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Superconducting energy gap in $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ studied by photoemission spectroscopy

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We report photoemission measurements on highly textured polycrystalline samples of $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223, $T_c = 104$ K). High-resolution data show a superconducting gap opening below T_c. The gap-spectrum line shape suggests an anisotropic gap structure in the Brillouin zone. The maximum gap in Bi-2223 is estimated to be 29 meV so that $2\Delta/kT_c \sim 6.5$, somewhat larger than the reduced gap in $Bi_2Sr_2CaCu_2O_8$ (Bi-2212). A spectral dip feature is observed at 72 meV in the superconducting state. The results are compared with angle-resolved experiments on Bi-2212 single crystals.

Since the superconducting gap in $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) was successfully measured with high-resolution photoemission spectroscopy (PES),[1,2] a number of important findings have been revealed with this technique. It was reported[3] and confirmed[4] that significant gap anisotropy exists within the a-b plane in Bi-2212. The maximum gap was found along the Cu-O bond direction near the Brillouin zone boundary of the Cu-O_2 lattice (near the M point),[3,4] where, in the normal state, an unusually flat band exists near the Fermi level (extended Van Hove singularity).[5–11] The observed maximum gap value is much larger than the BCS weak-coupling prediction.[1,4] The gap appears to be minimal along the diagonal directions of the Cu-O_2 lattice [Γ-(X/Y) in Bi-2212]. In addition, an anomalous spectral dip feature was observed, below T_c, at the higher binding energy side of the electron condensation peak.[12,13] These photoemission observations have been incorporated in descriptions of new pairing mechanisms for cuprate superconductors. The anisotropic gap structure is consistent with theories that imply d-wave pairing[14] or anisotropic s-wave order parameters.[15] It has also been suggested that an extended Van Hove singularity band near E_F might play a key role in the enhancement of T_c in the cuprate superconductors[16] and in driving the metal-insulator transition.[17] Regarding the spectral dip feature, several distinctly different explanations have been offered, but no consensus description to account for this feature has been achieved.[18–22]

To date, Bi-2212 is the only cuprate superconductor that consistently shows an observable superconducting gap in photoemission measurements. It is very important to find other high-T_c cuprates that can be studied to obtain order-parameter information and to explore their common electronic properties. We have undertaken an ultrahigh-resolution study on polycrystalline, but highly textured (c-axis oriented) $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) and have measured energy distribution curves at low electron binding energies. Below T_c, the spectral function clearly exhibits a superconducting gap and electronic condensation. The results are compared with measurements on Bi-2212 single crystals.

The Bi-2223 samples were synthesized by a two-step process.[23] Processed powders of $Bi_{1.8}Pb_{0.4}Sr_2CaCu_2O_x$, Ca_2CuO_3, and CuO were packed into a silver tube, which was drawn, rolled and extensively heat treated. The resulting tape contains high-purity, dense $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ polycrystals that are approximately c-axis oriented. The Ag-clad tape (25×5 mm^2) has a T_c transition at 104 K (~3 K transition width) and a large transport critical current density of ~17 000 A/cm^2 at 77 K in the tape plane, measured in zero field. The photoemission experiment was carried out at the Synchrotron Radiation Center, Stoughton, WI, using the 4m-NIM beamline, and at Brookhaven National Laboratory, using the U3C beamline. Sections of the Bi-2223 tape were cleaved at 13 K in a vacuum of 3×10^{-11} Torr. The cleaved surface was later examined with electron and optical microscopes, showing densely packed grains (1–10 μm in size) with specular a-b planes exposed.

Figure 1 shows an energy distribution curve (EDC) from the Fermi level to Bi 5d levels measured from Bi-2223 with 74 eV photons. The valence band spectrum was also studied with 19 eV photons with 0.05 eV resolution; an EDC is shown in the inset. Like Bi-2212 and $YBa_2Cu_3O_{6.9}$,[24] these materials are highly two-dimensional, so that significant valence band dispersion in the a-b plane, but very little dispersion in the c direction are expected. Since the samples are polycrystalline, however, valence band spectra show little angle dependence, and they should be viewed as (a-b plane) momentum integrated. A Fermi edge cutoff at the top of the

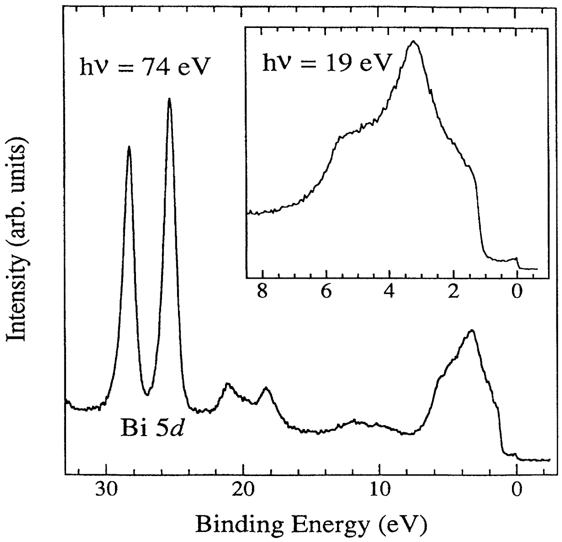

FIG. 1. Energy distribution curve (EDC) taken, with $h\nu$=74 eV, from Bi-2223, scanning the valence band from E_F to Bi $5d$ levels. The inset shows the valence band in greater detail; these data were taken with 19 eV photons. Because samples are polycrystalline, data are effectively angle integrated.

valence band is clearly seen in Fig. 1. The valence bandwidth (~6.5 eV) is in close agreement with PES studies of other cuprate superconductors.[24] The Bi $5d_{5/2}$ peak is located at 25.38 eV binding energy with a FWHM (full width at half maximum) of 0.96 eV after correcting for the instrument broadening (0.18 eV). For Bi-2212 single crystals, the Bi $5d_{5/2}$ level was found at 25.2–25.4 eV (depending on oxygen doping) with a width of ~1.05 eV.[25,26] The sharp Bi $5d$ data indicate a pure Bi bonding configuration for the cleaved Bi-2223. Other features in Fig. 1 include Pb $5d$ at 18.3 and 21 eV, which overlap O $2s$, and Bi $6s$ near 11 eV.[25] A Cu d^8 satellite resonance feature near 12 eV was also reported for cuprate superconductors;[27] this might also appear in the spectrum of Fig. 1. No (contaminant) C $1s$ level was detectable. These results suggest that a clean cleaved surface is obtained which represents the metallic Bi-2223 material. The successful cleavage of the polycrystalline Bi-2223 tape is probably due to the exceptionally good bonding between grains in this highly textured material.[28]

The superconducting energy gap, that opens below T_c in Bi-2223, is illustrated in Fig. 2. The leading edge of the valence band was measured at 106 K and 13 K, respectively, with an overall instrument resolution of 14 meV. The Fermi-level position was referenced to the Fermi edge of a co-grounded platinum sheet. Electronic drift, which can cause uncertainty in the Fermi edge position, was less than 0.2 meV. At T=13 K, the leading edge of the valence band shifts to higher binding energy and a spectral pileup appears at 25–35 meV. In addition to the formation of the gap and electron condensation, a dip or weight loss feature is apparent in the spectrum at ~72 meV binding energy when measured at T=13 K.

It is useful to compare these spectral changes, that occur as the sample goes superconducting, to those reported in pre-

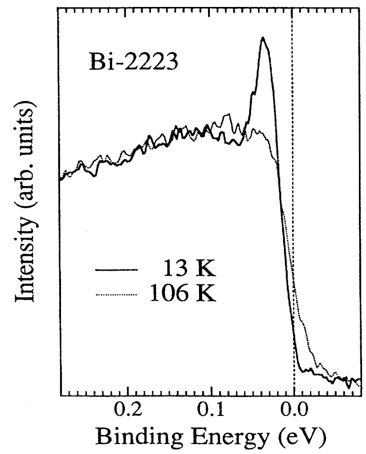

FIG. 2. EDC's taken from Bi-2223, with high resolution, in the normal (T=106 K) and superconducting (T=13 K) states. At T=13 K, a superconducting gap opens at the leading edge of the valence band.

vious studies of Bi-2212. Angle-resolved photoemission spectroscopy (ARPES) measurements on Bi-2212 single crystals showed significant gap anisotropy within the a-b plane.[3,4] Figure 3 shows a comparison of the Bi-2223 spectrum and an angle-resolved EDC for Bi-2212 taken near M (along Γ-M, from Ref. 4), where a maximum gap opening (22 meV) was observed. The condensation peak and dip feature in Bi-2223 are located at ~7 meV higher binding energies than they are in the Bi-2212, indicating a larger gap opening in Bi-2223. The leading edge of the Bi-2223 condensation peak, however, does not shift rigidly to higher

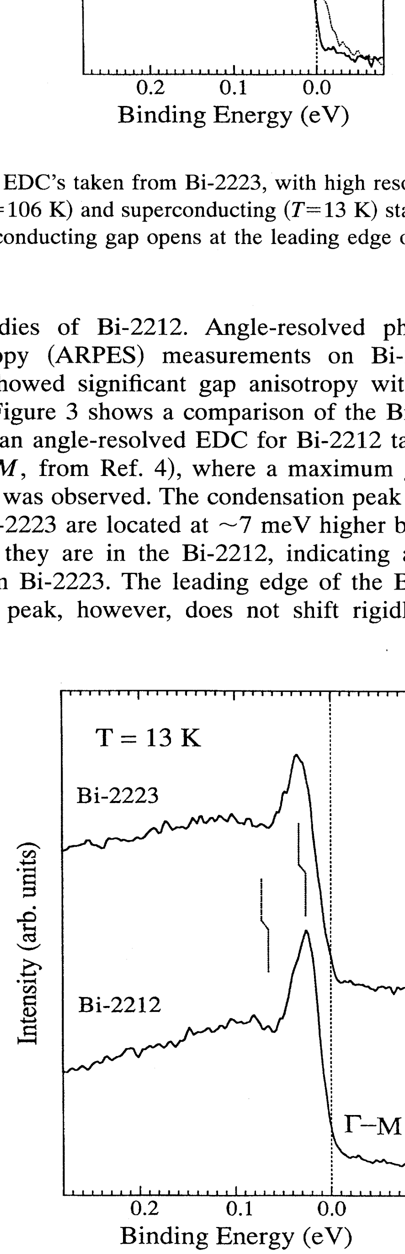

FIG. 3. Comparison of the Bi-2223 data at 13 K with the angle-resolved spectrum from Bi-2212 (T_c=85 K, taken from Ref. 4). The Bi-2212 data were collected along Γ-M where the energy gap is largest.

binding energy. Some spectral weight still remains at very low energies near the Fermi level. In fact, the leading edge of the Bi-2223 data at 13 K is ~25 meV wide (measured at 10–90 % of peak intensity), which is broader than the combined instrument and thermal broadening measured from the reference platinum Fermi edge at 13 K (15 meV). It is likely that the broadened edge in the Bi-2223 data at $T=13$ K is caused by a gap structure that is nonuniform throughout the Brillouin zone.

In Bi-2212, electronic states near E_F measured from different regions of the Brillouin zone show large intensity variations. EDC's taken near the M point, where the gap opening is largest, were typically more intense than EDC's taken along Γ-(X/Y), where the gap has its minimum value.[4] It is likely that the Bi-2223 gap spectrum (Fig. 3) will be broadened near E_F by the low-intensity contributions from regions of the zone where the gap is small (or zero). Further, ARPES studies on $YBa_2Cu_3O_{7-\delta}$, Bi-2212, and Bi-2201 have found an extended flat band near the zone edge (CuO_2 plane) along the Cu-O bond direction (near M for Bi-2212).[5–11] If a flat band near E_F also exists in Bi-2223 and it has a significant photoemission cross section, it should contribute significantly to the k-integrated data because of its extensive spread in k space. The Bi-2223 data in Figs. 2 and 3, contributed by all states near E_F, might represent a substantial spectral weight from the extended flat band where the gap is largest. Weaker spectral contributions near E_F, from elsewhere in the zone, where the gap is small, cause broadening of the leading edge.

The similarity of the Bi-2223 data and the Bi-2212 spectrum near M enables us to estimate the maximum gap value in Bi-2223. From the Bi-2212 data, a gap value of 22 meV ($2\Delta/kT_c \sim 6.1$) was obtained by a fit in Ref. 4. We estimate the maximum gap for Bi-2223 to be at least 29 meV (we add the 7 meV shift in the condensation peak to the gap value for Bi-2212). The resulting reduced gap $2\Delta/kT_c = 6.5$ for Bi-2223, suggesting that the scaling factor for cuprates increases with increasing T_c. Tunneling measurements of the gap in Bi-2201 ($T_c \sim 6$ K, $2\Delta/kT_c \sim 3.5$) (Ref. 29) are also consistent with this conclusion.

We have have noted that, in addition to the formation of the superconducting gap and the spectral pileup, a dip feature is also apparent in the spectrum at ~72 meV binding energy when measured at $T=13$ K (Fig. 3). A dip feature was also observed in electron tunneling experiments on a number of high-T_c superconductors, including Bi-2212, Bi-2201, $Nd_{2-x}Ce_xCuO_4$ (Ref. 29), and $YBa_2Cu_3O_{6.9}$.[30] So far there is no consensus explanation for physical origin of the dip feature. Dessau *et al.* have argued that the dip might be an intrinsic feature of the superconducting state.[12] Anderson[18] suggested that the dip is a consequence of band splitting in the superconducting state that appears as a result of an interlayer coupling interaction. Arnold *et al.*[19] have considered that it might be caused by a bosonic interaction with electrons near E_F. Modeling the PES results, they obtained a strong peak at 10 meV in the Eliashberg spectral function α^2F. However, bosonic mechanisms in high-T_c cuprates that could give rise to such behavior in α^2F have not been verified.[19] Littlewood and Varma[20] have shown that in the marginal-Fermi liquid model a two-peak spectral structure might appear at the superconducting transition, with one sharp peak between Δ and 3Δ, and a second broad peak appearing at higher energies with an onset at 3Δ. Coffey and Coffey[21] argued that the dip feature observed in the tunneling and photoemission data is an effect resulting from quasiparticle decay in the two-dimensional superconductors. They argued that the energy where the dip occurs in the tunneling conductance spectra (about three times the gap) tends to support a d-wave, rather than isotropic s-wave, pairing order parameter. Liu and Klemm[22] suggested that interband pairing, with hopping energies comparable to the critical temperature, might induce two peaks (separated by a diplike feature) in the electronic spectrum. The energy positions and strengths of these peaks appear to be strongly dependent on the model parameters.[22] The present photoemission observation of the dip structure at ~72 meV in Bi-2223, with $T_c = 104$ K shifted by ~7 meV from the dip in Bi-2212 ($T_c = 85$ K) provides additional information to assist in the development of a satisfactory quantitative theory of the high-T_c cuprates.

To summarize, we have successfully used high-resolution photoemission spectroscopy to measure electronic structure in the superconducting state of Bi-2223. Using highly textured (c-axis aligned) polycrystalline samples, measurements were effectively momentum integrated. A superconducting gap was observed; the gap appears to display a nonuniform structure in the Brillouin zone. A maximum gap value of ~29 meV was estimated (about 7 meV larger than Bi-2212). The resulting reduced gap ($2\Delta/kT_c \sim 6.5$) is larger than the reduced gap for Bi-2212 ($2\Delta/kT_c \sim 6.1$). A spectral weight loss (dip) feature is observed at 72 meV in the superconducting state, also shifted by ~7 meV from a corresponding feature in Bi-2212.

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