Anisotropy of Heat Conduction in $YBa_2Cu_3O_{6.9}$: A Probe of Chain Superconductivity

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(Received 2 December 1996)

The thermal conductivity κ of $YBa_2Cu_3O_{6.9}$ was measured along the a and b axes of detwinned single crystals. Both κ_a and κ_b show the usual peak below $T_c = 93.8$ K, but a clear additional contribution to the b-axis conduction sets in well below T_c. The difference $\kappa_b - \kappa_a$ exhibits a peak similar to the peak in the plane conductivity κ_a but with an onset temperature of 55 K. This result suggests that the CuO chains give rise to a sudden growth in superfluid density at that temperature, as predicted by models of single-electron tunneling between chains and planes. [S0031-9007(97)02695-1]

PACS numbers: 74.72.Bk, 74.25.Fy

$YBa_2Cu_3O_{7-\delta}$ is the best characterized, and the most studied, of the high-T_c superconductors. However, it is by no means the simplest system, as it contains quasi-1D CuO chains (along the b axis of the orthorhombic crystal structure) in addition to the CuO_2 planes (parallel to the ab plane) thought to be essential to high-temperature superconductivity. There have been numerous theoretical investigations of the role of the CuO chains in determining the gap structure in $YBa_2Cu_3O_{7-\delta}$. These studies have largely been driven by two experimental facts, namely, that certain tunneling experiments give results inconsistent with the $d_{x^2-y^2}$ symmetry allowed in a purely tetragonal system (see Ref. [1], and references therein), and that measurements of penetration depth anisotropy show that the superfluid densities along a and b have the same functional form and differ only in magnitude [2]. The latter data, which are indicative of similar nodal structures in the chains and planes, require an understanding of the plane-chain coupling below T_c. Broadly speaking, the theories rely on either single-electron tunneling ("proximity effect") or pair tunneling between the plane and chain Fermi surface sheets. A general feature of the proximity effect models appears to be pronounced upward curvature in the superfluid density along the b axis at a temperature well below T_c [3,4]. This is not surprising, as pointed out by Xiang and Wheatley, since these theories continuously approach that of independently superconducting planes and chains (with $T_c^{\text{plane}} > T_c^{\text{chain}}$) as the plane-chain coupling is reduced [3]. To date, these models have been rejected because they did not agree with the penetration depth anisotropy results of Zhang *et al.* [2], leading theorists to consider, for example, pair tunneling models [3].

In this Letter, we use thermal conductivity to investigate the role of CuO chains in the superconductivity of $YBa_2Cu_3O_{7-\delta}$. Although it is not a direct measure of the superfluid density, the conduction of heat in these systems is very sensitive to the onset of pair condensation. Our main finding is that chain carriers experience a sudden increase in mean free path below $T_{\text{onset}} \approx 55$ K which is similar to that experienced by the carriers in the CuO_2 planes at T_c, pointing to the onset of pair condensation or a significant increase in superfluid density in the chains at 55 K. In light of these results, and considering the new penetration depth data of Srikanth *et al.* [5], the above-mentioned single-electron tunneling theories should be reappraised. This may have implications for the symmetry of the order parameter insofar as these theories admit non-d-wave gaps and complex nodal structures imposed by, e.g., Fermi surface effects [1,4].

The thermal conductivity was measured in the temperature range between 5 and 150 K using the standard one-heater two-thermometers steady-state method. The sensors were attached to the sample via silver wires and diffused silver-epoxy contacts. The samples are untwinned single crystals of $YBa_2Cu_3O_{6.9}$ with either the a or the b axis along the length. They came from the same batch, grown by a self-decanting flux method using yttria-stabilized zirconia crucibles, as described elsewhere [6]. The crystals were oxygenated for 10 days at 500 °C in flowing O_2 and quenched to room temperature. They were then detwinned by applying about 50 MPa of uniaxial stress at 550 °C in air for 30 min, followed by reoxygenation for one day at 500 °C in O_2. Electrical contacts were made with silver epoxy annealed at 500 °C in O_2 for 1 h and quenched to room temperature. Contact resistances were typically 50 mΩ. The resistive transitions are narrow (0.2 K) and the T_c high (93.8 K) in both crystals. The extent of detwinning was measured by polarized light microscopy, and found to be complete between the two inner contacts. The dimension of the crystals and the separation between contacts (which serve to measure both voltage and temperature gradient) were measured by scanning electron microscopy. The a-axis (b-axis) crystal has a thickness of 86 (81) μm, a width of 0.74 (1.29) mm, and a separation between contacts of 1.31 (1.43) mm. The uncertainty on the geometric factor used to calculate the absolute value of the conductivity is $\pm 6\%$ (5%).

There is a qualitative difference in the temperature dependence of the resistivity along a and b [6]. While $\rho_a(T)$ is found to be perfectly linear between 130 and

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250 K, i.e., $\rho_a = \rho_a^0 + A_a T$, with $\rho_a^0 = -14\ \mu\Omega\,\mathrm{cm}$ and $A_a = 0.94\ \mu\Omega\,\mathrm{cm\,K^{-1}}$, ρ_b has upward curvature as a result of the chain contribution. At 250 K, $\rho_b = 95\ \mu\Omega\,\mathrm{cm}$ and the anisotropy ratio $\rho_a/\rho_b = 2.32$. The chain conductivity, defined as $\sigma_{\mathrm{chain}} = \sigma_b - \sigma_a$, converts to a chain resistivity which roughly obeys $\rho_{\mathrm{chain}} = \rho^0_{\mathrm{chain}} + A_{\mathrm{chain}} T^2$ above about 150 K [6]. In our crystals, $\rho^0_{\mathrm{chain}} = 66\ \mu\Omega\,\mathrm{cm}$ and $A_{\mathrm{chain}} = 0.0016\ \mu\Omega\,\mathrm{cm\,K^{-2}}$, and ρ_a (110 K) = ρ_{chain} (110 K), i.e., the two channels conduct equally well just above T_c.

The thermal conductivity κ of the two crystals is shown in Fig. 1. Essentially identical results were obtained on another pair of a and b untwinned crystals from another batch grown at McGill University, as well as on another crystal grown at the University of British Columbia. The data reproduce the two established features. First, $\kappa(T)$ exhibits the well-known increase just below T_c, characteristic of all high-T_c superconductors [7], which leads to a peak typically centered around $T_c/2$ or lower. The enhancement of heat conduction following the condensation of electrons into Cooper pairs is simply due to the concomitant reduction in the electron scattering of the heat carriers. Second, conduction is better along b over the whole temperature range from 5 to 150 K, which reflects at least in part the additional contribution of the chain electrons. The anisotropy in the normal state is roughly constant and the difference $\kappa_b - \kappa_a$ hovers between 3.0 and 3.5 $\mathrm{W\,m^{-1}\,K^{-1}}$ with an absolute uncertainty of $\pm 10\%$. Note that the Wiedemann-Franz law applied to the chain electrical conductivity above T_c gives $L_0 \sigma_{\mathrm{chain}} T = 3.5\ \mathrm{W\,m^{-1}\,K^{-1}}$, where $L_0 = 2.44 \times 10^{-8}\ \Omega\,\mathrm{W\,K^{-2}}$ is the Sommerfeld value of the Lorenz number.

These features were established by Yu *et al.* [8]. However, what the measurements of these authors did not clearly reveal is the significant departure from a constant difference below 60 K, which we find to grow dramatically as the temperature is lowered. This is best seen in Fig. 2 where $\kappa_b - \kappa_a$ is plotted as a function of temperature. Two aspects are striking: there is not a trace of an anomaly at $T_c = 93.8$ K, in contrast to the plane behavior (i.e., κ_a), and a sizable increase sets in rather suddenly at a much lower temperature, below about 55 K, giving rise to a peak centered around 15 K. The threefold increase in what we might call "chain" conductivity taking place between 55 and 15 K is reminiscent of the increase in plane conductivity between 90 and 30 K.

The distinct increase in $\kappa_a(T)$ right at T_c shows that heat conduction can be used as a measure of the onset of superconductivity, just like the electrical resistivity or the magnetic susceptibility. The arrow in Fig. 1 shows the resistively determined transition temperature, in good agreement with the change in κ. More generally, we can view κ as a detector of sudden changes in the superfluid density, not only at T_c but also below T_c. This will work as long as electrons are a major source of scattering for the carriers of heat. The increase in mean free path that follows the condensation of those electrons into pairs, thereby removing them as sources of scattering, is a well-known phenomenon for phonons in superconducting alloys [7]. The same will apply to electronic heat carriers if electron-electron scattering is strong enough. The effect will be all the more pronounced in high-quality samples since the growth in mean free path is ultimately limited by defects. Consequently, we propose that one can characterize sample quality by the ratio of $\kappa(\mathrm{peak})/\kappa(T_c)$, which is 2.3 for our a-axis crystal, the highest value reported so far (e.g., 2.1 for the crystals of Yu *et al.* [8] and Cohn *et al.* [9]).

In Fig. 3(a) we compare qualitatively the behavior of planes (κ_a) and chains ($\kappa_{\mathrm{chain}} = \kappa_b - \kappa_a$) in their response to the onset of superfluid growth at their respective onset temperatures T^* of 93.8 and 55 K. For ease of comparison, the data of Figs. 1 and 2 are normalized in such a way that the two peaks have the same height once a constant offset has been subtracted. This normalized $\Delta\kappa$ is plotted versus reduced temperature T/T^*.

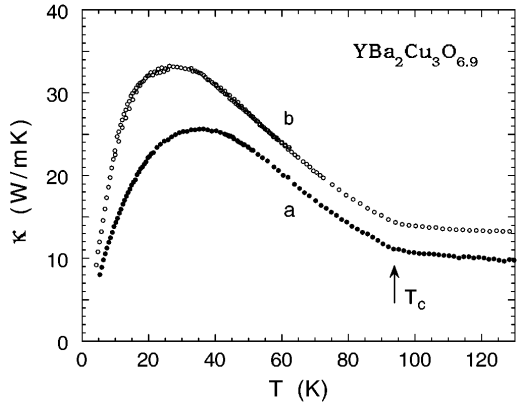

FIG. 1. Temperature dependence of the thermal conductivity in the a (solid circles) and b (open circles) directions. The arrow shows the resistively determined T_c.

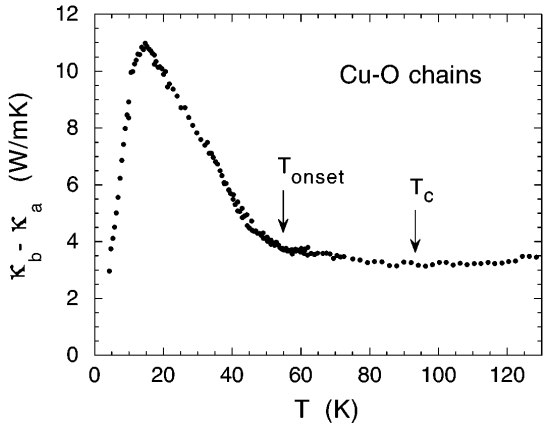

FIG. 2. Difference in the thermal conductivity along b and a. The larger conduction along the b axis is at least partly due to electrons in the CuO chains. $T_c = 93.8$ K is the onset of the peak in κ_a and $T_{\mathrm{onset}} = 55$ K.

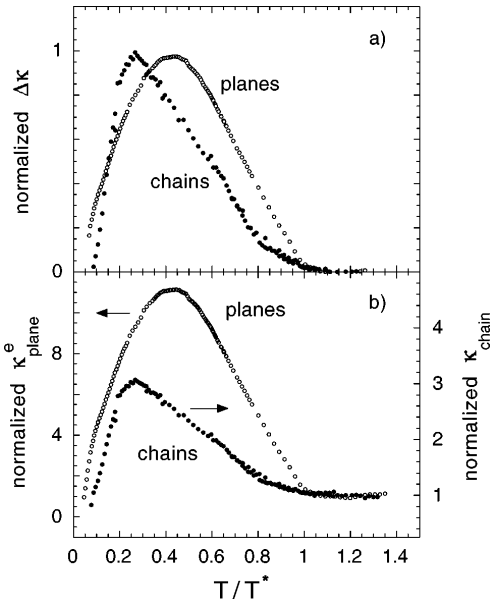

FIG. 3. (a) Comparison of plane (κ_a: open circles) and chain ($\kappa_b - \kappa_a$: solid circles) conductivities, normalized to 1 after subtracting a constant offset from the data of Figs. 1 and 2. (b) Comparison of the electronic part of the plane and chain conductivities, as discussed in the text. $T^* = T_c$ for planes and $T_{\rm onset}$ for chains (see Fig. 2).

The qualitatively similar behavior of $\kappa_{\rm chain}$ and κ_a below T^* and the absence of any anomaly in $\kappa_{\rm chain}$ at T_c suggest the following simple scenario: planes and chains are largely decoupled and each electronic system undergoes its own superconducting transition. This is what single-electron tunneling models predict [3,4], with the lower "transition" corresponding to the onset of superfluid growth in the chains rather than to a real transition when the coupling is not actually zero. Recently, Srikanth *et al.* observed a sudden growth in superfluid density below about 60 K in microwave measurements of $\sigma_2(T)$ [5], which may be related to the peak we see developing in $\kappa_{\rm chain}$ at about the same temperature. However, because these authors used twinned crystals, they were unable to say what role the chains play in this "two-component superconductivity."

At this stage, our proposal of a two-component superconductivity with the chains contributing only below 55 K is phenomenological. To be more specific, an understanding of the underlying carriers of heat and their scattering mechanisms is needed. A reasonably satisfactory understanding now exists for the planes. By measuring the thermal Hall effect, Krishana *et al.* were able to extract the electronic contribution to κ_a [10]. They find that in the normal state it is roughly 10% of the total conductivity and that the peak below T_c is in large part due to electronic carriers, as originally proposed by Yu *et al.* [8]. The ratio $\kappa_e(\text{peak})/\kappa_e(T_c)$ is about 10, reflecting an increase in electronic mean free path by a factor of about 30 in twinned crystals, and about 60 in untwinned crystals [11]. Recently, Taillefer *et al.* measured $\kappa_a(T)$ as a function of Zn impurity concentration, and they find that the peak is rapidly suppressed by low levels of Zn (less than 1%) [12], in a manner similar to the suppression of the peak in the charge conductivity $\sigma_1(T)$ at microwave frequencies [13]. The parallel suppression of the peak in κ and σ_1 is further evidence for an electronic mechanism responsible for the peak in κ_a. However, even when the concentration of Zn is increased to 3%, so that the electronic mean free path is decreased by a factor of 30 or so relative to the pure crystal, a small peak in κ still remains, which is attributed to phonons [12]. The theory of Hirschfeld and Putikka [14], based on a gap with d-wave symmetry and inelastic scattering of quasiparticles by antiferromagnetic spin fluctuations, can account for the Zn-doped thermal conductivity data in terms of a varying impurity scattering rate for the electrons. However, this theory neglects the chain contribution, and is therefore only applicable to κ_a.

There is at present very little information about transport in the chains. The relative importance of electrons and phonons as heat carriers is not known and there is no direct evidence for strong electron-electron scattering as there is for the planes. We will therefore adopt the simplest approach, namely, assume a phonon spectrum that is roughly isotropic in the ab plane, not unreasonable in this almost tetragonal crystal structure, and hence attribute most of the anisotropy in κ to chain electrons. This anisotropy is in the right direction ($\kappa_b > \kappa_a$) and of the right magnitude when compared with the electrical conductivity (see also Ref. [8]). Under this assumption, we can make a quantitative comparison of the *electronic* κ_a and $\kappa_{\rm chain}$, where the former is obtained either from the thermal Hall data [10] or equivalently from a subtraction of κ_a for the 3% Zn crystal [12] from the data on the pure crystal (Fig. 1). In Fig. 3(b), we show this "subtracted" κ_a and compare it with $\kappa_{\rm chain} = \kappa_b - \kappa_a$. It is seen that the enhancement of chain conduction below 55 K is a factor of 3 whereas it is a factor of about 10 for the planes. A larger enhancement of the electronic mean free path in the CuO_2 planes is not surprising: because $T_c > T_{\rm onset}$, the inelastic scattering is likely to be all the more pronounced. Furthermore, the elastic scattering from defects is expected to be much more significant in a quasi-1D channel like the chains. An extrapolation of the resistivities $\rho_a(T)$ and $\rho_{\rm chain}(T)$ to low temperatures certainly supports the view that the ratio of inelastic to elastic scattering is much weaker in the chains. In fact, the numbers suggest that it is so small in the chains that it could never give rise to a peak in $\kappa_{\rm chain}$. Our observation of a peak value well in excess of the upper bound imposed by the Wiedemann-Franz law using an extrapolated residual $\rho_{\rm chain}$ ($= 66\ \mu\Omega$ cm) implies either that the resistivity does not follow the T^2 "law" at low temperature or that phonons susceptible to phonon-electron scattering contribute significantly to the chain thermal conductivity. It may also be that the

Wiedemann-Franz limit $\kappa_e < L_0\sigma T$ fails for the chains. Indeed, it has recently been shown that the Lorenz number can diverge at low temperature in a 1D interacting electron gas [15]. All this obviously points to the need for a better understanding of the anisotropy of phonon transport in the basal plane and electron transport in the chains.

Empirically, one approach is to tune the ratio of inelastic to elastic scattering in the chains just as was done for κ_a by introducing controlled amounts of impurities that go specifically in the chains, such as Au. An investigation of this kind is currently under way. Just as it was for Zn doping in the planes, a high sensitivity to impurities would be evidence for an electronic origin to the peak in κ_{chain}. This would then imply that the peak in κ_{chain} is due to pair condensation of chain electrons, given that electrons in the chains are more likely to be scattered by other electrons in the chains than by electrons in the planes (the absence of a feature in κ_{chain} at T_c is evidence for weak plane-chain coupling). Now, there is already some indication that the peak in the chain conductivity is highly sensitive to defects. The fact that the additional contribution to κ_b below 60 K was only glimpsed at in the measurements of Yu *et al.*, for which the ratio $\kappa_a(\text{peak})/\kappa_a(T_c)$ is equal to 2.1 [8], while it shows up as a threefold increase in $\kappa_b - \kappa_a$ in our own crystals, where the same ratio is equal to 2.3, suggests that the chain peak is even more sensitive to defects than the plane peak. Indeed, the corresponding ratio for the b axis is, respectively, equal to 1.8 [8] and 2.4.

The issue of sample quality is connected with the crucible used to grow the crystals. In particular, Srikanth *et al.* [5] showed that the microwave feature in the vicinity of 60 K is present only in samples grown in $BaZrO_3$ crucibles (and absent in those prepared in ZrO_2 crucibles). Since microwave measurements probe only a small distance into the sample, this is probably correlated with the established difference in the surface characteristics of $BaZrO_3$-grown crystals. The fact that thermal conductivity probes the entire bulk of a sample might then explain why our measurements detect a chain anomaly in crystals where previous microwave data show no unusual behavior [2,13]. More generally, there is now a clear need for an in-depth comparison of charge and heat transport in $YBa_2Cu_3O_{7-\delta}$.

To conclude, we have observed a pronounced peak in the difference between the thermal conductivities of $YBa_2Cu_3O_{6.9}$ along the b axis (planes + chains) and the a axis (planes only). By analogy with the well-studied, qualitatively similar peak in κ_a, we interpret this feature as a sudden increase in superfluid density at about 55 K. This is in qualitative agreement with recent microwave conductivity data on the superfluid density in twinned crystals [5]. Our results suggest that the additional superfluid growth observed below 60 K is associated with the CuO chains. Theories of chain superconductivity rejected in the past specifically because such a feature had not been observed previously should be revisited, and further theoretical and experimental work to understand the role of electrons and phonons in the anisotropy of transport in the basal plane is called for.

We thank R. Besserling for his help with the experiment, K. Behnia for useful discussions, and D. Bonn for providing us with a crystal grown at UBC for a comparative test. This work was funded by NSERC of Canada, FCAR of Québec, and the Canadian Institute for Advanced Research. L. T. acknowledges the support of the Alfred P. Sloan Foundation.

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