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To cite this article: J. Demsar *et al* 1999 *EPL* **45** 381

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Evidence for crossover from a Bose-Einstein condensate to a BCS-like superconductor with doping in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ from quasiparticle relaxation dynamics experiments

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Abstract. – Time-resolved measurements of quasiparticle (QP) relaxation dynamics on the femtosecond timescale are reported as a function of temperature and doping in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ for $(0.48 < \delta < 0.1)$. In the underdoped state $(\delta > 0.15)$, there is no evidence for any changes in the low-energy gap structure at T_c from either photoinduced QP absorption or QP relaxation time data. In combination with the sum rule, this implies the existence of pre-formed pairs up to a much higher temperature T^*. Near $\delta = 0.1$ a rapid cross-over is observed, to a state where the QP recombination time diverges and the photoinduced QP density falls to zero at T_c, indicating the existence of a temperature-dependent superconducting gap which closes at T_c.

Combining the universal correlations between T_c, the ratio of carrier density to effective mass n_s/m^* and pseudogap behaviour in the underdoped region, Uemura [1] suggested that the phase diagram of high-temperature superconducting cuprates could be described in terms of a crossover from Bose-Einstein (BE) to BCS-like condensation. According to this scenario, in the underdoped state hole pairs form at temperatures above T_c which subsequently form a phase-coherent superconducting condensate at T_c with no associated change of pairing amplitude at this temperature, while in the BCS-like state —suggested to exist in the overdoped cuprates— an energy gap, phase coherence and superconductivity would all occur more or less simultaneously close to T_c as a result of a collective phenomenon.

Using time-resolved (TR) optical spectroscopy to measure quasiparticle (QP) relaxation dynamics in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (YBCO) on the femtosecond timescale, we present experimental evidence for such a crossover near optimum doping from a BE-like superconductor with pre-formed pairs in the underdoped state to a BCS-like superconductor which shows a gap opening close to T_c. The photoinduced optical transmission through a superconductor thin film is proportional to the photoexcited QP density, so it can be used to probe changes in the low-energy excitation spectrum. Time-resolved measurements also provide independent
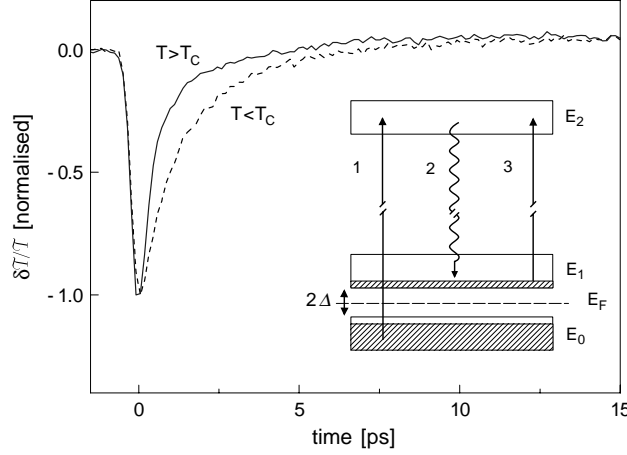
Fig. 1. – The normalised time-resolved induced transmission as a function of time delay just above and just below T_c for YBCO with $\delta = 0.1$. The schematic diagram shows the optical absorption and QP relaxation processes involved in the experiment.

direct information about the gap from analysis of the QP recombination time, where for a superconductor $\tau_s \propto 1/\Delta(T)$ [2]. Consistent with the appearance of a superconducting gap, previous TR measurements on optimally doped cuprate superconductors have shown large changes in both the photoinduced optical constants [3, 4] and relaxation time [5] near T_c. In this paper the data for a large range of O doping δ are presented for $YBa_2Cu_3O_{7-\delta}$ and analysed using a theoretical model for the temperature dependence of the photoinduced QP density [6], giving systematic and quantitative information about the evolution of the energy gap with δ and T in underdoped and near optimally doped samples.

The experiments were performed on a number of ~ 100 nm thick epitaxial YBCO films on either $SrTiO_3$ or MgO substrates which were annealed to obtain δ in the range $0.48 < \delta < 0.1$. AC magnetic susceptibility measurements show narrow (single) superconducting transitions of less than 2 K for $\delta \sim 0.1$ and 4–7 K for $\delta > 0.2$ (defined by a 90% drop in the real part of the susceptibiliy χ'). The optical processes involved in the photoinduced experiments are shown schematically in fig. 1. First carriers are excited by the absorption of a 200 fs pump laser pulse (step 1 in fig. 1). After photoexcitation, the carriers relax to QP states near the Fermi level within 10–100 fs by carrier-carrier scattering and carrier-phonon scattering (step 2) [7-9]. Subsequently, QPs accumulate above the energy gap, forming a near-equilibrium distribution of QPs due to a relaxation bottleneck. This bottleneck occurs because the gap in the low-energy spectrum limits further QP energy relaxation to recombination processes which include only high-energy phonons with energy greater than the gap [2, 6]. This near-steady state QP population, which is intimately related to the properties of the gap itself, can be detected by a second, suitably delayed laser pulse (step 3). To maximize the induced absorption signal, we use 200 fs pulses with a laser wavelength of 800 nm (1.5 eV photon energy) from a Ti:Sapphire laser, which coincides with a O-Cu charge transfer optical resonance in YBCO [4, 10]. The initial states for the probe pulse absorption are QP states at E_F and the final unoccupied states are in a band 1.5 eV above E_F. The probe pulse was polarized in the (a, b)-plane and hence probes primarily the CuO-plane excitations. The number of QPs photoexcited by each laser pulse is approximately $n_Q = n_P \frac{E_P}{2\Delta(0)}$, where $\Delta(0)$ is the gap magnitude and n_P is the number of absorbed photons in each laser pulse. With $\Delta(0) = 30$ meV and with a pump power of typically
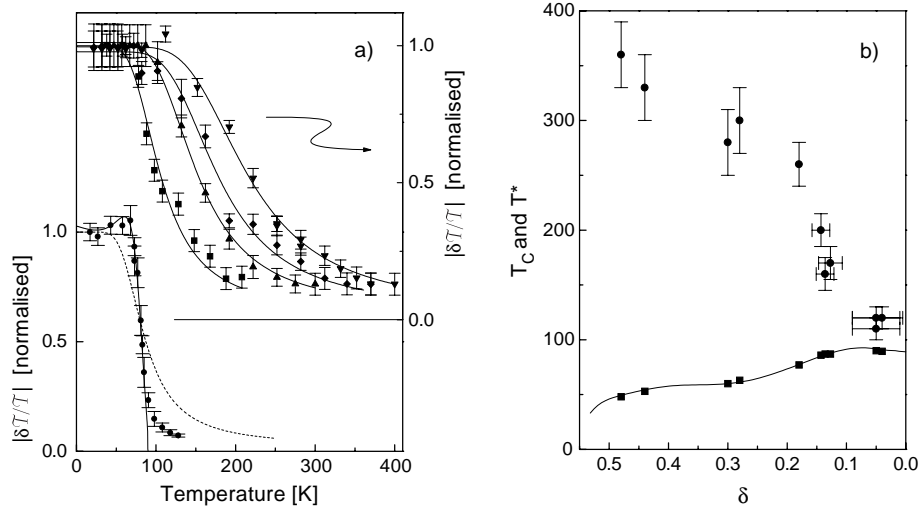
Fig. 2. – a) The normalized amplitude of the induced transmission $\Delta\mathcal{T}/\mathcal{T}$ for near-optimally doped sample with $\delta \sim 0.05$, $T_{\mathrm{c}} = 90$ K (circles) and for underdoped samples with $\delta = 0.14$, $T_{\mathrm{c}} = 84$ K (squares), $\delta = 0.18$, $T_{\mathrm{c}} = 77$ K (up triangles), $\delta = 0.44$, $T_{\mathrm{c}} = 53$ K (diamonds) and $\delta = 48$, $T_{\mathrm{c}} = 48$ K (down triangles), respectively. The underdoped-sample data are displaced for clarity. The lines are theoretical fits to the data from the model of Kabanov *et al.* [6]. b) T^* (full circles) and T_{c} (line and squares) as a function of δ.

10 mW, we calculate the photoinduced carrier density to be $n_{\mathrm{Q}} = 2 \times 10^{19}$–$3 \times 10^{20}$ cm^{-3}. Since the superconducting carrier density is $n_{\mathrm{s}} \sim 5 \times 10^{21}$ cm^{-3}, $n_{\mathrm{Q}} \ll n_{\mathrm{s}}$, the photoexcited QPs are only a very small perturbation on the system.

A typical normalized photoinduced transmission signal $\delta\mathcal{T}/\mathcal{T}$ as a function of time delay below and above T_{c} on a near-optimally doped sample with $\delta = 0.1$ is shown in fig. 1. The risetime —which is characteristic of the establishment of the QP near-equilibrium state— is not resolved with our 200 fs pulses, while the decay ranges from 300 to 3000 fs and characterises the QP recombination time. A longer-lived decay component, which was already reported in optimally doped samples [4] is also observed at all doping levels, but will not be discussed further in this paper. The normalized peak amplitude of the observed photoinduced transmission amplitude $|\delta\mathcal{T}/\mathcal{T}|$ as a function of T for different δ is shown in fig. 2a). Near optimum doping ($\delta \sim 0.1$), the signal amplitude drops rapidly and nearly dissappears close to T_{c}. With $\delta > 0.1$ however, in spite of the fact that T_{c} is lower, the amplitude drops at progressively *higher* temperatures above T_{c}. To fit the temperature dependence of the induced absorption signal, we use the theoretical formula derived for the photoinduced QP absorption [6]. For underdoped samples ($\delta > 0.1$) we assume the gap is temperature independent, and then the induced transmission is given by

$$-\delta\mathcal{T}/\mathcal{T} \propto \frac{E}{\Delta}\left[1 + \frac{2\nu}{N(0)\Omega_{\mathrm{D}}}\exp[-\Delta/k_{\mathrm{B}}T]\right]^{-1},$$

where $\mathcal{E}$ is the pump excitation energy density per unit cell, $\nu \sim 8$ is the number of phonon modes participating in the relaxation, $N(0) = 2.2$ eV^{-1}spin^{-1}cell^{-1} and $\Omega_{\mathrm{D}} = 0.1$ eV is a typical phonon frequency. The value of Δ used in the fits shown by the solid lines in fig. 2a) is given by $2\Delta = \beta k_{\mathrm{B}}T^*$, where T^* is defined as the temperature at which the amplitude $|\delta\mathcal{T}/\mathcal{T}|$ drops to 5% of its maximum low-temperature value and $\beta = 5 \pm 1$. Although the
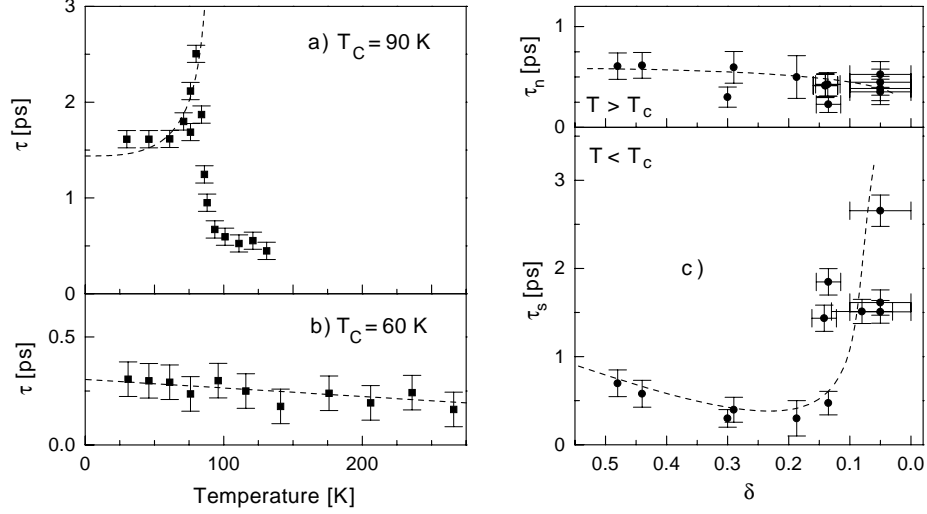
Fig. 3. – τ_s as a function of T for a) $\delta = 0.05$ ($T_c = 90$ K) and b) $\delta = 0.3$ ($T_c = 60$ K). The dashed line in a) is a fit with $\tau = A/\Delta(T)$, where A is a constant and $\Delta(T)$ is a BCS-like T-dependent gap. c) The relaxation time τ as a function of δ for $T > T_c$ and $T < T_c$ (at $T = 100$ K and 20 K, respectively). The relaxation time τ_s in the superconducting state shows a cross-over near optimum doping, while τ_n ($T > T_c$) is nearly doping- and temperature-independent.

choice of ν is somewhat arbitrary, the fit is relatively insensitive to its actual value and only has a small effect on the magnitude of β. The data for the underdoped samples are seen to be in good agreement with the predicted temperature dependence of $|\delta\mathcal{T}/\mathcal{T}|$ with a constant Δ. However, attempting to use the formula above to describe the near-optimally doped sample $\delta = 0.1$ proves impossible as shown by the dashed line in fig. 2a). If, however we assume instead that Δ is tempereture *dependent,* and using a gap $\Delta = \Delta_{\mathrm{BCS}}(T)$ of BCS form with $2\Delta_{\mathrm{BCS}}(0) = 10k_BT_c$ (not T^*), the agreement with the data becomes again very good over a wide range of temperatures below T_c (solid line in fig. 2a)). We note that the slight cusp in the data below T_c, which is present in all optimally doped samples, can only be reproduced by using a temperature-dependent gap $\Delta(T)$ which closes at T_c. Above T_c, where $\Delta_{\mathrm{BCS}}(T) = 0$, a small $|\delta\mathcal{T}/\mathcal{T}|$ signal remains, which presumably corresponds to some remains of a T-independent gap. We conclude that the underdoped and near-optimally doped sample data cannot be described by the same form of temperature-dependent gap, but a cross-over from a T-independent gap to a dominant T-dependent gap occurs near optimum doping. The T^* obtained from fig. 2a) are plotted together with T_c as a function of δ on the phase diagram in fig. 2b). They coincide rather well with the "pseudogap" temperature T_p, where a drop in $N(0)$ has been deduced from NMR [11], infrared [12] and specific-heat [13] measurements amongst others.

Turning our attention to the QP recombination time τ_s obtained from a single exponential fit of the data near optimum doping, a sharp divergence is observed just below T_c which then drops to a near-constant value at low temperatures (fig. 3a)). From the existence of this divergence in τ_s and the fact that below T_c, $\tau_s \propto 1/\Delta(T)$ [2,6], we can unambiguously deduce the presence of a gap $\Delta(T)$ which *closes at T_c*. With increasing δ however, this divergence of τ_s near T_c rapidly dissappears. As shown in fig. 3b) for $\delta = 0.3$, τ is nearly constant with temperature above and below T_c and shows no visible anomaly at T_c or T^* (fig. 3b)). A plot of the normal-state relaxation time τ_n for $T > T_c$ (at 100 K) and τ_s for $T < T_c$ (at 20 K) as a function of δ in fig. 3c) shows a step-like change of τ_s near optimum doping clearly suggesting

the existence of a cross-over in behaviour.

Let us now discuss the possible origins of the observed cross-over. Near optimum doping the gap appears to be formed by a *collective effect* implying a BCS-like scenario where the creation of pairs occurs simultaneously with macroscopic phase coherence and the opening of a gap. With such a BCS-like gap $\Delta_{\mathrm{BCS}}(T)$ we can explain quantitatively the divergence of τ_{s} at T_{c} (fig. 3a)) and the temperature dependence of $|\delta\mathcal{T}/\mathcal{T}|$ (eq. (1) and fig. 2a)) together with the fact that $\delta\mathcal{T}/\mathcal{T} \to 0$ at T_{c} near optimum doping.

In the underdoped state with $\delta > 0.15$, the anomaly of τ_{s} at T_{c} is no longer visible. Noting that energy conservation together with the sum rule dictate that pairing *must* involve a change in the single-particle DOS, the absence of anomaly in τ at T_{c} together with the relation $\tau \propto 1/\Delta$ imply that there is no change in the pairing amplitude at T_{c} itself. Moreover, within experimental error, $|\delta\mathcal{T}/\mathcal{T}|$ also shows no change at T_{c}, which, considering eq. (1) also implies that there is no change in the DOS at this temperature ([1]) and certainly that no gap opens *at T_{c}*. In fact, from the T-dependence of both $|\delta\mathcal{T}/\mathcal{T}|$ and τ_{s} (figs. 2a) and 3b), respectively), the gap appears to be more or less T-independent.

Let us now consider these underdoped sample data in the gereneralised framework of Boson condensation superconductivity theories, where the experimentally verifyable consequences arise from the fact that no collective pairing effect occurs at T_{c}, but rather bosons, which are already present at T_{c} condense into a phase-coherent macroscopic superconducting ground state without any change in pair density at this temperature. In the BEC scenario as applied to the underdoped cuprates, pairing starts to take place well above T_{c} and is governed by the thermal excitations from the pair ground state at E_0 to single particle states E_1 at an energy 2Δ above it (fig. 1). The gap 2Δ now signifies the local pair binding energy E_{B} and is T-independent, consistent with the T-dependence of $|\delta\mathcal{T}/\mathcal{T}|$ and τ. Its magnitude should decrease with increasing doping because of screening [16], which is also consistent with the data on T^* in fig. 2b). This scenario with a constant splitting between the pair ground state and the unpaired excited state thus explains why $|\delta\mathcal{T}/\mathcal{T}|$ does not vanish at T_{c} in underdoped samples, but is dominated by "pseudogap" behaviour with asymptotic temperature dependence above T_{c} resulting from the statistics of the 2-level system [6].

To understand better the behaviour of photoexcited charge carriers in this scenario, let us consider the relaxation process in more microscopic terms. After inital photoexcited e-h pair relaxation by e-e scattering and phonon emission —a process which is insensitive to the low-energy structure— the particles end up in *single particle states* near E_{F}. The next relaxation step involves pairing of these carriers into the pair ground state with the release of E_{B} per pair. This pairing process is similar as for QP recombination in the BCS case, except that the gap $\Delta_{\mathrm{BCS}}(T)$ is now replaced by a T-independent E_{B} [6]. Because of the large dielectric constant in YBCO at low frequencies ($\varepsilon_{\mathrm{r}} > 100$ [17]) the Coulomb repulsion for carriers on adjacent sites is small compared to either the typical bipolaronic binding energy or the exchange interaction energy J. Thus pairs on adjacent lattice sites can form relatively easily, irrespective of whether the pairing mechanism is bipolaronic, electronic, or some combination of the two. Since the in-plane coherence length $\xi > a$, where a is the intersite carrier spacing, to first approximation the pairs can be treated as local bosons, which is a condition for BEC to occur. Macroscopic phase coherence and condensation in the superconducting ground state occurs when thermal phase fluctuations of such bosonic pairs are sufficiently reduced to enable phase locking between neighbouring boson wave functions. This phase locking at T_{c} is manifested by the appearance of a macroscopically coherent Meissner state and zero resistivity, but is not visible in the

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([1]) A similar conspicuous absence of anomalies at T_{c} in underdoped samples is also observed in other experiments which probe the DOS, for example infrared spectroscopy [12, 14], specific heat [13, 14] and single-particle tunneling [15] etc.

pairing amplitude or in the single-particle DOS, and hence also not measurable in $\delta\mathcal{T}/\mathcal{T}$ or τ_s. By heuristic argument, phase coherence should occur when the pair deBroglie wavelength λ becomes comparable to the coherence length ξ. Estimating T_c from $k_B T_c \sim h/(m^*\xi^2)$, with $m^* = 3m_e$ and $\xi = 18$ Å (in-plane for YBCO) we obtain $T_c \sim 100$ K. More rigorously, applying the Bose-Einstein formula $T_c \simeq \hbar^2 n_s^{2/3}/(2m^*)k_B$ to YBCO with the same $m^* = 3m_e$ and $n_s \sim 10^{21}$ cm^{-3} gives values consistent with the observed T_c's [1].

We conclude that the distinct differences of the low-energy carrier dynamics in YBCO underdoped state compared to the optimally doped state imply the existence of a cross-over near $\delta \sim 0.1$ from a state in which pre-formed bosonic pairs condense at T_c with no observable change in the DOS at this temperature, to a BCS-like state exhibiting clear anomalies related to a gap opening at T_c. Throughout the discussion of the present data we have discussed the concept of condensation in general terms and intentionally kept it separate from the issue of the microscopic pairing mechanism. For a recent survey of some of the high-T_c theories which rely on condensation for achieving a macroscopically coherent superconducting ground state —ranging from the generalized Hubbard model to bipolaronic superconductivity— we refer the reader to ref. [18].

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