Angular Position of Nodes in the Superconducting Gap of YBCO

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The thermal conductivity of a $YBa_2Cu_3O_{6.9}$ detwinned single crystal has been studied as a function of the relative orientation of the crystal axes and a magnetic field rotating in the Cu-O planes. Measurements were carried out at several different temperatures below T_c for a field of 30 kOe. A fourfold symmetry characteristic of a superconducting gap with nodes at odd multiples of 45° in k space was resolved. Experiments were performed to exclude a possible macroscopic origin for such a fourfold symmetry and our results impose an upper limit of 10% on the weight of the s-wave component of the essentially d-wave superconducting order parameter of YBCO. [S0031-9007(97)02826-3]

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Over the last years, there has been accumulating evidence that the pairing state of high temperature superconductors may be the so-called $d_{x^2-y^2}$ state. Among the wealth of experimental data, one can mention the results from magnetic penetration depth [1–3], angular resolved photoemission [4], and nuclear spin relaxation rate [5], which provide strong evidence for nodes in the superconducting gap of the cuprates. Furthermore, quantum phase interference experiments [6], which look directly at the symmetry of the order parameter as a function of its argument, generally confirm the presence of the nodes and the sign change of the gap function over the Fermi surface.

Most of these experiments suggest, as a recent review by Annett *et al.* [7] concludes, that a $d_{x^2-y^2}$ order parameter is the most plausible candidate to describe the superconducting state in these systems. However, in the case of optimally doped $YBa_2Cu_3O_{7-\delta}$ (YBCO), it has been argued that a possible slight s-wave component could arise from the orthorhombic distortion [8]. The in-plane anisotropy observed below T_c in thermal conductivity [9] and penetration depth [2,3] suggest that the CuO chains play a role in the thermodynamic and transport properties of the superconducting state. Furthermore, it was recently pointed out that the in-plane penetration depth anisotropy is difficult to understand within a proximity model with only a pure d-wave pairing in the Cu-O plane [10]. One consequence of the existence of a s-wave component would be a shift of the nodal positions from the principal diagonal directions over the Fermi surface. Thus, the precise angular location of the gap nodes on the Fermi surface would be useful information in the current debate on the symmetry of the order parameter in YBCO.

We present here a study of the thermal conductivity of a YBCO single crystal, κ, rotating in a magnetic field parallel to the Cu-O planes. A pioneer work by Salamon and coworkers [11,12] showed that, thanks to the Andreev scattering of quasiparticles by rotating vortices, such an experiment can be a relevant probe of the k-space anisotropy of the superconducting gap. This work was criticized by Klemm *et al.* [13] who contested a microscopic interpretation of the data. Moreover, error bars on the angular dependence of the longitudinal thermal conductivity were comparable to the magnitude of the periodical oscillations [11], making it difficult, if not impossible, to resolve a fourfold symmetry of $\kappa(\theta)$ which is the qualitative distinction of d-wave superconductivity. In this Letter, we begin by reporting on high-resolution experimental results which establish such a fourfold symmetry, and then we address objections to a microscopic interpretation of this angular dependence. Finally, we show that our data impose an upper limit on the relative weight of the s-wave component of the essentially d-wave state of YBCO.

Our YBCO single crystal was prepared by a self-flux method described elsewhere [14]. Absence of twins was checked using polarized light microscopy. Measurements were performed in a dilution refrigerator using a one-heater-two-thermometer steady state method. The sample was anchored at one end to a Cu heat sink, and a heater resistor was attached to the other. The heat current (J) was injected along the b-axis direction (i.e., parallel to the chains), and the thermal gradient was measured along the same direction with two Lakeshore Cernox thermometers. The experimental setup was rotated at the center of a superconducting coil with the rotation axis along the c axis and the magnetic field parallel to the Cu-O planes. The precise relative orientation of the magnetic field and the crystal was determined through a Hall probe rigidly fixed on the setup. The maximal available rotation was about 200°. Below 5 K, due to the slightly anisotropic magnetoresistance of the thermometers, we used a dynamic method which allowed us to calibrate the thermometers for each measured θ direction.

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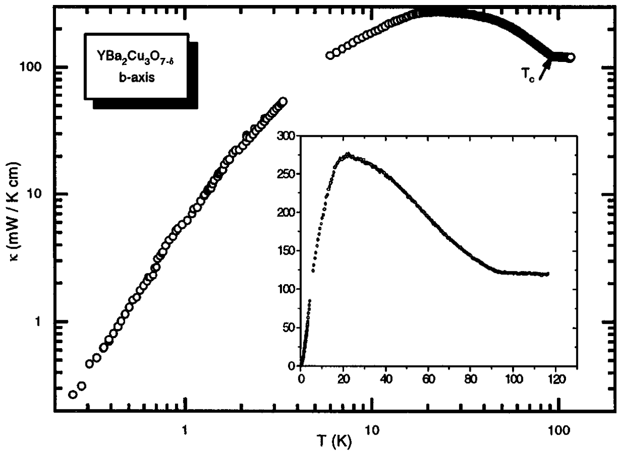

FIG. 1. Main panel: The temperature dependence of the thermal conductivity in a log-log plot. Inset shows a linear plot. Note the sharp increase at T_c leading to a peak at 23 K.

Figure 1 shows the thermal conductivity of the YBCO sample as a function of temperature over a wide temperature range. A few years ago, it was suggested that the steep increase of the thermal conductivity at the superconducting transition is induced by the electronic contribution in the Cu-O planes which, due to the strongly suppressed quasiparticle scattering rate in the superconducting state, increases rapidly below T_c [9]. Early evidence for such a suppression came from optical absorption studies [15] and microwave conductivity data [16]. Later, thermal Hall effect measurements [17] confirmed this pattern, and it is now generally accepted [18] that the peak of the thermal conductivity below T_c is in large part due to electrons. In our sample this peak is higher $[\kappa_{\max}/\kappa(T_c) = 2.2]$ and occurs at a lower temperature ($\sim$23 K) than what has been previously reported [9]. Both these features point to a long maximum quasiparticle mean-free path in the sample studied in this work. Because of this large electronic contribution, thermal conductivity is a useful probe of the quasiparticle excitation spectrum.

The angular variation of the thermal conductivity of YBCO, $\kappa(\theta)$ with $\theta = (\mathbf{b}, \mathbf{H})$, at 24 K is shown in Fig. 2. The full range of angular variation ($0° < \theta < 360°$) was obtained by inverting the direction of the magnetic field. Thermal conductivity shows a clear fourfold variation superposed on a hysteretic background. This hysteresis, observed between successive rotations, is related to the pinning of vortices, which might induce some variation of the vortex density between two consecutive crossings of the magnetic field at a θ direction. This hysteresis continues to be present at lower temperatures where the pinning is stronger. But, somewhat surprisingly, the monotonic background disappears. As shown in Fig. 3(a), the angular variation has a clear fourfold symmetry at 6.8 K. This is the first time that such a symmetry of thermal conductivity is unambiguously established well beyond the experimental resolution in a high-T_c superconductor.

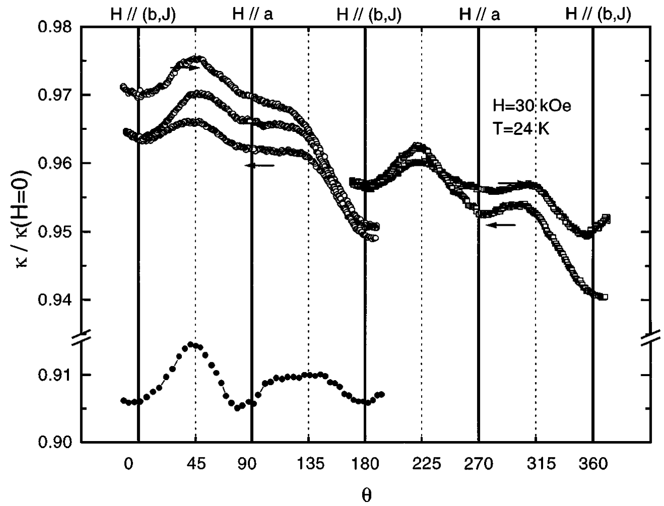

FIG. 2. Open squares and circles show the angular variation of the thermal conductivity at $T = 24$ K and $H = 30$ kOe. There are minima for the field parallel and perpendicular to the b-axis direction (heat current), and maxima when the field is parallel to the main diagonal directions. Arrows indicate the rotating direction. Solid circles indicate the results obtained with an alternative procedure of field cooling at every angle (see text).

Next, we consider possible objections to a microscopic interpretation of this fourfold symmetry such as raised by Klemm *et al.* [13]. These authors suggested that the angular structure might be "due to the demagnetization and flux pinning effects associated with a rectangular sample." To check this hypothesis, we performed complementary verifications. First, we used an alternative experimental procedure by rotating the crystal in the normal phase:

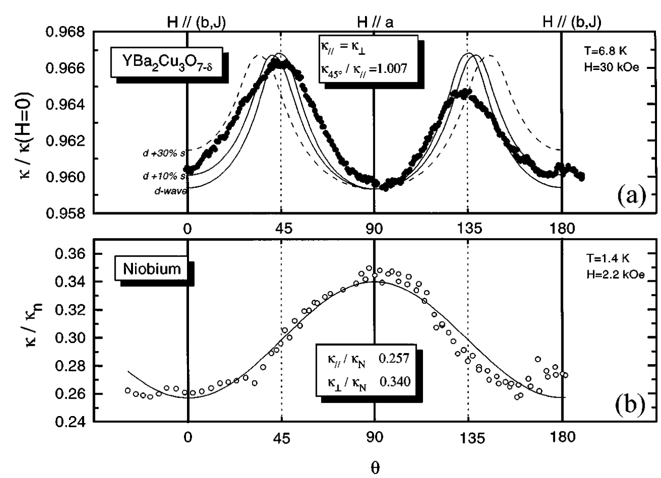

FIG. 3. The fourfold variation of the thermal conductivity in YBCO (a) is compared with the twofold variation for the Nb crystal (b). For YBCO the numerical results are shown for a pure d wave, $d + 10\%s -$ wave ($r = 0.1$) (solid line) and $d + 30\%s -$ wave ($r = 0.3$) (dashed line). For Nb the solid line is a fit using the cosine-squared dependence expected for a conventional gap.

After each rotation of about 1°, the sample was heated to a temperature above T_c (93 K) before cooling down to the measurement temperature. The angular variation obtained in this way (Fig. 2) presented the same behavior without the sloping background. Second, to rule out the possibility of a morphological origin related to the demagnetization, for example, we studied carefully the thermal conductivity of a niobium (Nb) sample of similar shape (flat rectangular slab) and size, and our results reproduce previous measurements on Nb [19]. As shown in Fig. 3(b), the angular variation of the thermal conductivity for this sample has an obvious twofold symmetry. This anisotropy changes sign with decreasing temperature reflecting the nature of the dominant quasiparticle carriers [20], but the symmetry always remains twofold. Thus, the relative orientation of vortices and the applied current, and not the sample geometry, governs the angular structure seen in Fig. 3(b).

Now, with the elimination of a macroscopic origin for the fourfold variation observed in the case of YBCO, we can turn to the microscopic picture which was originally formulated by Yu *et al.* [12] and is based on the anisotropic scattering of the quasiparticles by the vortices. It is well known [21] that the vortices have dramatic effects on the heat transport in type II superconductors. Even in the case of the cuprates with a magnetic field parallel to the basal plane, the coreless vortices lying between the Cu-O planes can act as scatterers of the BCS-like quasiparticles. This scattering mechanism was expressed [12] in terms of Andreev reflection [22] which is a process of retroreflection of excitations where spatial variations of the amplitude or the phase of the order parameter induce branch conversion of electronlike excitations into holelike excitations, and vice versa. In other words, the excited states distributed above the superconducting gap exhibit in the presence of a phase gradient (superfluid flow, v_s), a Doppler shift of their energies, $E = E_0 - \mathbf{p} \cdot \mathbf{v}_s$, so, when a quasiparticle approaches the vortex core, its energy in the superfluid frame reaches the energy gap and is converted to a quasihole, halting its contribution to the heat transport. This scattering process is strongly dependent on the relative orientation of the quasiparticle momentum ($\mathbf{p}$) and the superfluid velocity ($\mathbf{v}_s$). The latter is imposed by the magnetic field. Indeed, no Andreev reflection occurs when the quasiparticle momentum is normal to the supercurrent and parallel to the magnetic field. Thus, thanks to the directionality of this scattering mechanism, thermal conductivity can identify the preferential momentum orientation of the excitations above the superconducting gap.

Qualitatively, the observed behavior, i.e., a fourfold variation with maxima for odd multiples of 45°, indicates that there are maxima in the angular distribution of the quasiparticle momentum in the vicinity of $|k_x| = |k_y|$. When the field is aligned along these particular directions, most quasiparticles are not Andreev reflected, and the thermal resistance is lower.

The predominance of the fourfold variation at 6.8 K enables us to compare the curve to a 2D version of the usual Bardeen-Richayzen-Tewordt (BRT) expression of the electronic thermal conductivity [12],

$$\kappa_b^{qp} = \frac{1}{2\pi^2 c k_B T^2 \hbar^2} \int d^2p \, \frac{v_{gb}^2 E_p^2}{\Gamma(\mathbf{H},\mathbf{p})} \operatorname{sech}^2\!\left(\frac{E_p}{2k_b T}\right),$$

where v_{gb} is the b axis component of the group velocity, c is the c axis lattice parameter, and the effective rate of scattering

$$\Gamma(\mathbf{H},\mathbf{p}) = \frac{1}{\tau_0}\left(1 + \frac{\tau_0}{\tau_{v_0}} \times \exp\left\{\frac{-m^2 a_v^2 [E_p - |\Delta(\mathbf{p})|]^2}{p_F^2 \hbar^2 \ln(a_v/\xi_0) \sin^2\psi(\mathbf{p})}\right\}\right)$$

depends on a_v, the intervortex mean distance, and on $\psi(\mathbf{p})$, the angle between the magnetic field and the quasimomentum direction $\mathbf{p}$. $1/\tau_0$ and $1/\tau_{v_0}$ are, respectively, zero-field and maximum Andreev scattering rates. The gap function is a mixture of d-wave and s-wave components,

$$\Delta = \Delta_0\left\{r + \frac{\cos(p_x a/\hbar) - \cos(p_y a/\hbar)}{1 - \cos(p_F a/\hbar)}\right\},$$

where r represents the relative weight of the s component. As mentioned above, a finite r would shift the nodal positions from the main diagonal directions, and the angular interval between the peak positions of the thermal conductivity would differ from 90°. Numerical calculations using realistic physical parameters ($E_F = 1$ eV, $\tau_0 = 3\tau_{v_0} = 10^{-12}$ s, and $\kappa^{qp}/\kappa = 0.05$) are shown in Fig. 3(a) for pure d-wave ($r = 0$), $d + 10\%\, s$ ($r = 0.1$), and $d + 30\%\, s$ ($r = 0.3$) cases. The interval (2θ) between the two peaks is shifted from 90° (pure $d -$ wave wave) to 96 (10%) and 108 (30%), following the relation $2\theta = \arccos(r)$. However, in our experimental curve, the two peaks are separated by $90 \pm 6°$. Thus, according to our results, the upper limit to r, i.e., the relative weight of the s component of the superconducting order parameter, $[\Delta = \Delta_d(r + \cos(2\theta))]$, is about 0.1. This is significantly lower than what is suggested through a recent examination [23] of the in-plane penetration depth anisotropy [1]. On the other hand, it is compatible with the absence of any detectable difference in the zero-field thermal conductivity along the a axis and the b axis at very low temperatures which also suggest an essentially d-wave state [24].

We also studied the temperature dependence of this angular variation down to 0.5 K. Figure 4 shows the curves for 24, 6.8, and 0.8 K plotted together. Data at 1.2 and 0.5 K present the same behavior as the 0.5 K curve and are not shown here. A striking change in the

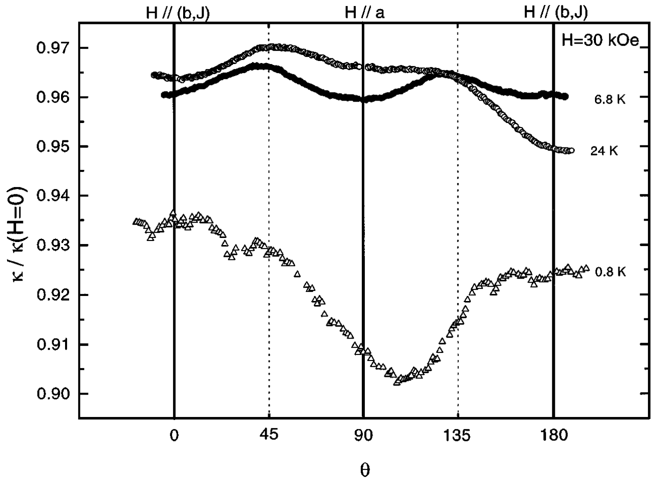

FIG. 4. Angular variation of the thermal conductivity at 24, 6.8, and 0.8 K, at $H = 30$ kOe.

structure of $\kappa(\theta)$ is detected between 6.8 and 1.2 K where the fourfold symmetry fades away. The minimum for the field perpendicular to the thermal current (b axis) develops significantly (i.e., $\kappa_{\parallel} > \kappa_{\perp}$). We have found that this minimum becomes deeper with decreasing temperature or for increasing magnetic field. The origin of this crossover between these two regimes (6.8 and 1.2 K) is not yet fully understood. However, it may be related to the dramatic change in the relative importance of electrons and phonons as heat carriers: while at 5 K and above the electronic contribution is large [25], it becomes negligible below 1 K [26]. Indeed, our analysis neglects the effect of vortices in the plane on both phonons and quasiparticles in the chains. The former may provide an explanation for the twofold variation developed at low temperatures. On the other hand, as a careful study of the in-plane anisotropy of thermal conductivity at various temperatures suggests [25], the chain contribution to the thermal conductivity increases significantly below 50 K passing by a maximum around 15 K. In our geometry, with the heat current applied along the chain orientation, a twofold angular structure due to the scattering of chain quasiparticles by vortices could well be present. Additional experiments of this type on a-oriented YBCO crystals will be necessary to elucidate the effect of a rotating magnetic field on different types of heat carriers at different temperatures.

In conclusion, our results support the existence of nodes in the superconducting gap at angular positions close to what is expected for a purely d-wave state and impose an upper limit of about 0.1 to the relative weight of the s component.

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