Exploring the Dynamics of Superconductors by Time-Resolved Far-Infrared Spectroscopy

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(Received 27 January 2000)

We have examined the recombination of excess quasiparticles in superconducting Pb by time-resolved far-infrared spectroscopy using a pulsed synchrotron source. The energy gap shift calculated by Owen and Scalapino [Phys. Rev. Lett. **28**, 1559 (1972)] is directly observed, as is the associated reduction in the Cooper pair density. The relaxation process involves a two-component decay; the faster (~200 ps) is associated with the actual (effective) recombination process, while the slower (~10 to 100 ns) is due to heat transport across the film/substrate interface. The temperature dependence of the recombination process between $0.5T_c$ and $0.85T_c$ is in good agreement with theory.

PACS numbers: 74.40.+k, 74.25.Gz, 78.47.+p

When excess unpaired electrons are injected into a superconductor, they appear in excited states (quasiparticle excitations) that eventually relax by emitting a phonon (or other excitation) and forming pairs. BCS calculations by Schrieffer and Ginsberg [1] and by Rothwarf and Cohen [2] took into account the electron-phonon interaction and the availability of quasiparticles to determine a temperature-dependent recombination time valid for temperatures well below the critical temperature T_c. For metallic superconductors such as Sn and Pb, the typical time scale is ~100 ps for $T \sim T_c/2$. Subsequently, Rothwarf and Taylor [3] showed that the measured (or effective) lifetime was longer than the "bare" or intrinsic recombination time, due to phonon trapping effects. Kaplan *et al.* [4] calculated the various scattering and relaxation times for both quasiparticles and phonons in a number of elemental superconductors, including strong-coupling effects in Pb and Hg.

Exposure to light produces an excess (nonequilibrium) population of quasiparticles with each photon breaking one or more Cooper pairs, depending on the photon energy. As first shown by Testardi [5], light of sufficient intensity can actually destroy the superconducting state. This effect is not due to heating to a temperature above the critical temperature T_c. Instead, as Owen and Scalapino showed [6], an excess quasiparticle population reduces the superconductor's order parameter (the energy gap) to the point that it collapses to zero, even though the lattice temperature is still below T_c. A number of photoinduced pair-breaking experiments have been conducted since the 1970s. The change in the energy gap and strength of the pair condensate were explored in quasistatic measurements [7,8] that confirmed the Owen and Scalapino result for low fluences and indirectly gave a magnitude for the pair recombination time. At higher fluences, the system reverted gradually to the normal state, in contradiction to the abrupt first-order transition predicted by theory. The inferred lifetimes from these measurements were consistent with theory when phonon-trapping effects were included.

The majority of the time-resolved studies have been performed for $T \ll T_c$, where lifetimes are typically much greater than 1 ns. Hu, Dynes, and Narayanamurti [9] carried out direct time-resolved studies, though resolution was tens of nanoseconds at best. The more recent transient electrical photoresponse measurement by Johnson [10] was the first direct time-dependent study to achieve a time resolution of 100 ps. The observed relaxation consisted of a two-component decay, suggested as being intrinsic. Unfortunately, the observed electrical response was limited to temperatures near T_c and little information on the nature of the excited state could be extracted. One of the first time-resolved spectroscopy studies [11] made use of the newly developed coherent terahertz laser spectroscopy technique [12], and determined that the superconducting state could be completely destroyed in less than 1 ps. This time scale is consistent with theories for electron-electron and electron-phonon scattering of hot electrons. The recombination process was not explored. Similar techniques have been applied to high-T_c cuprate superconductors, detecting picosecond and even femtosecond relaxation times [13].

In this Letter, we report a pump-probe, far-infrared study of the time-dependent relaxation and recombination of excess quasiparticles in superconducting Pb films. We directly observe the reduction in the pair condensate and a concomitant drop in the energy gap, in accord with the theory of Owen and Scalapino [6]. A two-component decay is found, similar to the results of Johnson [10]. We identify the two components as excess quasiparticle recombination followed by heat flow, and extract the temperature dependence of the recombination time for a moderate range of temperatures. The results are in good agreement with the calculations of Kaplan *et al.* [4].

The detailed process through which excess quasiparticles are produced, following absorption of a light pulse, is quite complex. High-energy quasiparticles produced by photon absorption quickly relax by *e*-*e* and *e*-ph

scattering, creating additional quasiparticles and resulting in an excess population of low-energy ($\sim\Delta$) quasiparticles and phonons. The recombination of quasiparticles into Cooper pairs produces phonons of energy 2Δ; those phonons that do not decay anharmonically or escape the superconductor are destined to break other pairs. These two excess populations equilibrate on a time scale $\tau_{\rm eq} = (1/\tau_R + 1/\tau_B)^{-1}$ ($\leq$50 ps for Pb), where τ_R is the intrinsic quasiparticle recombination time and τ_B is the time for a 2Δ phonon to break a pair. From energy conservation, one can write the temperature-dependent fraction of quasiparticles as $n_{\rm qp}(T)/n_0 = [\Delta_0/\Delta(T)]/[1 + 2\tau_B/\tau_R]$ where n_0 is the number density when the excess population is all quasiparticles. The expected temperature dependence for τ_R and τ_B implies that the absorbed energy resides mostly in excess 2Δ phonons for T near T_c, changing over to predominantly excess quasiparticles for $T \ll T_c$. In the limit of $T = 0$ K, the energy is entirely in the excess quasiparticles, i.e., $n_{\rm qp}(0) = n_0$. This combined system then relaxes with an effective lifetime $\tau_{\rm eff} = \tau_\gamma + (1/2)\tau_R(1 + \tau_\gamma/\tau_B)$ where τ_γ is the time for a phonon to become unavailable for pair-breaking. Note that $1/\tau_R$ is defined as the rate for quasiparticle *recombination*, and that each recombination event removes two quasiparticles. At low temperatures τ_R is typically large compared to τ_γ and the effective lifetime becomes $(1/2)\tau_R(1 + \tau_\gamma/\tau_B) \cong \tau_R\tau_\gamma/2\tau_B$ when $\tau_\gamma \gg \tau_B$. At higher temperatures τ_R becomes small and the effective lifetime approaches τ_γ.

Our experiment uses the standard time-resolved technique of pump-probe spectroscopy. The Pb films were probed using infrared pulses of a few hundred picoseconds duration produced as synchrotron radiation at the U12IR far-infrared beam line of the National Synchrotron Light Source (NSLS) VUV ring [14]. A lamellar grating interferometer [15] in conjunction with a He cooled bolometer detector were used for the probe spectroscopy. The films were pumped (to break Cooper pairs) using a Ti:sapphire laser that produced near infrared picosecond-duration pulses synchronized to the infrared synchrotron radiation. The time resolution for the experiment was determined by the duration of the synchrotron pulses.

The superconducting Pb films were evaporated onto sapphire substrates held at $T = 80$ K. The film thicknesses were estimated from prior experience to be $\sim$5 to 10 nm. The films were cooled to 20 K immediately after deposition and maintained at that temperature, or lower, throughout the course of the measurement. A 6 mm diameter circular aperture restricted the illuminated area to the central portion of the film for both the far-infrared probe and laser pump sources. The far-infrared transmission through the films was measured for both the normal and superconducting states to characterize the films. Behavior typical of Pb was generally observed (e.g., $T_c \sim 7.2$ K; $2\Delta_0/hc = 22$ cm^{-1}; strong coupling). Figure 1 shows $\mathcal{T}_S/\mathcal{T}_N$, the ratio of the transmission at several temperatures below T_c (superconducting state) to that at 10 K (normal state), for a 50 $\Omega/\Box$, $\sim$10% transmitting film. Also shown is the BCS prediction including a first-order strong-coupling correction [16]. The agreement is generally very good.

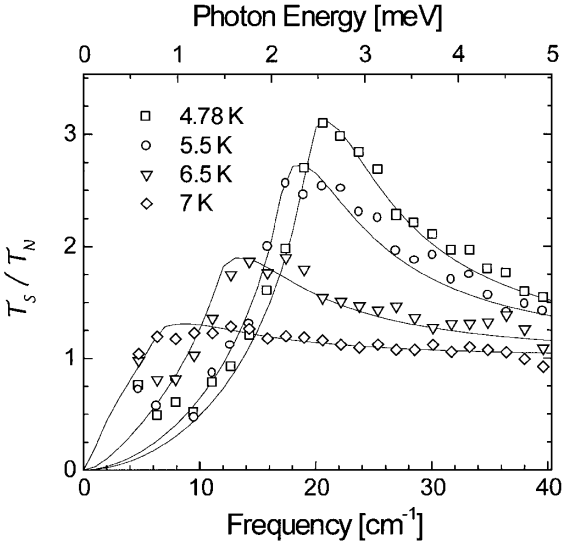

FIG. 1. Measured ratio of $\mathcal{T}_S/\mathcal{T}_N$ for a Pb film at four temperatures below T_c (symbols), and fits (solid curves) using the Mattis and Bardeen calculation plus a correction for strong coupling [17].

Our system (film, substrate, and copper clamp) has at least one thermal time constant larger than the 18.9 ns laser pulse separation, causing the train of laser pulses to heat the film (compared to the copper cold finger where the temperature sensor is located). The film's transmission is very temperature dependent and, when accurately measured, serves as an excellent thermometer. We used this transmission value to determine the temperature of the film just prior to the arrival of a laser pulse by setting the probe pulses to arrive just *before* the pump pulses, and then measuring the transmission with laser off and with laser on. The difference is compared to the T-dependent transmission to determine an average temperature rise of the film. Most of our time-resolved measurements were performed using 15 mW of laser power, which caused a temperature increase of 0.1 K at 4.5 K.

At the 15 mW power level, the laser delivered 0.3 nJ per pulse, about $\frac{1}{4}$ of which we expect to be absorbed in the film. If half eventually appears as excess low-energy quasiparticles, then about 10^{11} pairs are broken, resulting in a quasiparticle density of about 6×10^{17} cm^{-3} for a 10 nm thick film. This nonequilibrium density can be compared with the density of electrons strongly affected by entering the paired state, $n_{\rm pairs} \cong 4N(0)\Delta_0 = 5 \times 10^{19}$ cm^{-3} where $N(0)$ is the single spin density of states. The expected result is an excess quasiparticle density of about 1% of the "pair density." This is comparable to the thermal quasiparticle density for $T = 4$ K. Therefore, we always checked that our response was linear in excitation power, and reduced it when necessary to remain in the weak perturbation (linear) limit.

We used several different techniques to collect data on the pair-breaking and recombination process. When the shortest possible probe pulses (~300 ps) were used, our time-dependent transmission signal just began to resolve the recombination process. This signal is shown in Fig. 2 for $T = 3.7$ K, along with a fit to a two-component exponential decay. (The fit is convolved with a Gaussian to account for the width of the probe pulse.) The faster component has a lifetime of ~250 ps, with an uncertainty of ± 100 ps. This value is consistent with τ_{eff} for a Pb film on sapphire. As the temperature increased toward T_c, the decay time remained approximately constant (perhaps decreasing slightly), but the amplitude of the fast component decreased rapidly; it was barely detectable for temperatures greater than $T = 6$ K. The slow component is well described by an exponential with decay time ~20 ns and little dependence on temperature below T_c. Neither signal component was observed above T_c.

In Fig. 3 we show the photoinduced signal, $-\delta\mathcal{T}/\mathcal{T}$ for $T = 3.7$ K, where $\delta\mathcal{T}$ is the change in the infrared transmission of the film at the instant a laser pulse is incident. Results for two laser fluences are shown, along with BCS fits using the same parameters as for $\mathcal{T}_S/\mathcal{T}_N$ (see Fig. 1). In making the fits, we assumed a fixed temperature and allowed the gap to be reduced by a small amount $\delta\Delta$. Note that changes in the energy gap $\delta\Delta$ can be related to the excess quasiparticle density n_{qp} through $\delta\Delta/\Delta \cong n_{\text{qp}}/2N(0)\Delta_0 = 2n_{\text{qp}}/n_{\text{pairs}}$ (for weak perturbation and temperatures not near to T_c) [6,7]. A gap reduction of 0.1 cm^{-1} fits the 0.3 nJ pulse data, indicating that approximately 0.25% of the superconducting pairs were broken, in rough agreement with the estimate based on the photon fluence. This confirms our association of the fast decay process with the recombination of excess quasiparticles. The slow decay process is most likely thermal relaxation of the film where a portion of the deposited light energy, having fully thermalized, escapes as heat into the underlying substrate. We will return to this subject later.

Time-dependent decay measurements were performed at selected temperatures and fitted to a two-exponential decay for two Pb films. As mentioned above, a lifetime of 250 $\pm$ 100 ps is observed for all temperatures. Kaplan *et al.* [4] calculate $\tau_R < 20$ ps and $\tau_B > 40$ ps for most of this temperature range, so that $(1/2)\tau_R(1 + \tau_\gamma/\tau_B) < 50$ ps, implying that $\tau_{\text{eff}} \sim \tau_\gamma \sim 200$ ps. The magnitude of the decay signal is determined by the number density of excess quasiparticles. This depends on the laser pulse fluence and the fraction of laser energy in the form of quasiparticles, i.e., $n_{\text{qp}}(T)/n_0 = [\Delta_0/\Delta(T)]/[1 + 2\tau_B(T)/\tau_R(T)]$. Results for the signal magnitude at selected temperatures are shown in Fig. 4 (open and solid circles). Also shown is the calculated fraction of quasiparticles (solid curve) using theoretical results [4] for $\tau_R(T)$ and $\tau_B(T)$. The constant of proportionality between signal amplitude and quasiparticle fraction is not known, so the data were scaled until one point fell on the theoretical curve. We also used probe pulses much longer than the fast decay time, sensing only the average signal for the first ~1 ns. Such measurements could be performed while continuously sweeping the sample temperature. Though not temporally resolved, this signal is still proportional to the fast signal amplitude (since the lifetime is approximately constant). The results (again using a common factor to adjust the overall scale) are shown in Fig. 4, and are in good agreement with the calculated quasiparticle fraction.

The temperature-dependent, excess quasiparticle density results reported here suggest future experiments for testing theoretical calculations more directly. For example,

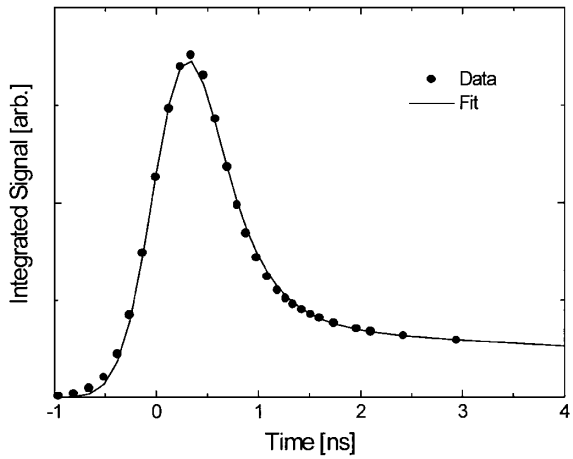

FIG. 2. Time-dependent far-infrared response of a Pb film at 3.8 K to a 0.4 nJ laser pulse. The solid curve is a fit using the convolution of a Gaussian (the synchrotron probe pulse) with the sum of two simple exponential decays.

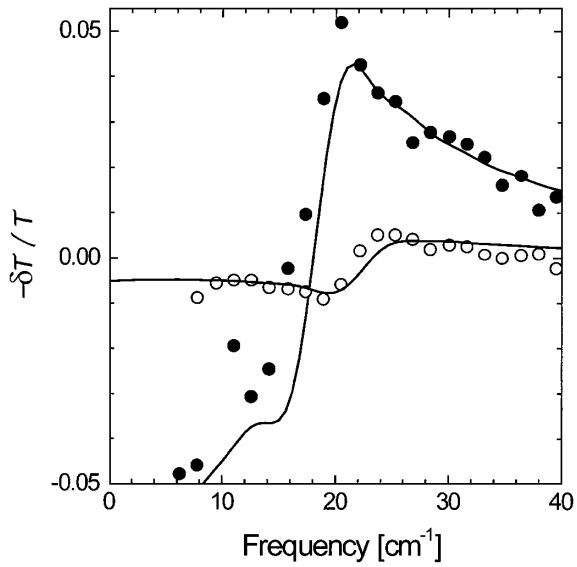

FIG. 3. Photoinduced spectral changes for two samples. The laser pulse energies were 1.8 nJ (solid circles) and 0.4 nJ (open circles). Also shown are fits (solid curves) assuming an ~3% and 0.6% reduction in the energy gap, respectively. All other parameters were held fixed at the values determined from the temperature-dependent $\mathcal{T}_S/\mathcal{T}_N$ fits.

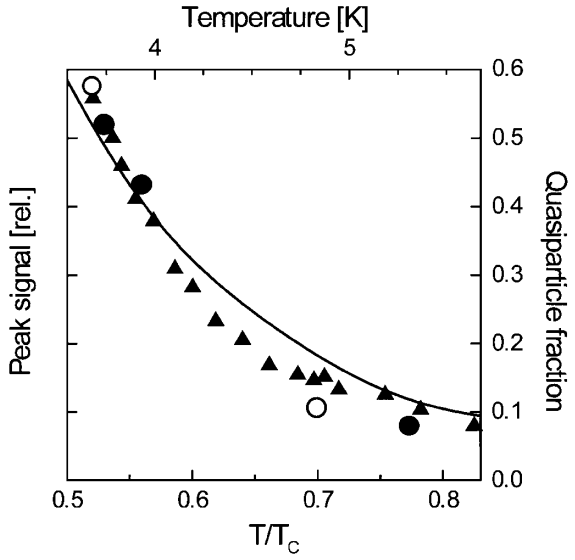

FIG. 4. The photoinduced signal magnitude as a function of temperature, determined by fitting individual time-dependent decay (open and solid circles) and from the signal averaged over the first nanosecond (solid triangles; see text). Also shown is the temperature-dependent excess quasiparticle fraction calculated from theory (solid line, right axis).

the excess quasiparticle density should saturate at low temperatures when $\tau_R \gg \tau_B$ and the energy resides entirely in the quasiparticle system. If S_0 is the signal magnitude for this situation, then $S(T)/S_0 = [\Delta_0/\Delta(T)]/[1 + n_{\rm ph}(T)/n_{\rm qp}(T)] = [\Delta_0/\Delta(T)]/[1 + 2\tau_B(T)/\tau_R(T)]$ (it is assumed that the excess quasiparticles and phonons have equilibrated) and the ratio τ_B/τ_R can be directly extracted from the temperature-dependent signal amplitude. In conjunction with accurate measurements of the temperature-dependent effective lifetime $\tau_{\rm eff} = \tau_\gamma + (1/2)\tau_R + \tau_\gamma\tau_R/2\tau_B$, it may prove possible to determine individual values for τ_R, τ_B, and τ_γ in some situations.

The two-component decay we observe for Pb is similar to that seen in the transient electrical response of Nb [10]. We interpret the slow decay component as thermal relaxation where heat flows from the film into the substrate. Such a process occurs by phonon transport across the film/substrate boundary with a lifetime $\tau_{\rm th} = C/G$ where C is the film heat capacity and $G_{\rm bd}$ is the thermal conductance across the boundary. Acoustic mismatch theory [17] predicts $G_{\rm bd} = AT^3$ where the coefficient A is determined by material properties, such as the relative sound velocity between the metal film and substrate. Lead has a low Debye temperature ($\theta_D = 100$ K) such that the film's heat capacity continues to have a dominant phonon (T^3) contribution for this temperature range. Thus, the thermal relaxation time $\tau_{\rm th}$ for a Pb film should be more or less independent of temperature, as observed. The same two-component decay should apply to other film systems. In the case of Nb on sapphire, the higher Debye temperature ($\theta_D = 275$ K) implies a heat capacity falling exponentially with temperature in the superconducting state, due to the more important contribution of electrons over phonons. In addition, the thermal boundary resistance for Nb should be less than for Pb on sapphire, leading to shorter, temperature-dependent decay times, as reported [10].

In conclusion, we have used time-resolved far-infrared spectroscopy to explore, for the first time, the relaxation of excess quasiparticles in a metallic superconductor. Fits to the far-infrared transmission change allow us to observe directly the associated energy gap shift and to extract a value for the fraction of broken pairs. This quantity can be compared with the thermal population of quasiparticles to provide definitive information on whether we are in the weak or strong perturbation regimes. Indeed, for higher fluences, where the light-induced quasiparticle population exceeded the thermal population, our signal amplitude showed signs of saturation indicating that the intrinsic recombination rate was becoming insensitive to the temperature and increasing with light intensity. In the low fluence, linear regime, the measured transient signal magnitude was found to vary with temperature, in good agreement with theoretical expectations based on the relative populations of excess quasiparticles and phonons. A method for determining the temperature-dependent ratio τ_R/τ_B was described. Such measurements should provide a more stringent test of theory.

This work was performed with the support of the U.S. Department of Energy through Contracts No. DE-FG02-96ER45584 at the University of Florida and No. DE-ACO2-98CH10886 at the NSLS. We are grateful to P. B. Allen and M. Strongin for useful conversations.

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