

PHOTOPYROELECTRIC MEASUREMENT OF THE THERMAL DIFFUSIVITY OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ AND $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$

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Thermal diffusivity measurements for superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ are reported over the temperature range from 50 to 300 K. The results were obtained using frequency-modulated time-delay photopyroelectric spectrometry (FM-TDPS), which consists of chirped laser excitation of the sample and detection of the associated impulse by a thin-film pyroelectric detector.

1. INTRODUCTION

Since the discovery of the high- T_c oxide superconductors,¹⁻³ much experimental effort has been expended to understand the physical properties which underlie their high transition temperatures. Several aspects of the thermal properties of these oxide superconductors have recently attracted great interest.⁴ In addition, the thermal parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and other compounds have been reported to exhibit anomalous behavior not only at T_c but also at elevated temperatures in the range from 150 to 250 K, both in ceramic⁵⁻⁹ and in single crystal samples.¹⁰ Our own studies of thermal wave transit times and transport properties^{11,12} in single-crystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ provide support for these observations. In this work we report thermal diffusivity measurements for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (BSCCO); the thermal diffusivity α is functionally dependent on the thermal conductivity κ and the specific heat C_p through the relation $\alpha = \kappa/\rho C_p$, where ρ is the density.

The measurements were made via frequency-modulated time-delay photopyroelectric spectrometry (FM-TDPS), a new alternative to the conventional laser flash method of measuring thermal diffusivity. Although the laser flash method has been the usual method for determining the thermal diffusivity of metals and oxides,¹³ recent studies have shown that fast optical excitation pulses may induce a rapid transition from the superconducting to the normal state in the new high- T_c materials due to nonequilibrium heat flow,¹⁴ which will affect any thermal measurements on the sample. It is thus useful to establish a technique in which this phenomenon does not occur. In FM-TDPS, or the chirped laser technique, the sample is heated by a chirp-modulated *cw* laser, and the associated thermal response detected at the sample back surface by a fast risetime thin-film pyroelectric detector. The thermal impulse response of the sample may then be calculated from the input and output waveforms. Because the fluence of the chirped laser excitation is orders of

magnitude lower than for pulsed lasers, the switching mechanism discussed above does not occur. Solution of the heat conduction equation for the sample-detector system yields a quantitative prediction for the temporal evolution of the induced heat pulse which can be compared to the experimental results, yielding the sample thermal diffusivity.

2. THEORETICAL

2a. Chirp Excitation

In the chirped excitation technique,^{15,16} a *cw* laser is modulated by a fast frequency sweep waveform $x(t)$ before being focussed onto the sample. If the power spectrum $G_{xx}(f)$ of the chirp is relatively flat across its frequency span, in the frequency domain the chirped excitation is equivalent to pulsed excitation. The equivalent pulse, in fact, approaches a Dirac delta function with increasing bandwidth of the chirp. If $y(t)$ is the instantaneous response of the sample to the exciting chirp $x(t)$, the impulse response may then be obtained by Fast Fourier Transform (FFT) and correlation analysis techniques as follows.

The cross spectrum $G_{xy}(f)$ and the input power spectrum $G_{xx}(f)$ are given by

$$G_{xy}(f) = F[x(t)] \times F[y(t)]^* \quad (1a)$$

$$G_{xx}(f) = F[x(t)] \times F[x(t)]^* \quad (1b)$$

where F and F^* indicate the Fourier transform and its complex conjugate, respectively. The impulse response is then obtained from the relation

$$h(t) = F^{-1}[G_{xy}(f)/G_{xx}(f)] \quad (2)$$

As a consequence, the chirped excitation technique yields the equivalent of pulsed excitation, while retaining the advantages of low incident power densities and high source stability inherent in *cw* laser systems.

2b. Pyroelectric Detection

Consider a pyroelectric detector with a thickness d , a pyroelectric coefficient p and a dielectric constant ϵ in contact with the back surface of the sample. The current impulse response of the detector due to heat flow through a sample of thickness l may be obtained by a Green's function treatment,¹⁷ yielding

$$I(t) = \frac{pdA}{\epsilon l^{3/2}} \sum_{n=0}^{\infty} (-1)^n \beta_{32}^n (\tau_{1n}^{1/2} e^{-\tau_{1n}/4t} - 2 \tau_{2n}^{1/2} e^{-\tau_{2n}/4t} + \tau_{3n}^{1/2} e^{-\tau_{3n}/4t}) \quad (3)$$

The thermal coupling coefficients between adjacent layers i and j in the air-sample-detector-backing system (layers 1 to 4, respectively) are given by $\beta_{ij} = (b_{ij} - 1)/$

($b_{ij} + 1$), where $b_{ij} = \kappa_i \alpha_j^{1/2} / \kappa_j \alpha_i^{1/2}$. Here κ_n and α_n are the thermal conductivities and diffusivities of the n th layer. The following definitions have been made:

$$\tau_{1n}^{1/2} = \frac{2nd}{\alpha_3^{1/2}} + \frac{l}{\alpha_2^{1/2}} \tag{4a}$$

$$\tau_{2n}^{1/2} = \frac{(2n + 1)d}{\alpha_3^{1/2}} + \frac{l}{\alpha_2^{1/2}} \tag{4b}$$

$$\tau_{3n}^{1/2} = \frac{2(n + 1)d}{\alpha_3^{1/2}} + \frac{l}{\alpha_2^{1/2}} \tag{4c}$$

and A is a constant incorporating the static thermal properties of the sample-pyroelectric system:

$$A = -\frac{2(\alpha_3 \alpha_2)^{1/2}}{4\sqrt{\pi} \alpha_2 (b_{32} + 1)} \tag{5}$$

Equation (3) was derived under three approximations: a large thermal mismatch at the sample front surface ($b_{12} \ll 1$ or $\beta_{12} \approx -1$); the use of a metal backing for the thin-film pyroelectric detector ($b_{43} \gg 1$ or $\beta_{43} \approx 1$); and a sample that is thermally thick compared to the detector ($\tau_2 \gg \tau_3$, where τ_n is the time for a unit heat impulse to travel through the n th layer; equivalently, $l^2/\alpha_2 \gg d^2/\alpha_3$). All these approximations are valid for our experimental arrangement.

Thermal diffusivity information is readily available from either the peak delay time τ_p or the zero-crossing point τ_0 of the pyroelectric current response.^{18,19} The shape of these current responses depends on the thermal properties of the particular detector considered; for a polyvinylidene fluoride (PVDF) detector, as in our case, $\alpha_3 = 8 \times 10^{-8}$ m²/s and $\kappa_3 = 0.19$ W/m-K for detector thermal diffusivity and conductivity, respectively.²⁰ Using these values in Equation (3), we obtain the curves shown in Figure 1. This shows the theoretical relationship between τ_p and τ_0 and the parameter l^2/α , for the case when $\kappa = 1$ W/m-K. The peak time τ_p is linear with l^2/α , and τ_0 very nearly linear, with correlation coefficient $R > 0.999$.

We should point out that these curves are no longer linear (or valid) for $l \approx 0$, since the theoretical development here is limited to thermally thick samples. Similar to work with thermally thick pyroelectric detectors,²¹ it is found that the τ vs l^2/α curves are identical for all values of κ . The absolute value of the thermal diffusivity may then be calculated using the slopes, through the relations

$$\alpha_p = F_p \frac{l^2}{\tau_p}, \quad \alpha_0 = F_0 \frac{l^2}{\tau_0} \tag{6}$$

where $F_p = 0.08$ and $F_0 = 0.24$; these coefficients are dependent only on the pyroelectric properties of the detector. For a given sample, the thermal diffusivities α_p and α_0 calculated from Equation (6) should correspond to each other, such that $\alpha = \alpha_p = \alpha_0$.

3. RESULTS AND DISCUSSION

The pyroelectric impulse responses were excited with 20 mW incident power from the 488 nm line of an Ar⁺ laser. The cw beam was chirped by an acousto-optic

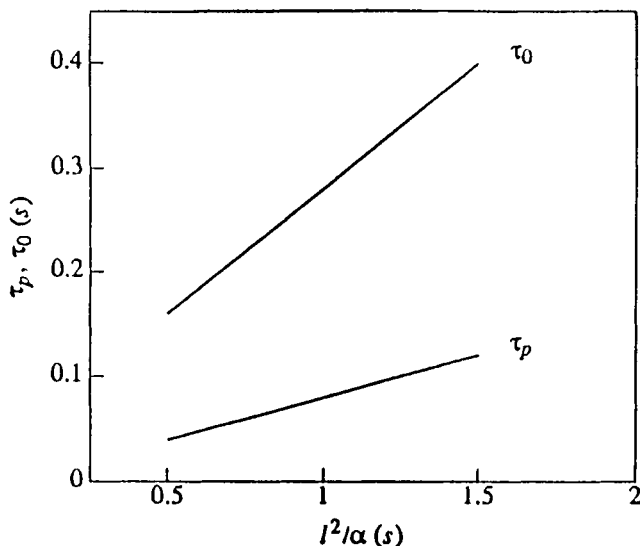


FIGURE 1 Dependence of the peak time τ_p and the zero-crossing time τ_0 on the parameter I^2/α .

modulator driven by a waveform synthesizer before being focussed onto the sample front surface. The driver waveform had a flat power spectrum over the modulation bandwidth (1 to 5 kHz), so that the resulting chirped *cw* laser beam satisfied the criterion for mathematical equivalence to pulsed excitation.

The samples consisted of single-phase YBCO or BSCCO ceramic compounds, prepared by standard solid state reaction of the corresponding binary oxide and carbonate powders: Y_2O_3 , $BaCO_3$ and CuO for the YBCO compounds and Bi_2O_3 , $CaCO_3$, $SrCO_3$ and CuO , for the BSCCO compounds. After mixing and pressing, the mixtures were heated for several hours before being cooled down again to room temperature. The pellets were roughly of size $3 \times 3 \times 1$ mm³, and the presence of the single-phase element was confirmed. The superconducting transition for YBCO was at $T_c = 75$ K and for BSCCO was at $T_c = 81$ K.

Photopyroelectric (PPE) measurements were carried out with the sample and detector housed in a cryogenic system²² with optical access through a vacuum-sealed quartz window. The experimental temperature range was 50 to 300 K, monitored by a gold/iron-constantan thermocouple at the end of a copper cold finger to which the sample/detector holder was also attached. The detector consisted of a 28 μ m PVDF film, surface-metallized with nickel electrodes and supported on a stainless steel backing. The YBCO samples were fixed to the detector by means of a thin thermal compound layer, whose contribution to the PPE signal was negligible above 50 K. It has been shown¹¹ that the response of the thin-film PVDF detector is nominally flat across the entire temperature range, such that the structure of the YBCO response is not affected. This is in contrast to a recent photothermal study²³ which was complicated by the fact that the piezoelectric detector exhibited marked changes in response throughout the temperature range involved. The output of the thin-film detector was fed to a fast current amplifier before being directed to $y(t)$ system input of a Fast Fourier Transform analyzer.

The PPE current response was then recovered by correlation and FFT operations on $x(t)$ and $y(t)$ as discussed above.

Figure 2 shows representative thermal impulse responses at 300 K, 75 K and 50 K for a 964 μm thick YBCO sample, normalized to unity at the peak value. The bandwidth for the chirped laser excitation was 1 kHz, and the responses have been processed by a digital noise filter. The same narrowing of the impulse response at lower temperatures was observed for a 422 μm thick BSCCO sample. The spike in the PPE signal at early times ($<50 \mu\text{s}$) is due to the detector response to light leakage onto the surface of the film. However, the fastest transit time through the

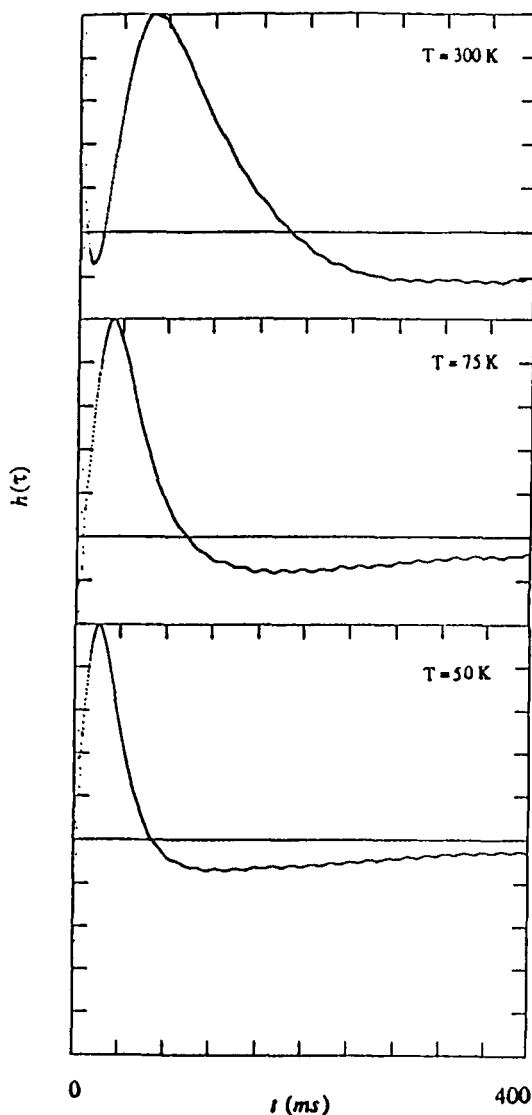


FIGURE 2 Representative impulse responses $h(\tau)$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at $T = 300 \text{ K}$, 75 K and 50 K . Sample thickness was 964 μm ; excitation laser chirped from 0–1 kHz. The responses have been normalized at the peak.

sample is on the order of tens of milliseconds, and so the initial PVDF spike is negligible in our analysis.

The narrowing of the impulse response at lower temperatures is more evident in Figure 3, which shows the behavior of the peak time τ_p and the zero-crossing time τ_0 of the impulse responses throughout the temperature range from 50 to 300 K for YBCO. A similar response was found for BSCCO. Because of the diffusive nature of thermal-wave propagation through the sample, any increase in α leads to a narrowing of the pulse, and a faster arrival of the detected temperature change at the sample back surface. Narrowing of the temperature-time profile also leads to an increase in the amplitude of the signal, which is a reason for the normalization applied in Figure 2. This decrease in τ_p and τ_0 at lower temperatures is thus indicative of a concomitant increase in the thermal diffusivity. The τ_0 curve, furthermore, exhibits a discontinuous jump at T_c ; the jump is also present in the τ_p curve. Note that τ_0 is inversely proportional to α_0 , and thus proportional to C_p/κ . Although both κ and C_p change around the transition temperature, the thermal conductivity change is continuous,^{24,25} and so the fractional jump $\Delta\tau_0/\tau_0$ will be approximately equal to the fractional change in specific heat $\Delta C_p/C_p$. From this relation we may estimate the specific heat jump to be 6% of the total specific heat. This value agrees well with other calorimetric measurements of the specific heat jump²⁶⁻²⁸ in YBCO.

Figure 4 shows the thermal diffusivity for YBCO, calculated from τ_p and τ_0 using Equation (6). The thermal diffusivities calculated using either parameter are in excellent quantitative agreement with each other. The curves consistently exhibit a dip near the transition from the normal to the superconducting state; again, the effect is more pronounced with the α_0 curve, for the same reason discussed above

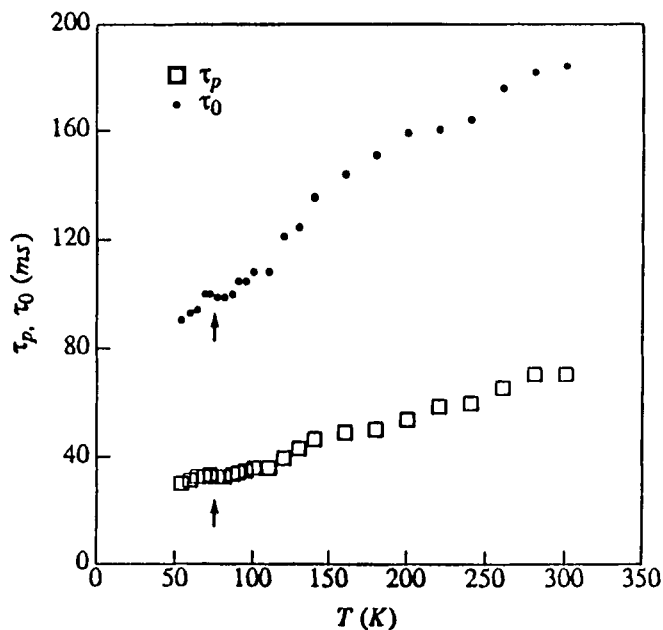


FIGURE 3 Temperature dependence of τ_p and τ_0 for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The arrow indicates the superconducting transition temperature.

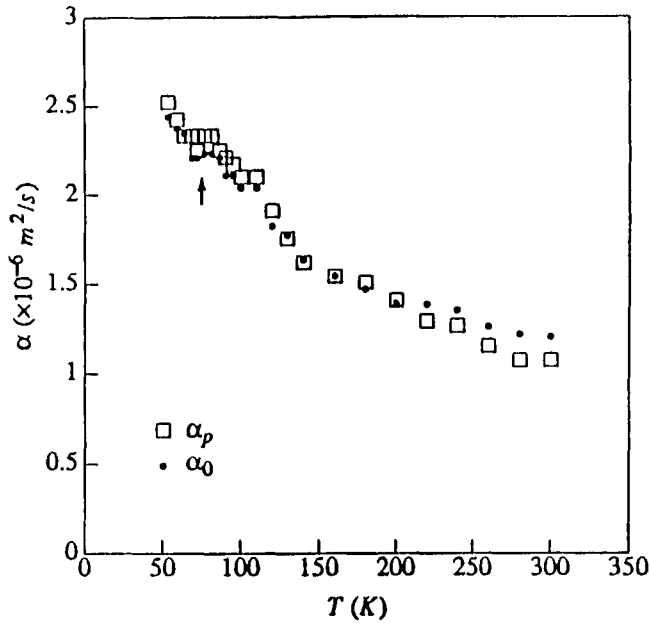


FIGURE 4 Temperature dependence of the thermal diffusivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The arrow indicates the superconducting transition temperature.

for the τ_0 graph. The α vs T profile is in good agreement with data obtained using photoacoustics and laser flash measurements,²⁶ the latter measurements taken with a slow detector, whose response time was much slower than the switching time from the normal to the superconducting state. Our thermal diffusivity values are approximately 25% higher than for the photoacoustic/laser flash measurement; this result is quite good, considering the large spread of thermal parameters for different YBCO samples.²⁹ In the photoacoustic/laser flash measurements themselves, different YBCO samples yielded diffusivity curves with a spread of 25%.

Figure 5 shows the corresponding thermal diffusivity graph for BSCCO. While there has been no previous work on the temperature dependence of α for BSCCO, our thermal diffusivity at 300 K is in excellent agreement with room temperature measurements of the diffusivity of single-crystal BSCCO fibers.^{30,31} Similar to YBCO, the thermal conductivity has been found to change continuously³² around T_c , and so the fractional change in specific heat can again be related to $\Delta\tau_0/\tau_0$. In contrast to the YBCO results, however, we detect no abrupt change in the thermal diffusivity or the τ_0 parameter around T_c ; this puts an upper limit of 1% on the fractional change of the specific heat $\Delta C_p/C_p$ for our sample. The anomalous change in the thermal diffusivity in the 240 K region can be understood if we assume that the BSCCO compounds contain a parasitic concentration of CuO, a precursor in the preparation process. This compound is known to undergo a phase transition, ordering antiferromagnetically in the 200–250 K temperature range.³³ Other previous works have shown that some anomalous behavior in the thermal parameters of the oxide superconductors can be attributed to this and other parasitic compounds^{34,35} such as BaCuO_2 .

In conclusion, we have measured the thermal diffusivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and

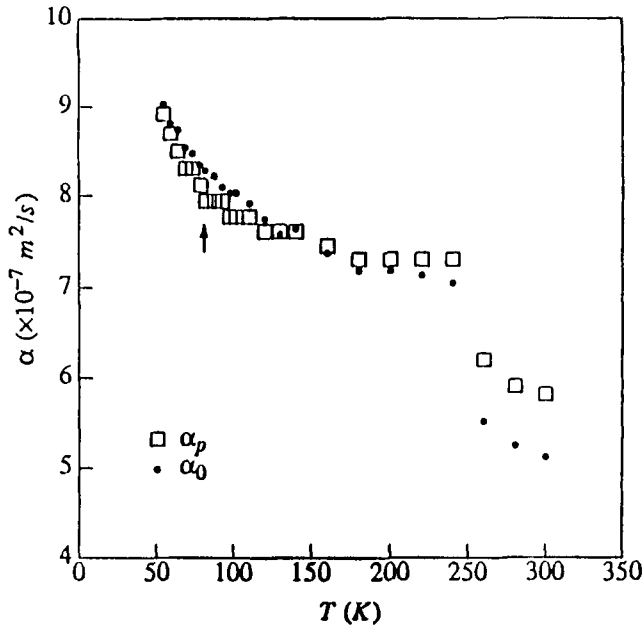


FIGURE 5 Temperature dependence of the thermal diffusivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$. The arrow indicates the superconducting transition temperature.

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ in the temperature range from 50 to 300 K. The techniques of chirped laser excitation and photopyroelectric detection, combined in FM-TDPS, have been shown to give results in excellent agreement with conventional means for measuring the thermal diffusivity.

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