Evidence for Two-Component High-Temperature Superconductivity in the Femtosecond Optical Response of $YBa_2Cu_3O_{7-\delta}$

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(Received 13 March 1996; revised manuscript received 11 September 1996)

Femtosecond time-resolved spectrocopy has been used to investigate electronic excitations contributing to the superconducting gap function $\Delta(\omega, T)$ in $YBa_2Cu_3O_{7-\delta}$. The optical response is strongly peaked at 1.5 eV, and contains two distinct components: one with a characteristic relaxation time of $\sim$5 ps, whose amplitude displays a two-fluid-like temperature dependence, and a long-lived component ($>$10 ns) which is consistent with localized quasiparticle states at the Fermi energy. The latter shows activated behavior below T_c with an activation energy $2\Delta_0 \approx 3.5kT_c$. [S0031-9007(97)02434-4]

PACS numbers: 74.72.Bk, 73.50.Gr, 78.47.+p

The microscopic origin of the boson exchange mechanism responsible for electron pairing in high-temperature superconductors remains unresolved, despite numerous investigations during the past ten years or so since their discovery [1]. Existing experimental data support two quite different scenarios in which the charge carriers are either localized polaronic states or extended band-like states, with deviations from canonical Fermi liquid behavior arising from strong anisotropy and damping [2]. In the case of conventional low-temperature superconductors, tunneling spectroscopy in conjunction with Eliashberg theory convincingly demonstrated the fundamental role of electron-phonon interactions, providing a spectral density that closely matches the phonon frequency distribution. With high-temperature superconductors this technique has been limited to energies $\leq$ 200 meV because it has not been possible to fabricate junctions which can sustain substantially higher voltages. This situation has been significantly changed by the recent work of Holcomb *et al.* [3] who have measured the spectral function up to $\sim$5 eV using thermal modulation spectroscopy (TMS). This work found clear evidence of an excitonic contribution to the pairing mechanism with a characteristic energy $\sim$1.5 eV in $YBa_2Cu_3O_{7-\delta}$. A self-consistent Eliashberg analysis gives impressive agreement between the predicted T_c, the calculated gap function $\Delta(\omega, T)$, and the TMS spectra [4].

Guided by these developments, we have investigated the ultrafast dynamical optical response of $YBa_2Cu_3O_{7-\delta}$. Previous studies of carrier dynamics in high-T_c superconductors using degenerate pump/probe spectroscopy have already established that the optical response in the neighborhood of 2 eV is sensitive to the occupancy of quasiparticle states near the Fermi level, and the relaxation rate is reported to be dependent on the magnitude of the energy gap [5–7]. In this Letter we show that the dynamical response at 1.5 eV includes a fast ($\sim$5 ps) component, with a temperature-dependent amplitude which displays two-fluid behavior, and a long-lived ($>$10 ns) component which shows thermally activated behavior below T_c with an activation energy $2\Delta_0 \approx 3.5kT_c$. The dispersion of the fast response over the energy range 0.8–3.0 eV closely follows the behavior of TMS data.

The samples used in this investigation included *c*-oriented films of thickness $\sim$1000 Å, i.e., approximately one absorption length, and crystals with well-developed *a*-*c* and *a*-*b* planes. The optical absorbance measured at 4 K is shown in Fig. 1 for as-grown film, and also for insulating material which had undergone oxygen depletion. The latter shows a sharp charge transfer (CT) transition at $\sim$1.8 eV, with a broad continuum extending to higher energies; it is essentially transparent at energies below the CT gap. In addition to a broad high-energy continuum, the superconducting material shows strong absorption at energies below $\sim$1 eV, which includes contributions from the extended Drude tail. The 1.8 eV CT exciton of the insulating phase disappears on doping and is not present in the superconducting material. In fact, a distinct new feature appears at $\sim$1.5 eV which does not evolve systematically from the 1.8 eV band, and which band structure calculations indicate may arise from chain-to-plane Cu-O transitions [8].

In the present investigation we have measured the dynamical response of the superconducting phase using nondegenerate pump and probe laser beams. The time dependence of the optical reflectance $\mathcal{R}$ and transmission

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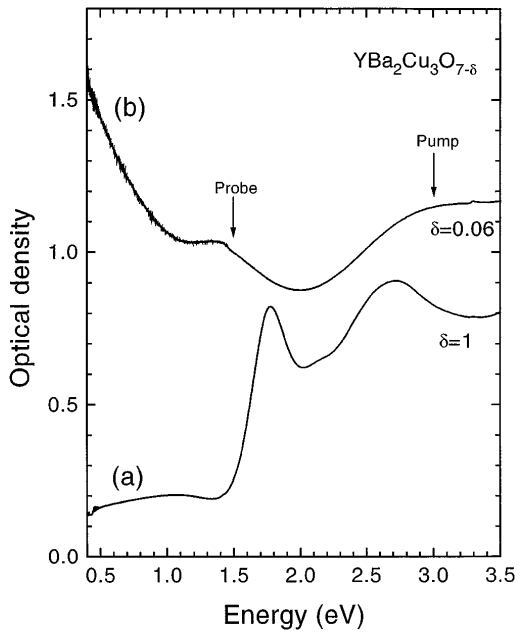

FIG. 1. Optical absorption spectrum of (a) insulating and (b) superconducting thin film $YBa_2Cu_3O_{7-\delta}$ at 4 K. The arrows indicate the energies of pump and probe photons in the time-resolved measurements.

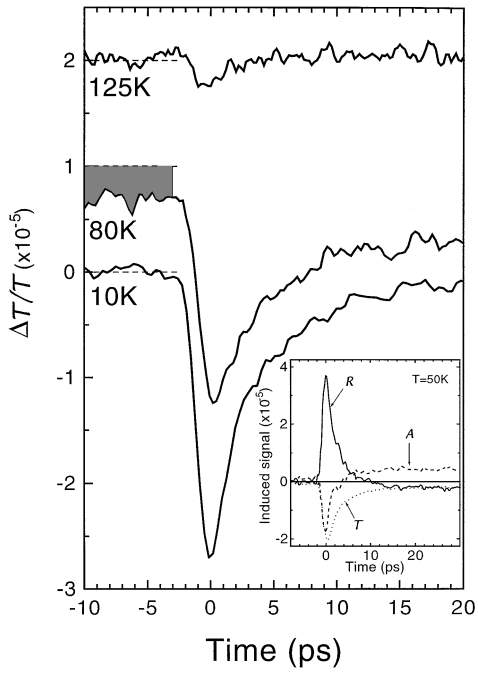

FIG. 2. Time-resolved differential transmittance of $YBa_2Cu_3O_{7-\delta}$ thin film at temperatures above and below T_c. The traces are displaced for clarity of presentation, the broken line indicating the baseline. The inset shows curves for the differential reflectance (solid) and transmittance (dotted) and differential absorption (broken) obtained at 50 K.

$\mathcal{T}$ of $YBa_2Cu_3O_{7-\delta}$ was measured at several energies following photoexcitation at 3.0 eV. The pump beam was the second harmonic of a mode-locked Ti:sapphire laser producing 150 fs pulses at a repetition frequency of 80 MHz. It was focused to a 200 μm diameter spot, with an average power of 60 mW. For the main set of measurements the probe beam was the laser fundamental at 1.5 eV. Measurements were also made at 0.8 eV using an optical parametric oscillator pumped by the Ti:sapphire laser, at 2.0 eV using a colliding pulse mode-locked dye laser, and at 3.0 eV using the frequency-doubled Ti:sapphire laser. We used high-frequency (2 MHz) modulation with phase sensitive detection to provide detection sensitivity of $\sim 10^{-6}$. Group velocity dispersion in the acoustooptic modulator broadened the excitation pulses to $\sim$1 ps. The induced reflectance $\Delta\mathcal{R}$ is highly dependent on the quality of the sample surface and the illumination conditions, (cf. [6,7]), and so we focus attention on transmission measurements of freshly prepared films, using a laser fluence that is more than an order of magnitude lower than that used previously.

Figure 2 presents the temporal evolution of $\Delta\mathcal{T}/\mathcal{T}$ measured at temperatures above and below T_c. In the superconducting phase there is a strongly reduced transmission at low temperature, which has a very fast recovery ($\sim$5 ps). The magnitude of the fast component decreases with increasing temperature, and vanishes above T_c. However, the most remarkable feature of the data, not previously observed, is the emergence of a slow component in the relaxation behavior. Its amplitude is vanishingly small at low temperature, but it increases with increasing temperature towards T_c, and vanishes again in the high-temperature phase. The decay is nonexponential, dropping to half maximum after $\sim$10 ns; this can be seen in the 80 K trace by the presence of a signal at negative time delays, which indicates incomplete relaxation before the arrival of the succeeding laser pulse (12.5 ns).

The inset in Fig. 2 shows the time dependence of the transmitted and reflected power measured simultaneously at 50 K. $\Delta\mathcal{R}/\mathcal{R}$ displays similar two-component relaxational behavior, but clearly changes sign after $\sim$10 ps (cf. [6,7]). The differential absorption $\Delta\mathcal{A}/\mathcal{A}$ derived from $\mathcal{R}$ and $\mathcal{T}$ is shown by the broken curve. This result clearly demonstrates that the fast process gives rise to *increased* reflectance and *decreased* absorption, whereas the slow process corresponds entirely to *increased* absorption. The picture that emerges, therefore, is that of two distinct relaxation processes: a fast relaxation of pump-excited carriers, and excited state absorption involving long-lived metastable states.

The reflectance measurement has the distinct advantage of being applicable to optically thick crystals, and permits the optical response to be probed in different crystallographic directions. The data in fact show a distinct anisotropy. The amplitudes of both the fast and slow components are independent of *pump* polarization, as shown in Fig. 3(a) for $\mathbf{E}_{\text{probe}} \perp \mathbf{c}$. Figure 3(b), on the other

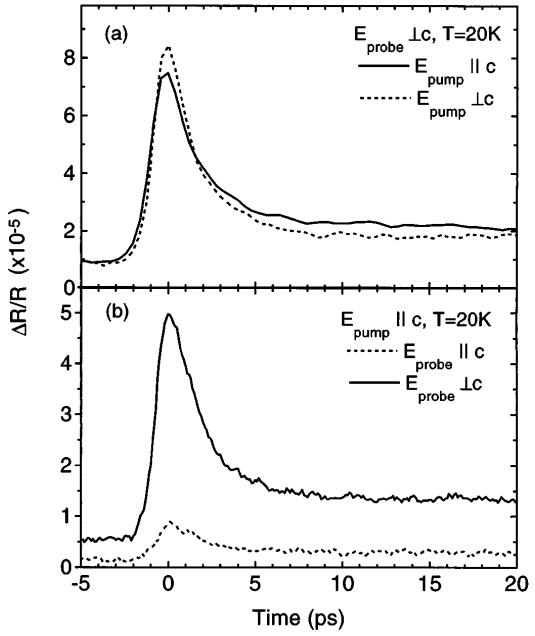

FIG. 3. Anisotropy of the differential reflectance of $YBa_2Cu_3O_{7-\delta}$ crystals measured at 20 K.

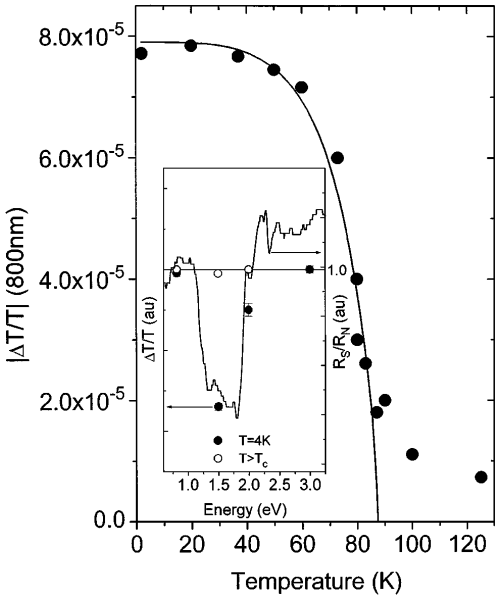

FIG. 4. Temperature dependence of the amplitude of the fast component in the differential transmittance. The solid curve is a fit to the two-fluid model for the gap function $\Delta(\omega, T)$. The inset shows a comparison of the TMS data 3 with the dispersion of the amplitude of the fast signal, measured both above and below T_c.

hand, shows that there is a strong dependence on *probe* polarization: the magnitudes of the differential reflection signals obtained with $\mathbf{E}_{\text{probe}} \perp \mathbf{c}$ and $\mathbf{E}_{\text{probe}} \parallel \mathbf{c}$ are approximately in the ratio of 5:1, which indicates that the states being probed have predominantly in-plane character. The data presented here correspond to $\mathbf{E}_{\text{pump}} \parallel \mathbf{c}$, but similar results are obtained with $\mathbf{E}_{\text{pump}} \perp \mathbf{c}$. The lack of dependence on pump polarization is most likely due to ultrafast dephasing by carrier-carrier and carrier-phonon scattering.

The temperature dependence of the fast component in $\Delta\mathcal{T}/\mathcal{T}$ is shown in Fig. 4. At 4 K the amplitude is $\approx 8 \times 10^{-5}$; on raising the temperature there is initially a slow decrease, but closer to $T_c \sim 87$ K it drops rapidly to a low background level. The solid curve shows that the functional form of temperature dependence closely follows the behavior of the BCS gap function $\Delta_{\text{BCS}}(T)$. This result indicates that the induced optical response is proportional to the energy gap, either through the optical matrix element or through the density of available states. The decay rate is relatively temperature independent below T_c with a value of $\approx 0.2\ \text{ps}^{-1}$; however, the presence of both fast and slow components of similar amplitudes at temperatures close to T_c does not allow us to measure the decay rate near the transition. The inset in Fig. 4 compares the amplitude of the signal measured at different energies, both above and below T_c, with the TMS results of Holcomb *et al.* [3]. This result demonstrates that the dynamical optical response peaks at 1.5 eV and has dispersion very similar to the TMS data.

In the early stage of photoexcited carrier relaxation paired hole states will necessarily be broken, resulting in an increased occupancy of quasiparticle states within an energy $\sim\Delta$ of the Fermi level, and the superconducting gap is thereby reduced. If the pair breaking is sufficiently strong, the illuminated volume can be driven normal, in which case the differential response is determined by the difference between the response of the superconductor (at a given temperature) and that of the normal phase. Han *et al.* [7] have suggested that the optical response is modified at frequencies above Δ, extending to 2 eV, via the Drude term in the conductivity. The TMS data of Holcomb *et al.* [3] do not support this contention, but show rather that the modified response at 1.5 eV is explained via Eliashberg theory by an excitonic contribution to the pairing mechanism.

The slow component, on the other hand, shows dramatically different temperature dependence. Its magnitude increases with increasing temperature until close to T_c, where it drops rapidly to zero (Fig. 5). The amplitude, in fact, follows activated behavior of the form $\Delta\mathcal{T}/\mathcal{T} \propto \exp(-2\Delta_0/kT)$, as shown by the solid curve. This signal therefore appears to arise from excited state absorption where, remarkably, the excited state population depends on cross-gap excitation. This behavior is distinctly different from the bolometric response which has been reported for high laser fluence by Han *et al.* [7]. Laser heating would be expected to produce an induced absorption which increases monotonically with increasing sample temperature, and cannot account for the rapid decrease in signal observed at T_c. We have also investigated freestanding films and films deposited on

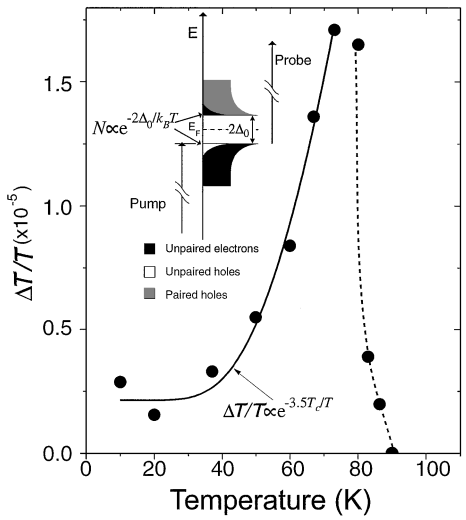

FIG. 5. Temperature dependence of the amplitude of the slow component in the differential transmittance. The solid curve is a fit to the data for thermally activated behavior. The broken curve is a guide to the eye, indicating the rapid decrease in the signal near T_c. The inset shows pump and probe optical transitions which can account for this behavior.

substrates, and bulk crystals—all with quite different thermal properties—but they display the same long-lived effect. Furthermore, the amplitude of the signal increases linearly with increasing laser power, and there is no evidence of "hot spot" formation. Finally, modeling of laser heating using published heat capacity and optical absorption data shows that the size of the effect and the temporal behavior are quite different from the experimental results. The long-lived effect is therefore electronic in origin.

The inset in Fig. 5 gives a schematic representation of states in the neighborhood of E_F, together with proposed optical transitions which can account for the observed behavior. It shows paired hole states, together with strongly peaked densities of unpaired electron and hole densities of states at energies close to the gap which are partially occupied at $T > 0$. Clearly, single electron transitions involving unpaired electron states cannot occur. However, the optical transitions indicated in Fig. 5 will display the observed behavior. The pump beam excites electrons from lower energy states within the valence band into unpaired hole states near E_F, and the probe beam excites this population to strongly nested plane or chain states lying 1.5 eV higher in energy. The induced absorption then depends on the density of unpaired hole states, which is thermally activated. The theoretical fit to the data gives a value for $2\Delta_0 \approx 3.5kT_c$, which corresponds to weak coupling BCS theory. The strong decrease in signal observed close to T_c can be understood as arising from the rapid decrease in the density of unpaired hole states close to the gap as the system reverts to normal Fermi liquid behavior.

Identification of the electronic processes probed in the optical spectrum is crucial for a microscopic understanding to be reached. Local-density approximation (LDA) band structure calculations yield densities of states and optical matrix elements which indicate that the main transition in $YBa_2Cu_3O_{7-\delta}$ at 1.5 eV is between Cu-O in-plane initial states and Cu-O chain final states [8], which is consistent with our polarization data. The two-fluid behavior of the fast component of the optical response, together with the TMS data, shows that these states are intimately involved in the pairing mechanism, and it will be important to evaluate the magnitude of this charge transfer contribution in theoretical models. The extremely long lifetime of the slow component is strongly indicative that the states may in fact be localized. Band structure calculations also show that there is a flat dispersionless band of states near E_F along the Y direction of the Brillouin zone: they are well known in angle-resolved photoemission emission measurements where they appear as an extended van Hove singularity [2]. The LDA calculations also show that optical transitions between the van Hove band and the chain bands have a large joint density of states and a significant matrix element at the probe energy of 1.5 eV, and should be polarized predominantly with $\mathbf{E} \parallel \mathbf{b}$. The issue of *s*-wave versus *d*-wave coupling might also be investigated by measuring the in-plane anisotropy of the optical response: the amplitude of the response and the activation energy should display anisotropy characteristic of the symmetry of the coupling mechanism. These experiments require polarization measurements of untwinned single crystals.

We acknowledge valuable comments from T. Mertelj, C. Ambrosch-Draxl, and K. A. Müller. This work was supported in part by the EU through the ULTRAFAST Network CHRXCT93-0133, and CIPA-CT93-0076.

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