LOW-TEMPERATURE PHOTOTHERMAL MEASUREMENTS OF HIGH-TC SUPERCONDUCTORS


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INTRODUCTION

Thermal conductivity provides important information on the scattering mechanisms in a material. In anisotropic materials, such as the high-temperature superconductors, the thermal conductivity depends on the anisotropy of both the charge carriers and the lattice contribution. The conductivity also depends intimately on the nature of the electron-phonon interactions which are a major source of the scattering. Since the electron-phonon interaction also plays a critical role in the Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity, measurements of the thermal conductivity can provide insight into the superconducting mechanism.

Measurements of the thermal conductivity of polycrystalline YBa$_2$Cu$_3$O$_{7-\delta}$ have shown an abrupt rise of a few percent in the thermal conductivity below the critical temperature ($T_c$) [1-3]. This increase is most likely a result of the reduction in electron-phonon scattering as the electrical carriers freeze into superconducting pairs; once the carriers have paired into the superconducting state, they can no longer transport heat or scatter phonons. Since the heat flow in these materials is predominantly through the lattice, the slight decrease in thermal conductivity due to the loss of the electrical component is more than offset by the enhancement of the lattice component. Thus, unlike the behavior in the metallic superconductors, the total thermal conductivity increases below $T_c$.

A recent analysis by Tewordt and Wölkhausen [4] applying the BCS theory to the electron-scattering-limited thermal conductivity (as originally put forth by Bardeen, Rickayzen, and Tewordt [5]) duplicated the observed measurements. Furthermore, the authors showed that the enhancement could be a useful measure of the electron-phonon coupling constant and the pairing energy, two fundamental microscopic parameters in the BCS theory. For the Y-Ba-Cu-O data published in the literature, the authors estimate a coupling constant of about 0.5, within the weak-coupling range.

The above studies, however, were all conducted on polycrystalline samples since single-crystal specimens are usually unsuitable for bulk measurements due to their small size.
and irregular shape. In polycrystalline materials, the mixed orientation of the crystallites in the ceramic makes it impossible to separate the contributions of conduction along the copper-oxide planes (ab-planes) from that across the planes (c-axis). Since the electrical behavior of these materials is extremely anisotropic (exhibiting two-dimensional superconductivity), it is essential to measure the various contributions individually. According to the explanation above, we should see a strong enhancement along the superconducting Cu-O planes, and very little enhancement in the direction of the c-axis for which the phonon momentum is normal to the superconducting planes and, hence, does not interact strongly with the superconducting pairs.

We have circumvented the size limitation of single-crystal superconductors by using a photothermal system to measure the thermal conductivity on a micron scale. This allows us to measure the conductivity along all three axes of a single specimen. By enclosing the sample in a high-vacuum cryostat, we can conduct these measurements at low temperatures. We present here our results on single-crystal B\textsubscript{2}Ca\textsubscript{2}Sr\textsubscript{2}Cu\textsubscript{2}O\textsubscript{8} materials.

OPTICAL CONFIGURATION

A schematic of the photothermal microscope is shown in Figure 1. The sample is heated periodically by a modulated argon-ion laser beam and the resulting periodically varying temperature profile is measured with a second, diode, laser. By using a microscope objective to focus the two beams, we achieve micron resolution. The physical mechanism which gives rise to our detected signal is the temperature dependence of the reflectivity of these materials (dR/dT); the temperature fluctuation gives rise to a small fluctuation in the intensity of the reflected probe beam. We also tried measuring the temperature by using a beam deflection technique to monitor the thermal expansion of the heated region, but we found that the refractive index effect was stronger. To remove any thermal expansion effects from our signal we underfill the lenses and the photodetector so that the reflected beam is not clipped by any apertures.

The heating and probe beams are normally separated by about 10 \( \mu \text{m} \) on the sample surface, as shown in Figure 2. While this entails a slight loss in resolution, it does allow us
to use the thermal phase, rather than the amplitude, as the source for our measurement. The advantages of using phase are twofold: it allows us to conduct anisotropic measurements since the phase lag depends mainly upon the conductivity in the direction of propagation between the two beams, and, unlike the amplitude, it is independent of the optical properties of the material. For a given separation of $\Delta x$, the phase lag from source to probe is approximately (for a point source)

$$\phi_{\text{thermal}} \equiv \sqrt{\frac{\omega}{2D}} \Delta x$$

where $D$ is the thermal diffusivity in the direction of the separation, and $\omega$ is the modulation frequency. Instead, a full three-dimensional model of the anisotropic heat flow that includes the effects of finite spot size is necessary [6]. Note that we actually measure the thermal diffusivity; to determine the thermal conductivity the heat capacity must also be measured by other means. Since the heat capacity is dominated by the lattice component, it is a relatively smooth function of temperature [7]; therefore errors in this term do not severely effect the relative size of the enhancement.

The ideal spot separation, $\Delta x$, depends on the spot size. If the separation is large, the size and shape of the spots become irrelevant. At very large separations, however, we sacrifice too much signal to $1/t$ decay. In practice, we place the probe at the point where the amplitude has fallen to about 10% of its peak value. For high-$T_c$ superconductors, this corresponds to a separation of about five or six spot widths (i.e. about 10 to 15 $\mu$m) in the high-conductivity direction, and only about two or three spot widths in the poor direction. The spot separation is measured by scanning the two beams across a sharp edge or step in reflectivity (such as a patterned silicon wafer) and recording the reflected intensities as a function of position. The uncertainty in the separation is about 0.5 $\mu$m due to the size of the spots and to jitter in the scanning actuators. Our technique and theory were confirmed by measuring the thermal anisotropy of single-crystal quartz, upon which a 50 $\AA$ layer of titanium was deposited to absorb the heating beam. The conductivities measured along the $a$- and $c$-axes were within a few percent of handbook values.

While we use the phase to infer the conductivity, we can also make use of the photothermal amplitude, or modulated reflectance, signal. The amplitude of our signal depends on $dR/dT$ as well as the thermal properties. Having determined the thermal properties with phase, we can use the amplitude to measure minute changes in the optical reflectivity as the sample is cooled. As we will show below, the reflectivity undergoes striking changes at the superconducting transition.
THE LOW-TEMPERATURE ENVIRONMENT

There are a number of practical issues to address when taking this experiment to low temperatures. The primary concerns are the formation of ice on the sample and the measurement of the ambient temperature. The first problem requires that we build a high-vacuum environment in which to conduct the experiment, the second requires that we use extremely low laser powers to avoid heating the surface by more than a degree or so.

The severity of the ice problem can be appreciated by considering that, at low pressures, ice accumulates on cold surfaces at a rate of $10^{-6} \frac{P}{\text{hour}}$, where $P$ is the pressure in Torr. Since our measurement takes place in a volume only a few microns on the side, it is important to avoid an accumulation of much more than a micron of ice. The experiment takes about 2 or 3 hours to complete, which means we need to obtain pressures in the $10^{-7}$ Torr range, a difficult task for a system that cannot be baked out before each run (to avoid damaging the samples).

We achieved the necessary vacuum conditions with the cryostat shown in Figure 3. The chamber is evacuated by a sorption pump and an ion pump. Both pumps are ideally suited for our needs because they are vibration free and introduce no pumping oils into the environment. Optical access to the sample is provided by a thin window in the vacuum shroud. To minimize the optical distortion of the focused beam we need to make this window as thin as possible. We found that 250 μm-thick sapphire withstands the vacuum and does not affect the spot size of the beams if the lens has an NA of less than 0.3.

The ambient temperature of the sample is measured with a diode thermometer imbedded in the sample mount. To ensure that the surface was within one degree of the bulk, the laser power had to be kept below 10 μW at the sample surface. This results in extremely weak signals, requiring signal integration times of a few seconds.

RESULTS

Our measurements of the thermal conductivity of single crystal Bi$_2$CaSr$_2$Cu$_2$O$_8$ reveal a strong anisotropy at room temperature. Measurements on the a-c face, shown in Figure 4, indicate that when the spots are oriented along the Cu-O planes, a thermal diffusivity of 1.9 mm$^2$/s is obtained. This value is consistent with that measured from the a-b face of the same sample. Using published values for the heat capability, the conductivity is about 3 W/m-K, which is in good agreement with the bulk measurements made on polycrystalline samples. However, when the spots are oriented along the c-axis, the conductivity is only one-sixth of

![Figure 3. High-vacuum cryostat used for low-temperature measurements.](image-url)
that of the Cu-O planes. Note that anisotropy measurement would be extremely difficult using bulk techniques since the crack-free regions are typically only about 20 μm wide.

While this is a large anisotropy for a single-crystal material, part of the anisotropy is due to the extreme difference of the electrical conductivity in the two directions. Using electrical resistivity measurements and the Wiedemann-Franz law, we find that about 40% of the heat is carried by electrons in the Cu-O planes, while the heat conduction along the c-axis is entirely due to phonons. Thus the lattice anisotropy is closer to 3.5 : 1.

The effect of the superconducting transition on the thermal conductivity is shown in Figure 5. The sample is a Bi-Ca-Sr-Cu-O crystal with a transition temperature of 88 K. To measure the temperature dependence of the thermal diffusivity, we fix the beam spacing and the modulation frequency and record the thermal phase lag as a function of temperature. The top trace shows the thermal conductivity of the Cu-O planes. Below $T_c$ we see a large
enhancement. Since this measurement is confined to the direction of superconductivity, the condensation of the carriers should have a strong effect. Very similar results are obtained for other samples from the same batch. However, we have found variations in the size of the enhancement in crystals grown at different times or under different conditions. Thus, it is not yet possible to assign firm values to the electron-phonon coupling constant.

The thermal conductivity along the c-axis (lower curve in Figure 5) shows no enhancement below $T_C$. This is a result of the two-dimensional nature of the superconductivity. Since the charge carriers in the Cu-O planes absorb or emit only the component of phonon momentum that also lies in the Cu-O plane, the transition should have little effect upon the lattice conductivity normal to the plane.

A surprising feature of our data is the apparent onset of the enhancement above $T_C$. The behavior of the photothermal amplitude ($dR/dT$) is even more striking as seen in Figure 6 (the electrical resistivity is plotted as well for comparison). The amplitude clearly begins to change as much as 12K above $T_C$, and then jumps by a factor of three to a peak at the transition temperature. Subsequent examinations of other phases of Bi-Ca-Sr-Cu-O revealed that the location of the peaks coincides with the transition temperature of the material being examined (with the solitary exception of an 80K-phase sample that exhibited a sudden drop in $dR/dT$ at $T_C$ rather than a peak). The fact that the location of the peak changes from sample to sample indicates that it is not an artifact of the environment. Furthermore, the ambient temperature readings were verified by conducting a simultaneous measurement of the electrical resistivity and the photothermal amplitude, which demonstrated that the peak does coincide with the electrical transition.

Current research is underway to determine the source of this high-temperature behavior. A likely cause is thermodynamic fluctuations in the superconducting-carrier wavefunction, $\Psi$. Unlike conventional superconductors which have long coherence lengths (100 to 1000Å) that result in millions of overlapping pairs, the short coherence lengths (~15Å in the Cu-O planes and 2-3Å along the c-axis) and two-dimensional nature of the bismuth materials cause the thermal fluctuations in $\Psi$ to be significant over a large temperature range [8]. Thus even at temperatures many degrees above $T_C$, there is a statistically significant amount of pairing. Such effects have been hypothesized as a reason for curvature in the electrical resistivity and magnetic susceptibility curves immediately above $T_C$ [8,9]. In fact,

![Figure 6](image-url)

Figure 6. Amplitude of the photothermal signal as measured on the a-b face of the 88K-phase Bi-Ca-Sr-Cu-O crystal.
our own resistivity measurements in Figure 6 depart from linear behavior near the same temperatures at which the photothermal amplitude begins to change. We are currently conducting a set of photothermal measurements on samples that exhibit varying degrees of curvature in the magnetic susceptibility to determine if the effects correlate.

CONCLUSION

We have developed a method to measure the full anisotropic thermal conductivity of single-crystal superconductors. The high resolution of our technique allows us to measure specimens as small as a few microns on a side. Our measurements clearly indicate large changes in both the thermal conductivity (along the Cu-O planes) and in the temperature dependence of the reflectivity as the sample is cooled below its transition. With further measurements on a range of samples, we hope to determine the strength of the electron-phonon coupling.

We have also discovered that thermal and optical changes associated with the transition start to appear as much as 10K above \( T_c \). We believe this early onset to be an indication of large thermodynamic fluctuations in the carrier wavefunction. If so, the dramatic changes in our signal, especially in the amplitude, could serve as the basis for a useful probe of these effects.

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REFERENCES