

Unambiguous evidence for extended s-wave pairing symmetry in hole-doped high-temperature superconductors

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ABSTRACT

We have analysed data from angle-resolved photo-emission spectroscopy, Fourier transform scanning tunneling spectroscopy, and low-temperature thermal conductivity for optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ in order to discriminate between d-wave and extended s-wave pairing symmetry. The combined data are inconsistent with d-wave symmetry, but quantitatively consistent with extended s-wave symmetry with eight line nodes. We also explain all phase-sensitive experiments in a consistent manner.

The phenomenon of superconductivity involves the pairing of electrons into Cooper pairs (Bardeen *et al.* 1957). The internal wavefunction (gap function) of these Cooper pairs obeys a certain symmetry which reflects the underlying pairing mechanism. It is known that conventional superconductors (e.g., Pb and Nb) possess an s-wave gap symmetry that reflects the phonon-mediated electron–electron pairing (Bardeen *et al.* 1957). On the other hand, the gap symmetry of high-temperature cuprate superconductors has been a topic of intense debate for over 15 years. Three symmetry contenders have been put forward, isotropic s wave, d wave and extended s wave, as depicted in figure 1. Both d wave and extended s wave have line nodes and change sign when a node is crossed. A majority of experiments testing the symmetry (e.g., penetration depth, thermal conductivity, and specific heat measurements) have pointed to the existence of line nodes in the gap function (Hardy *et al.* 1993, Jacobs *et al.* 1995, Lee *et al.* 1996, Chiao *et al.* 2000). Qualitatively, these experiments are consistent with both d-wave and extended s-wave gap functions.

There has been much experimental evidence for a d-wave symmetry of superconducting condensate (order parameter) for hole-doped cuprate superconductors. In particular, phase-sensitive experiments based on planar Josephson tunneling (Tsuei and Kirtley 2000) appear to provide compelling evidence for a d-wave order parameter symmetry. Further, some angle-resolved photo-emission spectroscopy (ARPES) studies of nearly optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ (BSCCO) (Shen *et al.* 1993, Ding *et al.* 1996) show a very anisotropic gap that may be consistent with d-wave symmetry. As a result, there is a widespread belief that the d-wave gap

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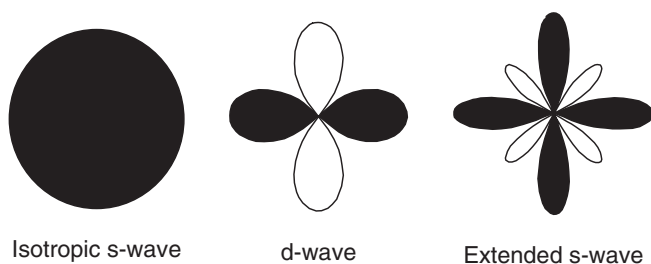


Figure 1. Three allowed pairing symmetries appropriate for CuO_2 planes in high- T_c superconductors. Both d wave and extended s wave have line nodes and change sign when a node is crossed.

symmetry is now firmly established. Nevertheless, there is also overwhelming evidence favouring an extended s-wave gap (A_{1g} symmetry) (Zhao 2001, Brandow 2002). This evidence includes data from phase-sensitive experiments based on out-of-plane Josephson tunnelling (Sun *et al.* 1994, Li *et al.* 1999, Bille *et al.* 2001), ARPES studies on heavily overdoped BSCCO (Vobornik *et al.* 1999), single-particle tunnelling spectroscopy (Maggio-Aprile *et al.* 1995), Raman spectroscopy of heavily overdoped cuprates (Kendziora *et al.* 1996), the nonlinear Meissner effect (Bhattacharya *et al.* 1999), and inelastic neutron scattering (Zhao 2003). Measurements of the physical properties related to low-energy quasiparticle excitations (Hardy *et al.* 1993, Jacobs *et al.* 1995, Lee *et al.* 1996, Chiao *et al.* 2000) have definitively excluded a nodeless s-wave gap symmetry, but cannot distinguish between d wave and extended s wave unless one makes quantitative comparisons between theory and experiment.

Although there are more experiments favouring extended s-wave than d-wave gap symmetry (Zhao 2001, Brandow 2002), the extended s-wave evidence is less well known and has been undervalued. If the gap symmetry for hole-doped cuprate superconductors is extended s wave, can we consistently explain all the phase-sensitive experiments?

The next question is: if the intrinsic bulk gap symmetry is extended s wave, can we definitively explain the ARPES data for BSCCO? The ARPES data reported in the 1995 paper (Ding *et al.* 1995) for a slightly overdoped BSCCO sample with $T_c = 87$ K are consistent with an extended s-wave gap symmetry. In contrast, the other ARPES data reported in the 1996 paper (Ding *et al.* 1996) for the same sample, which were measured by the same group with the same energy and momentum resolutions, are consistent with a simple d-wave gap function. Now a question arises: which ARPES data are more reliable? One can easily check that both the Fermi surface (FS) and superconducting gaps reported in the 1995 paper are in perfect agreement with those determined by independent and very precise Fourier transform scanning tunnelling spectroscopic (FT-STs) data (McElroy *et al.* 2003) (see also figure 2). The FS reported in the 1995 paper is also in excellent agreement with that recently determined using the symmetrisation method, the most reliable method to extract the FS from ARPES data (Mesot *et al.* 2001). This indicates that the 1995 ARPES data are reliable because they are in perfect agreement with three independent sets of data, which are very precise and in perfect agreement with each other. In contrast, the FS and superconducting gaps reported in the 1996 paper by Ding *et al.* are far from those determined from the very precise FT-STs data

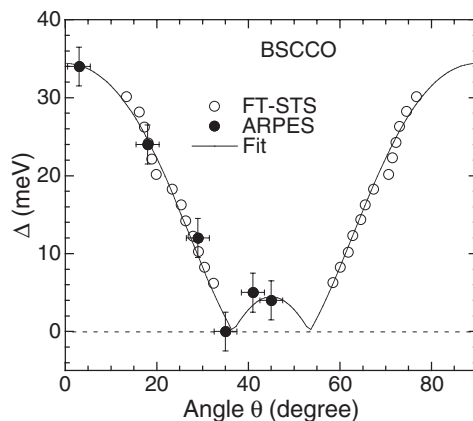


Figure 2. The angle dependence of the superconducting gap $\Delta(\theta)$ in the Y quadrant for slightly overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ crystals with $T_c = 86\text{--}87\text{ K}$. The gaps are extracted from ARPES data (Ding *et al.* 1995) (●) or from FT-STES data (McElroy *et al.* 2003) (○). The solid line is the best fitted curve using equation (1). Here θ is the angle measured from the Cu–O bonding direction.

(McElroy *et al.* 2003). Moreover, the FS reported in the 1996 paper by Ding *et al.* disagrees significantly with that determined recently from the reliable symmetrisation method (Mesot *et al.* 2001). This implies that the 1996 ARPES data are not reliable because they are not consistent with the other three independent sets of data, which are very precise and in perfect agreement with each other.

In figure 2 we plot the angle dependence of the superconducting gap $\Delta(\theta)$ in the Y quadrant for a slightly overdoped BSCCO with $T_c = 86\text{--}87\text{ K}$. The gaps were determined independently from ARPES (Ding *et al.* 1996) and FT-STES studies (McElroy *et al.* 2003) on similar BSCCO crystals. It is striking that two independent data sets overlap each other in the angle range accessible to both ARPES and FT-STES. The other two sets of ARPES data (Ding *et al.* 1996, Mesot *et al.* 1999) are far from the FT-STES data points (McElroy *et al.* 2003) due to the unreliable extraction of the FS (see the above discussion). Only the gap near the antinodal direction is found to be the same in all three measurements (Ding *et al.* 1995, 1996, Mesot *et al.* 1999), suggesting that the error in the FS has little effect on the accuracy of gap extraction along the antinodal direction. Based on the reliable 1995 ARPES data (see the above discussion), it is apparent that the gap at $\theta = 45^\circ$ is finite rather than zero for this nearly optimally doped BSCCO. This is further supported by another set of ARPES data for a heavily overdoped BSCCO with $T_c = 60\text{ K}$, which clearly shows that the gap at $\theta = 45^\circ$ is about $9 \pm 2\text{ meV}$ (Vobornik *et al.* 1999). These ARPES data thus suggest that the anisotropy between the gap at $\theta = 45^\circ$ and at $\theta = 0$ decreases with doping. This conclusion is also consistent with Raman scattering data, which indicate that the gap difference between $\theta = 0$ and 45° becomes negligibly small for heavily overdoped BSCCO and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$ (Kendziora *et al.* 1996).

We can fit the combined data points in figure 2 by an extended *s*-wave gap function

$$|\Delta(\theta)| = |\Delta(\cos 4\theta + s) + A \cos 8\theta|. \quad (1)$$

Here, we include the next harmonic term $\cos 8\theta$ of the extended s-wave symmetry to account for the high harmonic correction to the Fermi surface. One can clearly see that the fit is excellent with fitting parameters $\Delta = 19.43(46)$ meV, $s = 0.874(22)$ and $A = -2.01(41)$ meV. From the fitted curve, we find that the line nodes are located at $\theta_n = 36.7^\circ$ and 53.3° in the first quadrant, and the maximum gap is 34.3 meV. Since the intrinsic bulk maximum gap for optimally doped BSCCO is 33–34 meV, as determined from intrinsic tunnelling spectroscopy (Krasnov *et al.* 2000), we conclude that the top CuO_2 layer of this slightly overdoped BSCCO is optimally doped.

Because the ARPES determined gap near the antinodal direction is very accurate with an uncertainty of ± 1.5 meV (Ding *et al.* 1995), we can fit only the FT-STs data with the constraint that the fitted curve is exactly through one ARPES data point near the antinodal direction (the first ARPES data point in figure 2). Such a fit leads to almost the same fitting parameters as the fit that includes all the ARPES data points.

The FT-STs data points alone could also be consistent with a d-wave gap function

$$|\Delta(\theta)| = |\Delta_M[(1 - B)\cos 2\theta + B\cos 6\theta]|. \quad (2)$$

Here, $\cos 6\theta$ is the next harmonic term of the d-wave gap function. McElroy *et al.* (2003) fit their FT-STs data using equation (2). The best fit leads to the fitting parameters $\Delta_M = 39.3$ meV and $B = 0.182$. Although the d-wave fit is also good, the fitted maximum gap (39.3 meV) is well above the value (34 ± 1.5 meV) found from ARPES (Ding *et al.* 1995). Because the upper limit of the antinodal gap is bounded by the peak position of the spectrum, which is 35 meV below the Fermi level (Ding *et al.* 1995), the fitted maximum gap (39.3 meV) is unphysical.

In order to definitively exclude the d-wave gap symmetry, one could quantitatively compare both d-wave and extended s-wave predictions with other experiments. One such prediction is the linear slope of the low-temperature electronic thermal conductivity, κ_o/T , which is directly related to the Fermi velocity v_F and momentum k_F in the nodal directions, and the slope $S = d\Delta(\theta)/d\theta$ at nodes. The former two quantities can be obtained from ARPES data, while the latter can be readily calculated from the gap function deduced from a fit. The residual thermal conduction is due to a fluid of zero-energy quasiparticles induced by the pair-breaking effect of impurity scattering near the nodes in the gap. Calculations for the heat transport by nodal quasiparticles in two dimensions give the general expression (Durst and Lee 2000)

$$\frac{\kappa_o}{T} = N \frac{k_B^2}{3\hbar d} n \left(\frac{v_F}{v_2} + \frac{v_2}{v_F} \right), \quad (3)$$

where n/d is the stacking density of CuO_2 planes, $v_2 = S/(\hbar k_F)$, and N is the number of nodes per quadrant. Remarkably, theory (Durst and Lee 2000) predicts that κ_o/T is independent of the impurity concentration and that equation (3) is still valid even when vertex and Fermi-liquid corrections are taken into account. This makes thermal conductivity a very robust probe of the nodal quasiparticle spectrum in anisotropic superconductors.

A detailed ARPES study of BSCCO (Kaminski *et al.* 2001) showed that v_F depends on the angle θ being maximum at $\theta = 45^\circ$, while k_F only has a weak angle dependence ($k_F = 0.74 \text{ \AA}^{-1}$ near $\theta = 45^\circ$). The $v_F(\theta)$ can be evaluated from a linear fit to the band dispersions (energy distribution curves) above a kink energy

(about 50 meV below the Fermi level). From the middle column of figure 4 of Kaminski *et al.* (2001), we estimate that $\hbar v_F = 1.40 \text{ eV \AA}$ for $\theta = 45^\circ$ and $\hbar v_F = 1.16 \text{ eV \AA}$ for $\theta = 38.5^\circ$. If we linearly extrapolate v_F with θ , we obtain $\hbar v_F = 1.09 \text{ eV \AA}$ at an extended s-wave gap nodal angle of $\theta_n = 36.7^\circ$ deduced above for the optimally doped top CuO_2 layer of BSCCO. Similarly, we estimate $\hbar v_F = 0.69 \text{ eV \AA}$ for $\theta = 25.8^\circ$, which is one of the nodal directions of the extended s-wave gap function deduced for slightly overdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (see below). It is interesting to note that the value of v_F ($1.05 \times 10^5 \text{ m/s}$) at the nodal directions of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) estimated from ARPES is very close to the value $(1.2 \pm 0.2) \times 10^5 \text{ m/s}$, estimated from the field dependence of the in-plane magnetic penetration depth at low temperatures (Carrington *et al.* 2001).

With the values of $\hbar v_F$ and k_F , we can now calculate κ_o/T for the d-wave and the extended s-wave gap functions using equation (3). The calculated values of κ_o/T are shown in the last column of table 1. Since the top CuO_2 layer of this slightly overdoped BSCCO is optimally doped, as discussed above, we should compare the calculated values of κ_o/T with the measured value for an optimally doped BSCCO, which is not available. Fortunately, it is known that the value of κ_o/T for slightly underdoped cuprates is slightly higher than that for slightly overdoped cuprates. This can be seen clearly from the YBCO system: $\kappa_o/T = 0.17 \pm 0.01 \text{ mW/K}^2 \text{ cm}$ for slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.90}$ (Taillefer *et al.* 1997) and $\kappa_o/T = 0.12 \pm 0.02 \text{ mW/K}^2 \text{ cm}$ for overdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$ (Chiao *et al.* 2000). By analogy, we should take the experimental value of κ_o/T to be about $0.2 \text{ mW/K}^2 \text{ cm}$ for optimally doped BSCCO, which is slightly larger than that for slightly overdoped BSCCO ($0.15 \text{ mW/K}^2 \text{ cm}$) (Chiao *et al.* 2000).

From table 1, one can clearly see that the predicted value of κ_o/T from the d-wave gap function is larger than the experimental value by a factor of 2, while this value from an extended s-wave gap model is within 10% of the experimental value. This indicates that the gap symmetry for optimally doped BSCCO is not d wave, but extended s wave.

For optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$, the measured κ_o/T is about $0.17 \text{ mW/K}^2 \text{ cm}$ (Taillefer *et al.* 1997) and $\Delta_M \simeq 30 \text{ meV}$. Taking the d-wave gap form of equation (2) with $B = 0.182$ and $\Delta_M = 30 \text{ meV}$, we have $\kappa_o/T = 0.65 \text{ mW/K}^2 \text{ cm}$, which is larger than the measured value by a factor of 4.

On the other hand, an extended s-wave gap function $\Delta(\theta) = 24.5(\cos 4\theta + 0.225) \text{ meV}$ has been deduced from a single-particle tunnelling spectrum for slightly overdoped YBCO (Zhao 2001). This gap function has line nodes located at $\theta_n = 25.8^\circ$ and 64.2° in the first quadrant. With $\hbar v_F = 0.69 \text{ eV \AA}$ (see above),

Table 1. Calculated values of κ_o/T for optimally doped BSCCO in terms of the d-wave and extended s-wave gap functions deduced from the best fits to the ARPES and FT-STs data for the optimally doped top layer of BSCCO (see text). The experimental value of κ_o/T for optimally doped BSCCO is about $0.2 \text{ mW/K}^2 \text{ cm}$ (see text). Here, d/n is the average separation between CuO_2 planes stacked along the c axis, θ_n is the angle of the nodal direction, $S = d\Delta(\theta)/d\theta$ is the slope at the node and N is the number of nodes per quadrant.

	d/n (\AA)	θ (deg)	S/N (meV)	$\hbar v_F$ (eV \AA)	k_F (\AA ⁻¹)	v_F/v_2	κ_o/T (mW/K ² cm)
d wave	7.72	45	21.38	1.40	0.74	48.5	0.378
Extended s wave	7.72	36.7	28.6	1.09	0.74	28.2	0.220

$k_F = 0.74 \text{ \AA}^{-1}$, and $S = 47.7 \text{ meV}$ (evaluated from the extended s-wave gap function), we calculate $\kappa_o/T = 0.12 \text{ mW/K}^2 \text{ cm}$, in quantitative agreement with the measured value ($0.14 \pm 0.02 \text{ mW/K}^2 \text{ cm}$) (Chiao *et al.* 2000).

The above quantitative data analyses unambiguously show that the gap symmetry for optimally doped cuprates is extended s wave. How could this conclusion be compatible with all the phase-sensitive experiments? This issue can be resolved if we consider the fact that there are two types of charge carriers; one is intersite bipolarons of oxygen holes and the other Fermi-liquid type with a large Fermi surface (Müller *et al.* 1998). The Fermi-liquid component is nearly absent for hole doping $p < 0.1$, and increases monotonically with doping for $p > 0.1$ (Müller *et al.* 1998). Further, it has been shown that the Bose–Einstein condensate of bipolarons has d-wave symmetry (Alexandrov 1998). Because the interfaces of grain-boundary junctions consist of underdoped cuprates (Betouras and Joynt 1995), the d-wave component of the Bose–Einstein condensate of bipolarons is dominant at the surface, in agreement with phase-sensitive experiments based on grain-boundary Josephson junctions (Tsuei and Kirtley 2000). It was also shown that the surface layer of a cuprate crystal is underdoped when it is contacted with a normal metal (Mannhart and Hilgenkamp 1999). This can explain the observation of a dominant d-wave component in corner SQUID experiments (Mathai *et al.* 1995, Wollman *et al.* 1995). The extended s-wave symmetry for the Fermi-liquid component can naturally account for phase-sensitive experiments based on out-of-plane Josephson tunnelling (Sun *et al.* 1994).

In summary, we have analysed data from angle-resolved photo-emission spectroscopy, Fourier transform scanning tunneling spectroscopy, and low-temperature thermal conductivity for optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ in order to discriminate between d-wave and extended s-wave pairing symmetry. The combined data are inconsistent with d-wave symmetry, but quantitatively consistent with extended s-wave symmetry with eight line nodes.

ADDED TO PROOFS

After submission of the present paper, we learned about the new ARPES data for optimally doped BSCCO (Cuk *et al.* 2004). From the Bogoliubov-type gap opening in the band dispersion curves, we can reliably determine the superconducting gaps at $\theta = 21.86^\circ$ and 27.0° , which are 19.5 meV and 12.0 meV, respectively. These values are in excellent agreement with those predicted from the fitted curve in figure 2, which are 19.93 meV and 12.60 meV, respectively. Therefore, the data shown in figure 2 are the most reliable because three sets of data, which are measured from three different groups and deduced from three independent methods, overlap each other.

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