

Controlled Vaporization of the Superconducting Condensate in Cuprate Superconductors by Femtosecond Photoexcitation

P. Kugar,¹ V. V. Kabanov,¹ J. Demsar,^{1,3} T. Mertelj,¹ S. Sugai,² and D. Mihailovic¹

¹Complex Matter Department, Jozef Stefan Institute, Jamova 39, Ljubljana, SI-1000, Ljubljana, Slovenia

²Department of Physics, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan

³Physics Department, University of Konstanz, D-78457 Konstanz, Germany

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We use ultrashort intense laser pulses to study superconducting state vaporization dynamics in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.1$ and 0.15) on the femtosecond time scale. We find that the energy density required to vaporize the superconducting state is 2.0 ± 0.8 and 2.6 ± 1.0 K/Cu for $x = 0.1$ and 0.15 , respectively. This is significantly greater than the condensation energy density, indicating that the quasiparticles share a large amount of energy with the boson glue bath on this time scale. Considering in detail both spin and lattice energy relaxation pathways which take place on the relevant time scale of $\sim 10^{-12}$ s, the experiments appear to favor phonon-mediated pair-breaking mechanisms over spin-mediated pair breaking.

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The study of nonequilibrium phenomena in superconductors has been an important topic of condensed matter physics since the 1960s, and the fact that intense laser pulses can nonthermally destroy the superconducting state has been known for a long time [1]. After the discovery of high-temperature superconductivity in cuprates and the simultaneous rapid development of ultrashort pulsed lasers, real-time studies of quasiparticle (QP) dynamics became possible using pump-probe experiments [2–5]. Recent developments in phenomenological modeling and new systematic experimental studies of the nonequilibrium optical response [6–9] have enormously improved our understanding of the dynamics of photoexcited QPs on short time scales, and the response of the superconducting state to weak pulsed laser excitation in cuprates can now be unambiguously identified on the femtosecond time scale [7–16]. Rothwarf and Taylor (RT) originally proposed their phenomenological model for QP recombination in the framework of phonon-mediated pairing [6,8], but spin-fluctuation mediated recombination (which might be relevant for the cuprates) is not excluded by their model. Both high-energy phonons and spin excitations could in principle mediate QP recombination, and the nonequilibrium studies so far did not directly reveal the pairing boson.

In this Letter we specifically address the question of the mediating boson by carefully measuring and analyzing the energy and time needed to destroy (vaporize) the superconducting condensate in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) with $x = 0.1$ and 0.15 . We compare the measured vaporization energy with the thermodynamically measured condensation energy, and find that a substantial amount of energy is temporarily stored by the glue boson bath during the vaporization process. Since spin and lattice subsystems have vastly different heat capacities, this places significant constraints on the type of bosonic bath which can mediate pairing. By carefully considering the energy relaxation

pathways associated with pair-breaking dynamics we are able to conclude which bosonic excitations are involved in the destruction of the condensate, shedding light on the pairing boson responsible for superconductivity in these materials.

Outlining the sequence of events in our experiments microscopically, the laser pump pulses first excite electrons from occupied to unoccupied states within 1.5 eV of the Fermi level. Immediately afterwards, in an avalanche QP multiplication process which is well studied in metals, as well as cuprates, the photoexcited carriers relax to states near the Fermi energy via *intra*band electron-electron scattering, occurring on a typical time scale $\tau_{e-e} \leq 50$ fs [17], and scattering with phonons—preferentially interacting with those phonons which are most strongly coupled to the QPs [18]—resulting in significant nonequilibrium QP and phonon populations within ~ 100 fs of photoexcitation. The next relaxation step, QP recombination across a superconducting energy gap (or pseudogap) with the emission of a boson with energy $\geq 2\Delta$, takes significantly longer, and is typically described very well by the Rothwarf and Taylor model [6,8,9]. The model does not directly identify the pairing boson, but two crucial parameters in the model do depend on the electron-boson interaction, namely, the characteristic pair-breaking rate η and recombination rate r which define the pair-breaking and QP recombination time scales, respectively [6–8]. Importantly, η and r can be determined from the vaporization time τ_r [7].

There is a consensus in the literature that transient reflectivity changes in optical pump-probe experiments are proportional to the number of photoexcited quasiparticles n_p [10,13,19,20], which is corroborated by optical pump-THz probe experiments, where the imaginary component of the THz conductivity is directly proportional to the condensate density [21]. This makes it possible to

detect when the superconducting condensate is destroyed by measurement of the transient reflectivity [20].

In the experiments described here, we perturbed the superconducting condensate in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with 50 femtosecond laser pulses. The experiments were performed on freshly cleaved surfaces of high quality $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.1$ and 0.15) single crystals with $T_c = 30$ and 38 K, respectively [22]. The laser pulses were linearly polarized and incident along the c axis of the crystal with a wavelength of $\lambda = 810$ nm (~ 1.5 eV). We used a Ti:sapphire oscillator and a 250 kHz amplifier to cover the range of excitation fluences from $\mathcal{F} \sim 4 \times 10^{-2}$ to $100 \mu\text{J}/\text{cm}^2$. The pump and probe beam diameters were measured accurately with a pinhole and the absorbed energy density was accurately determined [23]. The low laser repetition rate of our laser ensured that there was no heat buildup between pulses even with the highest fluences used, and the temperature increase due to the laser was found to be less than 2 K (which can also be seen from a comparison of the T_c measured optically with the T_c from susceptibility measurements).

The photoinduced reflectivity change $\Delta R/R$ as a function of time delay for different \mathcal{F} is shown below T_c ($T = 4.5$ K) in Fig. 1(a) and above T_c ($T = 32$ K) in Fig. 1(b) for $x = 0.1$ (the data for $x = 0.15$ are qualitatively the same). Below T_c [Fig. 1(a)] we identify two relaxation processes with very different dynamics, which we label as A and B. Signal B is present from low T to well above T_c [Fig. 1(b)], and disappears gradually above the so-called

pseudogap temperature T^* . In agreement with many previous low- \mathcal{F} experiments [9,11–13], it is assigned to the carriers recombining across the pseudogap. Signal A is visible strictly only below T_c and is—in accordance with previous works [11,16]—assigned to QP recombination across the superconducting gap $\Delta_s(T)$, and has a relaxation time typically $\tau_A > 10$ ps at 4.5 K [11]. The rise time $\tau_r = 0.8 \pm 0.15$ ps of the superconducting signal $\Delta R/R_A$ is the time required for the QP population to build up [7,8] by pair-breaking from the condensate.

Examining Fig. 1 in more detail, we see that at low \mathcal{F} and T signal A is dominant. As fluence is increased, the amplitude of signal A first increases with \mathcal{F} and then starts to saturate for \mathcal{F} above $\approx 12 \mu\text{J}/\text{cm}^2$. As signal A starts to saturate, signal B starts to become more visible, and above the saturation threshold of signal A, a linear increase of the amplitude of signal B with increasing \mathcal{F} becomes clearly apparent.

The maximum amplitudes of $\Delta R_A/R$ and $\Delta R_B/R$ are shown in Fig. 2(a) for $x = 0.1$ and 0.15 as a function of \mathcal{F} . We see that $\Delta R_A/R$ is linear at low fluence for $\mathcal{F} < 8 \mu\text{J}/\text{cm}^2$. Above $8 \mu\text{J}/\text{cm}^2$, the signal amplitude departs from linearity, indicating an onset of saturation associated with vaporization of the condensate. $\Delta R_A/R$ soon saturates and becomes constant for $\mathcal{F} > 18 \mu\text{J}/\text{cm}^2$ (up to the highest fluences measured). In contrast, $\Delta R_B/R$ is linear with \mathcal{F} both below and above T_c .

To accurately determine the vaporization threshold, we carefully take into account the optical penetration depth λ_{op} for the pump and the probe beams and their spatial profile [23]. From fits of the measured dependence of $\Delta R_A/R$ on \mathcal{F} to the function provided by a straightforward model calculation [shown in Fig. 2(a)] [23], we obtain values for the threshold vaporization fluence at 4.5 K: $\mathcal{F}_T = 4.2 \pm 1.7 \mu\text{J}/\text{cm}^2$ for $x = 0.1$ and $\mathcal{F}_T = 5.8 \pm 2.3 \mu\text{J}/\text{cm}^2$ for $x = 0.15$.

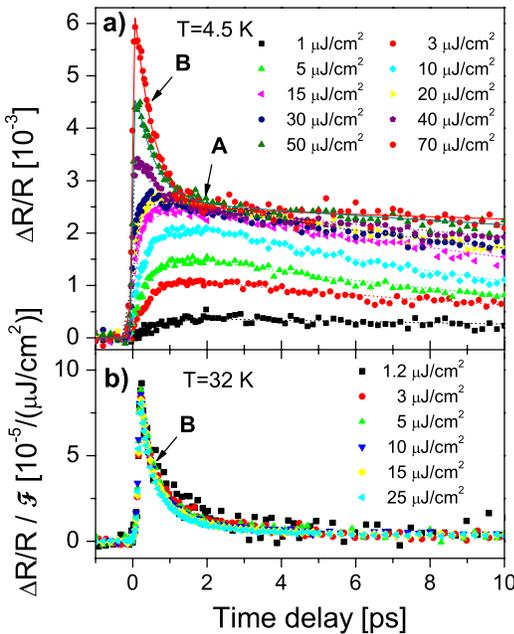


FIG. 1 (color online). The photoinduced reflectivity $\Delta R/R$ in $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ ($T_c = 30$ K) taken at various photoexcitation fluences (a) below and (b) above T_c . The data above T_c are normalized with respect to \mathcal{F} and fully overlap, showing that the response is linear. Below T_c the two distinct relaxation components are marked as A and B.

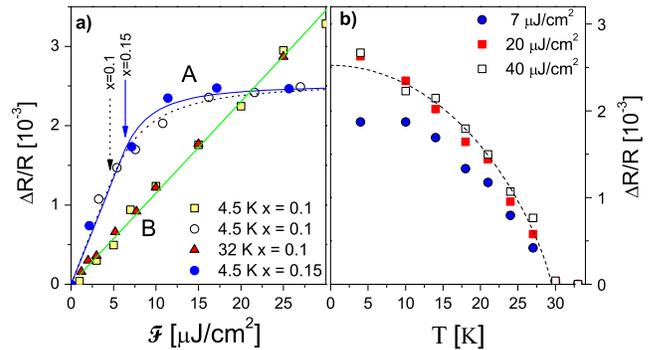


FIG. 2 (color online). (a) The maximum amplitude $\Delta R_A/R$ at 4.5 K for $x = 0.1$ (empty circles) and $x = 0.15$ (full circles), and $\Delta R_B/R$ at 4.5 K (squares) and 32 K (triangles) for $x = 0.1$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The arrows mark the vaporization thresholds $\mathcal{F}_T = 4.2 \pm 1.7 \mu\text{J}/\text{cm}^2$ and $\mathcal{F}_T = 5.8 \pm 2.3 \mu\text{J}/\text{cm}^2$ for $x = 0.1$ and $x = 0.15$, respectively, obtained from the fit [23] (lines). (b) The T dependence of $\Delta R_A/R$ for $x = 0.1$. The dashed line is a fit to the data using Eq. (1).

In Fig. 2(b) we plot the T dependence of $\Delta R_A/R$ for several excitation levels for the $x = 0.1$ sample. As expected, for $\mathcal{F} > \mathcal{F}_T$, the T dependence of $\Delta R_A/R$ does not depend on \mathcal{F} , since full vaporization is achieved at all $T < T_c$. Near the threshold, for $\mathcal{F} = 7 \mu\text{J}/\text{cm}^2$, only partial vaporization is evident and the amplitude $\Delta R_A/R$ merges with the high fluence data only as $T \rightarrow T_c$. We can understand the T dependence of the $\Delta R_A/R$ by considering the difference in reflectivity between the superconducting state and the normal state. The induced change in reflectivity for fluences above the vaporization threshold $A_s = |\frac{\Delta R}{R}|_{\mathcal{F} > \mathcal{F}_T}$ is proportional to $\sigma_1^n - \sigma_1^s$, where σ_1^n and σ_1^s are real parts of the complex conductivity in the normal and superconducting states, respectively. Using the Mattis-Bardeen formulas [24] it follows that [23]

$$A_s(T) \propto \frac{2\Delta(T)}{\hbar\omega} \ln\left(\frac{1.47\hbar\omega}{\Delta(T)}\right), \quad (1)$$

where $\hbar\omega$ is the photon energy and $\Delta(T)$ the T -dependent gap. Using $\Delta(T) = \Delta_0[1 - (T/T_c)^2]$ (Δ_0 is gap at 0 K), which was previously found to describe $\Delta(T)$ in cuprate superconductors [25], a very good agreement between Eq. (1) and the data for $\mathcal{F} > \mathcal{F}_T$ is obtained [see Fig. 2(b)].

Let us now examine the energy relaxation pathways on the pair-breaking time scale of ~ 1 ps. Phonons released during this time need at least $\lambda_{\text{op}}/v_s \sim 30$ ps to escape from the excited volume, v_s being the velocity of sound. The characteristic QP diffusion time from the excitation volume is also of the order of ~ 100 ps, calculated using the measured QP diffusion constant for very clean samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ at 4 K [26]. Therefore we can conclude that the absorbed optical pulse energy cannot diffuse or escape, and remains in the excitation volume on the time scale of 1 ps.

Next, let us analyze the microscopic energy relaxation processes within the excitation volume in more detail. The energy densities in the excitation volume at vaporization threshold for $x = 0.1$ and $x = 0.15$ shown in Fig. 2(a) are $U_p/k_B = \mathcal{F}_T/(\lambda_{\text{op}}k_B) = 2.0 \pm 0.8$ and 2.6 ± 1.0 K/Cu, respectively (using $\lambda_{\text{op}} = 150$ at 810 nm [27]). Both are significantly higher than the thermodynamically measured condensation energies extracted from specific heat data, which are $U_c/k_B = 0.12$ K/Cu for $x = 0.1$ and $U_c/k_B = 0.3$ K/Cu for $x = 0.15$ [28]. The ratios of the two energies are thus $U_p/U_c \approx 16$ and 8.5, respectively. This means that a significant amount of energy ($U_p - U_c$) is not directly used in the vaporization process, but is stored elsewhere on the time scale of τ_r .

There are excitations of the system, such as phonons of different symmetry, but also potentially spin fluctuations, etc., that make up the difference between the condensation energy and the measured optical vaporization energy. Let us consider spin excitations first. The energy required to heat the entire spin bath from 4.5 K to T_c for $x = 0.1$ is given by $U_M = \int_{4.5 \text{ K}}^{T_c=30 \text{ K}} C_M(T)dT$, where $C_M(T)$ is the magnetic specific heat. Using the published value [29] of

$C_M(T)$ for undoped La_2CuO_4 (C_M in doped $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ can only be smaller), we obtain $U_M \approx 80$ mJ/mol (0.01 K/Cu). Clearly, the magnetic system alone is not capable of absorbing $(U_p - U_c)/k_B \approx 1.9$ K/Cu, its heat capacity being too small by a factor of ~ 190 . Making the same estimate for the lattice excitations, we obtain $U_L = \int_{4.5 \text{ K}}^{T_c} C_p(T)dT \approx 77$ J/mol (9 K/Cu) for $x = 0.1$ ($T_c = 30$ K) and 240 J/mol (28 K/Cu) for $x = 0.15$ ($T_c = 38$ K), where $C_p(T)$ is the experimentally measured specific heat [28]. The phonon subsystem can thus easily absorb the excess supplied energy, with $U_L/U_p \sim 4.5$ for $x = 0.1$ (and 11.6 for $x = 0.15$).

This observed discrepancy between measured U_p and thermodynamically measured condensation energy, as well as the T and \mathcal{F} dependence of the superconducting state depletion process, can be naturally explained within the RT model in the bottleneck regime, where the pairing bosons are reaching quasiequilibrium with the QPs [8] on the 1 ps time scale and share some of the energy supplied by the optical pulses.

In the RT model, the pair-breaking time (which corresponds to the condensate vaporization time when $\mathcal{F} > \mathcal{F}_T$) is given by $\tau_r^{-1} = \eta\sqrt{1/4 + [4N(0) + 2n(0)]r}/\eta$, where the initial QP and boson densities are $n(0)$ and $N(0)$, respectively [7,8]. For weak photoexcitation, when both $n(0), N(0) < n_T$, where the threshold density is defined as $n_T = \eta/r$, τ_r is independent of \mathcal{F} , and $2\tau_r = \eta^{-1}$. For intense photoexcitation, when either $n(0), N(0) \geq n_T$, τ_r strongly depends on \mathcal{F} . A strong \mathcal{F} dependence of τ_r is not observed in our data, which implies that LSCO is in the “weak” perturbation regime over our range of \mathcal{F} , and so $\eta = 1/(2\tau_r) \approx 0.5 \times 10^{12} \text{ s}^{-1}$. To estimate n_T , we take $r/d = 0.1 \text{ cm}^2 \text{ s}^{-1}$, where d is the interplane distance, measured by Gedik *et al.* in YBCO [10], and obtain a threshold density $n_T = \eta/r \approx 0.8 \times 10^{20} \text{ cm}^{-3} \approx 0.8 \times 10^{-2}/\text{Cu}$. We can make an alternative microscopic estimate of n_T using the formula for the bare recombination rate from Ref. [30] (with phonons as the mediating bosons) $r = 8\pi\Lambda\Delta^2/\hbar^3\Omega_D^2N_0$, where N_0 is the density of states at the Fermi level, Δ is the superconducting gap, Ω_D is the characteristic phonon frequency, and Λ the electron-phonon coupling constant (which is the same as appears in the McMillan formula for T_c [30]). Taking typical values for LSCO $N_0 = 5/\text{eV Cu}$, $\Delta \approx 0.01 \text{ eV}$, $\hbar\Omega_D \approx 0.1 \text{ eV}$, and the measured $\Lambda = 0.9$ [31], we obtain $r = 0.7 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ which gives a very similar threshold density as the phenomenological estimate $n_T = \eta/r = 1.5 \times 10^{-2}/\text{Cu}$. Note that both are just slightly lower than the estimated photoexcited QP density at threshold fluence which is $n_p^s = \frac{\mathcal{F}}{\Delta_s\lambda_{\text{op}}} \frac{e-1}{e} \approx 2.7 \times 10^{-2}/\text{Cu}$. The arguments presented in our Letter do not rely on which limit (strong or weak bottleneck) of the RT model is used. However, the presented results are consistent only with the strong bottleneck regime, since there is a large discrepancy between the measured energy required to deplete the

superconductivity and the thermodynamically measured condensation energy. In the weak bottleneck regime the two should be roughly equal, in disagreement with the experimental data. We can conclude that the RT model in the strong bottleneck regime involving phonons in the pair-breaking process gives a self-consistent quantitative description of the vaporization dynamics.

Let us now see whether the relaxation processes on the sub-1 ps time scale might somehow involve spin excitations. In this scenario, energy might be initially transferred from photoexcited carriers to the spin subsystem on a time scale much shorter than 1 ps and QPs would then be excited from the condensate by absorbing energy from the hot bath of spin excitations. For energy relaxation only real (not virtual [22]) processes are relevant and the relevant interaction between QPs and spin excitations is spin-orbit coupling. Such a scenario is consistent with our data, provided that the spin-orbit relaxation time τ_{S-O} is equal to, or shorter than, the observed vaporization time of $\tau_r = 0.8 \pm 0.15$ ps. To estimate the vaporization time for this case, we use the fact that spin-lattice relaxation is a process in which electron-phonon relaxation follows spin-orbit relaxation, and $\tau_{S-L} \simeq \tau_{S-O} + \tau_{e-ph}$. So, for spin excitations to be involved in the pair breaking and QP relaxation process, τ_{S-L} needs to be of the order of 1 ps or less. Electron-paramagnetic resonance measurements of Cu spin relaxation in $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ give electron-paramagnetic resonance linewidths ranging from $\Delta H \sim 1$ kG at 30 K to $\Delta H = 3$ kG at 8 K. This corresponds to a lower limit of the relaxation time $\tau_{S-L} \simeq 100\text{--}340$ ps [32], which is much longer than observed. Assuming that the measured τ_{S-L} is correct, the pair breaking thus cannot proceed via the spin excitations, because the relaxation process at 4.5 K would take over 340 ps, instead of ~ 0.8 ps. Thus, if spin excitations were to be responsible for the destruction of the superconducting condensate, a new, as yet unknown mechanism would need to be present. This conclusion has important implications for the pairing mechanism in these compounds. The pair-breaking process discussed above is related to QP recombination (pairing) by time-reversal symmetry, and therefore both processes must involve the same mediating boson. We conclude that the present experiments appear to favor phonon-mediated over spin-mediated QP recombination and pairing.

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