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Superconducting gap and order parameter in $Bi_2Sr_2CaCu_2O_{8+x}$

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Using angle-resolved photoemission, we observed a nonzero superconducting gap and the presence of a superconducting condensate along all three major symmetry directions. We find that the gap is highly anisotropic, with a gap as small as 1-2 meV along Γ -Y, 4-8 meV along Γ -X, and 14-20 meV along Γ -M. We argue that our data imply either an anisotropic s-wave order parameter or an unconventional, two-component order parameter, and that measuring the size of the gap does not by itself distinguish between the two possibilities. We propose a phenomenological unconventional order parameter, and note the quantitative agreement between theory and experiment.

Several research groups have by now published angleresolved photoemission data from cuprate superconductors, in particular reports on the size of the superconducting gap.¹⁻¹¹ Such data have led to different conclusions as to the symmetry of the superconducting state. Further, the symmetry has been inferred by other means, with again different answers arising from various research groups.¹²⁻¹⁵ We present data showing that the size of the superconducting gap leads to one of two conclusions: (1) a conventional, anisotropic *s*-wave superconductor, $^{16-18}$ or (2) an unconventional, $^{19-21}$ two-component order parameter. 22,23 We emphasize (below) that measuring the size of the superconducting gap does not by itself distinguish between a conventional and an unconventional order parameter. If $Bi_2Sr_2CaCu_2O_{8+x}$ is an unconventional superconductor, we discuss how the relative weights of the two components depends on stoichiometry, which explains the apparently inconsistent results obtained in different laboratories. Our data specifically rule out any pure, single spherical harmonic order parameter, including isotropic s-wave and $d(x^2-y^2)$ symmetries.²⁴ In this report, we refer to a superconductor as "conventional" when the superconducting order parameter follows the symmetry of the crystal lattice, and exhibits no nodes, while "unconventional" refers to the superconducting order parameter exhibiting symmetry different from that of the lattice.

Our single-crystal samples were grown using literature methods.²⁵ Typical size was $7 \times 3 \times 0.2$ mm platelets. The samples were placed in a load-lock vacuum system, transferred to our ultrahigh vacuum system, and cleaved at low temperature (20-30 K) in ultrahigh vacuum (5-8×10⁻¹¹ tom).²⁶ Photoemission measurements were performed using the 4-m NIM monochromator at the Wisconsin Synchrotron Radiation Center. The total-energy resolution was 15-30 meV, depending on the measurement. Figure 1(a) illustrates susceptibility mea-

surements of the samples and Fig. 1(b) illustrates photoemission spectrum of a gold film Fermi edge. Note that the 10-90% susceptibility superconducting transition width of the sample is 1.3 K, comparable to the best Y-Ba-Cu-O untwinned single crystals and better than earlier reports on BSCCO-(2212) single crystals. Also note that the energy resolution from the gold film is 15-18 meV. These data establish the quality of samples used and the electron energy resolution that our equipment can provide.

We have provided elsewhere a report on the size of the superconducting gap in different directions in the Brillouin zone.¹⁰ The exact values of the gap inferred from photoemission data should not be taken too seriously because the theoretical photoemission line shape from a superconducting condensate has not been worked out.^{27,28} The ratio of the gap size in different directions is a much more robust quantity. We emphasize that we, and other research groups, observe a condensate and nonzero gap in all three major symmetry directions in the Brillouin zone.^{1–11,29} As illustrated in Fig. 2, for the large majority of our samples, the size of the superconducting gap is typically

$$0 < [(\Delta)_{\text{Gamma-}Y} = 1 - 2 \text{ meV}]$$

$$< [(\Delta)_{\text{Gamma-}X} = 4 - 8 \text{ meV}]$$

$$< [(\Delta)_{\text{Gamma-}M} = 14 - 20 \text{ meV}]$$
(1)

or a ratio of the size of the superconducting gap in different directions of approximately

$$(\Delta)_{\text{Gamma-}M}:(\Delta)_{\text{Gamma-}X}:(\Delta)_{\text{Gamma-}Y} \text{ of } 10:4:1 .$$
 (2)

Other investigators have reported ratios ranging from 10:1:1 to $1:6:1.^{1-11}$ The reports have sufficient energy resolution that differences in experimental instrumentation do not account for the wide range of results. We

concentrate in this work on providing an explanation for the wide range of experimental results.

Our data, for example, can naturally be thought of as composed of two levels of anisotropy, one between Γ -M



and Γ -X, and the other between Γ -X and Γ -Y. We have reported elsewhere that the size of the gap is, for our samples, very closely related to the normal-state density of states at the same location in the Brillouin zone.¹⁰ We emphasize that this relationship is consistent with an anisotropic s-wave superconducting order parameter, where the superconducting pairing mechanism is fairly short ranged in momentum space.

However, there is second alternative. Our data compel us to explain three important points: (i) the gap is nonzero along all three major symmetry directions; (ii) the gap along the Cu-O-Cu bond axis is larger than along either the a axis or the b axis; (iii) the a axis and b axis exhibit gaps of different sizes. Thus, there are two levels of anisotropy, one between the Cu-O-Cu bond axis direction and the Bi-O-Bi bond axis direction, and the other between the two Bi-O-Bi bond axis directions (a axis and b axis). The inequivalence of the a axis and b axis has also been established on the same samples using bulk-sensitive techniques, including infrared optical absorption³⁰ and resistivity measurements using the Montgomery technique, including a difference in zero resistivity.³¹ Any unconventional order parameter must be of the form (a+ib), since no node is observed along the three major symmetry directions. Associating (a) with the Cu-O-Cu bond axis compels one component to vanish along the Bi-O-Bi bond axes. Associating the (b) part with the Bi-O-Bi bond axes, to obtain an inequivalence of the a-axis and the b-axis, we must have an offset. Taking the possible symmetries tabulated by Annett³² into account, we



FIG. 1. (a) ac susceptibility measurements of our singlecrystal samples. The 10-90% signal width is 1.3 K. Note the absence of different phases, and the narrow temperature width, of these samples. (b) Angle-resolved photoemission spectrum, taken at normal emission with 21-eV photons, of a gold film deposited in vacuum. The 10-90% signal width is 15-17 meV. The electron energy analyzer pass energy used is 1 eV.

FIG. 2. Angle-resolved photoemission spectra taken along the Γ -M, Γ -X, and Γ -Y directions. The total-energy resolution was 20–25 meV, the sample temperature was 20 K, and the superconducting gap is determined by the shift of the leading edge (the Fermi edge) compared to the same sample at 90 K. The dotted line is the Fermi energy determined by a gold film. Note that all three directions exhibit a condensate, and also a superconducting gap. Also, the size of the superconducting gap is different in each of the three directions.

are thus lead to an order parameter of the form

$$\Delta = \gamma_1 \cos(2\varphi) + i\gamma_2 \cos(\varphi + \varphi_0) , \qquad (3)$$

where γ_1 and γ_2 are the weighting factors of the two components, φ is the angle with respect to the Γ -M direction (Cu-O-Cu direction in real space), and φ_0 is a phase angle used to account for anisotropy between the Γ -X and Γ -Y directions. The first term $[\gamma_1 \cos(2\varphi)]$ possesses $d(x^2-y^2)$ symmetry, while the second term $[\gamma_2 \cos(\varphi + \varphi_0)]$ possesses d(xz) + d(yz) symmetry. Equation (3) is the simplest, but not the only, way to express a two-component order parameter. Note that Eq. (3) naturally separates the strictly in-plane component from the interplanar part. In this sense, our reasoning is similar to that of Chakravarty et al.¹⁷ who argued that the gap arises from both an in-plane and interplanar coupling. In fact, Eq. (3) implies that there is always an in-plane contribution to the gap, while the second contribution can be more or less significant, depending on the precise stoichiometry of the sample.

Using Eq. (3), we can account for the various reports as to the size of the superconducting gap from different investigators. The essential point to realize is that the weighting factors change with stoichiometry, since the chemical potential, hybridization, and interlayer coupling³³⁻⁴² are all affected by the stoichiometry. For example, Eq. (3) agrees quantitatively with our data for the parameter values:

$$\gamma_1 = 13.1 \text{ meV}$$
, $\gamma_2 = 6.09 \text{ meV}$, and $\varphi_0 = 118.0^\circ$.
(4)

For such parameters, most of the gap possesses $d(x^2-y^2)$ symmetry, with a non-negligible d(xz)+d(yz) component. Also, note that the two Γ -*M* directions would have a gap that differs by only 0.7 meV, which renders them identical within experimental resolution.

It is noteworthy that Eq. (3) for an unconventional superconductor was derived strictly from symmetry considerations. That is, once it is recognized that the gap never vanishes, and has two levels of anisotropy, an order parameter with more than one component is mandatory for an unconventional superconductor. The reason is that a one-component order parameter can account only for the anisotropy between Γ -M and Γ -X(Y). Whether the material is viewed as having tetragonal or orthorhombic symmetry, the anisotropy between Γ -X and Γ -Y implies a second component to the order parameter. Equation (3) is simply a particularly useful form for representing such a two-component order parameter. Considering reports⁵ of a larger anisotropy of 20 meV:2 meV yields parameters

$$\gamma_1 = 19.8 \text{ meV}$$
, $\gamma_2 = 2.82 \text{ meV}$, and $\varphi_0 = 0^\circ$, (5)

which is overwhelmingly $d(x^2 - y^2)$.

In addition to the majority of our samples, described by parameters close to those of Eq. (4), there is a small fraction for which the size of the superconducting gap is approximately 20:8:14.⁴³ Such samples, again, exhibit a nonzero gap, and condensate, along all three major symmetry directions. The anisotropy yields parameters

$$\gamma_1 = 12.6$$
, $\gamma_2 = 16.1$, $\varphi_0 = 15.3^\circ$, (6)

which is roughly equally weighted toward $d(x^2-y^2)$ and d(xz)+d(yz) symmetries. Such averaging is exactly what one would expect to arise from scattering. For these particular samples, our normal-state photoemission data indicate an unusually high scattering rate.⁴³ Although we do not have a complete understanding of the material properties that affect the relative weights of the two components of the order parameter, all that is necessary to infer a two-component order parameter is that there be two levels of anisotropy, between Γ -M and Γ -X and between Γ -X and Γ -Y.

In summary, we have observed two levels of anisotropy in the superconducting gap. We conclude that either (1) the superconducting order parameter is an anisotropic s wave, with the degree of anisotropy affected by material parameters, or (2) the unconventional superconducting order parameter possesses two components. We present a simple phenomenological equation (3) for such an order parameter, and demonstrate that we obtain quantitative agreement with various experimental reports by using equation (3). We emphasize that our main goal in this report is to demonstrate, via Eq. (3), that simply measuring the size of the superconducting gap does not by itself distinguish between a conventional and an unconventional order parameter. However, to be consistent with data in the literature¹⁻¹¹ any unconventional order parameter must have at least two components.

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