Superconducting Gap Δ_c, the Pseudogap Δ_p, and Pair Fluctuations above T_c in Overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ from Femtosecond Time-Domain Spectroscopy

J. Demsar,[1] B. Podobnik,[1] V. V. Kabanov,[1] Th. Wolf,[2] and D. Mihailovic[1]
[1]*Jozef Stefan Institute, Jamova 39, 1001 Ljubljana, Slovenia*
[2]*Forschungszentrum Karlsruhe, Institut fur Technische Physik, D-76021, Karlsruhe, Germany*
(Received 12 October 1998)

The gap structure in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ single crystals is investigated by real-time measurements of the quasiparticle (QP) relaxation dynamics with femtosecond optical spectroscopy. We find evidence for the coexistence of two distinct gaps. One is a *T-independent* pseudogap Δ_p and the other is a *T-dependent* gap $\Delta_c(T)$ with a BCS-like T dependence. From QP relaxation time measurements above T_c we ascertain that fluctuations associated with the latter are consistent with time-dependent Ginzburg-Landau theory and are distinct from the pseudogap whose presence is apparent well above T_c for all x. [S0031-9007(99)09415-6]

PACS numbers: 74.25.Dw, 74.25.Jb, 78.47.+p

The phase diagram of high-temperature superconducting copper oxides is thought to describe the evolution from a Mott-Hubbard insulator at one end to a more conventional metal on the other. The crossover from localized states in the ground state on one side to itinerant electrons on the other is a general and still open problem. Theoretical calculations [1] have led to suggestions that this crossover may proceed via a spontaneous self-organization into an inhomogeneous state with short range charge (and spin) ordering, rather than through a continuous transition. Supporting this view, on the experimental side [2] there has been mounting evidence in the last few years for an inhomogeneous charge distribution in the Cu-O planes. The two relevant energy scales in this state are (i) the critical temperature T_c, at which macroscopic phase coherence is established between hole pairs, experimentally exhibiting the Meissner state with zero resistivity and (ii) one or more so-called pseudogaps with energy $\Delta_p > kT_c$, which manifest themselves through an apparent reduction in the density of states (DOS) above T_c. To determine the temperature and doping dependence of all the energy gaps in such a multicomponent system from frequency-domain spectroscopy means extracting gap information by deconvolution of all the different spectral components. This inevitably leads to ambiguity in the interpretation of the data, as highlighted by the numerous controversies regarding the interpretation of infrared, Raman, and photoemission spectra among others.

As an experimental alternative, *time-domain* spectroscopy (TDS) can distinguish between different excitations by their different relaxation dynamics, potentially giving new and complementary information on the low-lying electronic structure [3,4]. From the temperature dependence of quasiparticle (QP) dynamics in $YBa_2Cu_3O_{7-\delta}$ (YBCO) it was shown that a T-independent charge gap $\Delta_p(x)$ is dominant in the underdoped state, whose magnitude is inversely proportional to doping [4] in good agreement with other measurements on cuprates [5]. Near optimum doping, however, the same measurements show a dominant T-dependent gap $\Delta_c(T)$ which closes at T_c. The question of how the two gaps evolve near optimum doping and into the overdoped state still needs to be answered experimentally. In this Letter we report the first direct and detailed TDS measurements of the evolution of the QP recombination dynamics from optimum doping to the overdoped region of the phase diagram of a high-T_c superconductor $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ as a function of T and x, paying particular attention to the multicomponent response and the evolution of the pseudogap $\Delta_p(x)$ and the collective gap $\Delta_c(T)$ with x. The time-domain information on the relaxation of the QP density above T_c enables us to clarify the connection between the pseudogap and pair fluctuations in the overdoped region.

In time-resolved pump-probe experiments, a laser pulse first excites electron-hole pairs which then rapidly relax to states close to the Fermi energy by e-e and e-ph scattering creating a nonequilibrium QP population. This initial avalanche QP multiplication process occurs within $\tau_m \sim 100$ fs [4,6]. The presence of a gap near E_F causes a bottleneck, so that carriers accumulate in QP states above the gap, giving rise to a transient change in absorbance or reflectivity which is detected by a second probe laser pulse. A detailed description of the experimental technique and theory of femtosecond time-resolved QP spectroscopy can be found elsewhere [4,7]. We used light pulses from a Ti:sapphire laser producing $\tau_L \lesssim 80$ fs pulses at 800 nm ($\approx$1.5 eV) for both the pump and the probe. The photoinduced (PI) change in reflectivity $\Delta\mathcal{R}/\mathcal{R}$ was measured using a photodiode and lock-in detection. The pump laser power was <10 mW, exciting approximately 10^{19}–10^{20} carriers per cm^3, and the pump/probe intensity ratio was $\sim$100. The steady-state heating effect was accounted for as described in Ref. [7], giving an uncertainty in sample temperature of ± 2 K. The experiments were performed on four $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ single crystals with $x = 0$, 0.016, 0.101, and 0.132 and T_cs of 93, 89.5, 83, and 75 K,

 0031-9007/99/82(24)/4918(4)$15.00

respectively, grown by the self-flux method in Y or Ca stabilized ZrO_2 crucibles. The Ca content was determined by energy-dispersive x-ray spectroscopy and neutron diffraction analysis. The oxygen content δ was adjusted by heat treatment and adjustment of oxygen pressure to give $\delta = 6.94, 6.986, 6.943$, and 6.928 for $x = 0, 0.016, 0.101$, and 0.132, respectively. T_c was measured by dc magnetization for each x and δ as shown in the inset to Fig. 1(b).

The time evolution of the PI reflection, $\Delta\mathcal{R}/\mathcal{R}$, is shown for $x = 0$ and 0.132 at a few temperatures in Figs. 1(a) and 1(b). Above T_c, a single exponential gives a very good fit to the data with a relaxation time of $\tau_B \sim 0.5$ ps. We note that beyond 3 ps ($\simeq 6\tau_B$) the signal has decayed to nearly a constant value, indicating that *no other* relaxation process is present on this time scale [8]. This is true for all $0 < x < 0.132$. This is also evident from the logarithmic plots in Figs. 1(c) and 1(d). *Below* T_c, however, the logarithmic plots of $\Delta\mathcal{R}/\mathcal{R}$ shown in Figs. 1(c) and 1(d) reveal a break in the slope near $t = 3$ ps, indicating the presence of two distinct relaxation times, one with $\tau_B \approx 0.5$ ps and the other with $\tau_A \approx 3$ ps. This implies that a two-component fit to the data is necessary for an accurate description. We therefore model the response as a sum of two components, each given by the solution of $dr/dt = -r/\tau + G(t)$, where $r = \Delta\mathcal{R}/\mathcal{R}$ and $G(t)$ is the excitation temporal profile approximated by $G(t) = G_0 \exp(-2t^2/\tau_m^2)$. For $t > 200$ fs, we can simplify the solution to $\Delta\mathcal{R}/\mathcal{R}(t) = A(T)\exp(-t/\tau_A) + B(T)\exp(-t/\tau_B)$, where both amplitudes $A(T)$ and $B(T)$ are T dependent and $A(T) = 0$ for $T > T_c$.

In Fig. 2 we have plotted the relaxation times τ_A and τ_B as a function of temperature for different x. The common feature for all x is the divergence of τ_A just below T_c similar to that reported previously near optimum doping [4,9]. In contrast, τ_B is found to be completely T independent, as previously observed in underdoped $YBa_2Cu_3O_{7-\delta}$ [4,10].

Below T_c the QP recombination time of the superconductor with a gap $\Delta(T)$ can be expressed as [4]

$$\tau = \frac{\hbar\omega^2 \ln\{(\frac{\mathcal{E}_I}{2N(0)[\Delta(0)]^2} + e^{-\Delta(T)/k_BT})^{-1}\}}{12\Gamma_\omega[\Delta(T)]^2}, \qquad (1)$$

where ω is a typical phonon frequency, Γ_ω is a characteristic anharmonic phonon linewidth, $N(0)$ is the DOS, and $\Delta(0)$ is the gap at zero temperature. The important feature of Eq. (1) is that near T_c, $\tau \propto 1/\Delta(T)$ [4]. On

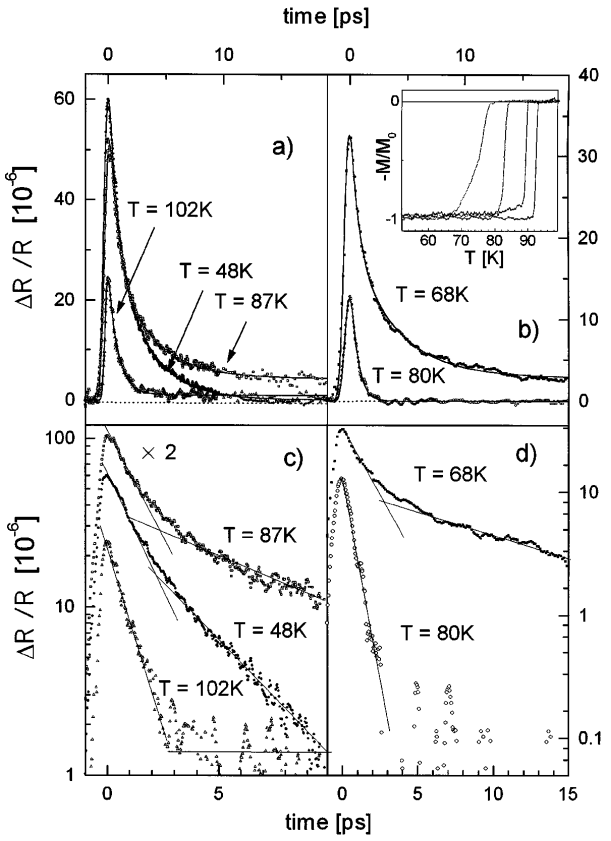

FIG. 1. The photoinduced reflection $\Delta\mathcal{R}/\mathcal{R}$ from $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ above and below T_c as a function of time (a) for $x = 0$ ($T_c = 93$ K) and (b) $x = 0.132$ ($T_c = 75$ K) at different temperatures. A two-exponential fit is made below T_c and a single exponential fit above T_c. In (c) and (d) the same data for $x = 0$ and $x = 0.132$, respectively, are presented on a logarithmic scale. The inset to (b) shows the dc magnetization curves for the four samples.

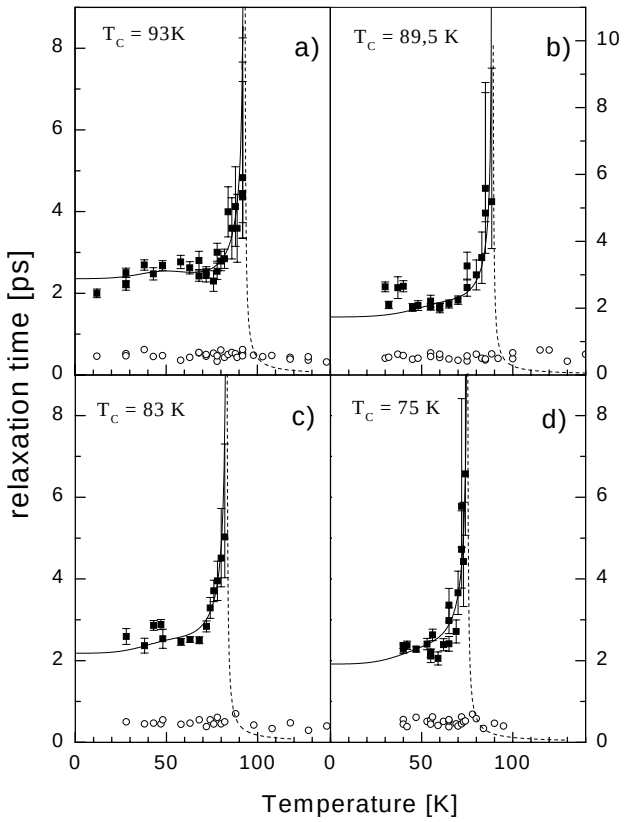

FIG. 2. The relaxation times τ_A (squares) and τ_B (open circles) as a function of T for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with (a) $x = 0$, (b) $x = 0.016$, (c) $x = 0.101$, and (d) $x = 0.132$. The solid line is the relaxation time below T_c given by Eq. (1). The dashed line describes QP relaxation time above T_c given by $\tau_{GL} = \pi\hbar[8k(T - T_c)]^{-1}$.

the other hand, if τ is constant, this implies that Δ is T independent. To model the divergent signal (component A) below T_c, we substitute $N(0) = 5\ \mathrm{eV}^{-1}\,\mathrm{cell}^{-1}\,\mathrm{spin}^{-1}$, $\Gamma_\omega = 10\ \mathrm{cm}^{-1}$ [11], and $\omega = 400\ \mathrm{cm}^{-1}$, with—for simplicity—a BCS functional form for $\Delta(T) = \Delta_c(T)$ and $\Delta_c(0) = 4kT_c$. The result is shown by the solid curves in Fig. 2. The divergence of τ at T_c is evidence for the existence of a collective gap in the entire overdoped region. The simultaneous presence of a T-independent τ_B indicates the *coexistence* of a T-independent gap Δ_p also over the whole overdoped region.

To obtain quantitative information on $\Delta_c(T)$ and Δ_p we analyze the temperature dependence of $|\Delta\mathcal{R}/\mathcal{R}|$ plotted in Fig. 3 as a function of T. Qualitatively similar behavior is observed for all x: at low T, $|\Delta\mathcal{R}/\mathcal{R}|$ is nearly constant exhibiting a slight upturn near $0.7T_c$ and then a rapid drop to approximately 30% of maximum amplitude just below T_c. Close to T_c, there is a clear break in the response and $|\Delta\mathcal{R}/\mathcal{R}|$ reverts to a much slower asymptotic temperature dependence above T_c extending to 150 K or more.

In the limit of small photoexcited carrier density, we can assume that all possible contributions to $\Delta\mathcal{R}/\mathcal{R}$—arising from excited state absorption and photoinduced band-gap changes, for example—are linear in the photoexcited carrier density. So, for a T-dependent gap $\Delta_c(T)$, the temperature dependence of the amplitude of the photoinduced reflectivity $\Delta\mathcal{R}/\mathcal{R}$ is given by [4]

$$A(T) = \frac{\mathcal{E}_I/[\mathbf{\Delta}_c(T) + k_BT/2]}{1 + \frac{2\nu}{N(0)\hbar\Omega_c}\sqrt{2k_BT/\pi\mathbf{\Delta}_c(T)}\,e^{-\mathbf{\Delta}_c(T)/k_BT}}, \quad (2)$$

where $\mathcal{E}_I$ is the incident energy density per unit cell of the pump pulse, ν is the number of phonon modes interacting with the QPs, $N(0)$ is the DOS, and Ω_c is a typical phonon cutoff frequency. A similar expression gives the amplitude for a T-independent gap Δ_p:

$$B(T) = \frac{\mathcal{E}_I/\mathbf{\Delta}_p}{1 + \frac{2\nu}{N(0)\hbar\Omega_c}\,e^{-\mathbf{\Delta}_p/k_BT}}. \quad (3)$$

The two expressions predict qualitatively different T dependence for $|\Delta\mathcal{R}/\mathcal{R}|$. As T_c is approached from below, Eq. (2) predicts that $A(T) \to 0$ as $\Delta(T) \to 0$. In contrast, Eq. (3) predicts an asymptotic (exponential) fall of the amplitude at high T. Moreover, Eq. (2) predicts a slight maximum at $T/T_c \approx 0.7$, which is not present for the case of a T-independent gap [Eq. (3)]. These differences between the two predictions allow us to unambiguously identify the temperature dependence of the QP gaps and determine their magnitude. Using $\nu = 18$, $\Omega_c = 0.1$ eV, and $N(0) = 5\ \mathrm{eV}^{-1}\,\mathrm{cell}^{-1}\,\mathrm{spin}^{-1}$ as before, fits to the temperature dependence of $|\Delta\mathcal{R}/\mathcal{R}|$ with the sum of (2) and (3) are plotted in Fig. 3. The values of $\Delta_c(0)$ and Δ_p are shown in each case. It is evident from the plots that the total amplitude $|\Delta\mathcal{R}/\mathcal{R}|$ can be described accurately only by a two-component fit and cannot be described by either component separately. The gap ratios obtained from the fits are $\Delta_c/k_BT_c \approx 5 \pm 0.5$, depending slightly on x. Δ_p and $\Delta_c(0)$ from the fits of the T dependences of $|\Delta\mathcal{R}/\mathcal{R}|$ as a function of doping are shown in Fig. 4. (The data on Δ_p for underdoped YBCO [4] have also been included for completeness.) In the crossover region the two gaps converge $\Delta_p \to \Delta_c(0)$, but they *remain clearly distinct*, as indicated by the two-component decay in Figs. 1(c) and 1(d), as well as in Figs. 2(a)–2(d) and in the T-dependence analysis of $|\Delta\mathcal{R}/\mathcal{R}|$ (Fig. 3).

Turning our attention to the relaxation dynamics of the order parameter *above* T_c, if we assume that Ginzburg-Landau (GL) theory can be applied to the collective state which exhibits a T-dependent gap $\Delta_c(T)$, then the only contribution relevant to the present experiments is from nonequilibrium pair density fluctuations. Time-dependent GL (TDGL) theory [13] predicts the relaxation time for the amplitude of these fluctuations above T_c to be $\tau_{\mathrm{GL}} = \pi\hbar[8k(T - T_c)]^{-1} \simeq 3.0/(T - T_c)$ ps K. Plotting this (parameterless) expression for τ_{GL} as a function of T above T_c in Fig. 2, we see that τ_{GL} drops to zero within a few K of T_c, consistent with the data on τ_A. Any QP density extending *significantly above* that predicted by TDGL theory would be evident in the data above T_c, but it is not. We conclude that pair fluctuations associated with the *collective phase* are consistent with TDGL theory and are quite unrelated to the pseudogap behavior.

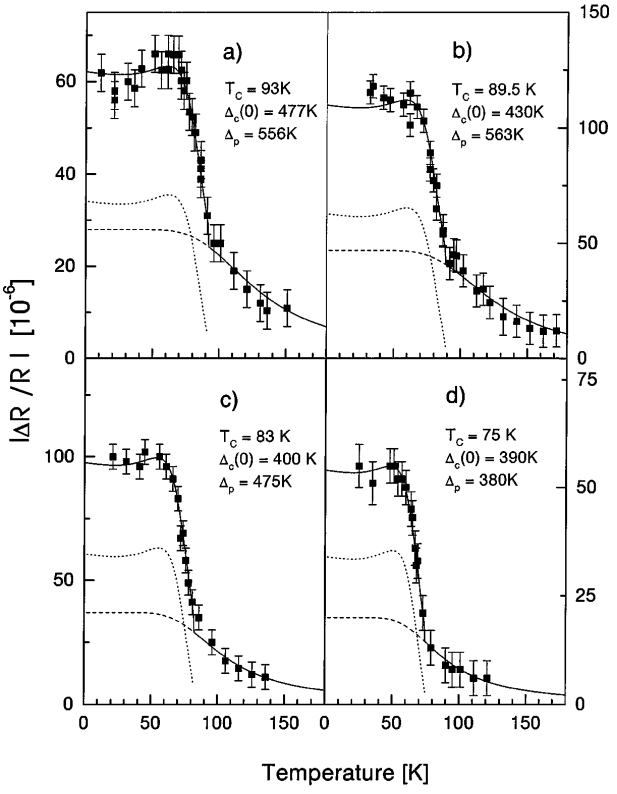

FIG. 3. The PI reflection amplitude, $|\Delta\mathcal{R}/\mathcal{R}|$, as a function of T for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with (a) $x = 0$, (b) $x = 0.016$, (c) $x = 0.101$, and (d) $x = 0.132$. The fits are made using the sum of Eqs. (2) and (3). The values of $\Delta_c(0)$ and Δ_p used in the fit are shown. The separate $A(T)$ and $B(T)$ are also shown as a dotted line and a dashed line, respectively.

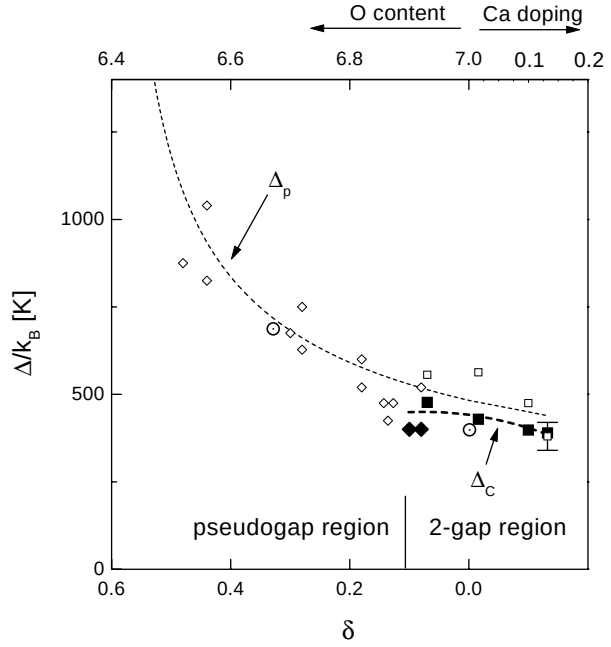

FIG. 4. The energy gaps Δ_p and $\Delta_c(0)$ as a function of doping in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ obtained from fits to the data in Fig. 3. The open squares represent Δ_p, while the solid symbols are for $\Delta_c(0)$. The open and filled diamonds represent the Δ_p and $\Delta_c(0)$, respectively, from Ref. [4]. The upper dashed line represents $\Delta_p \propto 1/x$, where x is the carrier concentration. The lower dashed line is a guide to the eye emphasizing the behavior of $\Delta_c(0)$. The circles are from tunneling data [12].

To put the present results in the context of other spectroscopy experiments, the data on τ_A and τ_B suggest that above T_c we should expect a broad peak (gap) at Δ_p of width $\Delta E_A \gtrsim h/\pi c\tau_A$ ($\simeq$4 meV). Below T_c in addition to this peak, a narrower QP peak should be present with $\Delta_c \simeq 5kT_c$, with $\Delta E_B \gtrsim 0.5$ meV. The simultaneous presence of two gaps has been previously reported in tunneling spectra [12] and microwave experiments [14] on optimally doped YBCO. Comparing our $\Delta_p(x)$ with the gap from Giever (single-particle) tunneling on YBCO, we find very good agreement (see Fig. 4) [12]. Extending the discussion to other cuprates, two-component behavior was reported in $La_{2-x}Sr_xCuO_4$ over a large portion of the phase diagram, although so far only a T-independent pseudogap was observed. A T-independent pseudogap has also been reported in overdoped $Bi_2Sr_2(Ca,Y)Cu_2O_8$ [12,15,16]. The coexistence of Δ_p and $\Delta_c(T)$ is also consistent with the T dependence of the photoemission line shapes in $Bi_2Sr_2CaCu_2O_{8-\delta}$ [17].

Speculating on the origins of the two-gap behavior in the spatially inhomogeneous phase picture [2], it is natural to associate the behavior of $\Delta_c(T)$ with high carrier density areas, where the gap in the QP spectrum is formed as a collective effect. Pairing there occurs simultaneously with macroscopic phase coherence at T_c and the fluctuation region above T_c is small. In low-density regions, where no collective effects are present, Δ_p signifies the individual pair binding energy. The pseudogap behavior arises due to the fluctuating presence of pairs in the ground state, whose density is determined by kT. At T_c macroscopic phase coherence is established across both regions into a common superconducting state.

To conclude, the TDS experiments on the time and temperature dependence of the photoinduced QP response give a self-consistent and systematic picture of the low-energy charge excitation spectrum of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. They suggest that the crossover from the underdoped to the overdoped region of the phase diagram occurs via a two-component inhomogeneous state with two coexisting gaps, one T independent and one with a BCS-like T dependence. According to present TDS experiments the mixed gap region is present over most of the overdoped and optimally doped phase. To what extent the two gap behavior is universal in the cuprates remains to be shown.

We thank Airton A. Martin for kindly processing and characterizing the samples.

[1] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **64**, 475 (1990); articles by E. Sigmund, V. Hizhnyakov, and G. Seibold, in *Phase Separation in Cuprate Superconductors*, edited by K. A. Muller and G. Bendek (World Scientific, Singapore, 1992); C. Di Castro and M. Grilli, *ibid.*

[2] D. Mihailovic and K. A. Müller, in *High-T_c Superconductivity 1996: Ten Years after the Discovery*, edited by E. Kaldis, E. Liarokapis, and K. A. Müller, NATO ASI, Ser. E, Vol. 343 (Kluwer, Dordrecht, 1997), p. 243.

[3] C. J. Stevens *et al.*, Phys. Rev. Lett **78**, 2212 (1997).

[4] V. V. Kabanov, J. Demsar, B. Podobnik, and D. Mihailovic, Phys. Rev. B **59**, 1497 (1999).

[5] K. A. Müller, G. Zhao, K. Conder, and H. Keller, J. Phys. Condens. Matter **10**, L291 (1998).

[6] S. D. Brorson *et al.*, Solid State Commun. **74**, 1305 (1990).

[7] D. Mihailovic and J. Demsar, in *Spectrosopy of Superconducting Materials*, edited by E. Faulques, ACS Symposium Series, Vol. 730 (ACS, Washington, 1999).

[8] In addition, a much slower component is also observed, similar as in Ref. [3], but this will not be discussed further in this paper.

[9] S. G. Han *et al.*, Phys. Rev. Lett. **65**, 2708 (1990); D. H. Reitze *et al.*, Phys. Rev. B **46**, 14 309 (1992); see also Refs. [4,10].

[10] D. Mihailovic *et al.*, J. Phys. Chem Solids **59**, 1937 (1998).

[11] D. Mihailovic, K. F. McCarty, and D. S. Ginley, Phys. Rev. B **47**, 8910 (1993).

[12] G. Deutscher, Nature (London) **397**, 410 (1999).

[13] L. P. Gorkov and G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **54**, 612 (1968) [Sov. Phys. JETP **27**, 328 (1968)].

[14] H. Srikanth *et al.*, Phys. Rev. B **57**, 7986 (1998).

[15] R. Nemetschek *et al.*, Phys. Rev. Lett. **78**, 4837 (1997).

[16] Ch. Renner *et al.*, Phys. Rev. Lett. **80**, 149 (1998); **80**, 3606 (1998).

[17] M. R. Norman *et al.*, Phys. Rev. Lett. **79**, 3506 (1997); Phys. Rev. B **57**, R11 093 (1998).