DIVERGENCE OF THE QUASIPARTICLE LIFETIME WITH DOPING AND EVIDENCE FOR PRE-FORMED PAIRS BELOW T* IN YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-d} DIRECT MEASUREMENTS BY FEMTOSECOND TIME-RESOLVED SPECTROSCOPY

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Abstract—We report new time-resolved data of quasiparticle relaxation and Cooper pair recombination dynamics in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-d} measured as a function of temperature and doping \(d\) using femtosecond optical spectroscopy. The data show the existence of a normal state pseudo-gap for in-plane charge excitations below \(T^*\) and an unusual divergence of the quasiparticle relaxation time in the superconducting state \(t_s\) with \(d\) towards optimum doping. In the underdoped state, no change in the amplitude of the induced transmission (which is proportional to the DOS at \(E_F\)), or relaxation time \(t_s\) is observed at \(T_c\). From the sum rule, both observations signify that no gap opens at \(T_c\) in underdoped YBCO for \(d<0.15\). \(T_c\) in this case only signifies the onset of phase coherence. The presented data thus suggest pair formation with an associated redistribution of the DOS starting at \(T^*\) and the establishment of phase coherence at \(T_c\) consistent with Bose–Einstein condensation. In the optimally doped material, \(d<0.1\), on the other hand, both a divergence in lifetime and a change of the DOS occur at \(T_c\), signifying the opening of a gap and the occurrence of pairing takes place simultaneously.

Keywords: YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-d}, time-resolved optical spectroscopy

1. INTRODUCTION

The low-energy electronic excitation spectrum in high-temperature superconducting cuprates has been controversial ever since the first experimental data were reported on the subject more than 10 years ago. The standard measurement techniques used to obtain experimental data have been mainly infrared reflectivity, transmission and ellipsometry together with electronic Raman scattering. Although there was significant agreement regarding the raw data between different groups \[1\], controversy arose when interpretation of the spectra was attempted. The single particle spectrum on the other hand was very successfully investigated by angle-resolved photoemission (ARPES) \[2\]. However in this case, just as for optical spectroscopy, the complexity of the observed multi-component spectral features necessitates the use of a model in interpreting the data. Furthermore, in all time-integrated spectroscopies the issue of whether the spectrum shows homogeneous or inhomogeneous line-width cannot be easily circumvented, so particle lifetimes determined by these techniques are necessarily ambiguous.

In this paper we describe an example of the application of time-resolved optical spectroscopy to the direct investigation of low-energy electronic excitation dynamics. The method by default directly gives quasiparticle lifetimes in the case of high-temperature superconductor materials. From such measurements as a function of temperature and doping \(d\) in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-d} we are able to infer the occurrence of Bose–Einstein condensation of quasiparticles at \(T_c\) in the underdoped state and a cross-over to BCS-like state near optimum doping.

2. EXPERIMENTS

The success of the time-resolved spectroscopy method relies on two factors. Firstly, the technological developments of femtosecond lasers and related technology, with the recent development of high-frequency lock-in amplifiers. Secondly, a particularly important generic feature of the cuprate materials, the existence of a charge-transfer resonance in the wavelength region of 800 nm easily accessible by these lasers. The assignment of this resonance by use of laser wavelengths ranging from 1500 to 350 nm has been particularly important for understanding the time-resolved measurements \[3\]. In previous work \[4, 5\], the spectroscopy off-resonance (usually at 2 eV) showed features which were substantially more difficult to interpret.

The laser used in the present time-resolved experiment was a Ti:sapphire mode-locked laser giving 150 fs pulses at 800 nm with a repetition rate of 88 MHz. The pump pulse train average power was typically between 10 and 120 mW, while the probe pulse train was typically 0.2 mW or less. The two beams were focussed onto the
sample mounted onto a copper block in an Oxford Instruments Microstat. The pump beam was modulated at 200 kHz and the probe detected via an amplified photodiode and a high-frequency digital lock-in amplifier (EG&G 7260).

For the understanding of the present experiments, it is important to establish that the optical transitions involve excitations from the ground state (of predominantly O character) near $E_F$ to unoccupied states (of predominantly Cu orbitals) 1.5 eV above in energy. In such a resonance case, the changes in the ground state DOS occurring with temperature, particularly at $T_c$ and $T^*$, can thus be measured by pump-probe spectroscopy. The evidence for the assignment given above is summarized below.

From early X-ray work of Bianconi and others [6] it emerged that the charge carriers (holes) are located mainly on the O ions, while the Cu $d$ (upper Hubbard) band is approximately 1.5–1.8 eV higher in energy (depending on the material and level of doping). Experiments on YBa$_2$Cu$_3$O$_x$, for example, have shown that the charge transfer (CT) transition between O and Cu is strongly observed in optical conductivity, optical ellipsometry [7] and absorption spectra [8] as well as photoconductivity [8] at 1.8 eV with a typical width of 0.1 eV. Upon doping it splits into two bands approximately 0.1 eV apart at the insulator-to-metal transition [7, 9] and eventually at optimum doping only a peak at 1.5 eV is clearly visible. A feature at 1.5 eV is clearly observed also in large-shift electronic Raman scattering [10] with an apparent splitting observed at $\delta \sim 0.6$. This probably indicates that the local symmetry for the CT transition is lower than orthorhombic and has no center of inversion, otherwise the 1.5 eV feature would not be seen both in gerade (Raman) and ungerade (infrared) transitions.

Further confirmation that the initial states for optical excitations at 1.5 eV cross $E_F$ comes from thermal differential reflectance (TDR) [11] and time-resolved (TR) optical spectroscopies [3]. The former measures the change in reflectivity which occurs at $T_c$ as a result of the redistribution of the DOS and shows distinctly a double peak at 1.5 eV similar to the one seen in the optical conductivity and Raman spectra. TR spectroscopy shows the same feature at 1.5 eV in the optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$—albeit with much lower resolution—also appearing below $T_\text{tr}$ and is similarly

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**Fig. 1.** A schematic diagram of the pump and probe processes in resonance with the 1.5 eV CT transition in YBaCuO. The carriers relax rapidly to a quasi-steady state between the pump and the probe pulses.

**Fig. 2.** The amplitude of the induced transmission (squares) increases with doping, following $T_c$. The data for $T_c$ are from Conder et al. [19].
thought to be caused by a redistribution of initial states for the optical transitions at $E_F$. In this case the 4:1 in-plane to out-of-plane polarization ratio also confirms this assignment. Yet more independent confirmation that the initial states for absorption are at $E_F$ comes from ARPES [2] in conjunction with theoretical calculations, while the effect of doped holes on the 1.5 eV transition was nicely demonstrated by Matsuda et al. [12].

The schematic diagram for the resonant pump and probe processes which is based on the assignment discussed above is shown in Fig. 1. The carriers are first excited by the pump pulse from occupied states at or below $E_F$. The second, probing step involves determining—as a function of time—the resulting changes in the density of states at $E_F$, caused by the photoexcited quasiparticles by measuring the change in transmission $T$ of the sample with a delayed weak laser probe pulse. In the adiabatic approximation, the golden rule gives the change in optical absorbance of the probe pulse to be proportional to the change in the DOS at $E_F$ i.e. $\frac{dA}{dT} \propto \frac{dN(0)}{dT}$ caused by the pump pulse. Since, as was discussed above, this is in turn proportional to $N(0)$, the time-resolved changes in optical transmission $\delta T/T(= -\frac{dA}{dT})$ can directly probe temperature- and $k$-dependence of $N(0)$. The probe pulse was polarized in the $a$–$b$ plane to probe predominantly CuO plane excitations (the signal was found previously to be independent of pump polarization [3]).

3. EXPERIMENTAL RESULTS

The induced transmission $\delta T/T$ following the pump pulse typically shows a relatively fast relaxation of $t \approx 0.5$–3 ps, followed by a distinct long-lived component with a decay time of 10 ns or more [3, 13], which is most evident in optimally doped YBCO with $x = 6.94$ and also for $x \approx 6.75$. This long-lived component is attributed to quasiparticle relaxation in localized states and was discussed in detail by Stevens et al. [3]. In this paper we will only discuss the fast component of the relaxation. The amplitude of this component was measured well below $T_c$ as a function of doping $x$ in YBCO over a wide range of doping. The results shown in Fig. 2 indicate that the integrated amplitude—which is proportional to the total number of particles excited,

$$n = \int (dn/dt) dt \propto \int \frac{\delta T}{T} dt$$

—increases almost linearly with doping, starting at the insulator-to-metal transition at $x = 6.4$. (Near optimum doping, the non-integrated amplitude of the signal actually decreases, but this is not attributed to a drop in the DOS, but rather to the fact that the relaxation time $\tau$ starts to increase dramatically for $x \approx 6.9$.)

An important feature of the data is that the amplitude is strongly temperature dependent (Fig. 3). At low temperature ($T < T_c$) the amplitude is nearly temperature independent. With increasing temperature the amplitude starts to drop and eventually vanishes, such that at room temperature the signal is usually not visible, or very small. The temperature $T^*$ at which the amplitude of the induced transmission $\delta T/T$ drops to zero—indicating a change (drop) in the DOS at $E_F$—increases with decreasing carrier concentration in the underdoped phase in close agreement with the "pseudogap" temperatures for YBCO determined from other experiments [14]. Importantly, in near optimum doping the amplitude vanishes near $T_c$, which has already been noted previously [3]. In underdoped samples on the other hand, the amplitude shows no change at $T_c$, suggesting no changes in the DOS take place at $T_c$, which as we shall discuss below is presented as evidence for Bose–Einstein condensation.

![Fig. 3. The temperature dependence of the amplitude of the induced transmission for a number of different samples (the small T-independent signal—approx. 10% of maximum $|\delta T/T|$—was subtracted). The $T_c$'s are shown in the plot. The temperature at which $\delta T/T$ drops to zero is close to the pseudogap temperature $T^*$.

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1939 Quasiparticle lifetime divergence with doping
Fig. 4. The relaxation time measured as a function of doping in the normal state at 100 K (top panel) and at 20 K (lower panel). A clear divergence of $\tau_0$ is observed near optimum doping.

As already mentioned briefly above, the quasiparticle lifetime $\tau_0$ in the superconducting state—determined by fitting a single exponential to the time-resolved trace—shows a divergence with increasing carrier concentration $1 - \delta$, in the region close to optimum doping as shown in Fig. 4. In contrast, almost no change in lifetime with $\delta$ is observed above $T_c$, and is $\tau_0 = 0.5 \pm 0.1$ ps at 100 K over the whole range of doping. Importantly, the lifetimes below and above $T_c$ in the underdoped state are typically the same below $\sim 6.85$. Approaching optimum doping, this is no longer the case, and a clear divergence of $\tau_0$ is observed at $T_c$, behavior which is well known in BCS superconductors [15] and is thought to be due to a quasiparticle relaxation bottleneck at $T \rightarrow T_c$ from below (not a Hebel–Slichter peak).

4. DISCUSSION

The systematic investigation of the amplitude and relaxation time $\tau_0$ of the photoinduced optical transmission through thin film samples shows rather well the crossover in behavior which occurs near optimum doping. In the underdoped state, neither the amplitude (which is related to the DOS at $E_F$) nor the lifetime $\tau_0$ show any effect at $T_c$. Instead, both show a gradual change with temperature, the amplitude vanishing at $T^*$, while the lifetime showing only very gradual change up to $T^*$. The simplest way to explain the behavior in the underdoped state is to assume that no change in amplitude or relaxation time is observed at $T_c$ because no change in DOS (i.e., gap) occurs at $T_c$. Instead, in a typical Bose–Einstein scenario, the pairs which are formed at $T^*$ only acquire phase coherence at $T_c$.

The onset of a macroscopically coherent condensed state occurs when the wavefunctions of adjacent pairs overlap sufficiently for phase coherence to be established between them. We can estimate the temperature at which the phase coherence is established by considering when the DeBroglie wavelength $\lambda$ becomes comparable to the superconducting coherence length $\xi$. Thus, $k_B T_c = h^2 / (m^* \xi^2)$, which, using measured values of $\xi = 18 A$ for YBaCuO$^{15}$ and $m^* = m_{ec}$, gives $T_c = 91 K$, which is close to the observed $T_c$ in this material. The density of carriers at the point of condensation is given by Einstein [17] as $(N/\hbar^2)^{1/2} = 2.612 \times 10^{21} m_{ec} T_c / (2 \pi \hbar^2)$, which, using the same value of $m^*$ and $T_c$ as above, gives $n_c = N / V = 10^{21} cm^{-3}$ which is close to the value estimated from Hall data [16].

The data in the near-optimally doped material with $\delta > 6.85$ are distinctly different to the underdoped state. Both the amplitude and the relaxation time show a dramatic change at $T_c$, the latter exhibiting diverging behavior as $T$ approaches $T_c$ similar to BCS superconductors like Al [18]. The amplitude, on the other hand, shows a rapid drop to zero very close to $T_c$, also with a BCS-like $T$-dependence, suggesting that a gap opens simultaneously with pair formation (and phase coherence) as in the BCS case.

To conclude, time-resolved optical spectroscopy is demonstrated to be a powerful tool for the investigation of quasiparticle dynamics in HTS. The occurrence of BE condensation in underdoped YBCO—as suggested by the absence of any observable change in the quasiparticle relaxation time $\tau_0$ or density of states $N(0)$ at $T_c$ in our experiments—is consistent with simple theoretical expectations. Obeyance of the sum rule implies that pairs must form above $T_c$ (the observed changes in the DOS from $\delta > T$) suggest that this occurs at $T^*$. In contrast, the optimally doped and overdoped state appears to show a divergence in the quasiparticle lifetime with doping and a BCS-like temperature dependence of both the intensity and lifetime is also apparent.

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REFERENCES


