

Unconventional Electronic Structure Evolution with Hole Doping in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$: Angle-Resolved Photoemission Results

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We report angle-resolved photoemission results on $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_{8+\delta}$ and oxygen depleted $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ investigating the electronic structure changes above T_c in materials with hole doping levels ranging from insulating to slightly overdoped. Near optimal hole doping, the Fermi surface is large and consistent with band calculations. In underdoped samples with T_c of 60–70 K, portions of this Fermi surface are not seen. This change is related to the opening of an energy gap near $(\pi, 0)$ above T_c . [S0031-9007(96)00356-0]

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The evolution of the electronic structure from a Mott insulator with long-range antiferromagnetic (AF) order to a high T_c superconductor without long-range AF correlations may be a key to unlocking the mystery of the cuprates. It is now believed that the Fermi surfaces of optimally doped superconductors are very similar to those predicted by the local density approximation (LDA) [1]. On the other hand, recent data from the related insulator $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ clearly shows that the AF order imposes a new unit cell with 45° rotated $\sqrt{2} \times \sqrt{2}$ periodicity and shifts the band maximum from (π, π) to $(\pi/2, \pi/2)$ of the original Brillouin zone (BZ) [2]. Extrapolating from $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, one might expect the Fermi contours of the cuprates at extremely small hole doping levels to be pockets centered at $(\pi/2, \pi/2)$, consistent with transport and optical data [3].

In this paper, we address the evolution of the electronic structure between the above two limiting cases using angle-resolved photoemission spectroscopy (ARPES) from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) crystals with hole concentrations ranging from nearly optimal (for T_c) to very low (near the AF insulating regime). A dramatic change in the electronic structure near $(\pi, 0)$ with doping is observed. Just below the optimal hole concentration, the features near $(\pi, 0)$ move to higher binding energy and a portion of the large Fermi surface disappears. The data can be interpreted as the opening of an energy gap maximized near $(\pi, 0)$.

The ARPES data were obtained with a VSW analyzer at a base pressure of $(3-5) \times 10^{-11}$ torr using beam line 5-3 of Stanford Synchrotron Radiation Laboratory (SSRL) as the 22.4 eV light source, described elsewhere [4]. The overall resolution of this system was 35–45 meV from the gold Fermi edge. All samples were cleaved and measured *in situ* at 110 K. Our bulk crystals were grown

by directional solidification, and their T_c 's were measured by SQUID magnetometry [5]. A 600 °C air postanneal yielded slightly overdoped material with $T_c = 85$ K. A 550 °C argon anneal yielded underdoped material with $T_c \sim 67$ K. Overdoped and underdoped refer to the hole doping with respect to "optimal" (highest T_c). Our thin film crystals were grown by molecular beam epitaxy. Their hole doping was controlled by Dy substitution of Ca [6]. The samples with 1%, 10%, and 17.5% Dy had superconducting transition temperatures of 85, 65, and 25 K, respectively, from the zero resistance point of the ρ vs T curves. At Dy levels of 50%, the material was insulating.

Figure 1, panels a1, a2, b1, b2, and d1, show photoemission from single crystal thin films of Bi2212 with various Dy concentrations. The data in panels a1 and a2 are similar in every detail to that from typical, slightly overdoped Bi2212 with Fermi level (FL) crossings near 45% along the $(0,0)-(\pi, \pi)$ line and near 25% along the $(\pi, 0)-(\pi, \pi)$ line [4]. The spectra in panel d1 are from an insulating 50% Dy substituted sample. These data have very broad features (possibly due to Dy-induced scattering) on a large sloping background with virtually no weight at E_F . In spite of this, the remaining spectral features disperse similarly to the much narrower peaks of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, reaching a maximum in energy about halfway between $(0,0)$ and (π, π) . However, the broadness of the feature and the large background makes it hard to quantify the relative energy. In a qualitative fashion, our data reaffirm the results at the doping extremes in a single material system with controlled doping variation. The 10% Dy material in panels b1 and b2 has electronic structure indicative of the transition between these two limiting cases. This material has a well-defined FL crossing near 45% along the $(0,0)-(\pi, \pi)$ line (panel b1), like the 1% Dy sample. However, the spectra

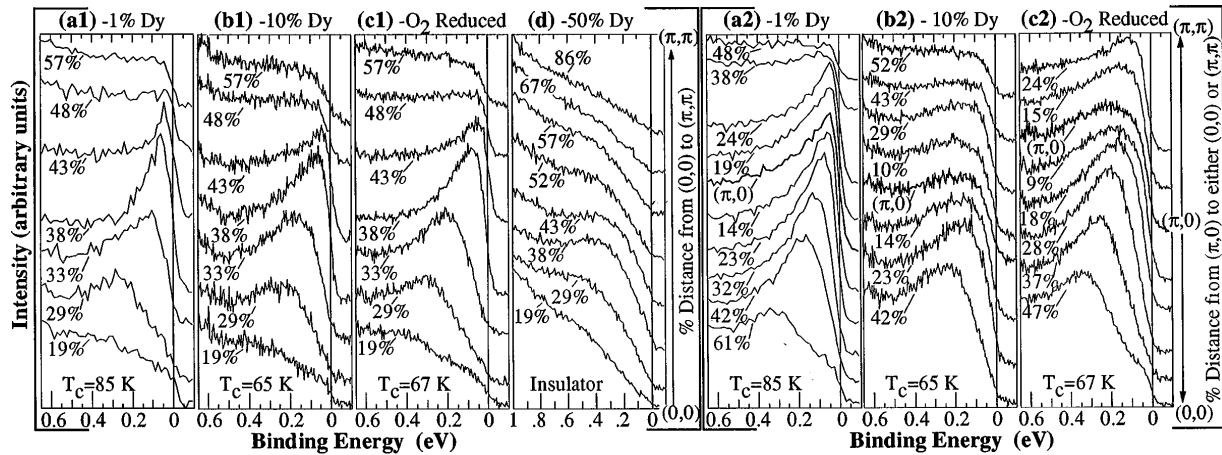


FIG. 1. ARPES spectra from $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_{8+\delta}$ single crystal thin films and deoxygenated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ bulk crystals. The symmetry points identified correspond to those indicated in the two-dimensional Brillouin zone of Fig. 4.

near $(\pi, 0)$ (panel b2) are dramatically different. Those features are relatively broad, the features nearest $(\pi, 0)$ appear shifted to higher binding energy, and none reaches E_F [no FL crossing between $(\pi, 0)$ and (π, π)]. Bear in mind that the spectral line shapes from this same sample between $(0, 0)$ and (π, π) are similar to those of the optimally doped material, setting an upper limit on the amount of scattering due to the Dy. This indicates that the primary changes near $(\pi, 0)$ are not due to impurity scattering, but rather are inherent electronic structure modifications with doping. The data in panels c1 and c2 are further evidence of the inherent nature of these changes. The spectra here are from underdoped, O_2 reduced *bulk* material with $T_c \sim 67$ K. In similar fashion to the 10% Dy sample, the O_2 reduced sample maintains fairly narrow spectral features and a clear FL crossing near 45% along the $(0, 0)$ - (π, π) line (panel c1) with similar modifications in its spectra near $(\pi, 0)$ (panel c2). These two doping methods are complementary. Dy substitution of Ca takes place between the CuO_2 planes while removal of oxygen occurs mainly from (or between) the BiO planes. While structurally these methods of regulating the hole doping are different, the resulting electronic structure changes are similar.

Figure 2 is a one-to-one comparison of the leading edges (lowest binding energy edges) of the 10% and 1% Dy samples near $(\pi, 0)$. The leading edge of each spectrum, which is indicative of the lowest binding energy excitations, is systematically shifted of order 20–30 meV. Similar results are obtained from oxygen reduced bulk samples.

Because the photoemission line shape is not well understood [7], one can only define approximate quantities to reflect the energy scales of the data, with the centroid of spectral features and positions of leading edges as possibilities. We will use both quantities in our discussions and emphasize that the qualitative conclusion is independent of the choice. The quantitative values, however, must be

taken with respect to the specific characterization quantity chosen. Figure 3 shows the spectral feature energy centroids vs k along high symmetry lines of samples with varying hole density [8]. The data for 50% Dy material resulted in large error bars. What the other samples in Fig. 3 show is that as the hole doping is reduced below optimal, the spectral weight near $(\pi, 0)$ shifts to higher binding energy, while the features near $(\pi/2, \pi/2)$ still cross E_F . This is visible in both the 10% and 17.5% Dy substituted thin films of Fig. 3(a), and from the argon annealed bulk crystal of Fig. 3(b).

Figure 4 maps the FL crossings [9] in one-quarter of the BZ for bulk Bi2212 crystals of two doping

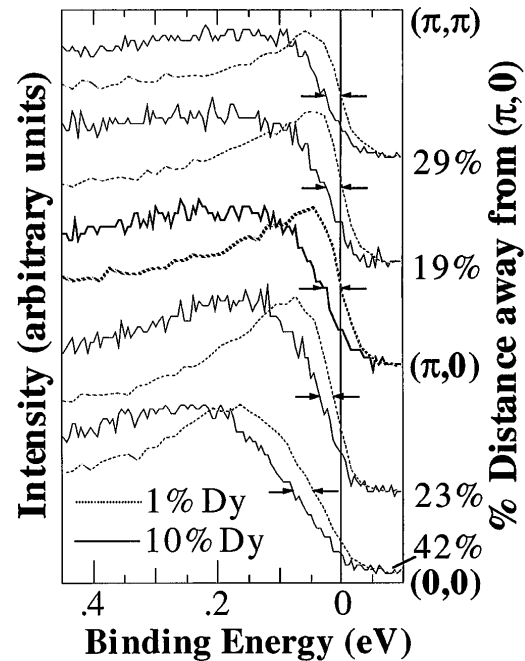


FIG. 2. Comparison of leading edge positions from 1% and 10% Dy samples.

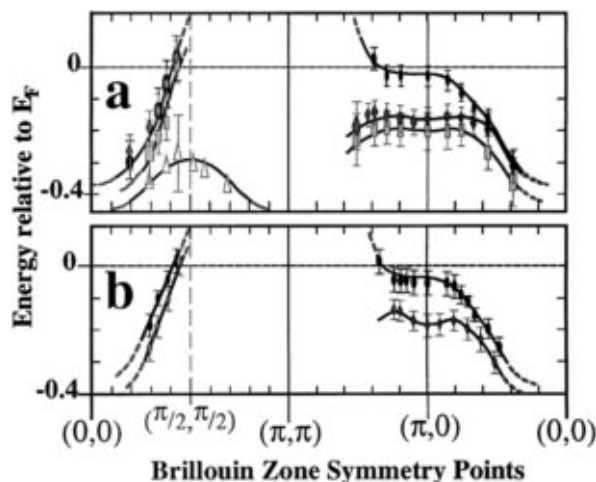


FIG. 3. (a),(b) Map peak centroids vs k for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_{8+\delta}$ thin films and deoxygenated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ bulk samples, respectively, with various hole doping levels. (a) Filled oval, 1% Dy—near optimal doping with $T_c = 85$ K; gray diamond, 10% Dy—underdoped with $T_c = 65$ K; gray rectangular, 17.5% Dy—underdoped with $T_c = 25$ K; triangle, 50% Dy—insulator. (b) Filled oval, 600 air anneal—slightly overdoped with $T_c = 85$ K; gray diamond, 550 argonne annealed—underdoped with $T_c = 67$ K.

levels: slightly overdoped ($T_c = 85$ K) and underdoped via oxygen reduction ($T_c \sim 67$ K). Of the two possible FS pieces [10], we plot the generally accepted piece of FS centered at (π, π) . The error bars indicate our uncertainty in k . The slightly overdoped sample ($T_c = 85$ K) has well-defined FL crossings that yield a large Fermi surface centered at (π, π) , consistent with the Luttinger theorem [1]. The sample with less holes has clear FL crossings over a smaller portion of the BZ and its Fermi contour does not extend to the BZ edge. The observations made in Figs. 3 and 4 from underdoped but still metallic and superconducting ($T_c = 65$ – 67 K) samples are not what one expects from a typical metal, certainly not within the band picture. As doping is reduced below optimal, band theory predicts that the Fermi surface would only shrink in area but still keep its general shape [as indicated by the dashed FS centered at (π, π)]. This means that there should always be a FL crossing between $(\pi, 0)$ and (π, π) , in contrast to our data. However, these observations are consistent with the opening of an energy gap at the underlying FS near the $(\pi, 0)$ to (π, π) line.

There are several possibilities for the origin of this gap in underdoped material. The first possibility is quasiparticle pairing without pair-pair coherence in the normal state. This would open an energy gap without the existence of a coherent superconducting state. Two classes of pairing above T_c have previously been discussed. The first class is the pairing of quasiparticles [11–14], as discussed in terms of generalized Ginzburg-Landau theory for d -wave superconductivity [11]. It has also been argued

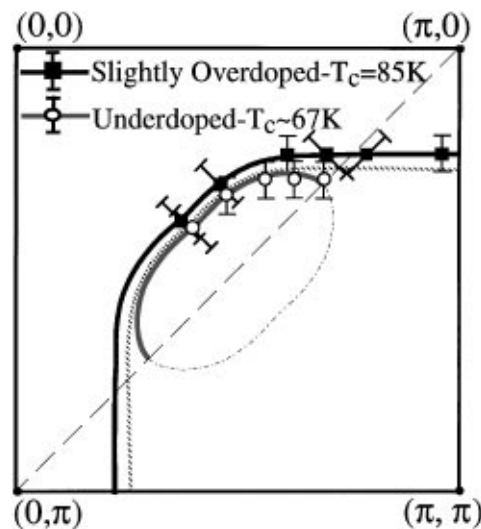


FIG. 4. Fermi level crossings from two Bi2212 samples of differing oxygen content. The entire BZ can be reconstructed by fourfold rotation about $(0, 0)$.

that the phase fluctuation is the limiting factor for T_c in these underdoped samples where the pairs are formed well above T_c [12–14]. The second class is d -wave pairing of spinons [15], discussed in a prediction extending the original resonating valence bond idea [16]. Both classes of pairing above T_c explain the binding energy shift near $(\pi, 0)$ as a $d_x^2 - y^2$ gap which is largest near $(\pi, 0)$ and is nonexistent along the $(0, 0)$ - (π, π) line. Impurity scattering may cause a region of near zero gap about the $(0, 0)$ - (π, π) line explaining why we see a section of Fermi surface [17]. Because the lowest binding energy excitations are indicative of gap magnitudes, the 20–30 meV leading edge shift in the data among the samples of Fig. 2 should be used when assigning gap values. This method is similar to the one used to characterize the superconducting gap [18].

Another possible origin of the gap is the formation of a 45° -rotated, $\sqrt{2} \times \sqrt{2}$ symmetry (as seen in AF insulating material) induced by either the increased AF correlations in the underdoped material or by some other effect with this same symmetry (such as a structural distortion). If this new symmetry has rigorous long-range order, it results in a new BZ also centered at $(0, 0)$ (the edge of which is indicated in Fig. 4 by the dashed line) causing $(0, 0)$ and (π, π) to be equivalent. The bands on the (π, π) side of the new BZ edge become mirrored replicas of those on the $(0, 0)$ side. Their mixing with the original bands opens a gap near $(\pi, 0)$ similar to a spin density wave gap [19]. In our case, the new symmetry could be relatively short range and fluctuating in time, but it may still cause this “gapping” behavior, although it does not force $(0, 0)$ and (π, π) to be exactly equivalent. The Fermi contour in this picture terminates at the edge of the first BZ of the new periodicity, and is made

continuous by the dash-dotted line in Fig. 4 resulting in Fermi contour pockets centered at $(\pm\pi/2, \pm\pi/2)$. Similar results are also obtained in stronger coupling models such as the t - J and large “ U ” Hubbard models [20]. We have observed some weak features in the dash-dotted area, but we are not certain if they are of magnetic or structural origin. A similarly weak feature was previously observed by Aebi *et al.* who only investigated the near optimally doped samples that do not have the gap discussed above [21]. They interpreted the data as due to the magnetic (π, π) scattering of the large Fermi surface. The interpretation is still controversial [22], and is different from our conjecture of small hole pockets in the underdoped samples.

A third possibility is related to recent theoretical approaches that have the same basic ingredients as those discussed in Ref. [15], but incorporate additional features such as the SU(2) symmetry [23], or the van Hove singularity [24]. These theories have the spirit of the mixture between the hole pocket picture and the d -wave pairing of spinons. The SU(2) symmetry at half filling yields results that can either be described by d -wave pairing of spinons, or a π -flux phase state whose dispersion resembles that observed in Sr₂CuO₂Cl₂ [2].

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 [8] We approximate the centroid by fitting each spectrum with a Fermi distribution cutting off a Lorentzian while including an integrated background. The fitting procedure is meant to serve as a systematic method for locating intensity maxima and relative positions. Broader as-fitted peaks were given proportionally larger error bars.
 [9] Our choice for a FL crossing can be illustrated using the data of Fig. 1, panel a1, where a peak is dispersing up through E_F decreasing in intensity as it is cut by the Fermi function and pushing its leading edge slightly above E_F (due to instrument broadening of a sharp peak at E_F). Our choice for the crossing is where the feature intensity is reduced by approximately 50%, and, simultaneously, the leading edge is pushed above E_F as observed 43% of the way from (0,0) to (π, π) .
 [10] Here we concentrate on the Fermi surface centered at (π, π) only, which is sufficient for the discussion of this paper. An earlier study found another Fermi surface centered at (0,0) [D. S. Dessau *et al.*, Phys. Rev. Lett. **71**, 2781 (1993)]. However, a more recent work with data at lower photon energy suggest that the other piece of Fermi surface is caused by the superstructure [H. Ding *et al.*, Phys. Rev. Lett. **76**, 1533 (1996)]. Details of these issues will be discussed in the future.
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