PHYSICAL REVIEW B VOLUME 46, NUMBER 21 1 DECEMBER 1992-I

Fermi-level dependence of femtosecond response in nonequilibrium high-T_c superconductors

D. H. Reitze, A. M. Weiner, A. Inam, and S. Etemad
Bell Communications Research, Red Bank, New Jersey 07701
(Received 26 June 1992; revised manuscript received 28 August 1992)

We have investigated the temperature dependence of the femtosecond optical reflectivity response, ΔR, in the superconducting series $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ as a function of Pr concentration, x. The sign of ΔR changes with the onset of superconductivity for all samples; in the superconducting state, the sign of ΔR changes as a function of x. Systematic analysis of these results demonstrates that the observed ultrafast optical response does not follow a simple two-fluid model, suggesting that the details of the electronic band structure significantly influence the magnitude and sign of the optical response.

Interest in the ultrafast optical response of high-T_c superconductors was initially motivated by the desire to obtain a measure of the electron-phonon coupling constant, λ,[1] using the rate of relaxation of hot electrons in the normal state.[2] More recently, considerable excitement has been generated by experiments which have investigated the ultrafast optical response near and below the superconducting transition temperature in these systems.[3-6] In particular, it has been found that the differential reflectance (ΔR) in $YBa_2Cu_3O_{7-\delta}$ (YBCO) reverses sign at the transition temperature T_c from a positive ΔR ($+\Delta R$) in the normal state to a negative ΔR ($-\Delta R$) in the superconducting state.[4,5] The observed correlation of the sign change of ΔR, measured at ~ 2 eV, with the onset of superconductivity has been interpreted as a direct measure of the dynamics of quasiparticles[4] and/or the order parameter[5] in high-T_c materials. Moreover, the temperature independence of the sign of ΔR in nonsuperconducting isomorphs, such as $PrBa_2Cu_3O_{7-\delta}$, has been used to confirm this assignment.[4]

The rapid, transient, $+\Delta R$ in *the normal state* has been interpreted as monitoring the change in the electronic Fermi-Dirac distribution caused by the absorption of the pump pulse which heats the carriers and induces a shift of the occupied electronic state from below to above E_F.[7] The sign of this signal depends on the position of the Fermi level with respect to the probe photon energy.[8] For example, in a thick film, the probe would detect a $-\Delta R$ ($+\Delta R$) for energies above (below) E_F. On the other hand, *in the superconducting state* of YBCO, the opposite, $-\Delta R$ signal has been interpreted in terms of a partial restoration of oscillator strength from the condensate into the superconducting energy gap. Within this picture, the complex conductivity of the condensate, given by $\sigma(\omega)=\delta(\omega)$ is restored to the $\sigma(\omega)$ of Drude carriers with a finite scattering rate of τ_n^{-1}, which has nonvanishing strength at optical frequencies. The relaxation time of the signal in the superconducting state has been assigned to the ultrafast recombination of photogenerated quasiparticles in the context of a simple, two-fluid model.[4]

Nevertheless, several key issues remain unresolved, including the exact origin of the optical response (be it quasiparticles and/or order parameter dynamics), the role of heating during femtosecond excitation, and the influence of sample quality upon the femtosecond optical response. In this paper, we present a systematic study of the femtosecond response in the isostructural series of epitaxial films based on $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ (Pr_xY_{1-x}BCO) in an attempt to answer these questions. As demonstrated in Hall effect,[9] resistivity and thermopower,[10] and x-ray photoemission spectroscopy[11] measurements on Pr_xY_{1-x}BCO, the incorporation of Pr into YBCO is consistent with a band-filling model in which free carriers are localized and/or removed from the Cu-O planes, resulting in both a change of the position of the Fermi level and a reduced T_c. Although alternative explanations based on magnetic-impurity pair breaking have been put forth,[12] room-temperature femtosecond reflectivity measurements,[8] which our measurements generalize and extend into the superconducting state, support the band-filling model. In particular, they have shown that increasing the Pr content moves E_F upward, enabling a fixed wavelength, 2-eV probe pulse to access optical transitions slightly below ($x=0.0$), very near ($x=0.1$), or slightly above ($x=0.25$) the Fermi level. Thus, in these films we have been able to study the effect of changing both the Fermi level and T_c on the temperature dependence of the femtosecond response without resorting to high-intensity excitation and continuum probing,[6] thus avoiding the deleterious effects of large transient temperature increases. Our quantitative analysis of these results questions the validity of the simplified picture of the femtosecond dynamics of the optical response solely in terms of the quasiparticle lifetime within the context of the two-fluid model.

The samples used in our studies are epitaxial, single-crystal films of various thicknesses (from 1400 to ~ 5000 Å) grown by the pulsed-laser ablation technique[13] on $LaAlO_3$ and MgO. Most films have a transition width $\Delta T_c < 0.5$ K, with the worst having a ΔT_c of 2 K, as measured by an ac susceptibility technique, and an ion channeling yield of $\sim 3\%$, which is comparable to that of single crystals, evidencing the high quality of the films. Their transition temperature varies with the Pr fraction, x, in Pr_xY_{1-x}BCO; typically $T_c=91,81$, and 62 K for

$x=0$, 0.10, and 0.25, respectively. The samples have been cooled using a Janis flow-through cold-finger cryostat, and their transition temperature has been monitored *in situ* by measuring their resistance. We note that earlier femtosecond optical studies were conducted on samples with $\Delta T_c \geq 2$ K. As discussed in more detail below, we have found that the femtosecond response depends sensitively on the transition width.

Our measurements use a colliding pulse mode-locked laser system operating at 620 nm which produces a 125-MHz train of 60 fsec, 20-pJ pulses. The beam is focused at near normal incidence to a spot size of about 30 μm in diameter on the surface of the superconducting films. The pump and probe are orthogonally polarized to reduce scattering of pump into the detector, and the pump is chopped for phase sensitive detection with detection capability approaching 10^{-6}. Pump fluences are maintained at 3 μJ/cm^2 or less, and the ratio of pump to probe pulse energy is 10:1. The fluence dependence of the signal was checked by attenuating the pump beam and runs were performed in different regions of the sample to check uniformity. In all cases, we found no difference in the temporal response of the signals. In order to assess the magnitude of laser-induced heating in our samples, the pump-induced rise in the temperature of the films has been quantified using the bolometeric response near T_c of a pattered YBCO bridge of width less than the beam spot. A maximum rise of ~ 6 K in film temperature associated with KHz rate chopping of the pulse train was measured for our focusing conditions, and we estimate a 0.02-K transient rise caused by individual pulses based on the measured thermal properties of YBCO,[14] comparable to estimates in other degenerate pump-probe experiments.[3,4,5]

In Fig. 1, we compare the temperature dependence of the reflectivity response from two optically thick (5000 Å) *superconducting films;* a YBCO film with $T_c=90$ K and a $Pr_{0.25}Y_{0.75}$ BCO film with $T_c=62$ K. The absolute values of the differential reflectivity at the lowest temperatures are typically on the order of 7×10^{-4}, consistent with other studies.[4,5] Qualitatively, both films have similar dynamics; a pulsewidth limited feature at $\Delta t=0$, followed by a fast, resolvable turnon of the superconducting response and subsequent relaxation back to equilibrium. The striking feature, however, is the behavior of the $Pr_{0.25}Y_{0.75}$BCO film, in which *the sign of* ΔR *is reversed to that of the YBCO film.* As we discuss below, the polarity reversal of ΔR is inconsistent with a simple two-fluid model, which predicts that the sign of the transient response of the reflectance due to conversion of superconducting to normal carriers is independent of Pr doping. The other significant feature of our data is that for all doping fractions x, *the polarity of* ΔR *changes sign in the vicinity of* T_c. The sign flip of ΔR at T_c has been observed for YBCO, as documented in previous works.[4,5,6,8] We note that these optical signatures are typical of all samples studied. Above T_c, a fast reflectivity transient of opposite sign is observed. This response continues as the temperature is increased. At room temperature, we observe differential reflectivities consistent both in sign, magnitude, and temporal dependence with earlier studies.[1,8]

In Fig. 2 we show the variation in the femtosecond relaxation time in the superconducting state, τ_s, below T_c and in the normal state, τ_n, above T_c as a function of reduced temperature T/T_c for the films in Fig. 1, as well as two other YBCO films, sample II (1400 Å, $T_c=92$ K, $\Delta T_c=0.25$ K) and sample III (1560 Å, $T_c=89$ K, $\Delta T_c=2.0$ K), as well as a $Pr_{0.1}Y_{0.9}$BCO (1400 Å, $T_c=81$ K, $\Delta T_c=0.5$ K) film. These points were obtained by fitting the observed reflectivity changes phenomenologically to an impulse response function given by $G(t)=A[1-\exp(-t/\tau_g)]\exp(-t/\tau_s)-B\exp(-t/\tau_n)$ convolved with the measured pulse autocorrelation function. Here $\tau_{g,s,n}$ are the generation (g) and relaxation times of the reflectivity signal in the superconducting (s) and normal state (n), respectively. A typical example of these fits is shown in the inset in Fig. 2. For all cases except sample II, the fit errors were less than 3%. The time constants obtained from the data for sample II overestimated the actual response times by as much as 10%, as the data could not be cleanly fit by a simple exponential decay. In all cases, we find a tendency for τ_s to the

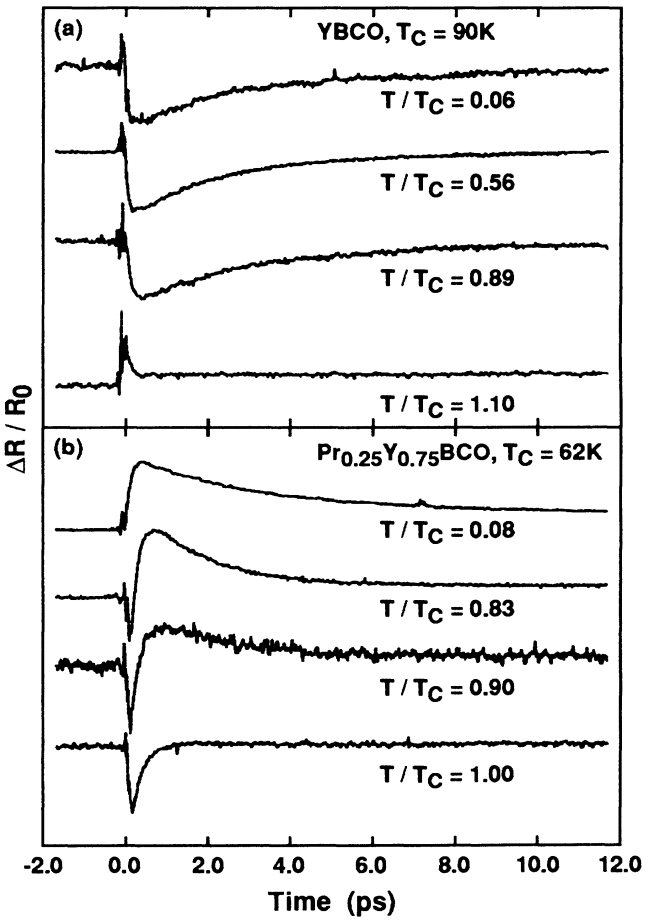

FIG. 1. The temperature dependence (displayed as reduced temperature T/T_c) of the transient reflectivity response of 5000 Å YBCO sample I ($T_c=90$ K) and 5000 Å $Pr_{0.25}Y_{0.75}$BCO ($T_c=62$ K). The curves are normalized and offset for clarity.

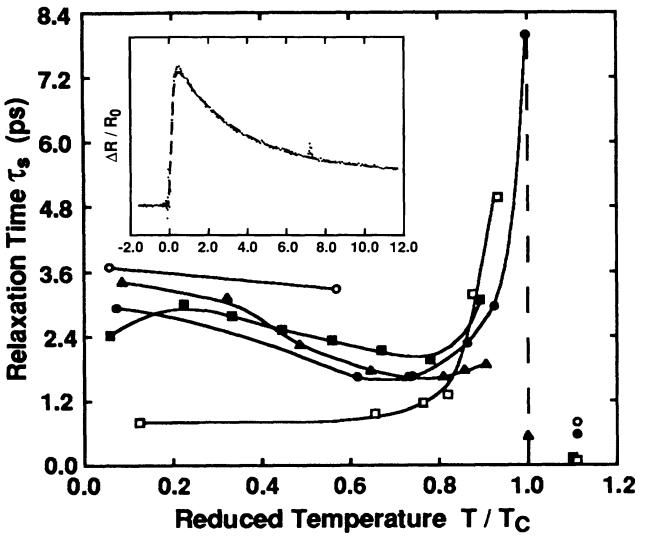

FIG. 2. The relaxation times τ_s (below T_c) and τ_n (above T_c) plotted as a function of reduced temperature T/T_c for the films of Fig. 1, YBCO sample I, $T_c=90$ K (■), and $Pr_{0.25}Y_{0.75}BCO$, $T_c=62$ K (▲), as well as YBCO sample II, $T_c=92$ K (□), YBCO sample III, $T_c=89$ K (○), and $Pr_{0.1}Y_{0.9}BCO$, $T_c=81$ K (●). The solid lines are guides to the eye. Inset: Typical example of the fits used to obtain τ_s and τ_n.

"diverge" near T_c, an observation that has been explained previously in terms of the decrease of the superconducting order parameter.[5]

Identifying the origin of the femtosecond response at *optical frequencies* is imperative to understanding the underlying physics. What makes this task difficult, however, is the fact that the redistribution of the free carrier oscillator strength associated with the onset of superconductivity occurs in the energy range well below the optical frequencies, even though a 2-eV probe directly accesses optical transitions near E_F, where a gap is expected to open. Although a strong correlation of the relaxation time with the onset of superconductivity is clear in our systematic study of the $Pr_xY_{1-x}BCO$ series, our data present three new lines of evidence which demonstrate that the simple two-fluid model is inadequate to explain the observed responses and that τ_s should not be assigned as a *direct* measurement of quasiparticle lifetimes in these measurements.

First, we consider the magnitude of $\Delta R/R$ measured in our experiments. Within the simple two-fluid model, the dielectric response at optical frequencies due to the creation of quasiparticles can be written as

$$\varepsilon_1(\omega)\approx\varepsilon_1+\frac{\omega_p^2}{\omega^2}\frac{\Delta f}{\omega^2\tau^2}\ ,\quad \varepsilon_2(\omega)\approx\varepsilon_2+\frac{\omega_p^2}{\omega^2}\frac{\Delta f}{\omega\tau}\ , \qquad (1)$$

where $\varepsilon_1=3.4$ and $\varepsilon_2=2.2$ are the the high-frequency dielectric background at 2 eV,[15] Δf is the number fraction of photogenerated quasiparticles, ω_p is the plasma frequency, and $1/\tau$ is the scattering rate of Drude carriers. For the samples used in our measurements, the plasma frequency $\omega_p(\sim 8000\ \mathrm{cm}^{-1})$ and scattering rate $1/\tau(\sim 100\ \mathrm{cm}^{-1})$ have been measured near the transition temperature using infrared spectroscopy.[16] For our excitation fluences, we find that $\Delta f\approx 0.01$ and that the shift of oscillator from the $\sigma(\omega=0)$ condensate into a Drude absorption of free carriers results in $\Delta\varepsilon_2\sim 10^{-4}$, $\Delta\varepsilon_1\sim 10^{-6}$. These are the same as the estimates of Han *et al.*[4] whose experiment used comparable fluence. While estimating $\Delta R/R$ is in general complicated for thin films, in the thick-film limit where significant absorption suppresses multiple reflections ($d>3000$ Å), the differential reflectivity is given by $\Delta R/R=4\,\mathrm{Re}[(\Delta n+i\Delta k)/(\varepsilon+1)]$ which yields a change in reflectivity of $\Delta R/R\approx 4\times 10^{-5}$, over one order of magnitude less than the experimentally measured $\Delta R/R\approx 7\times 10^{-4}$ observed in our data.

Second, we consider the sign of $\Delta R/R$ in the superconducting state in our measurements. Experimentally, we observe a positive $\Delta R/R$ in the superconducting state for $Pr_{0.25}Y_{0.75}BCO$ and a negative $\Delta R/R$ for YBCO. However, the above calculation results in the *sign* of $\Delta R/R$ being fixed and positive, contrary to experimental observations. Moreover, we have examined the effect of Pr incorporation on the sign and magnitude of $\Delta R/R$ in the two-fluid model by treating ε_1 and ε_2 as adjustable parameters in the above calculation to account for changes in the dielectric response as the Pr-doping fraction increases. We also examined the effect of varying the probe frequency ω. In the range $3.2<\varepsilon_1<3.5$, $2.0<\varepsilon_2<2.4$, and $1.8<h\omega<2.2$ eV (these limits overestimate the change in dielectric response based on linear reflectivity measurements of these materials), we find that $\Delta R/R$ maintains a positive sign and magnitudes of $\sim 10^{-5}$. Thus, simple redistribution of oscillator strength in a two-fluid model is insufficient to explain both the magnitude and the change in sign of $\Delta R/R$ of $Pr_xY_{1-x}BCO$ as a function of x in the superconducting state. We do not rule out the possibility that laser generation and subsequent recombination of quasiparticles is linked to the femtosecond response. However, the large values of the experimentally measured $\Delta R/R$ suggest that a redistribution of oscillator strength at optical frequencies, not simply the total number of quasiparticles and Cooper pairs associated with a two-fluid model dynamics associated with a simple two-fluid model, is the origin of the observed response. A more detailed picture considering the intrinsic structure of the energy bands accessed by the 2-eV laser probe and the energy distribution functions of electron and hole quasiparticles and Cooper pairs is necessary to fully explain the results of these measurements below T_c.

Finally, we examine the dependence of the relaxation time τ_s with Pr doping fraction displayed in Fig. 2. Note that there is a wide variation in the magnitude of τ_s within YBCO samples at temperatures below $T/T_c=0.7$, where τ_s is relatively insensitive to temperature. In addition, the abruptness of the divergence near T_c differs from sample to sample. Although this may be partially attributable to average heating (~ 6 K temperature rise), it is also influenced by intrinsic sample characteristics, since the measured responses are fluence independent in the range 0.75–3.0 μJ/cm^2. Most significantly, the superconducting component of sample III had completely

disappeared well below T_c, at $T/T_c=0.91$. Nevertheless, the difference in T_c between the best sample (II) and the worst sample (III) was only 3 K, and the width of the transition ΔT_c for sample III was only 2 K. Therefore, the assignment of any physical meaning to measured relaxation times is at best qualitative in these experiments unless care is taken to accurately characterize sample quality.

For the series $Pr_xY_{1-x}BCO$ ($x=0,0.1,0.25$) with comparable ΔT_c's and thus of *comparable* quality, we find that τ_s decreases with decreasing T_c (or, equivalently, increasing Pr content) for temperatures near T_c. However, for a BCS superconductor near T_c, where the number of photogenerated quasiparticles δN_{qp} is a small fraction of the thermal quasiparticle background, Kaplan *et al.* have calculated the temperature dependence of quasiparticle lifetimes,[17] and predicts that, for a fixed T/T_c, quasiparticle lifetimes should *increase* with decreasing T_c. This scaling is not significantly altered after taking into account the lifetime enhancement due to the phonon trapping factor,[18] $\tau_{qp,eff}=\tau_\gamma+\tau_{qp}(1+\tau_\gamma/\tau_B)$, where $\tau_{qp,eff}$ is the measured lifetime, τ_γ is the phonon lifetime (with contributions from phonon scattering and diffusion), τ_{qp} is the intrinsic quasiparticle lifetime, and τ_B is the time it takes to break Cooper pairs. We cite two possibilities for such behavior. First, as noted above, the effects of band structure are neglected in this model. For different doping concentrations, a 2-eV laser pulse is probing different positions in the energy bands. Thus, it monitors not only the generation and recombination of quasiparticles, but also the position and relaxation of quasiparticles at localized energy states within the bands. Second, the BCS theory may not adequately describe superconductivity in these materials, and, in particular, nonequilibrium superconductivity.

Note added in proof. Tsuei *et al.* have recently investigated the specific-heat discontinuity at T_c in $YBa_2Cu_3O_{7-\delta}$ to show that the energy dependence of the density of states is dominated by a sharp peak (two-dimensional van Hove singularity) lying near the Fermi level for small δ.[19] The presence of such a peak in the density of states would sensitively influence the transient optical response for wavelengths which access states near the Fermi level.

We thank G. Eesley, M. Johnson, P. Allen, G. Focht, T. Gong, F. Gao, and C. Levey for insightful discussions and K. Luther-Myers for technical assistance.

[1]S. D. Brorson, A. Kazeroonian, D. W. Face, T. K. Cheng, G. L. Doll, M. S. Dresselhaus, G. Dresselhaus, E. P. Ippen, T. Venkatesan, X. D. Wu, and A. Inam, Solid State Commun. **74**, 1305 (1990).

[2]P. B. Allen, Phys. Rev. Lett. **59**, 1460 (1987).

[3]J. Chwalek, C. Uher, J. F. Whitaker, G. A. Mourou, J. Agostinelli, and M. Lelental, Appl. Phys. Lett. **57**, 1696 (1990).

[4]S. G. Han, Z. V. Vardeny, K. S. Wong, O. G. Symko, and G. Koren, Phys. Rev. Lett. **65**, 2708 (1990); **67**, 1053 (1991).

[5]G. Eesley, J. Heremans, M. S. Meyer, G. L. Doll, and S. H. Liou, Phys. Rev. Lett. **65**, 3445 (1990); **67**, 1054 (1991).

[6]S. V. Chekalin, V. M. Farztdinov, V. V. Golovlyov, V. S. Letokhov, Yu E. Lozovik, Yu A. Matveets, and A. G. Stepanov, Phys. Rev. Lett. **67**, 3860 (1991).

[7]G. L. Eesley, Phys. Rev. Lett. **51**, 2140 (1983).

[8]A. Kazeroonian, T. K. Cheng, S. D. Brorson, Q. Li, E. P. Ippen, X. D. Wu, T. Venkatesan, S. Etemad, M. S. Dresselhaus, and G. Dresselhaus, Solid State Commun. **78**, 95 (1991).

[9]A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe, and T. Yamada, Phys. Rev. B **38**, 2910 (1988).

[10]A. P. Goncalves, I. C. Santos, E. B. Lopes, R. T. Henriques, M. Almeida, and M. O. Figueiredo, Phys. Rev. B **37**, 7476 (1988).

[11]S. Horn, J. Cai, S. A. Shaheen, Y. Jeon, M. Croft, C. L. Chang, and M. L. denBoer, Phys. Rev. B **36**, 3895 (1987).

[12]G. Guo and X. Timmerman, Phys. Rev. B **41**, 6372 (1990).

[13]A. Inam, M. S. Hedge, X. D. Wu, T. S. Venketesan, P. England, P. F. Miceli, E. W. Chase, C. C. Chang, J. M. Tarascon, and J. B. Wachtman, Appl. Phys. Lett. **53**, 908 (1988).

[14]S. E. Inderhees, M. B. Salamon, T. A. Friedmann, and D. M. Ginsberg, Phys. Rev. B **36**, 2401 (1987).

[15]M. K. Kelly, P. Barboux, J.-M. Tarascon, and D. E. Aspnes, Phys. Rev. B **40**, 6797 (1989).

[16]F. Gao, G. L. Carr, C. D. Porter, D. B. Tanner, S. Etemad, T. Venkatesan, A. Inam, B. Dutta, X. D. Wu, G. P. Williams, and C. J. Hirschmugl, Phys. Rev. B **43**, 10 383 (1991).

[17]S. B. Kaplan, C. C. Chi, D. N. Langenberg, J. J. Chang, S. Jafarey, and D. J. Scalapino, Phys. Rev. B **14**, 4854 (1976).

[18]K. E. Grey, J. Phys. F **1**, 290 (1971).

[19]C. C. Tsuei, C. C. Chi, D. M. Newns, P. C. Pattnaik, and M. Daumling, Phys. Rev. Lett. **69**, 2134 (1992).