Femtosecond Optical Detection of Quasiparticle Dynamics in High-T_c $YBa_2Cu_3O_{7-\delta}$ Superconducting Thin Films

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Femtosecond dynamics of photogenerated quasiparticles in $YBa_2Cu_3O_{7-\delta}$ superconducting thin films shows at $T \leq T_c$ two main electronic processes: (i) quasiparticle avalanche production during hot-carrier thermalization, which takes about 300 fsec; (ii) recombination of quasiparticles to form Cooper pairs which is completed within 5 psec. In contrast, nonsuperconducting epitaxial films such as $PrBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ show regular picosecond electronic response.

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The discovery of high-T_c superconductors in copper oxide compounds[1] has attracted wide interest in the mechanisms leading to superconductivity and in possible applications. One area in particular, the transient optical response, has been the subject of recent studies[2-8] dealing with the dynamics of pair breaking and applications to high-speed optical detectors with wide spectral range. Moreover, the optical interaction in these materials determines the nonequilibrium superconducting properties which may reflect pairing mechanisms. Several models[2,4,7,8] have been proposed to explain the optical response of $YBa_2Cu_3O_{7-\delta}$ films to cw excitation and pulsed radiation of nanosecond time duration, but the full picture is still unclear. One of the main issues appears to be[2-8] whether the optical response is predominantly bolometric (thermal) or due to nonequilibrium mechanisms associated with quasiparticle photogeneration.

In the present study, using femtosecond time-resolved spectroscopy we have clearly observed, for the first time, quasiparticle (QP) dynamics following 60-fsec pulsed excitation in superconducting Y-Ba-Cu-O thin films. We have resolved two main QP dynamic processes: (i) Avalanche multiplication of QP following photon absorption. This takes about 300 fsec with a QP production gain of order 100, thus making it possible to study electron–Cooper-pair inelastic-scattering processes. (ii) Recombination of the photogenerated QP to form Cooper pairs via nonlinear kinetics of order 5 psec, which is dominated by the escape time of 2Δ phonons released in the recombination process. In contrast, we found that the carrier dynamics for nonsuperconducting epitaxial films such as $YBa_2Cu_3O_6$ and $PrBa_2Cu_3O_7$ is normal, similar to other thin films without a superconducting transition.

Photoinduced changes in reflectivity, ΔR, were measured between 10 fsec and 3 nsec using the polarized pump and probe technique.[9] The pump beam excites carriers across the optical gap and the delayed probe beam monitors $\Delta R(t)$ due to the excited carriers as a function of the time delay t between the two beams. Both beams were derived from a passively mode-locked ring dye laser[10] which produces 60-fsec pulses at 625 nm (2 eV). The energy per pulse was 50 pJ and the repetition rate was 80 MHz. The pump and probe beams were focused onto a 30-μm-diam spot on the sample which was placed in a continuous-flow cryostat producing temperatures from 5 to 300 K. The intensity of the pump beam was modulated at 4 MHz using an acousto-optic modulator. The in-phase signal $\Delta R(t)$ associated with the probe beam was measured using a moderately fast Si photodiode, a preamplifier tuned to 4 MHz, and a fast lock-in amplifier; this provided an overall system resolution of $\Delta R/R \approx 10^{-6}$.

Measurements were made with perpendicular pump-probe polarizations in the a-b plane of epitaxial thin films of high-T_c materials, about 10 mm^2 in area. The films were deposited on (100) $SrTiO_3$ substrates by laser ablation using a UV laser.[11] Their c axis was perpendicular to the substrate and the best had sharp superconducting transitions (2 K wide) at $T_c = 90$ K and high critical currents. A $PrBa_2Cu_3O_7$ and four $YBa_2Cu_3O_{7-\delta}$ films with thicknesses ranging from 1000 to 4000 Å were used. The pump beam was absorbed within the optical skin depth ($\sim$1000 Å) and the initial density of photoexcited carriers was estimated to be 10^{18} cm^{-3}.

Figure 1 shows a typical transient $\Delta R/R$ response of a superconducting $YBa_2Cu_3O_7$ film above and below T_c, the temperatures being respectively 300 and 40 K. For $T > T_c$, Fig. 1(a), there is a step-function response of $\Delta R > 0$ and it decays with a characteristic time of 3 nsec [Fig. 1(a), inset]; it is much slower at 100 K. This behavior is a typical bolometric response in a metal.[12,13] Our measurements of the temperature dependence of the reflectivity R show a positive dR/dT of 5×10^{-5} K^{-1} and this allows us to estimate a sample temperature rise per pulse at 300 K of $\Delta T \approx 0.7$ K, consistent with calculations based on the absorbed energy and the sample

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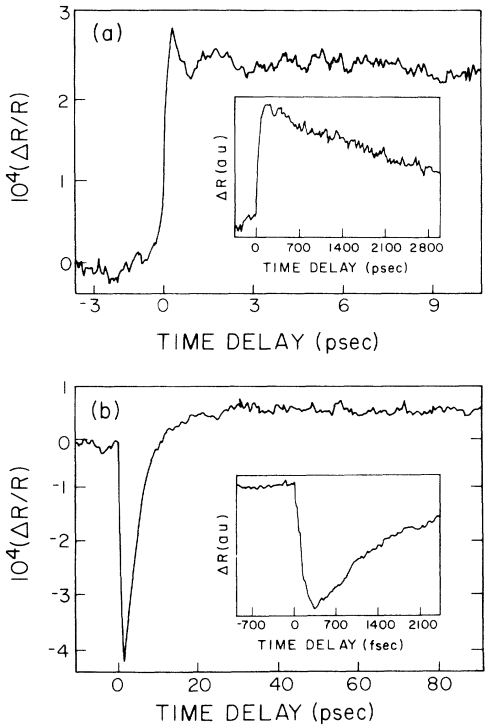

FIG. 1. Transient photoinduced reflectivity $\Delta R/R$ of superconducting 3000-Å $YBa_2Cu_3O_7$ film at (a) 300 K, bolometric response, and (b) at 40 K, quasiparticle to bolometric response.

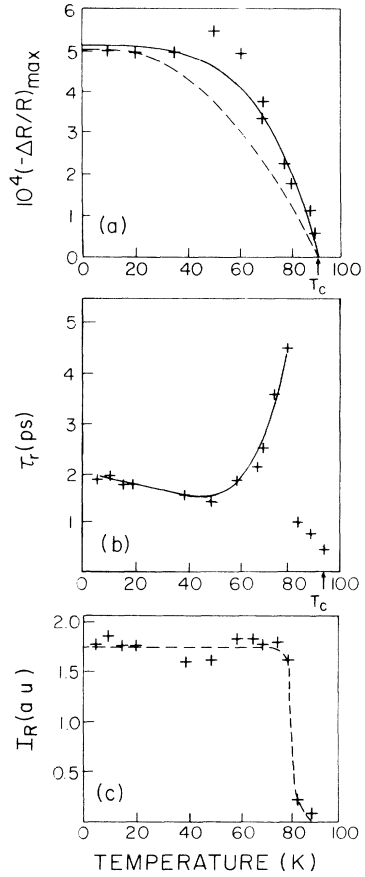

FIG. 2. (a) Temperature dependence of $\Delta R < 0$ quasiparticle peak $(-\Delta R/R)_{max}$ in $YBa_2Cu_3O_7$ for $T \leq T_c$; excitation intensity (Ref. 14) 3 $\mu J cm^{-2}$. The lines are theoretical fits to the data; the solid line is based on the two-fluid model (Ref. 15) and the dashed line is based on BCS theory (Ref. 16). (b) Temperature dependence of the recombination time τ_r for the $\Delta R < 0$ response (Ref. 14). The line is a guide to the eye. (c) Product of (a) and (b) showing the temperature dependence of I_R ($=\Delta R_{max}\tau_r$). The line is a guide to the eye.

heat capacity. The generated ΔR decays due to longitudinal heat diffusion into the film.[13]

A completely different transient response for this film is observed for $T \leq T_c$, Fig. 1(b). At $t=0$, ΔR builds up toward a negative peak with a characteristic time $\tau \simeq 300$ fsec, as shown in Fig. 1(b), inset, followed by a longer recovery of several psec duration with $\Delta R < 0$ and a crossing of the zero signal line into a plateau with $\Delta R > 0$. Since $R(T)$ increases with T even when $T < T_c$, the initial rapid $\Delta R < 0$ response cannot be bolometric; it is due to an electronic response associated with photogenerated QP in the film. This is further substantiated by the results in Fig. 2(a) where the peak value of the reflectivity change, $(-\Delta R/R)_{max}$, is measured as a function of temperature at a constant excitation intensity of 3 $\mu J cm^{-2}$.[14] This peak value increases from zero at $T \lesssim T_c$ to a saturation value of 5×10^{-4}. A negative response of ΔR is not observed for $T > T_c$. The data in Fig. 2(a) are best fitted by a two-fluid model[15] $[1-(T/T_c)^4]$ of the relative density of Cooper pairs, with $T_c \approx 90$ K. A fit within BCS theory by a superconducting electron density obtained from the penetration-depth function in the weak-coupling limit[16] is not as good. Thus the negative ΔR response is associated with QP generated by the breaking of Cooper pairs following photon excitation.

Such dramatic changes in the photocarrier response as a function of temperature are not observed for nonsuperconducting epitaxial thin films, as shown in Fig. 3 for $PrBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. We have observed in these films an instantaneous onset in electronic ΔR (no delay as in $YBa_2Cu_3O_7$) followed by an ultrafast relaxation of order 2–4 psec into a plateau. This is a typical response of nonsuperconducting films[12,13] where the ultrafast dynamics has been identified[12] as due to hot electrons and the plateau is bolometric in origin. To compare this behavior with that in $YBa_2Cu_3O_7$, we have measured the values of $\Delta R/R$ at the peak response as a function of temperature. As shown in Fig. 3, insets, these values are almost temperature independent for both films. This is again typical of nonsuperconducting films, and in contrast with all of our $YBa_2Cu_3O_7$ films [Fig. 2(a)].

The $YBa_2Cu_3O_7$ results in Fig. 1(b) show two main processes associated with the QP response: a fast build-

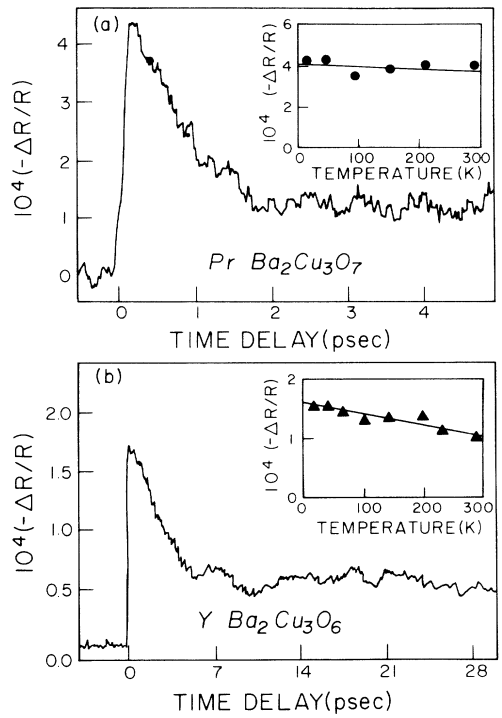

FIG. 3. Transient $\Delta R/R$ for nonsuperconducting (a) $PrBa_2Cu_3O_7$ and (b) $YBa_2Cu_3O_6$ thin films. Insets: The respective temperature dependence of the peak in $\Delta R/R$.

up and a relatively longer relaxation followed by a positive ΔR plateau. We interpret the first process as an avalanche multiplication of QP due to hot-carrier thermalization which lasts for about 300 fsec and which occurs immediately after photon absorption. The second process is interpreted as a QP recombination into Cooper pairs followed by a thermal relaxation producing a bolometric signal with $\Delta R > 0$, similar to $T > T_c$.

Following 2-eV photon absorption in $YBa_2Cu_3O_7$, highly excited QP dissipate their excess energy to other electrons near the Fermi level, Cooper pairs across 2Δ, and phonons. The observed rise time τ is a typical electron inelastic-scattering time which describes the thermalization process.[12,17] This τ of order 300 fsec is in agreement with the carrier scattering rate inferred from Drude cw optical response[18] and may be associated with electron-phonon scattering.[19] The maximum number of QP that can be created as a result of a single-photon absorption is roughly $g = 2\hbar\omega/2\Delta(0)$; here it is ~ 100 for $2\Delta(0) \simeq 5kT_c$,[20] and $\hbar\omega = 2$ eV. From g and the excitation intensity, the QP density δN_0 after the electronic thermalization process ends is estimated to be $\delta N_0 \simeq 10^{20}$ cm^{-3}. This amplification process is very important for observing QP response in superconductors; in many studies it has not been taken into account.

The optical QP response giving $\Delta R < 0$ may be explained within the superconducting extreme-clean-limit model,[15,21] which is compatible with the two-fluid model used previously in Fig. 2(a). Various ir spectroscopic studies of $YBa_2Cu_3O_7$ have shown[18] that the Drude contribution to the optical conductivity $\sigma(\omega)$, which is usually present in metals, shifts to zero frequency (clean limit) at $T \ll T_c$. Therefore, generation of QP over the gap partially restores the Drude contribution $\Delta\sigma$ to $\sigma(\omega)$. Assuming that all other optical transitions do not change substantially upon irradiation, $\Delta\sigma$ may be calculated by taking the difference due to the photogenerated QP δN_0 between a Drude contribution of 200-cm^{-1} width and one that is very narrow, representing the condensate in the two-fluid model.[15] The changes $\Delta\tilde{\epsilon}$ in the dielectric constant $\epsilon_1 + i\epsilon_2$ can then be calculated:

$$\Delta\epsilon_2 = \delta N_0 \omega_p^2 / N_t \omega^3 \tau_s \quad (1)$$

and $\Delta\epsilon_1 = \Delta\epsilon_2/\omega\tau_s$. In Eq. (1), ω_p is the plasma frequency ($\simeq 1$ eV),[18] τ_s is the scattering time ($1/\tau_s \simeq 200$ cm^{-1}),[18] and N_t is the total electron density ($N_t \simeq 6 \times 10^{21}$ cm^{-3}).[18] Using Eq. (1) with $\delta N_0 = 10^{20}$ cm^{-3}, we calculate $\Delta\tilde{\epsilon}$ of order 10^{-4}; this is consistent with our measurements.

To obtain $\Delta R/R$ from $\Delta\tilde{\epsilon}$ for a thin metallic film, one has to do tedious calculations[13] involving various integrals of the QP distribution function with distance over the film thickness, and to take into account the optical interference fringes which usually appear in thin films.[22] It is therefore possible to obtain a sign change in[13,22] ΔR such that $\Delta R < 0$ even though $\Delta\tilde{\epsilon} > 0$, as is probably the case for the QP response of the 3000-Å $YBa_2Cu_3O_7$ film shown in Fig. 1(b). The negative sign in ΔR (QP) is consistent with the positive sign of ΔR for the bolometric contribution. Measurements of $\tilde{\epsilon}$ as a function of temperature[23] give $\Delta\tilde{\epsilon} < 0$ for a temperature increase. However, since from Fig. 1(a) $\Delta R > 0$ for the bolometric response, then ΔR has the opposite sign of $\Delta\tilde{\epsilon}$. The observed QP response in this case, with $\Delta R < 0$, is due to $\Delta\tilde{\epsilon} > 0$, in agreement with the proposed model.

QP recombination may be described as quasielectron-quasihole recombination across 2Δ, in analogy with semiconductors. As is evident in Fig. 1(b) the recombination rate is very fast; the transient decays are not purely exponentials. We define a recombination time τ_r as the time for the ΔR (QP) signal to decay to half its maximum value and hence we measure it at various temperatures as shown in Fig. 2(b). For $T < 40$ K, τ_r decreases with T, and then starts to increase, reaching a value of 4.5 psec at 79 K.[14] Since this increase in τ_r occurs at temperatures where δN_0 decreases, we plot the product $I_R = (\Delta R/R)_{QP}\tau_r$ in Fig. 2(c); this is proportional to the integrated signal as a function of T. A constant behavior of I_R at temperature where δN_0 and τ_r change dramatically indicates that the QP generation and recombination processes are related.

QP recombination kinetics in superconductors was discussed by Rothwarf and Taylor[24] in terms of two rate equations for the excess QP (δN) and the 2Δ phonons (δn) released in the QP recombination process. For $\delta N \gg N_T$, where N_T is the QP density in thermal equi-

librium, these equations are given by[25]

$$\frac{d}{dt}(\delta N) = -r(\delta N)^2 + 2\tau_B^{-1}(\delta n), \quad (2)$$

$$\frac{d}{dt}(\delta n) = -(\tau_B^{-1} + \tau_\gamma^{-1})(\delta n) + \tfrac{1}{2} r(\delta N)^2, \quad (3)$$

where r is the QP recombination rate, τ_B is the Cooper-pair breaking time, and τ_γ is the phonon decay (escape) time.

The 2Δ phonons released in the QP recombination are trapped within the excited volume and can further rebreak Cooper pairs; hence they act as a bottleneck for QP recombination.[24,25] Under these conditions $\tau_r \simeq 2\tau_\gamma$,[25] rather than $\tau_r \sim (\delta N)^{-1}$ as is the usual nonlinear recombination kinetics in semiconductors. We checked the QP relaxation by changing the excitation intensity at 20 K; we verified that the QP dynamics did not change with $\delta N(0)$.

We attribute the 2-psec QP decay to the 2Δ-phonon relaxation time. Recent Raman-scattering measurements[20] have shown that the optical phonons (A_g and B_{1g}) are in resonance with 2Δ in $YBa_2Cu_3O_7$. τ_γ is therefore determined by the decay of the 2Δ optical phonons to acoustical phonons. From our data, $\tau_\gamma \simeq 1$ psec; this corresponds to a phonon with a homogeneous Lorentzian line shape of 15-cm^{-1} width, in good agreement with the measured A_g phonon linewidth at $T \simeq T_c$ in $YBa_2Cu_3O_7$.[20]

There are two possible explanations for the increase in τ_r at $T \geq 40$ K. Acoustical phonons may be released during the QP recombination at the higher temperatures causing τ_γ to increase; it is determined by the escape time of these phonons from the illuminated volume.[25] It is also possible that the QP recombination is accompanied by relaxation in Δ,[26] causing a divergence in τ_r as T_c is approached from the superconducting side; i.e., $\tau_r \sim \Delta^{-1}$, as can be inferred from Fig. 2(c).

In conclusion, we have resolved the photogenerated QP dynamics in superconducting Y-Ba-Cu-O thin films using femtosecond spectroscopy. We identified two main ultrafast electronic processes: an avalanche production of QP during the thermalization of hot electrons following photon absorption, and QP recombination to form Cooper pairs with a rate dominated by the coupled optical-phonon decay.

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Note added.—Chwalek *et al.*[27] have measured femtosecond transient transmission in high-T_c superconducting $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ and $YBa_2Cu_3O_{7-\delta}$ and found for both compounds nonequilibrium heating with a dramatic increase in relaxation time at temperatures below T_c.

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