Anomalous superconducting state gap size versus T_c behavior in underdoped $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$

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We report angle-resolved photoemission spectroscopy measurements of the excitation gap in underdoped superconducting thin films of $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$. As T_c is reduced by a factor of 2 by underdoping, the superconducting state gap Δ does not fall proportionally, but instead stays constant or increases slightly, in violation of the BCS mean-field theory result. The different doping dependences of Δ and kT_c indicate that they represent different energy scales. The measurements also show that Δ is highly anisotropic and consistent with a $d_{x^2-y^2}$ order parameter, as in previous studies of samples with higher dopings. However, in these underdoped samples, the anisotropic gap persists well above T_c. The existence of a normal state gap is related to the failure of Δ to scale with T_c in theoretical models that predict pairing without phase coherence above T_c. [S0163-1829(96)51146-X]

The superconducting state of a metal is characterized by an energy gap in the spectrum of electronic excitations. BCS-Eliashberg mean-field theory[1] has been used successfully for decades in describing the superconducting state gap Δ in conventional superconductors such as Al or Nb. The typical mean-field theory result that the superconducting transition temperature T_c is proportional to Δ has been abundantly confirmed for conventional superconductors. Here we report data from angle-resolved photoemission spectroscopy showing that this proportionality is violated in underdoped samples of the high temperature superconductor (HTSC) $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$, implying a novel transition into the superconducting state.

A large variety of experimental measurements in underdoped HTSC have shown evidence for a suppression in the intensity of low-energy excitations *above* T_c, including NMR,[2] resistivity,[3,4] specific heat,[5] and c-axis optical conductivity.[6] The relation, if any, between the superconducting state gap and this pseudogap or normal state gap is still an open question. Angle-resolved photoemission spectroscopy (ARPES) is uniquely able to measure the gap magnitude anisotropy. Measurements on slightly overdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) below T_c are consistent with the four-lobed $d_{x^2-y^2}$ gap[7] and show no normal state gap (or a very small one). The present results on *underdoped* BSCCO samples with a wide range of transition temperatures show the same strong angular dependence of the superconducting state gap, but in addition they show a *normal state* gap with very similar magnitude and angular dependence, in agreement with other recent ARPES work.[8–10] The normal state gap persists to temperatures well above T_c. These observations can be related to our finding that the superconducting state gap fails to scale with T_c as expected from mean-field theory. We discuss below how models with phase fluctuations in the order parameter predict pairing in the normal state of underdoped HTSC up to a characteristic mean-field temperature T_{MF}, giving the two gaps a common origin and accounting for the non-mean-field gap size vs T_c dependence. In these models, T_c is the temperature for phase coherence between pairs rather than the onset of pairing.

The angle-resolved gap measurements were carried out using a Scienta hemispherical analyzer operating with 20 meV full width at half maximum (FWHM) resolution ($\sigma=9$ meV) as measured by a Au reference Fermi edge. The photon energy was 21.2 eV, and the base pressure of the vacuum system was 5×10^{-11} torr. The analyzer acceptance angle was $\pm1°$, corresponding to a k-space window of radius $0.045\pi/a$ or 0.037 Å^{-1}. Our BSCCO samples were untwinned thin-film crystals[11] grown by atomic layer-by-layer molecular-beam epitaxy[12] and an underdoped bulk single crystal. Underdoping was accomplished by substituting trivalent Dy for divalent Ca and/or reducing the oxygen content. The nine thin-film samples measured were cut from three larger samples with $T_c=46$, 78, and 89 K, respectively, determined from ρ vs T superconducting transition midpoints. The samples were cleaved in ultrahigh vacuum using a top-post method. The thin films give results that are similar to those from bulk single crystals for the same hole doping.[13]

Raw data on underdoped BSCCO of two different oxygen dopings are plotted in Fig. 1 for temperatures well below and well above T_c. The data are taken as energy distribution curves (EDC's) consisting of photoemission intensity vs energy at fixed **k**. The superconducting state gap magnitude $|\Delta_k|$ can be found using the usual expression for excitations from the superconducting ground state, $E_k=\sqrt{(\varepsilon_k^2+|\Delta_k|^2)}$, where ε_k is the normal state (or ungapped) single-particle energy relative to E_F. At the Fermi surface (FS), $\varepsilon_k=0$ by definition, and the gap is simply the minimum energy excitation. In ARPES the gap can be found by stepping through k space along a particular direction and finding where the quasiparticle feature is closest to E_F.

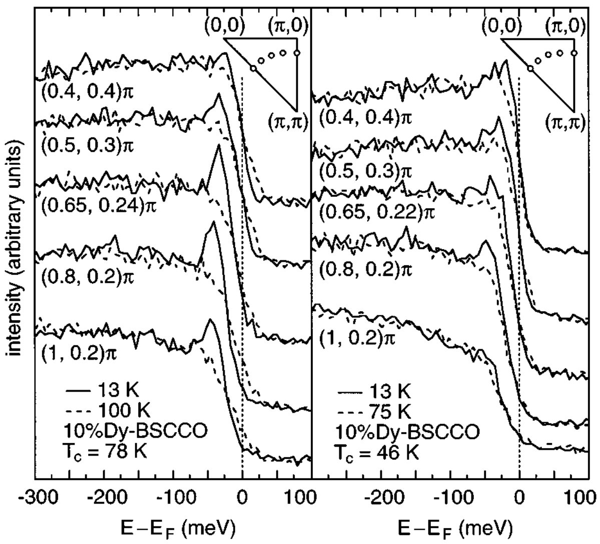

FIG. 1. ARPES spectra near the Fermi energy for underdoped single-crystal thin films of $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$ in the superconducting and normal states. k-space positions were selected on the underlying FS to facilitate measuring the energy gap. The systematic shift of leading edge position with k shows an anisotropic energy gap.

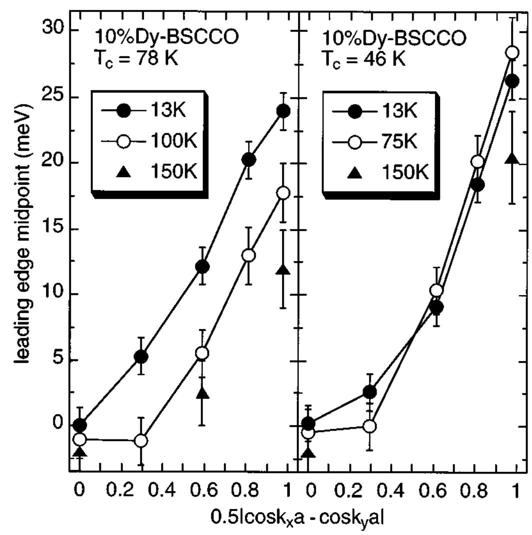

FIG. 2. Leading edge midpoint shifts from E_F, indicative of an anisotropic energy gap, in the superconducting and normal states of $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$ extracted from the ARPES spectra of Fig. 1. The abscissa, $0.5|\cos k_xa - \cos k_ya|$, was selected for comparison to a $d_{x^2-y^2}$ gap, which would be a straight line on this plot. The ''dirty d-wave'' scenario predicts flattening near the origin.

Data from BSCCO are more difficult to interpret than data from conventional materials since the EDC line shapes are broad and are not currently well understood. The samples that are more strongly underdoped have even broader features, especially in the vicinity of $(\pi,0)$ in the normal state. In order to avoid the ambiguities of picking a particular spectral function and background to fit the line shapes, we instead characterize the gap using the midpoint energy of the leading edge (the edge nearest E_F or 0 in Fig. 1) as in previous work.[7] As in optimally doped BSCCO,[14] gap values below T_c from leading edge shifts were found to be somewhat smaller than those extracted from fits to a broadened BCS spectral function; however, we stress that the trends in our data are insensitive to the specific method of characterizing the gap.

The five k-space positions shown (Fig. 1 inset) were chosen by taking five cuts in the Brillouin zone and selecting **k** so that the leading edge is closest in energy to E_F (i.e., on the underlying FS). It is evident that the leading edge positions change monotonically with angle, and that the superconducting and normal state leading edge positions are quite similar. Characteristic narrow peaks appear in the superconducting state near E_F. They are especially clear away from the $(0.4\pi,0.4\pi)$ Fermi surface crossing. The observation of the narrow peaks indicates that the broad normal state lineshape is intrinsic to the doping level and not primarily the effect of disorder or impurity scattering, since the scattering would also be expected to broaden the features below T_c. Also, we note a strong and systematic increase in the low-temperature height of the peaks with doping in the underdoped regime.

The leading edge midpoints of the EDC's of Fig. 1 are plotted vs $0.5|\cos k_xa - \cos k_ya|$ in Fig. 2. On this plot the $d_{x^2-y^2}$ gap prediction is a straight line that passes through the origin. The error bars are a combination of uncertainty in the leading edge midpoint position and uncertainty in E_F (± 1 meV). The data agree reasonably well with the strong anisotropy of the d-wave gap, but in some cases the measured values show a flattening near the d-wave node position (i.e., the origin in Fig. 2). One explanation is the ''dirty d-wave'' scenario[15,16] where impurity scattering broadens the point node into a region of finite width. Systematic impurity doping studies using ARPES would be useful to clarify this point. Another contribution to the flattening is finite k resolution combined with the strong energy dispersion in the node direction.[17]

The superconducting (13 K) and normal state (75 K) leading edge shift vs k curves for the T_c=46 K sample agree very well, suggesting the two gaps are intimately related. In the T_c=78 K sample, the anisotropy of the gap is similar above and below T_c, but the magnitude shows a marked reduction at 100 and 150 K. These observations raise two questions: Does the gap change continuously through T_c, and does the gap close at some higher temperature? To clarify these issues, more detailed temperature-dependence measurements are shown in Fig. 3. The leading edge midpoint energies on the FS for the maximum [along $(\pi,0)$ to (π,π)] and minimum gap [along (0,0) to (π,π)] are plotted for an underdoped single-crystal sample with T_c=85 K. Measuring the temperature dependence of the gap with ARPES requires caution because thermal broadening and line-shape changes may affect the leading edge positions. To partially cancel these effects, we take the gap to be the difference between the leading edge midpoints at the two k-space positions (the leading edge shift). This gives a gap of 28 ± 2 meV ($\sim$20% larger than a thin film of the same T_c) that changes smoothly above and below T_c, supporting the idea of a single gap function evolving with temperature. The gap becomes consistent with zero around 225 K.

Next, we focus on the superconducting state gap Δ_{sc} as a function of T_c (Fig. 4), using the maximum difference between the leading edge midpoints on the underlying FS. For

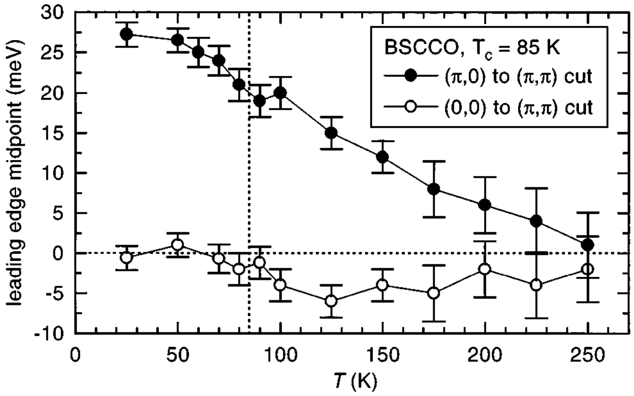

FIG. 3. The temperature dependence of leading edge midpoints for spectra taken at FS crossings near (π,0.2π) and (0.4π,0.4π) of an underdoped BSCCO single crystal. The difference between the two represents an energy gap that decreases continuously from 28 $\pm$2 at 25 K to near zero at 225 K.

these measurements, this ''internally referenced'' gap shows the same trend as the leading edge midpoint near (π,0) (the *d*-wave gap maximum) vs T_c since the FS crossing near (0.4π,0.4π) shows a gap consistent with zero. The nine samples measured fall into three T_c groupings (all underdoped) representing three thin-film crystal growth and annealing runs. In spite of substantial error bars, it is clear that the familiar BCS mean-field result of $\Delta_{sc} \propto T_c$ is violated [for example, $\Delta_{sc}(0) = 2.14kT_c$ for a weak-coupling $d_{x^2-y^2}$ solution[18]]. Instead Δ_{sc} stays constant or increases slightly as T_c is reduced.

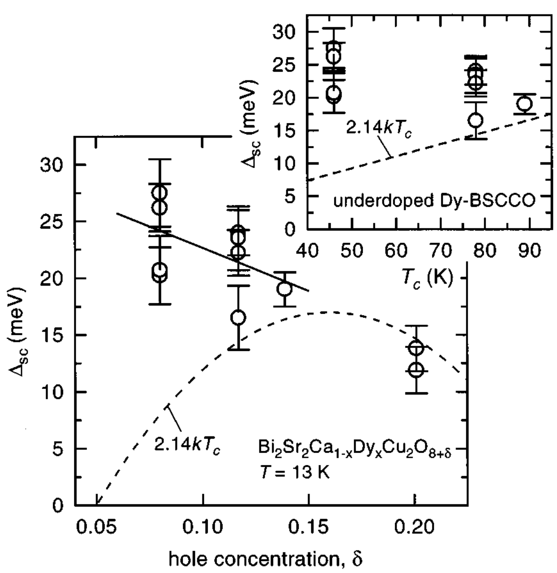

FIG. 4. Inset: The superconducting state gap Δ_{sc} from leading edge shifts measured at 13 K on $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+\delta}$ plotted vs T_c. The nine samples measured came from three growth and annealing runs, and therefore fall into three T_c groups. The dashed line is the standard BCS mean-field *d*-wave prediction (Ref. 17) with $\Delta_{sc} = 2.14kT_c$, shown to highlight the non-mean-field trend of the data. Main panel: Δ_{sc} vs doping δ, with δ inferred from $T_c/T_{c,\max}$ (Ref. 19). The energy scale from T_c (2.14kT_c, dashed line) shows very different behavior from the linear fit to the Δ_{sc} data points (straight line) from underdoped samples. By contrast, the gap values for overdoped samples (Ref. 20) decrease in the conventional way.

For comparison with phase diagrams, Fig. 4 shows Δ_{sc} vs doping δ (hole concentration per planar Cu) for the same underdoped samples, with each T_c converted to δ using the empirical relation $T_c/T_{c,\max} = 1 - 82.6(\delta - 0.16)^2$.[19] Once again, the predicted BCS weak-coupling *d*-wave result, $\Delta_{sc} = 2.14kT_c$ (Fig. 4 dashed line), shows no resemblance to the observed doping dependence. By contrast, as T_c decreases on the overdoped side, the gap falls rapidly[20] (although it may not be in quantitative agreement with the mean-field calculation because of the *ad hoc* leading edge midpoint criterion for the gap). The failure of the mean-field theory prediction for Δ_{sc} as a function of T_c (or doping) in the underdoped regime is our main result; it indicates the Δ_{sc} and T_c represent two distinct energy scales for underdoped BSCCO.

The non-mean-field Δ_{sc} vs T_c behavior is naturally related to the similarity of Δ above and below T_c in models with phase fluctuations in the complex superconducting state order parameter.[21,22] Paired electrons, and therefore a gap, exist below a mean-field temperature T_{MF} that is proportional to Δ. The zero-resistance T_c is the temperature at which long-range phase coherence is established. T_{MF} and T_c are the same in BCS theory since fluctuations are not considered, but T_c may be lower than T_{MF} in underdoped cuprates where the phase stiffness is expected to be small. Photoemission is insensitive to phase, so it measures a gap below T_{MF}. The phase stiffness is proportional to the superfluid density n_s. Thus if the phase stiffness energy scale instead of the gap determines T_c, then T_c should decrease as the doping is lowered, quite apart from any changes in Δ and T_{MF}, in agreement with the data of Fig. 4. In this model Δ is determined by the same pairing interaction in the superconducting and normal states. Muon spin relaxation (μSR) measurements support the idea that T_c is determined by n_s. A ''universal curve'' with $T_c \propto n_s$ from μSR has been reported for a large number of underdoped cuprate superconductors.[23] Also, magnetoresistance measurements of 60 K Y-Ba-Cu-O (underdoped) show a Lorentz-force independent contribution persisting to 200 K (Ref. 24) that may be consistent with phase fluctuations in the order parameter.

Various extensions to Anderson's original resonating valence bond (RVB) idea[25] give a possible microscopic justification in terms of spin-charge separation for the phase fluctuation model, including the two energy scales (kT_c and Δ) and a distinct pseudogap regime.[26–30] Spin-charge separation provides a means of producing pairing of excitations without superconductivity. The fermionic spin excitations (spinons) pair into singlets at a temperature $T_s > T_c$ for underdoped cuprates, where T_s is proportional to the gap. T_s is similar to T_{MF} and may represent a crossover instead of a true phase transition. Also, T_s decreases with increasing δ in agreement with the trend of the upper line in Fig. 4. The pairing was predicted to be *d*-wave, another area of agreement with the data. Because of the apparent flattening of the normal state gap near the *d*-wave node position (Fig. 2), the data could also be consistent with recent work predicting the pseudogap regime to be a mixture of *d*-wave spinon pairing and pockets of spinon FS.[28] In either case, the charge excitations (holons) Bose condense at T_c, so once again $T_c \propto n_s$, the two-dimensional Bose condensation result. T_c is also the temperature at which phase coherence between the singlet pairs appears. These models are in agreement with the ARPES data in the doping dependence of the gap, and in the existence of *d*-wave pairing well above T_c for underdoped samples.

In summary, the increase in the superconducting state gap with decreasing T_c violates the BCS mean-field theory prediction and suggests the existence of an energy scale for pairing that is separate from, and higher than, kT_c. This energy scale accounts for the pseudogap above T_c (normal state gap) seen by a variety of experimental probes in underdoped cuprate superconductors. As measured by ARPES, the normal state gap is highly anisotropic, and it is similar in magnitude and *k* dependence to the superconducting state gap, supporting the idea of a common underlying pairing interaction.

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[1] J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964).

[2] M. Takigawa, A. P. Reyes, P. C. Hammel, J. D. Thompson, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. B **43**, 247 (1991).

[3] T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993).

[4] B. Bucher, P. Steiner, J. Karpinski, E. Kaldis, and P. Wachter, Phys. Rev. Lett. **70**, 2012 (1993).

[5] J. W. Loram, K. A. Mirza, J. R. Cooper, and W. Y. Liang, Phys. Rev. Lett. **71**, 1740 (1994).

[6] C. C. Homes, T. Timusk, R. Liang, D. A. Bonn, and W. N. Hardy, Phys. Rev. Lett. **71**, 1645 (1993).

[7] Z.-X. Shen *et al.*, Phys. Rev. Lett. **70**, 1553 (1993).

[8] A. G. Loeser *et al.*, Science **273**, 325 (1996).

[9] D. S. Marshall *et al.*, Phys. Rev. Lett. **76**, 4841 (1996).

[10] H. Ding *et al.*, Nature (London) **382**, 51 (1996).

[11] J. N. Eckstein, I. Bozovic, D. G. Schlom, and J. S. Harris, Jr., Appl. Phys. Lett. **57**, 1049 (1990).

[12] J. N. Eckstein and I. Bozovic, Annu. Rev. Mater. Sci. **25**, 679 (1990).

[13] In particular, thin films and bulk single crystals give very similar gap anisotropy. However, thin films may show less strongly peaked normal state line shapes and slightly smaller gap values than bulk single crystals.

[14] H. Ding *et al.*, Phys. Rev. Lett. **74**, 2784 (1995).

[15] L. S. Borkowski and P. J. Hirschfeld, Phys. Rev. B **49**, 15 404 (1994).

[16] R. Fehrenbacher and M. R. Norman, Phys. Rev. B **50**, 3495 (1994).

[17] R. Fehrenbacher (unpublished).

[18] H. Won and K. Maki, Phys. Rev. B **49**, 1397 (1994).

[19] M. R. Presland *et al.*, Physica C **176**, 95 (1991); W. A. Groen, D. M. de Leeuw, and L. F. Feiner, *ibid.* **165**, 55 (1990).

[20] The gap measurements on overdoped BSCCO single crystals come from P. J. White *et al.*, Phys. Rev. B (to be published). The gap values have been reduced by 23% to compensate for the slightly lower gap values for thin films compared to bulk single crystals at optimal doping.

[21] V. J. Emery and S. A. Kivelson, Nature (London) **374**, 434 (1995).

[22] S. Doniach and M. Inui, Phys. Rev. B **41**, 6668 (1990).

[23] Y. J. Uemura *et al.*, Phys. Rev. Lett. **66**, 2665 (1991).

[24] J. M. Harris, Y. F. Yan, P. Matl, N. P. Ong, P. W. Anderson, T. Kimura, and K. Kitazawa, Phys. Rev. Lett. **75**, 1391 (1995).

[25] P. W. Anderson, Science **235**, 1196 (1987).

[26] G. Kotliar and J. Liu, Phys. Rev. B **38**, 5142 (1988).

[27] G. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[28] T. Tanamoto, H. Kohno, and H. Fukuyama, J. Phys. Soc. Jpn. **61**, 1886 (1992).

[29] X.-G. Wen and P. A. Lee, Phys. Rev. Lett. **76**, 503 (1996).

[30] B. L. Altshuler, L. B. Ioffe, and A. J. Millis, Phys. Rev. B **53**, 415 (1996).