The superconducting gap $\Delta_c$, the pseudogap $\Delta_p$, and pair fluctuations above $T_c$ in overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-x}$ from femtosecond time-domain spectroscopy.

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The low-energy electronic excitation spectrum and gap structure in optimally doped and overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-x}$ single crystals are investigated by real-time measurements of the quasiparticle relaxation dynamics with femtosecond optical spectroscopy. From the amplitude of the photoinduced reflectivity as a function of time, temperature and doping $x$ we find clear evidence for the coexistence of two distinct gaps in the entire overdoped phase. One is a temperature-independent "pseudogap" $\Delta_p$, and the other is a $T$-dependent collective gap $\Delta_c(T)$ which has a BCS-like $T$-dependence closing at $T_c$. From quasiparticle relaxation time measurements above $T_c$ we ascertain that fluctuations associated with the collective gap $\Delta_c(T)$ are limited to a few K, consistent with time-dependent Ginzburg-Landau theory and are distinct from the pseudogap whose presence is apparent well above $T_c$ for all $x$.

The phase diagram of high-temperature superconducting copper oxides is commonly thought to describe the evolution from a Mott-Hubbard insulator at one end to a more conventional metal on the other. However, the cross-over from localised states in the ground state on one side to itinerant electrons on the other is a general and still open problem. Recently, theoretical calculations [1] have led to suggestions that this cross-over may proceed via a spontaneous self-organisation 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 gap(s) in such a multi-component system from frequency-domain spectroscopy (FDS) 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 amongst 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]. For example, from the temperature dependence of the quasiparticle (QP) dynamics in YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) it was recently shown that a $T$-independent charge gap $\Delta_p(x)$ is dominant in the underdoped state, whose magnitude is inversely proportional to doping as $\Delta_p(x) \propto 1/x$ [4] in good agreement with other measurements on cuprates [4]. Near optimum doping however, the same measurements show a dominant $T$-dependent gap $\Delta_c(T)$ which closes at $T_c$. However, the fundamental 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 $Y_{1-x}Ca_xBa_2Cu_3O_{7-x}$ 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 $T_c$ also 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 non-equilibrium QP population. This initial avalanche QP multiplication process occurs within $\tau_m \sim 100$ fs [4]. The presence of a gap near $E_F$ causes a bottleneck in the final stage of relaxation, 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]. We used light pulses from a Ti:Sapphire laser producing $\tau_L \simeq 80$ fs pulses at 800 nm (approx.1.5 eV) for both the
pump and the probe. The photoinduced (PI) change in reflectivity $\Delta R/R$ 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. [1], giving an uncertainty in sample temperature of $\pm 2\text{K}$. The experiments were performed on four Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ single crystals with $x = 0$, 0.016, 0.101 and 0.132 and $T_c$s of 93K, 89.5K, 83 K and 75 K respectively, grown by the self flux method in Y- or Ca stabilized ZrO$_2$ crucibles. The Ca-content was determined by EDX and neutron diffraction analysis. The oxygen content $\delta$ was adjusted by heat treatment and adjustment of oxygen pressure to give $\delta = 0.94$ for $x = 0$, and 6.986, 6.943 and 6.928 for $x = 0.016, 0.101$ and 0.132 respectively. $T_c$ was measured by dc magnetization for each $x$ and $\delta$ as shown in the insert to Fig. 1b).

The time-evolution of the PI reflection, $\Delta R/R$, is shown for $x = 0$ and 0.132 at a few temperatures in Figures 1a) and b). Above $T_c$, a single exponential gives a very good fit to the data with a relaxation time of $\tau_B ~ 5$ ps. Importantly, we note that beyond 3 ps ($\sim 6\tau_B$) the signal has decayed to nearly a constant value, indicating that no other relaxation process is present on this timescale [8]. This is true for all $0 < x < 0.132$. This is also evident from the logarithmic plots in Fig. 1c) and d). Below $T_c$ however, the logarithmic plots of $\Delta R/R$ shown in Figs. 1c) and 1d) reveal a clear 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 clearly 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 $r = \Delta R/R$ and $G(t)$ is the excitation temporal profile approximated by $G(t) = G_0 \exp[-2(t/\tau_m)^2]$. For $t > 200$ fs, we can simplify the solution to $\Delta R/R(t) = A(T) \exp(-t/\tau_A) + B(T) \exp(-t/\tau_B)$, 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 $\tau_A$ and $\tau_B$ as a function of temperature for different $x$. The common feature for all $x$ is the divergence of $\tau_A$ just below $T_c$ similar to that reported previously near optimum doping [8,9]. In contrast, $\tau_B$ is found to be completely $T$-independent, as previously observed in underdoped YBa$_2$Cu$_3$O$_{7-\delta}$ [5,10].

Below $T_c$ the QP recombination time of the superconductor with a gap $\Delta(T)$ can be expressed as [11]:

$$\tau = \frac{\hbar \omega^2 \ln \left\{ \frac{(2 \pi N(0) \Omega I)^{\frac{1}{2}}}{12 \Gamma_\omega \Delta(T)} + e^{-\Delta(T)/k_B T} \right\}^{-1}}{\omega}$$

where $\omega$ is a typical phonon frequency, $\Gamma_\omega$ 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 $T_c$, we can expand the formula for small $\Delta(T) \to 0$, giving $\tau \propto 1/\Delta(T)$ [11], which means that $\tau$ must diverge at $T_c$. On the other hand, if $\tau$ is constant, this implies that $\Delta$ is $T$-independent. To model the divergent signal (component A) below $T_c$, we substitute $N(0) = 5$ eV$^{-1}$cell$^{-1}$spin$^{-1}$, $\Gamma_\omega = 10$ cm$^{-1}$ [11] and $\omega = 400$ 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 clear divergence of $\tau$ at $T_c$ is evidence for the existence of a collective gap in the entire overdoped region. On the other hand, the simultaneous presence of a $T$-independent $\tau_B$ indicates the co-existence of a $T$-independent gap $\Delta_p$ also over the whole overdoped region.

To obtain more quantitative information on $\Delta_c(T)$ and $\Delta_p$ we analyse the temperature-dependence of $|\Delta R/R|$ plotted in Fig.3 as a function of $T$. Qualitatively similar behavior is observed for all $x$: at low $T$, $|\Delta R/R|$ is nearly constant exhibiting a slight upturn near 0.7 $T_c$ 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 $|\Delta R/R|$ 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 $\Delta R/R$ - 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 $\Delta R/R$ is given by [4]:

$$A(T) = \frac{\mathcal{E}_I/(\Delta_c(T) + k_BT/2)}{1 + \frac{2\nu}{N(0)\Omega_c} \sqrt{\pi \Delta_c(T)} e^{-\Delta_c(T)/k_BT}$$

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

$$B(T) = \frac{\mathcal{E}_I/\Delta_p}{1 + \frac{2\nu}{N(0)\Omega_c} e^{-\Delta_p/k_BT}}.$$
The two expressions predict qualitatively different $T$-dependence for $|\Delta R/R|$. 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 $\nu = 18$, $\Omega_s = 0.1$ eV and $N(0) = 5eV^{-1}cm^{-1}spin^{-1}$ as before, fits to the temperature-dependence of $|\Delta R/R|$ with the sum of (2) and (3) are plotted in Fig.3. The values of $\Delta_c(0)$ and $\Delta_p$ are also shown in each case. It is evident from the plots that the total amplitude $|\Delta R/R|$ can only be described accurately by a two component fit and cannot be described by either component separately. The gap ratios obtained from the fits are $\Delta_c/k_B T_c \approx 5 \pm 0.5$, depending slightly on $x$. $\Delta_p$ and $\Delta_c(0)$ from the fits of the $T$-dependences of $|\Delta R/R|$ as a function of doping are shown in Fig. 4. (The data on $\Delta_p$ for underdoped YBCO [8] have also been included for completeness.). Remarkably, in the cross-over region the two gaps converge $\Delta_p \to \Delta_c(0)$, but they remain clearly distinct, as indicated by the 2-component decay in Figs. 1c) and d), as well as in Fig.2a)-d) and in the $T$-dependence analysis of $|\Delta R/R|$ (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 non-equilibrium pair density fluctuations. Time-dependent GL (TDGL) theory [12] predicts the relaxation time for the amplitude of these fluctuations above $T_c$ to be $\tau_{GL} = \pi \hbar [8k(T - T_c)]^{-1} \approx 3.0/(T - T_c) \text{psK}$. Plotting this (parameterless) expression for $\tau_{GL}$ as a function of $T$ above $T_c$ in Fig.2, we see that $\tau_{GL}$ drops to zero within a few Kelvin of $T_c$, consistent with the data on $\tau_A$. Any QP density extending significantly above that predicted by TDGL theory would be clearly 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.

To put the present results in the context of other spectroscopy experiments, the data on $\tau_A$ and $\tau_B$ suggest that above $T_c$ we should expect a broad peak (gap) at $\Delta_p$ of width $\Delta E_A \gt \hbar/(\pi c \tau_A) (\approx 4$ meV). Below $T_c$ in addition to this peak, a narrower QP peak should be present with $\Delta_c \sim 5kT_c$, with $\Delta E_B \gt 0.5$ meV. The simultaneous presence of two gaps have been previously reported in tunneling spectra [3] 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) [3]. Extending the discussion to other cuprates, two-component behavior was reported in La$_{2-x}$Sr$_x$CuO$_4$ 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$_2$Sr$_2$(Ca,Y)Cu$_2$O$_8$ (BISCO) [15,16,13]. The co-existence of $\Delta_p$ and $\Delta_c(T)$ is also consistent with the $T$-dependence of the photoemission lineshapes in BISCO [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, consistent with TDGL theory. On the other hand, in low-density regions, where no collective effects are present, $\Delta_c$ 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 thermal occupancy. However, 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$_x$Ba$_2$Cu$_3$O$_{7-\delta}$. They suggest that the cross-over from the underdoped to the overdoped region of the phase diagram occurs via a 2-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.

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Figure 1. The photoinduced reflection $\Delta R/R$ for Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ 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 2-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, clearly showing the single-exponential decay above $T_c$ and the 2-exponential decay below $T_c$ with a break near 3 ps. The insert to b) shows the dc magnetization curves for the four samples. Figure 2. The relaxation times $\tau_A$ (squares) and $\tau_B$ (open circles) as a function of $T$ for Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ with $a)$ $x=0$, $b)$ $x=0.016$, $c)$ $x=0.101$ and $d)$ $x=0.132$. The solid line is the prediction of the relaxation time below $T_c$ given by Eq.(1). The dashed line describes the expected QP relaxation time above $T_c$ given by $\tau_{GL} = \pi \hbar [8k(T - T_c)]^{-1}$. 

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Figure 3. The PI reflection amplitude, $|\Delta R/R|$, 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 $\Delta_p$ used in the fit are shown. The separate $A(T)$ and $B(T)$ are also shown dotted and dashed respectively.

Figure 4. The energy gaps $\Delta_p$ 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 Figure 3. The open squares represent $\Delta_p$, while the solid symbols are for $\Delta_c(0)$ obtained from the fits in Fig. 3. The open and filled diamonds represent the $\Delta_p$ and $\Delta_c(0)$ respectively from Kabanov et al. [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 behaviour of $\Delta_c(0)$. The circles are from tunneling data [13].

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FIG. 1
Fig. 2

(a) $T_c = 93\, \text{K}$

(b) $T_c = 89.5\, \text{K}$

(c) $T_c = 83\, \text{K}$

(d) $T_c = 75\, \text{K}$

Relaxation time [ps]

Temperature [K]

- $T_c$ denotes the critical temperature for superconductivity.
a) $T_c = 93K$
$\Delta_c(0) = 477K$
$\Delta_p = 556K$

b) $T_c = 89.5 K$
$\Delta_c(0) = 430K$
$\Delta_p = 563K$

c) $T_c = 83 K$
$\Delta_c(0) = 400 K$
$\Delta_p = 475K$

d) $T_c = 75 K$
$\Delta_c(0) = 390K$
$\Delta_p = 380K$
Figure 4

Ca content, $x$

$0.0 \ 0.1 \ 0.2$

$\Delta c$

$\Delta p$

$\frac{\Delta}{k_B} [K]$

$\delta$

$0 \ 0.2 \ 0.4 \ 0.6$