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Nature of the high-binding-energy dip in the low-temperature photoemission spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$

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At the transition to superconductivity, an anomalous high-binding-energy (≈ -90 meV) dip appears in the low-temperature photoemission spectra taken along the Γ-$\bar{M}$ high-symmetry direction of $Bi_2Sr_2CaCu_2O_{8+\delta}$. This paper details experiments which further characterize the energy and **k**-space dependence of this dip structure. The dip occurs over a wide portion of the Γ-$\bar{M}$ zone diagonal (110), yet shows minimal energy dispersion. In the spectra taken along the Γ-X zone edge (100), the dip is very weak or not present. We show that these results imply that the dip is not an artifact dependent on the experiment or special features of the band structure and therefore is an intrinsic feature of the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$. The behavior of the normal-state bands along Γ-$\bar{M}$ in relation to the local-density-approximation prediction of a Bi-O-based electron "pocket" is also discussed, with our data explained most naturally if the Bi-O band remains above the Fermi level for all **k**.

In an earlier paper we brought attention to an anomalous high-binding-energy dip which appears in the angle-resolved photoemission spectra of the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$.[1] This dip, which is centered at around -90 meV in the photoemission spectra, was found to occur in the superconducting state spectra taken along Γ-$\bar{M}$ [see Fig. 1(a)][2] but was very weak or not present in those taken along Γ-X. The existence of this dip cannot be understood in the context of a simple weak-coupling Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity and could have profound implications for a theoretical understanding of the mechanism of the superconductivity in the high-temperature superconductors. Indeed, a number of theories have been proposed to explain its existence, each of which details new and very interesting physics.[3-5] It is therefore important to more fully characterize the energy and **k**-space dependence of this dip. In this paper we show that the dip occurs over quite a wide portion of the Γ-$\bar{M}$ zone diagonal, yet shows minimal energy dispersion. In addition, we show that this result implies that the dip is not a by-product of the experiment or of the detailed electronic structure of $Bi_2Sr_2CaCu_2O_{8+\delta}$. Hence, this dip is in fact an intrinsic feature of the excitation spectrum (spectral weight function) of the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and so could provide vital information about the mechanism of the high-temperature superconductivity. The very difficult question of the existence of the Bi-O electron pocket centered at $\bar{M}$ will also be discussed, with our evidence pointing away from a separate Bi-O based electron pocket centered at $\bar{M}$.

Figure 1(a) shows our previously reported[1] experimental results for the temperature dependence of the photoemission specta of $Bi_2Sr_2CaCu_2O_{8+\delta}$ taken along Γ-$\bar{M}$ (near the $\bar{M}$ point). As the temperature is lowered into the superconducting state there is a pullback of the edge and corresponding pileup of intensity at energies above the gap. This behavior is in qualitative agreement with the predictions of BCS theory. However, there is an additional feature in the spectra of Fig. 1(a) that is not predicted by the BCS theory. This is the high-binding-energy (≈ -90 meV) dip that appears in the low-temperature spectra. Our studies have shown that this feature is present only below T_c, and to within our experimental accuracy (a few kelvin), opens up at T_c. It thus seems to be intimately related to the sample going superconducting, and perhaps may hold clues as to the mechanism of the high-temperature superconductivity.

It is crucial to perform more detailed studies to characterize this dip, and to establish that it is not due to a by-product of the experiment or of the detailed electronic structure of $Bi_2Sr_2CaCu_2O_{8+\delta}$. This can be done best by ruling out other possible scenarios for the existence of the dip which assume that the dip is not an intrinsic feature of the excitation spectrum. Figures 1(b) and 1(c) schematically illustrate two such possible scenarios. In Fig. 1(b) there is a quite broad feature which in the normal state has appreciable strength at E_F. As the temperature is lowered through T_c, the weight that was near E_F is pushed away into a pileup, and a dip appears as a valley between the pileup peak and the original peak position. The main problem with this scenario is that it cannot accurately reproduce the shape of the experimental spectra. The main difference is that in the scenario of Fig. 1(b) the lowest point of the dip remains above the normal-state spectrum, instead of dipping below it as in the experimental spectra of Fig. 1(a). A more difficult scenario to rule out is the possibility that there are two bands in close

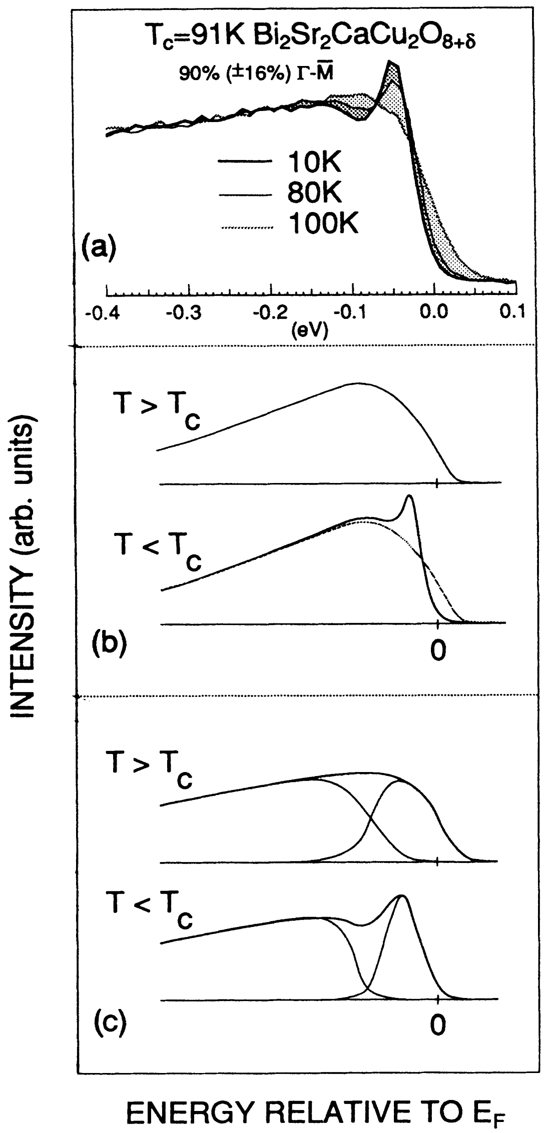

FIG. 1. (a) Angle-resolved photoemission spectra of a $T_c = 91$ K $Bi_2Sr_2CaCu_2O_{8+\delta}$ single-crystal sample taken along the Γ-$\bar{M}$ zone diagonal. Note the dip at ≈ -90 meV that appears as the temperature is lowered into the superconducting state. The photon energy was 21.2 eV and the angular resolution $\pm 4°$ ($\pm 16\%$ Γ-$\bar{M}$). (b),(c) Schematic illustrations of two possible origins of the dip. As discussed in the text, neither of these simplistic scenarios appear to be able to explain the experimental data.

proximity to each other along Γ-$\bar{M}$ which by coincidence superimpose to form one feature in the normal state. As the temperature is lowered, one or both of these bands sharpen up and the dip appears between them. This scenario is schematically illustrated in Fig. 1(c). We note that the sharpening of the bands must be directly related to the sample going superconducting, for the dip appears only below T_c. Based upon the data of Fig. 1(a) it is very difficult to rule out such a scenario. However, because this argument is based upon the coincidental arrangement of two bands, experiments done at a wide variety of **k** points can help lend insight into its applicability to the photoemission data. Such data will be presented in the remainder of this paper, and from it we will see that the two-band scenario of Fig. 1(c) is very unlikely. We feel that the data as a whole strongly imply that the high-binding-energy dip is an intrinsic feature of the excitation spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and presumably of the high-T_c superconductors in general.

Before we discuss the dip issue further, we will examine the normal-state data along Γ-$\bar{M}$. These data are necessary background information for our discussion of the origin and **k** dependence of the high-binding-energy dip. In addition, these data will shed light on the very difficult question of the existence of a separate Bi-O based electron "pocket" centered at $\bar{M}$. Figure 2 shows normal-state dispersion data taken along the Γ-$\bar{M}$ direction for a $T_c = 79$ K heavily oxygenated $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystal. Each of the curves corresponds to a different emission angle (and hence **k** value), with the Γ point at approximately 0% and $\bar{M}$ at 100%. We observe a feature starting some 200 meV below the Fermi level and then dispersing upwards towards the Fermi level as the electron emission angle is changed from near the Γ point out to the $\bar{M}$ point.[6] At approximately 70%–80% of the way out to $\bar{M}$, the feature reaches the Fermi level and its intensity be-

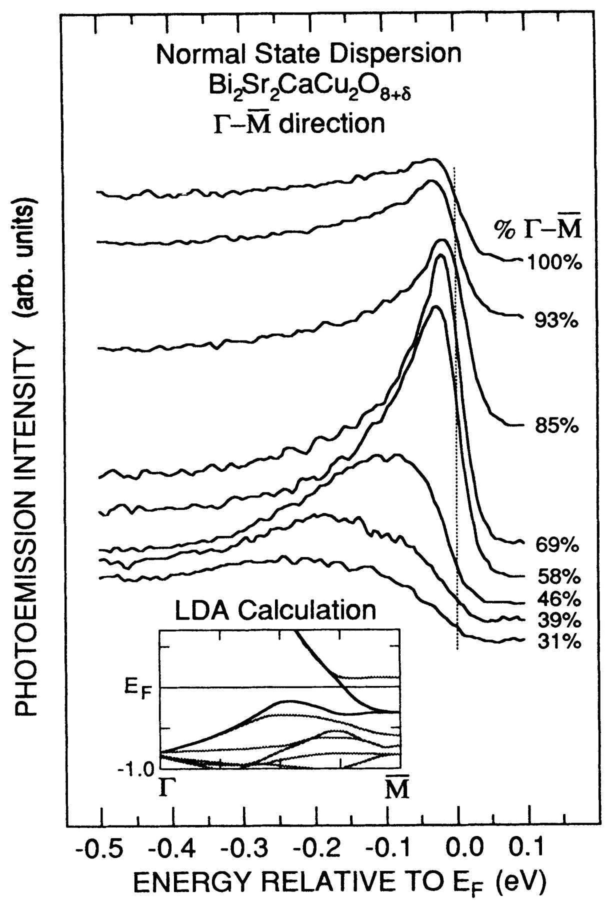

FIG. 2. Normal-state dispersion along the Γ-$\bar{M}$ direction for a $T_c = 79$ K $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystal. The photon energy was 19 eV and the angular resolution $\pm 1°$ ($\pm 4\%$ Γ-$\bar{M}$). Inset: The calculated band structure along Γ-$\bar{M}$ from Ref. 8.

gins to fall off rapidly.[7] The most natural explanation for this falloff is that the feature has begun to cross through the Fermi level. However, this crossing is not predicted to occur by the band theory calculations. The results of a representative calculation are shown in the inset to the figure.[8] A band of primarily Cu-O character starts at Γ and disperses upwards towards the Fermi level and, because it has the same symmetry as the Bi-O band at $\bar{M}$, hybridizes with and cannot cross the Bi-O band. It thus turns around to avoid the Bi-O band at its base. It does not, according to the calculation, cross the Fermi level. We feel that the most natural explanation of our data is that we are observing the Cu-O band cross the Fermi level. To achieve this, the only required alteration to the band theory result is that the Bi-O band lie above the Fermi level (i.e., be nonmetallic) instead of dipping below it and forming the electron pocket centered at $\bar{M}$. Due to the finite temperature and resolution broadening (a combined 60 meV for our data) it is of course impossible to rule out entirely the possibility that the Bi-O band dips only very slightly below the Fermi level (by say 10 meV). Likewise, the possibility exists that severe changes in matrix elements weaken the (Cu-O) feature right as it bends back around, making it appear as if it has crossed the Fermi level. We feel that neither of these possibilities are likely, and suggest that the Cu-O band does indeed cross the Fermi level. Of course the Cu-O band must still be strongly hybridized with the Bi-O band and would thus have significant Bi character. This possibility is therefore consistent with our earlier experimental evidence that the states along Γ-$\bar{M}$ have significant Bi character.[9] The literature contains other arguments both for[10] and against[11,12] the existence of the Bi-O pocket, and thus this is still very much an open question.

Moving back to our discussion of possible scenarios for the formation of the high-binding-energy dip, we observe that for all **k** values sampled, we only observe one normal-state feature, even though that feature is dispersing in energy and being strongly modulated in intensity (see Fig. 2). If that feature was made up of two separate features as in the scenario of Fig. 1(c), they must each disperse and be modulated in intensity in such a way that they always superimpose to form one feature. This places great constraints on the possible arrangements of the two bands making up the feature. The only plausible scenario is that the two bands disperse up from Γ together at a similar rate and with a relatively constant separation. They would then be modulated in intensity in a similar way and could conceivably always superimpose to form one feature. In this case we would expect to observe that the dip, if it is indeed due to a valley between the two bands, must disperse in energy with these bands. As we will show in Fig. 3, the dip does not disperse in energy.

Figure 3 shows both normal and superconducting state spectra taken along Γ-$\bar{M}$ for a different $T_c = 79$ K (heavily oxygenated) sample than was used for the data of Fig. 2. From the inset in the figure we can see that the normal-state behavior is qualitatively similar to that of Fig. 2; as we change the emission angle, a feature disperses up towards the Fermi level, growing in intensity and sharpening up in the process. As the electron's **k** gets near the $\bar{M}$ point, the strength of the feature begins to weaken as if it is beginning to cross through the Fermi level. When the sample is cooled into the superconducting state, we observe the characteristic pullback, pileup, and dip for each set of curves. As mentioned in the preceding paragraph, we would expect, within the confines of the scenario presented in Fig. 1(c), that the energy position of the dip should be a strong function of the photoelectron emission angle. This is clearly not happening in the data shown in Fig. 3; the dip is at approximately the same energy for each of the emission angles. Thus the scenario presented in Fig. 1(c) does not appear to be able to explain the experimental data. Our data therefore clearly suggest that the dip is an intrinsic feature of the excitation spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$. Even further support for this is taken from recent tunneling measurements on both $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Ref. 13) and $YBa_2Cu_3O_{7-\delta}$ (Ref. 14) which show a high-binding-energy dip very reminiscent of that seen in our photoemission data.

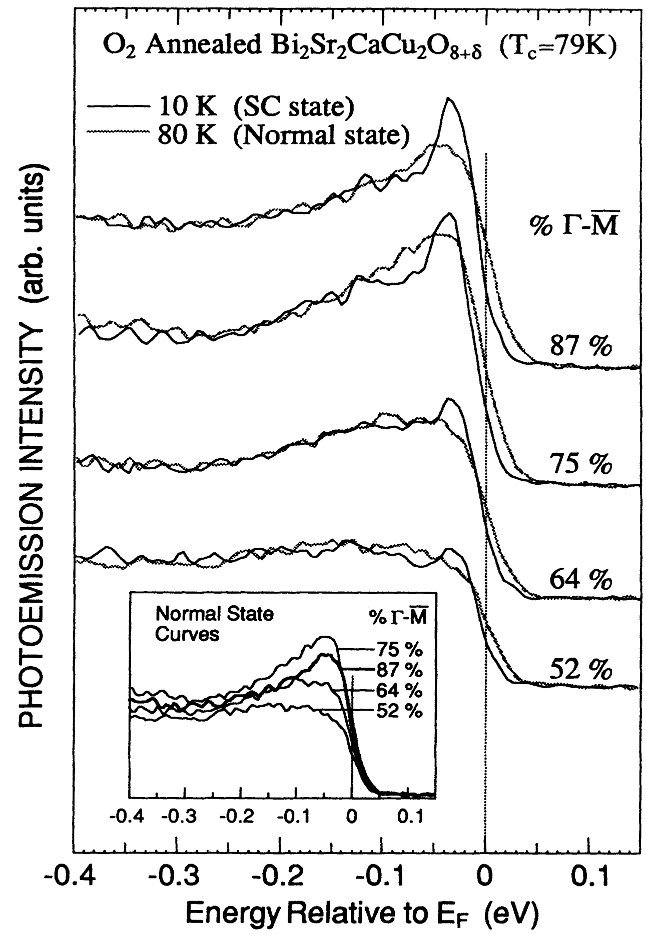

FIG. 3. Temperature-dependent data taken along Γ-$\bar{M}$ for a $T_c = 79$ K $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystal. Inset: The normal-state data stacked for easy comparison. The photon energy was 21.2 eV and the angular resolution ±1° (±4% Γ-$\bar{M}$).

The information presented in Fig. 3 may also provide essential clues needed in the development of a theory for the dip and for the mechanism of the high-temperature superconductivity in general. We feel that particularly important information is the fact that the dip exists over a wide portion of the Brillioun-zone diagonal, yet shows minimal energy dispersion. The lack of dispersion may, for instance, speak against Anderson's idea of degenerate parallel bands which split below T_c.[3]

In conclusion, we have performed extensive high-energy and angular resolution photoemission studies on the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. In this paper we have placed particular emphasis on the nature of the states along the Γ-$\overline{M}$ high-symmetry direction. Our normal-state dispersion data show no indication of the band theory prediction of a separate Bi-O based electron pocket centered at $\overline{M}$. As the sample temperature is lowered through its superconducting transition temperature (T_c), an anomalous high-binding-energy (≈ -90 meV) dip appears in the spectra taken along the Γ-$\overline{M}$ high-symmetry direction, while the dip is very weak or not present in the spectra taken along Γ-X. This dip occurs over quite a wide portion of the Γ-$\overline{M}$ zone diagonal yet shows minimal energy dispersion. The photoemission data as a whole, along with some very nice tunneling data taken by other groups,[13,14] strongly implies that the dip is an intrinsic feature of the excitation spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and probably of the high-T_c superconducting cuprates in general.

Note added.— Very recently Hwu *et al.*[15] published an angle-resolved photoemission study which confirmed the existence of the high-binding-energy dip in the superconducting state spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$. A significant difference between the two studies is that the dip of Hwu *et al.* showed little **k** dependence while we see very clear differences between the superconducting state spectra taken along the Γ-X and Γ-$\overline{M}$ directions. This surprised us until we realized how inconsistent their normal-state data [Figs. 2(a) and 2(b) of Ref. 15] are with the established results published independently by our group[16] and by Olson *et al.*[17] (even though they claimed consistency). The normal-state spectra of Fig. 2(a) of Hwu *et al.* show almost no dispersion, no intensity modulations, and no sign of the Fermi-surface crossing which should have occurred near 12°, curve *d* of their Fig. 2(a) and curve *e* of their Fig. 3. More details of the apparent inconsistencies in their data will be published later.[18] For now it is simply important to note their existence, and to note that the **k** dependence of their superconducting state results will almost certainly be affected.

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[2]The experiments were performed at high energy (30–40 meV full width at half maximum) and angular (±1° and ±4°) resolution on high-quality cleaved single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$. Details of the sample preparation process and characterization are available in D. B. Mitzi *et al.*, Phys. Rev. B **41**, 6564 (1990); and L. W. Lombardo *et al.*, J. Cryst. Growth (to be published). Details of the experimental apparatus and methods for the photoemission experiments are available in Ref. 1 and D. S. Dessau *et al.*, in *Proceedings of the Workshop on the Fermiology of High T_c Superconductors* [J. Phys. Chem. Solids **52**, 1401 (1991)].

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[6]We have studied two different classes of $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples: as-grown $T_c = 91$ K samples, and postannealed samples, with annealing-condition-dependent T_c's ranging from approximately 78 to 91 K. The as-grown $T_c = 91$ K samples studied previously (Ref. 9) showed little or no Fermi-level intensity along the Γ-$\overline{M}$ zone diagonal. This paper discusses results only from the annealed samples, which all show strong and distinct near-E_F features along the Γ-$\overline{M}$ direction. The reason for the lack of near-E_F strength along Γ-$\overline{M}$ in the as-grown samples is unclear, though we believe it is principally a result of disorder in the Bi-O layers due to the lack of a controlled oxygen stoichiometry.

[7]We notice that there is some sample-to-sample scatter in the exact **k** value (emission angle) that the intensity of the feature begins to fall off. We believe this scatter to be primarily a result of the difficulty in experimentally determining the surface normal. We do not yet have enough data to discuss differences in the crossing positions due to variations in the oxygen content of the samples.

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