquid concept for the cuprate superconductor materials.

A very successful example of a photoemission study of the cuprate superconductors is that of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi 2:2:1:2). These studies showed not only a clear Fermi edge and bandlike dispersive features, but also the opening of a superconducting gap in the density of states around E_F for $T < T_c$ with the characteristic peak at the edge of the gap in analogy to the BCS theory.[2,3,5] Further studies of Bi 2:2:1:2 have indicated that the peak is not entirely BCS like and that the spectra have anomalous features resembling those of the classical strong-coupling materials.[5]

Up to now, these studies have not addressed a very interesting question raised by the Bi related family of superconductors that might shed new light on our understanding of superconductivity in the cuprates, in general. In the Bi-based family of cuprate superconductors the superconducting transition temperature depends on the number of Cu-O planes. T_c's for the Bi 2:2:2:3 (three Cu-O layers), Bi 2:2:1:2 (two Cu-O layers), and Bi 2:2:0:1 (one Cu-O layer) compounds are 105, 85, and 10 K, respectively. This fact allows us to do a comparison-contrast study of the electronic structure and relate it to bulk superconducting properties. In this paper, we present exploratory angle-resolved photoemission study of the Pr stabilized $Bi_2Sr_2CuO_{6+\delta}$ (Bi 2:2:0:1) single crystal. The experimental data are analyzed and compared with that of Bi 2:2:1:2 in a comparative-contrast fashion. A natural complement to this study would have been to study single crystals of Bi 2:2:2:3; however, Bi 2:2:2:3 has been extremely difficult to make in single-crystal form and will have to await a future effort.

Our combined angle-resolved and angle-integrated photoemission spectroscopy study was carried out on $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ (Bi 2:2:0:1). The addition of Pr stabilizes the growth of the Bi 2:2:0:1 phase of the material and does not affect the T_c. We also present angle-integrated data on Bi 2:2:1:2 ($T_c = 77$ K) taken in an identical configuration for direct comparison. We compare our angle-resolved results to other experimental results performed on Bi 2:2:1:2 (photoemission and inverse photoemission), tight-binding calculations for Bi 2:2:0:1, and local-density approximation (LDA) calculations for Bi 2:2:1:2. The angle-integrated data are compared to earlier work on polycrystalline samples.

II. EXPERIMENT

The BiSrCaCuO superconductors occur in three basic stoichiometries, with the difference being the number of Cu-O layers and Ca layers between them. The addition of Pr at the appropriate stoichiometry stabilizes the 1 Cu

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layer single crystals. $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ single crystals were prepared by the directional solidification techniques. X-ray-diffraction measurements showed a single-phase structure with the c axis perpendicular to the plane. The samples had a T_c of approximately 10 K. The Bi 2:2:1:2 single crystals were, also, grown by the directional solidification technique and annealed in 12 atm of oxygen at 540 °C. The transition temperature was approximately 77 K. All the samples were single crystals of approximately 2 mm×2 mm×0.1 mm dimensions. They were epoxied to phosphorus-bronze sample holders and oriented with Laue precision measurements. The top posts were epoxied onto the samples, and the whole assembly was then screwed into a titanium holder that was screwed into the cryostat. The crystals were cleaved *in situ* in UHV (10^{-10} Torr) by knocking off the top posts. The surface of a sample gave a specular reflection after a cleave. All the cleavings and measurements were performed at liquid-nitrogen temperature (80 K). The angle-resolved photoemission data were taken at the Stanford Synchrotron Radiation Laboratory at the newly commissioned (undulator) beamline V. The spectra were recorded by a VSW hemispherical analyzer with a variable acceptance angle and equipped for multichannel counting. Some of the spectra were taken with a total acceptance angle of 1° and others with a total acceptance angle of 2°. Our experimental resolution was approximately 80 meV.

The angle-integrated data were taken at Stanford Synchotoron Radiation Laboratory Extended Grasshopper beamline 3-1. The data were recorded using a Varian cylindrical mirror analyzer with an acceptance angle of 60 °.

III. RESULTS AND DISCUSSION

A. Angle-integrated data

We performed angle-integrated measurements on single crystals of $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Fig. 1). The leftmost panel in the figure shows valence bands below and above Cu resonance energy for Bi 2:2:0:1 and Bi 2:2:1:2. The spectra are normalized to the main features of the valence band. The satellite associated with the Cu d^8 state is visible at the binding energy of 10–13 eV and enhanced slightly across the resonance energy. The Cu satellite is superimposed on the Bi 6s state near a binding energy of 11 eV. The distance of the Cu satellite from the main valence band is the same in Bi 2:2:0:1 and Bi 2:2:1:2 suggesting that the on-site correlation energy U_{dd} is approximately the same in the two compounds. The spectral weight difference in the satellite above and below the Cu resonance (shaded) has been interpreted as the number of copper sites in the given material.[7] The spectral weight difference is somewhat larger in Bi 2:2:1:2 than in Bi 2:2:0:1. Shen *et al.* had reported similar U_{dd} for polycrystalline samples of $Bi_2Sr_2CuO_{6+\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$.[8] The spectral weight of the satellite enhancement was more in a ratio of 2 to 1, since the polycrystalline samples are a collection of random surfaces. Unlike the polycrystalline samples, the single-crystal samples of Bi 2:2:0:1 material do show clear Fermi edges. The other two panels in the figure show $h\nu = 70$ eV data. The spectra are again normalized to the main feature of the VB. The signal at the Fermi level of Bi 2:2:1:2 is higher than that of Bi 2:2:0:1, supporting the idea that the states at the Fermi level are mostly Cu-O in character. The relatively fewer states near the Fermi level of the $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ compound would also suggest that the density of states near the Fermi level is a relevant parameter for T_c. We also see that the valence band is shifted to higher binding energy in the Bi 2:2:0:1 material with respect to Bi 2:2:1:2 (250 meV). The overall features of the valence bands are very similar indicating a similar electronic structure. With these materials there is always a question of phase intergrowth and the possibility that one is studying Bi 2:2:1:2 in a Bi 2:2:0:1 matrix. These angle-integrated spectra give us confidence that we are, indeed, studying Bi 2:2:0:1.

B. Angle-resolved data

We examined the near Fermi-level electronic structure of single-crystal $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ using $h\nu = 20.5$ eV light. Angle-resolved measurements were made on $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ along Γ-X, Γ-$\overline{M}$, and $\overline{M}$-X directions of the Brillouin zone. We obtained high-resolution angle-resolved data near the Fermi level. The spectra appear in Fig. 2 for Γ-X, Γ-$\overline{M}$, and $\overline{M}$-X. The Γ-X spectra were taken with the angular resolution of 2°, while the Γ-$\overline{M}$ and $\overline{M}$-X spectra were taken with the angular reso-

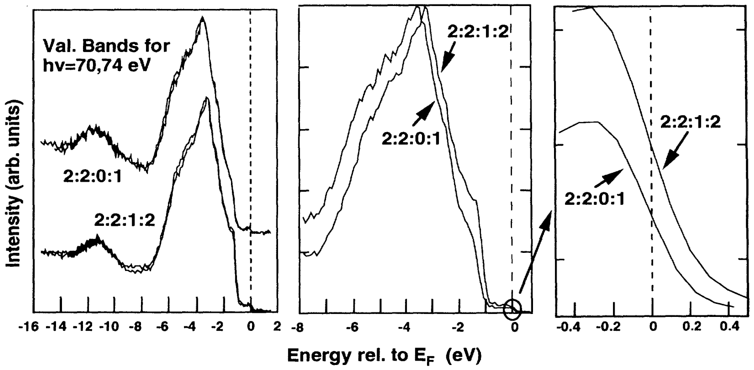

FIG. 1. Angle-integrated data comparing $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CuO_8$. The panel on the left shows the resonance enhancement of the Cu satellite (shaded). The two panels on the right are $h\nu = 70$ eV spectra. These show the higher relative DOS at the Fermi level in $Bi_2Sr_2CaCu_2O_8$.

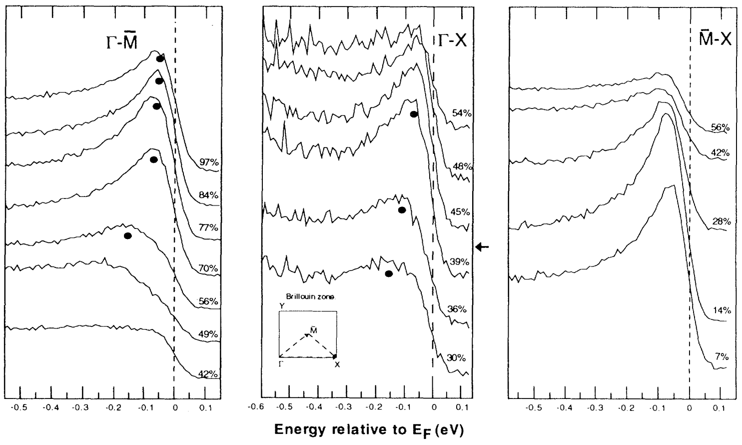

FIG. 2. Angle-resolved spectra along principal directions in Bi 2:2:0:1 ($h\nu=20.5$ eV). The arrow indicate the crossings.[14] The position in Brillouin zone are indicated as the fractional distance between the two symmetry points.

lution of 1°. We normalized the spectra to second-order light above the Fermi level. Normalization to the photon flux or beam current does not produce substantially different results. The spectra where the quasiparticle band crosses the Fermi level are marked in the figure. The Bi 2:2:0:1 band structure had been calculated by the tight-binding method along principal directions by Meshkov *et al.*[9] We compare our data to their results as well as the results from photoemission experiments and LDA calculations on Bi 2:2:1:2.[10–12] The fact that the samples studied were not stoichiometric $Bi_2Sr_2CuO_6$ suggests that a qualitative comparison of the calculation and the data are more appropriate.

Along Γ-$\bar{M}$, the calculation predicts one band (band No. 2) coming up to and trailing near the Fermi surface, but never crossing. Another band (band No. 2) comes up sharply toward the Fermi level at $\bar{M}$ and does not cross either. We do see a bandlike feature dispersing slowly toward the Fermi surface and then approaching very close to the Fermi level at approximately 80% of the distance to $\bar{M}$. Within the experimental error it is impossible to determine whether the band actually crosses. These superconducting Bi 2:2:0:1 crystals are hole doped with respect to the parent stoichiometric materials. We can thus identify this band as band No. 1 if we assume that the Fermi level is shifted slightly downward due to stoichiometry variations. We do not observe the dispersive peaks associated with band No. 2. This may be due to rapid dispersion of band No. 2 compared to band No. 1. The data only show one occupied band at $\bar{M}$. It is not clear whether this is a consequence of the experimental inability to resolve the two bands. Along $\bar{M}$-*X*, the results of the tight-binding calculations are, unfortunately, not available. We see strong intensity modulation near the Fermi level suggestive of a crossing. The intensity peaks at approximately 10% of the $\bar{M}$-*X* distance. Along Γ-*X*, there are again the two bands near the Fermi surface in the calculation. Band No. 2 comes through very sharply at approximately 45% to *X*, while band No. 1 peaks twice below the Fermi surface, once halfway to *X* and once at *X*. The band never actually crosses in the tight-binding calculation. We see a band come up and cross the Fermi surface approximately 43% of the way to *x*. The rapid dispersion and the dependence of the matrix elements on the polarization of the light are consistent with this being identified as band No. 2 (we will come back to this point later). This crossing is very similar to the Fermi level crossing in Bi 2:2:1:2,[12] and is also the first crossing observed by inverse angle-resolved photoemission on Bi 2:2:1:2.[13]

Even though we never actually resolve the two bands in our spectra, our results are consistent with the tight-binding calculation modulo experimental resolution and stoichiometry differences. Band No. 2 is predicted to have Cu $3d_{x^2-y^2}$-O $2p_{x,y}$ character, while band No. 1 is predicted to have mixed (Cu 3*d*-O 2*p*)-(Bi 6*s*-O 2*p*) character. We summarize the results in an *E* vs *k* diagram in Fig. 3. This resembles the photoemission evidence (as well as LDA results) on Bi 2:2:1:2 in that states at Fermi edge along Γ-$\bar{M}$ have some Bi-O character, while the states at the Fermi edge, at the Γ-*X* crossing, have pure Cu-O character.[3] This resemblance is based on identifying the experimental Bi 2:2:0:1 bands with the bands in the tight-binding calculation—independent experimental verification is still needed. Furthermore, the Bi 2:2:1:2 LDA calculation yields a Bi 6*p* derived electron pocket around **M**, while the calculation suggests that band no. 1 is made up of Bi 6*s* states.

The strong $3d_{x^2-y^2}$ component of the band along the

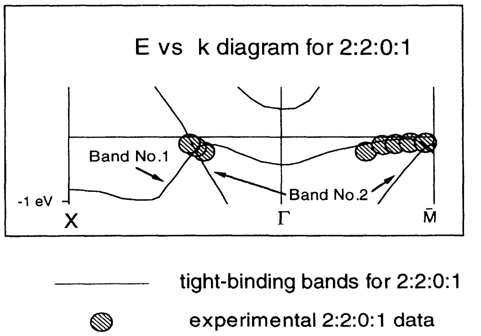

FIG. 3. *E* vs *k* diagram for $Bi_2Sr_2CuO_8$. Shown are measured points, as well as reproduced tight-binding bands.

Γ-X direction would result in very interesting polarization effects. The $d_{x^2-y^2}$ state is odd with respect to the Γ-X plane, while the final state is clearly even. Thus, if the polarization is even with respect to the Γ-X plane, the matrix element will vanish. On the other hand, odd polarization would result in a nonvanishing feature. This, in fact, is what we observe (Fig. 4). The dispersing peak is seen with the odd polarization, while in the even polarization spectra it does not appear. Takahashi *et al.*, however, claim strong O $2p$ character for the same band.[15] A possible resolution might be that Takahashi observes the photon energy dependence of the band matrix element at the Γ point, where the Cu $3d_{x^2-y^2}$ contribution would vanish due to symmetry considerations. Furthermore, we are looking at the band at a different point in k space, thus possibly resulting in different amounts of atomic character present in our spectra. While at present it is not possible to determine the exact origin of the background to the dispersive peaks, a possible explanation is that the background in the photoemission spectra consists of features due to secondary electrons as well as primary electrons from the incoherent part of the spectra. These features do not have simple mirror plane symmetry and thus are not expected to exhibit a polarization dependence. We thus have a natural way of subtracting the background and arriving at the quasiparticle contribution to the spectrum. Analyzing the line shape of the resulting peak could lead, in the future, to better understanding of these materials.

C. Pr states in the valence band

Pr is the only rare-earth element that quenches the superconductivity in $R\mathrm{Ba_2Cu_3O_7}$ (R = rare earth).[16] Earlier work (Kang *et al.*) suggests that Pr $4f$ states hybridized with the important Cu-O states and thus disrupted the superconductivity.[17] In another cuprate superconductor, $\mathrm{Pb_2Sr_2PrCu_2O_8}$, the Pr substitution did not affect the superconducting properties. The Pr states in that case were found to lie away from the Fermi level.[18]

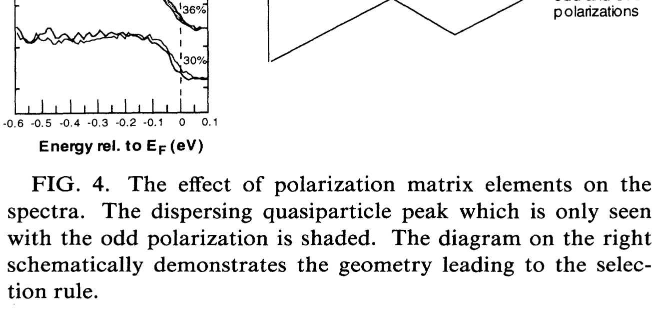

FIG. 4. The effect of polarization matrix elements on the spectra. The dispersing quasiparticle peak which is only seen with the odd polarization is shaded. The diagram on the right schematically demonstrates the geometry leading to the selection rule.

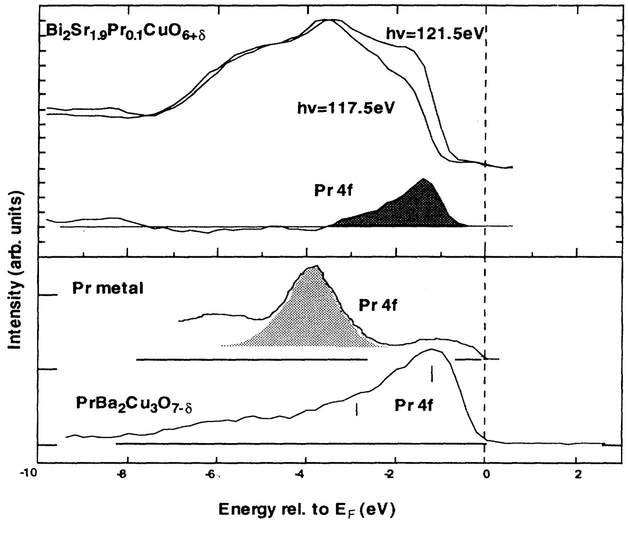

FIG. 5. The panel shows the Pr states. These extracted Pr states lie away from the Fermi level in Bi 2:2:0:1, and near it in PrBaCuO.

Since our compound is Pr stabilized, it is interesting to investigate the behavior of the Pr $4f$ state in this material. The Pr $4f$ states are extracted by taking a spectrum right above the Pr $4d$-$4f$ resonance, another one just below, and subtracting the second from the first. The resulting difference is a partial density of states for Pr $4f$ (Fig. 5). The top panel shows spectra for Bi 2:2:0:1 below and above the Pr $4f$ resonance energy. The change is almost entirely due to the Pr $4f$ contributing to the density of states. The lower panel shows the similarly extracted Pr $4f$ states in Pr metal and in Pr substituted Y-Ba-Cu-O for comparison. The full width at half maximum for the Pr $4f$ states in Bi 2:2:0:1 is approximately 1.5 eV, which is similiar to that of Pr metal and much smaller than that in $\mathrm{PrBa_2Cu_3O_{7-\delta}}$. This suggests that unlike in YBCO, the Pr $4f$ states in the Bi systems do not hybridize strongly. Furthermore, the Pr $4f$ states lie more than 0.5 eV away from the Fermi edge similarly to what was seen in $\mathrm{Pb_2Sr_2PrCu_3O_8}$, where the superconductivity was not affected. Thus, it appears that hybridization by Pr $4f$ with the Fermi-level electrons quenches the superconductivity inYBaCuO. However, in Bi 2:2:0:1 as in the Pb compound, Pr $4f$ states do not appear to interact strongly with the Fermi-level electrons and thus do not affect the superconductivity.

IV. SUMMARY

We studied Pr stabilized Bi 2:2:0:1 single crystals with angle-resolved and angle-integrated photoemission spectroscopy. We mapped the band dispersions near the Fermi level along high symmetry directions. The band structure derived from tight-binding calculations predicts the general trends of the near-Fermi level data, even though it does not agree in detail. We see strong polarization dependence of the matrix elements, yielding information about the symmetry of the states.

Angle-integrated photoemission data show the lower relative Cu content of Bi 2:2:0:1. We see suppression in the Cu valence-band satellites as well as a shift of the valence-band centroid as compared with Bi 2:2:1:2 data. The resonance extracted Pr $4f$ states lie away from the Fermi level and do not appear to hybridize as in Pr-doped YBaCuO.

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