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Thin-film photopyroelectric detection of thermal impulse response of single-crystalline $YBa_2Cu_3O_{7-x}$

I Alex Vitkin†, Samuel B Peralta†, Andreas Mandelis†, Wojciech Sadowski‡ and Eric Walker‡

† Photoacoustic and Photothermal Sciences Laboratory, Department of Mechanical Engineering, and Ontario Laser and Lightwave Research Center, University of Toronto, Toronto, Ontario M5S 1A4, Canada
‡ Department of Condensed Matter Physics, University of Geneva, CH-1211 Geneva 4, Switzerland

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Abstract. Photopyroelectric impulse response measurements carried out on single-crystalline $YBa_2Cu_3O_{7-x}$ are reported over the temperature range from 20 to 300 K. The photopyroelectric signal sensitivity to the superconducting transition is demonstrated; we also detect an increase in the impulse time delay at temperatures above 200 K. The results suggest the applicability of this simple and sensitive thermal wave technique to non-intrusive temperature studies of high-T_c superconductors.

1. Introduction

The recent discoveries of superconductivity in the La–Ba–Cu–O system, with onset around 30 K (Bednorz and Muller 1986), and the Y–Ba–Cu–O system, which has been observed to be superconducting at around 90 K (Wu *et al* 1987, Chu *et al* 1987), have led to a great deal of experimental effort in order to understand the structural and electronic properties which underlie the high transition temperatures in these materials. One research area which is beginning to yield useful information is the study of thermal parameters, particularly of the thermal conductivity, specific heat and thermoelectric power (Morelli *et al* 1987, Bayot *et al* 1987, Uher and Kaiser 1987, Freeman *et al* 1987). Most thermal measurements are accomplished by physically attaching a sensor to the material, an awkward and intrusive contact technique, with long thermal risetimes (seconds). This method has definite disadvantages, especially when one is testing large numbers of small-sized samples. This situation is typical of experimental work in ceramic superconductors at the present time because of the large variability in processing conditions which ultimately affect the characteristics of the sample. There exists, therefore, a need for a measurement method which does not rely on physical attachment of the sensor to the specimen.

The aim of this work is to assess the feasibility of a particular photothermal diagnostic method – that of photopyroelectric detection (Mandelis 1984, Mandelis and Zver 1985, Coufal 1984a, 1986) – to measuring the impulse response of high-T_c superconductor materials to an applied optical heating pulse. In this work we employ the technique of photopyroelectric detection, in which a voltage or current is produced in a thin-film pyroelectric sensor as a result of heat conduction through a sample excited by a laser beam and in intimate contact with the sensor. This experimental arrangement has the advantage of not requiring the troublesome electrode connection to the sample surface; since no additional soldering is required, no thermal perturbations due to the sample-contacting thermistor interface are involved, and sample changes may be readily made.

In this work we report photothermal impulse response measurements on single-crystalline $YBa_2Cu_3O_{7-x}$ heated by a modulated laser beam. Experiments on single crystal samples are important because the results will be minimally affected by polycrystalline effects (grain boundaries, non-stoichiometric phases and so on). Our measurements of the temperature dependence of the delay time of the impulse responses of single-crystal $YBa_2Cu_3O_{7-x}$ show a correlation with the reported temperature dependence of the sample thermal parameters, including the anomaly around the transition temperature, as well as anomalies in the region of 200 K, which is indicative of the potential usefulness of the photopyroelectric impulse response technique in unobtrusively probing transport mechanisms in high-T_c superconductors.

The broadband-modulated CW excitation used here has important advantages over pulsed laser excitation. Pulsed excitation techniques involve high energy fluxes at the sample surface, while the optical damage threshold for the single-crystalline superconductors is quite low.

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The stability of the CW intensity-modulated source is also an important asset. The only requirement for experiments involving broadband-modulated excitation is that the power spectrum of the input, $G_{xx}(f)$, where f is the modulation frequency, be flat (or 'white') relative to the power spectrum of the output $G_{yy}(f)$ (Coufal 1984b, Mandelis 1986). Fast Fourier transform (FFT) (Mandelis 1986, Coufal 1984b, Mandelis *et al* 1986a,b) and correlation analysis techniques (Bendat and Piersol 1980) may then be used to recover the associated impulse response in the time domain, $h(t)$.

The measured pyroelectric output $V(t)$ is essentially a measurement of $h(\tau)$, where τ is a time-delay variable which is a function of the material thickness d, the thermal conductivity k and the thermal diffusivity $\alpha = k/\rho C$, where ρ is the material density and C is the specific heat at constant pressure. In principle, the latter two parameters may be separately deduced from a photopyroelectric impulse response measurement provided that d is known (Power and Mandelis 1987a).

Because the broadband-modulated excitation is equivalent to an impulse, the experiment is analogous to applying a heat pulse at the sample front surface and measuring the diffusion time to the back surface. Intuitively, this diffusion time will be inversely proportional to some function of the sample thermal parameters such as its thermal conductivity and diffusivity. In this regard, measurement of heat-pulse transit times around the phase transition can yield information not only of the order of the transition, but also help understand the interaction between charge carriers and phonons, both of which conduct heat. Ultimately this may shed light on the strength of the carrier-phonon interaction in Y–Ba–Cu–O compounds and the underlying mechanism of superconduction.

2. Instrumentation and experimental methodology

The sample was a single crystal of $YBa_2Cu_3O_{7-x}$ of approximate dimensions $2 \times 2 \times 0.1$ mm^3. The Y–Ba–Cu–O compounds were prepared by mixing Y_2O_3, $BaCO_3$ and CuO in an agate ball mill with acetone added to assist the mixing process. After drying the powder, the mixture underwent a standard procedure: pressing, heating in a furnace for a growth run from room temperature to 1030 °C at a rate of 300 °C h^{-1}, keeping this temperature for 15 h, checking for liquid formation, heating at maximum temperature for another 12 to 15 h, cooling to 925 °C and then separating the grown crystals from residual flux by decanting. Annealing in pure O_2 was carried out after slowly cooling to room temperature: the crystal used in the present work was annealed at a temperature of 485 °C for 84 days. Resistivity and magnetic susceptibility measurements on the resulting crystals showed that the onset of superconductivity occurred at around 76 K, with a transition width (10–90%) of approximately 2.5 K. Additional details of the synthesis process have been presented elsewhere (Sadowski and Scheel 1990).

Figure 1 shows a schematic diagram of the experimental arrangement. The sample was placed in back-contact with a thin pyroelectric detector consisting of a 28 μm film of polyvinylidene fluoride (PVDF), metal-plated with nickel electrodes and supported on a stainless steel backing. The sample was sandwiched between the PVDF film and a transparent front window – thus eliminating the need for soldering of electrical contacts – and then enclosed in an Inficon housing assembly to extract the electrical signal and ensure shielding from RF interference (Coufal and Mandelis 1987). The entire assembly was placed in the experimental chamber of a helium-cooled cryogenic system, with optical access available through a vacuum-sealed quartz window. The operating pressures within the chamber were 10^{-5} to 10^{-3} Torr (about 10^{-3} to 10^{-1} Pa), and temperatures down to 20 K could be attained (Vitkin *et al* 1989). The results reported here were taken as the chamber temperature was increasing at a rate of approximately 2 K min^{-1}.

The excitation source was a CW argon-ion laser operating at 488 nm. The excitation power incident on the sample ranged from 20 to 30 mW. The Ar^+ beam was intensity-modulated by an acousto-optic modulator driven by the internal waveform synthesiser of an FFT analyser. In these experiments we employed a wide-band (0–1 kHz) pseudorandom noise excitation, as it was found to give cleaner signals than the corresponding chirp sweep for the integration time used. The acousto-optic modulator driver source had a 1 V amplitude, which yielded the highest signal-to-noise ratio at 1 kHz, and a flat power spectrum over the modulation bandwidth. The modulated laser beam was then directed through an achromat lens and focused onto the surface of

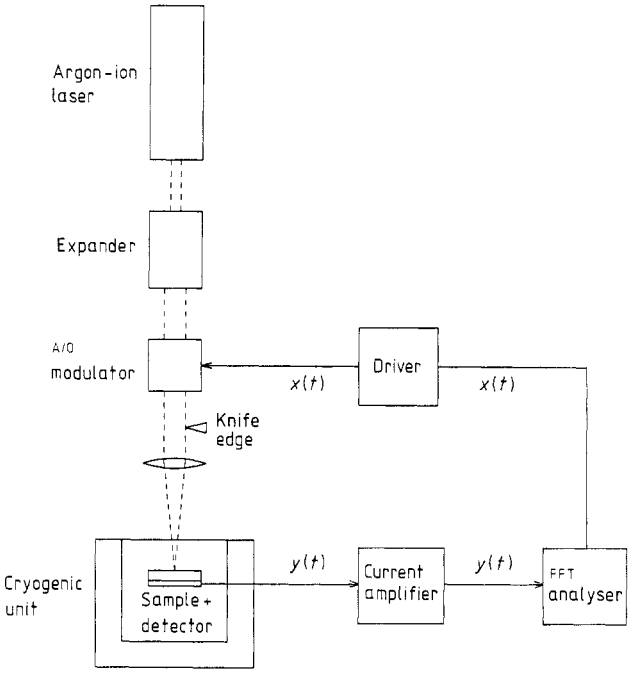

Figure 1. Experimental arrangement for photopyroelectric impulse response system.

the sample. The spot size of the exciting beam was approximately 0.2 mm in diameter.

The output of the photopyroelectric detector was fed to a preamplifier and then directed to the $y(t)$ system input of the FFT analyser, with the waveform synthesiser output used to supply the $x(t)$ waveform. The recovery of all impulse responses was accomplished via the internal correlation and FFT operations of the analyser. A detailed discussion of the signal processing techniques has been presented elsewhere (Power and Mandelis 1987b,c).

3. Results and discussion

In figure 2, we plot the susceptibility of our sample as a function of temperature, obtained using conventional AC susceptibility techniques. From this we estimate the transition temperature T_c to be 74.5 K, with a transition width (10–90%) of 2.5 K.

Figure 3 shows representative photopyroelectric impulse responses $h(\tau)$ at 50, 75 and 285 K. Similarly shaped responses were obtained throughout our temperature range. We can summarise these results by defining a quantity τ_d as the time delay at which the impulse response $h(\tau)$ has decreased to its DC (zero) level. The impulse responses of $YBa_2Cu_3O_{7-x}$ at temperatures from 20 to 300 K can then be summarised as shown in figure 4, where we plot the T dependence of τ_d. The data have been smoothed over two separate heating cycles; the absolute magnitudes of these responses were within 10% of each other except in the temperature range below about 50 K where the scatter was more significant. The corresponding curve for the PVDF detector is also included in the figure; this shows that the structure of the Y–Ba–Cu–O plot is affected only minimally by the PVDF temperature response. A recent photothermal study (Zhang *et al* 1989) on ceramic samples, which uses a piezoelectric detector displaying the same non-contact advantages of our arrangement, was complicated by the fact that the detector exhibited a sudden change in the signal at 200 K, a temperature range where anomalies in the thermal behaviour of the superconductor are also

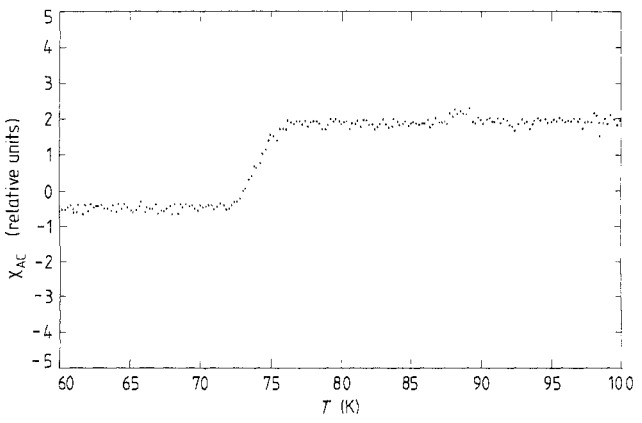

Figure 2. Measurements of AC magnetic susceptibility on single crystal $YBa_2Cu_3O_{7-x}$ sample, $T_c = 74.5 \pm 1.25$ K.

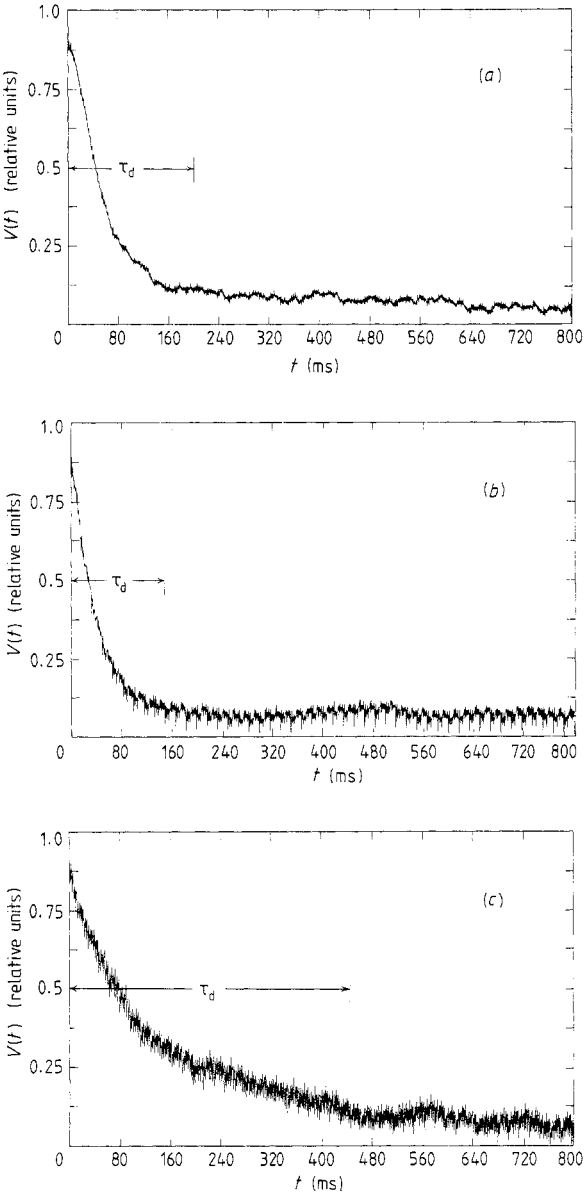

Figure 3. Normalised photopyroelectric impulse response of single crystal $YBa_2Cu_3O_{7-x}$ sample; (*a*) 50 ± 4 K, (*b*) 75 ± 3 K, (*c*) 285 ± 2 K.

observed. This implied a structural change in the detector material itself; this effect is not present in our thin-film PVDF detector.

The $YBa_2Cu_3O_{7-x}$ curves exhibit a decrease in τ_d as the temperature is decreased from 300 K to around 200 K. Below 200 K, τ_d remains nearly constant until T_c is approached, below which the delay time increases. To first order, our measured time delay response follows the previously reported thermal conductivity response in Y–Ba–Cu–O compounds (Morelli *et al.* 1987), Bayot *et al* 1987, Uher and Kaiser 1987, Freeman *et al* 1987). However, the pyroelectric response (as represented by the τ_d parameter) involves *both* the thermal conductivity and thermal diffusivity of the material. Thus the temperature dependence of the specific heat will also contribute to our measured signal. The specific heat of crystalline $YBa_2Cu_3O_{7-x}$ superconductors has been

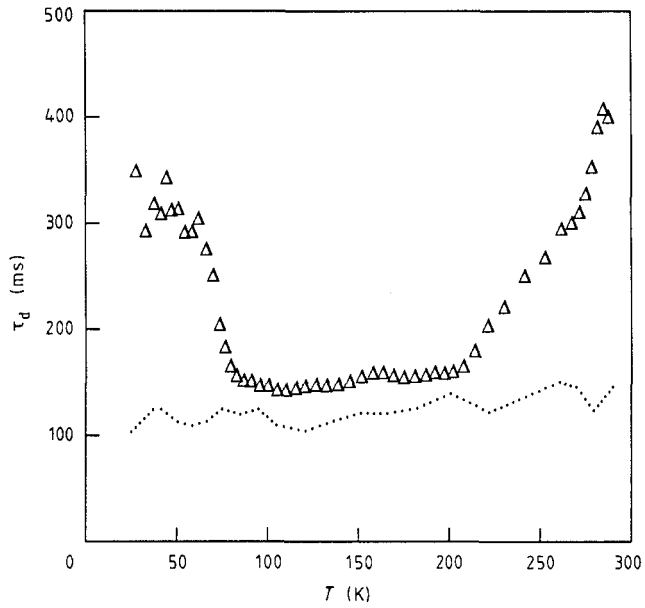

Figure 4. Temperature dependence of impulse-response delay time τ_d, of a single-crystalline $YBa_2Cu_3O_{7-x}$ sample of thickness 100 μm. The data have been smoothed over two separate heating cycles. The dotted curve shows the temperature dependence of τ_d for the PVDF detector, which serves as a reference.

shown to exhibit an anomalous maximum at the critical transition temperature (Fossheim *et al* 1989). Such a behaviour may also explain the results of thermal diffusivity measurements (Gomes *et al* 1988) which exhibit a discontinuity in α at the critical temperature.

The change in the behaviour of τ_d in the 200 K region warrants further discussion. Other experiments have also detected anomalies in the behaviour of the material parameters (specific heat, elastic constants, and so on) of Y–Ba–Cu–O compounds in this temperature range, both in ceramic (Laegreid *et al* 1987, Calemczuk *et al* 1988, Chen *et al* 1987, Almond *et al* 1987, Yening *et al* 1987) and in single crystal samples (Fossheim *et al* 1989, Inderhees *et al* 1988). Some workers contend that these indicate superconductivity at temperatures as high as 240 K, possibly in phases other than $YBa_2Cu_3O_{7-x}$.

The occurrence of a structural phase transition in this temperature range may also explain the impulse response of the superconductor samples. Although our experimentally measured τ_d parameter is dependent on the thermal properties of the sample, the properties themselves are affected by a structural change in the lattice of the compound, thus influencing τ_d near 200 K. This is supported by powder diffraction (Srinivasan *et al* 1988), Raman scattering (Chrzanowski *et al* 1988) and EXAFS measurements (Gygax *et al* 1987), all of which indicate some alteration in the unit cell of $YBa_2Cu_3O_{7-x}$ in this temperature range.

It is also possible that the behaviour near 200 K may be associated with the presence of parasitic compounds, such as $BaCuO_2$ (Kirby *et al* 1987, Liarokapis *et al* 1989), resulting from the preparation process. The present single crystals have been shown to contain $BaCuO_2$ inclusions and may contain CuO inclusions as well (Sadowski and Walker 1990); the latter compound is known to undergo a phase transition, ordering antiferromagnetically in the 200–250 K temperature range (Brockhouse 1954). From these considerations, it is apparent that the role of inclusions must be elucidated further, before a definite interpretation of the $\geqslant 200$ K data may be proposed. For now we simply note that our photopyroelectric measurements are sensitive to the previously observed 200 K anomaly in $YBa_2Cu_3O_{7-x}$.

In conclusion, we have demonstrated the feasibility of applying the photopyroelectric impulse response technique to study the temperature dependent response of a Y–Ba–Cu–O superconductor. Photopyroelectric impulse response measurements of single-crystalline $YBa_2Cu_3O_{7-x}$ over the temperature range from 50 to 300 K show that the technique is sensitive to both the superconducting phase transition at T_c, and to the previously reported anomaly near 200 K. A theoretical investigation of the time evolution of the photothermal impulse response is underway and is expected to yield quantitative information about the sample thermal diffusivity and conductivity. Furthermore, because no electrode connections to the sample are required, the photopyroelectric impulse response technique provides a fast, non-intrusive, sensitive and potentially useful method for evaluating the thermal characteristics of new high-T_c superconductors.

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