

Sharp resonant multiplet in femtosecond optical pair-breaking spectroscopy of optimally doped, underdoped, and Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: Transient insulating regions in the superconducting state

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(Received 6 November 2001; published 7 May 2002)

Femtosecond optical pair breaking spectroscopy is performed on optimally doped, underdoped, and Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) thin films near 1.5 eV. A sharp resonant triplet fine structure is seen. The systematics of the data for the three cases brings out the key role of Cu-O plane system in the attendant processes. The peak separations are attributable to the reported phonon and magnetic excitations in the system. These results strongly suggest the presence of insulating antiferromagnetic domains in the superconducting state of these YBCO systems on a subpicosecond time scale.

DOI: 10.1103/PhysRevB.65.184519

PACS number(s): 74.25.Gz, 74.72.Bk, 74.76.Bz, 78.47.+p

Since the discovery of high- T_C superconductivity (HTS) in 1986, several attempts have been made and are still being made to seek a theory for this phenomenon in terms of the Fermi-liquid picture, by suitably flexing the conventional picture to accommodate the characteristics that are unique to the cuprate systems. Experimental results have, however, continued to defy and challenge the norms laid out by such an established paradigm, and there is growing evidence to suggest that the presumption of a featureless quantum gas or liquid of quasiparticles may in fact be too naive and simplistic for these systems.¹ One physical picture which attempts to capture the essence of the existence of a complex quantum matter in high- T_C cuprates, as indicated by several recent experiments, is the electronic phase separation model; the so-called “stripe phase” scenario being one of its structured manifestations represented by a self-assembled array of conducting stripes separating hole-free antiferromagnetic insulating domains. The foundations of these concepts were laid by the works of Zaanen and Gunnarsson,² Emery, and co-workers,^{3,4} Schulz,⁵ and White and Scalapino.⁶ The notion of complex domain formation in high- T_C systems has also been advanced from the lattice strain point by Phillips,⁷ and experimentally by Bianconi *et al.*⁸ Experimentally, there is growing evidence for the existence of complex textures of charge and spin in HTS, especially in the La_2CuO_4 family of superconductors.⁹ However, the corresponding evidence is less direct¹⁰ in other key HTS materials such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, where the corresponding dynamics are suggested to be fast.

A key approach to understanding superconductivity is to probe the superconducting gap function $\Delta(\omega, \mathbf{k}, T)$ by inducing excitations in the system, and examining the corresponding quasiparticle behavior. Tunneling and inelastic neutron-scattering studies focus on low-energy excitations, while optical experiments generally employ high excitation energies. Holcomb, Collman and Little¹¹ used thermal-difference reflectance spectroscopy to obtain the superconducting to

normal reflectance ratio R_S/R_N for energies up to ~ 5 eV in different superconducting cuprates, and found considerable deviations of this ratio from unity for photon energies near 1.5 eV. They argued that these optical structures are hard to understand unless the electron-boson coupling function is assumed to consist of both a low-energy component (< 0.1 eV) and a high-energy component located around 1.5 eV. Stevens *et al.*¹² corroborated this claim by using femtosecond time-resolved pump-probe spectroscopy. In both these experiments, however, the measured physical quantities were the changes in the dielectric response, the correlation to electron pairing being only indirect. In this work, we selectively and directly measure the Cooper pair breaking rate via an *electrical* measurement¹³ on optimally doped, underdoped, and Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under femtosecond laser excitation. For this temporal condition, the dynamic electronic phase separation, if present, would appear frozen, thereby exposing both the insulating and superconducting regions to the optical-absorption process. The ability to selectively filter out the pair-breaking contribution from a host of other possible excitation effects afforded by this scheme (signal at a few parts in 10) distinguishes it clearly from other optical experiments,^{11,12} including the pump-probe ones, where the measurement channel is also optical (signal at a few parts in 10^4).

The YBCO thin films were prepared by pulsed laser deposition on (100)-oriented LaAlO_3 single-crystal substrates. The film thickness was 100 nm, nearly equal to the penetration depth of the laser beam at wavelength centered around 810 nm.¹⁴ The T_C for the optimally doped YBCO was ~ 90 K, and J_c was $> 10^6$ A/cm² at 77 K. The oxygen depleted YBCO thin films were obtained by vacuum annealing the optimally-doped samples at 250 °C for 6 h. The T_C was ~ 60 K corresponding to the single phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0.3 < \delta < 0.4$) with correlated oxygen vacancies along the Cu-O chain.¹⁵ The Zn-doped YBCO thin films were deposited from a target of $\text{YBa}_2\text{Cu}_{2.8}\text{Zn}_{0.2}\text{O}_{7-\delta}$, and the film T_C was ~ 38

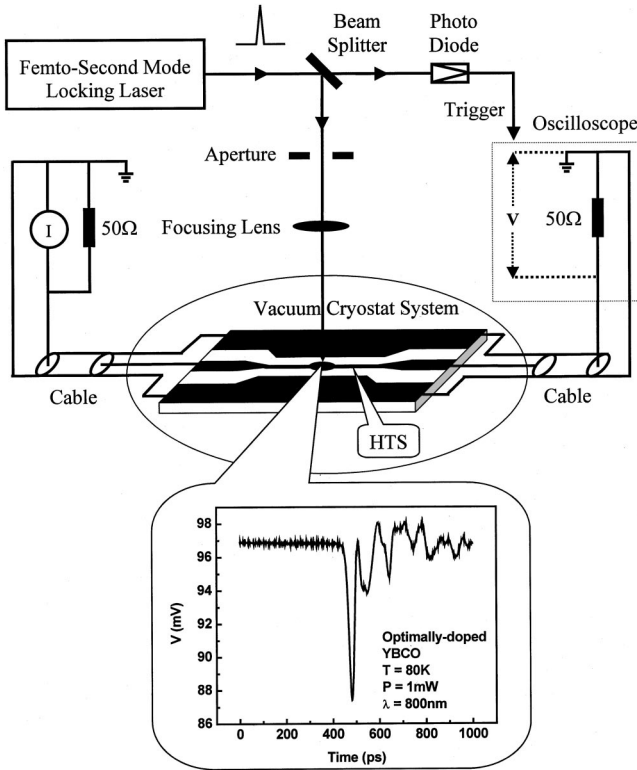


FIG. 1. Experimental setup, device schematic, and typical waveform for a fast optical response signal.

K. Since Zn is known to desorb partially during laser deposition,¹⁶ the actual Zn composition in the film was estimated¹⁷ from the T_C to be $\sim 5\%$. The films were patterned to obtain coplanar waveguide structures. The experimental setup and the device schematic are shown in Fig. 1. The size of the bridge at the center of the device was $5\text{ mm} \times 30\ \mu\text{m}$. The device was mounted on a cold finger located in a cryogenic system (vacuum $< 10^{-6}$ Torr), where the substrate temperature could be controlled between 10 and 300 K with a $\pm 0.1\text{-K}$ stability. The dc bias current was 4 mA. The device was illuminated with laser pulses from a Ti:sapphire laser system, consisting of an argon-ion pumping laser, an oscillator, and a regenerative amplifier, generating 100-fs laser pulses at up to $5\ \mu\text{J}/\text{pulse}$. The repetition rate was chosen to be 10 kHz, which eliminates accumulation of prior pulse effects, and leads only to a fast optical response (FOR) with rise and fall times of the order of picosecond.¹³ The corresponding waveforms were monitored by a fast digital sampling oscilloscope with a temporal resolution of 20 ps. The laser beam was focused onto the device by a cylindrical lens, resulting in a spot size of about $5\text{ mm} \times 200\ \mu\text{m}$. The typical laser fluence was $10\ \mu\text{J}/\text{cm}^2/\text{pulse}$. The wavelength of the laser was tunable within the range of 750–850 nm (1.65–1.45 eV).

A typical waveform of the FOR signal is also shown in Fig. 1. The strongest peak is the primary signal, while the weaker peaks are due to reflections off the impedance mismatch on the transmission line. Two mechanisms have been put forward to explain the FOR signal: the kinetic inductance (KI) model^{18,19} and the photo-activated flux flow model.²⁰

However, the KI model has gained favor, since it was shown that the amplitude of the FOR signal was not affected by applied magnetic field,¹⁸ in contradiction to the prediction of the photo-activated flux flow model. Moreover, the amplitude of the FOR signal shows a linear dc bias current dependence which is expected for the KI model,^{18,19} whereas the photoactivated flux flow model predicts a quadratic dependence. According to the KI model, the voltage transient across the superconducting device is proportional to the time derivative of the kinetic inductance (L_{kin}), it is initially positive during the pair-breaking stage of the process, and becomes negative at later times when the recombination process starts to dominate. The time scale for this entire process is on the order of $\sim \text{ps}$,^{12,21} and is beyond the temporal resolution ($\sim 20\ \text{ps}$) of the digital sampling oscilloscope used in this experiment. Therefore, the actual signal observed on the oscilloscope is related to both the amplitude and shape of the voltage transient generated across the device, as well as the impulse response function of the electric circuit in the oscilloscope. Generally speaking, the duration and shape of a voltage transient with a time scale shorter than the temporal resolution will not be reproduced faithfully by the oscilloscope. However, it was shown²² that the measured signal amplitude on the oscilloscope is proportional to the maximum voltage transient. The constant proportionality factor depends on both the pulse shape of the voltage transient signal and the impulse response function of the oscilloscope, but is invariant under the current experimental condition. Since the superconducting device and the $50\ \Omega$ internal impedance of the oscilloscope are connected in series, a positive (negative) voltage transient across the device would result in a negative (positive) signal on the oscilloscope. Therefore, a FOR proportional to $\Delta L_{\text{kin}}/\Delta t$ and $\Delta L_{\text{kin}}/\Delta t$ is related to the Cooper pair breaking rate (CPBR) by $\Delta L_{\text{kin}}/\Delta t = (m^* 1/e^* 2 w d n_{\text{sc}}^2) (\Delta n_{\text{sc}}/\Delta t)$, where m^* and e^* are the effective mass and the effective charge of the Cooper pairs, n_{sc} is the Cooper pair density, $\Delta n_{\text{sc}}/\Delta t$ is the CPBR, and l , w , and d are the length, width, and thickness of the superconducting bridge, respectively. The delay time of any possible reflections off the closest impedance mismatch point on the transmission line is estimated to be over 50 ps. While these reflections could in fact interfere with the secondary peaks, they would certainly have no effect on the amplitude of the primary peak which is the signal of interest in this paper. Thus our experiment does measure the CPBR directly and selectively; all the other processes which do not break pairs are excluded. This can probe the estimated fraction of less than 1% of the electromagnetic energy in the laser pulse contributing to pair breaking,¹³ which could be easily missed by other approaches.

The photon energy dependence of the FOR for optimally doped YBCO at different temperatures is shown in Fig. 2. The error bars were determined from five repeated measurements at each photon energy, and, for each measurement, a minimum of 1024 waveforms were averaged. Three sharp resonance peaks, indicated by A, B, and C, can be easily identified in all the spectra. The solid lines were obtained by fitting the data to three Lorentzians, the dotted lines being the individual Lorentzian functions (shown only for $T = 80\ \text{K}$).

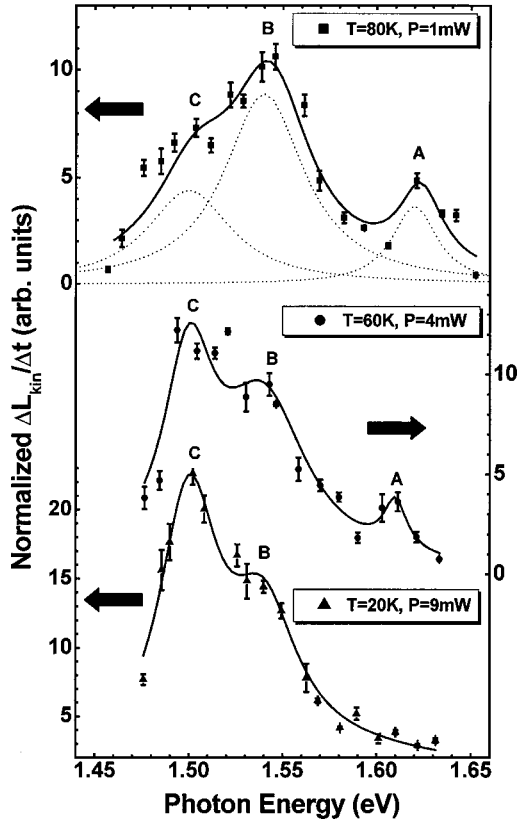


FIG. 2. Fast optical response as a function of photon energy at three different temperatures for optimally doped YBCO films.

At 80 K, the peak positions are $E_A = 1.62$ eV, $E_B = 1.54$ eV, and $E_C = 1.50$ eV. At 60 K, all the peak positions remain almost the same (within the resolution of ~ 10 meV afforded by a finite laser pulse width), but the relative spectral weights change. The contribution of C(A) grows (diminishes) with respect to B. At 20 K, the positions of peaks still hold, with C increasing even further relative to B; while peak A is merging with the background.

It is interesting to note that the energy difference between peaks B and C remains ~ 40 meV for all three temperatures, which is curiously close to the famous 41-meV peak observed in neutron-scattering experiment on YBCO systems.²³ Interestingly, the difference between peaks A and B is ~ 75 meV, which is close to the energy of longitudinal optical (LO) oxygen bond-stretching phonons (~ 70 – 80 meV) in the CuO_2 plane, observed in inelastic neutron-scattering measurements on HTS.²⁴ The reported zero-momentum energy separation between the optical and acoustic magnon branches is also close to 70 meV in YBCO.²⁵ However, since the LO-phonon mode and the 41-meV magnetic excitation are the only sharp collective modes in the system, they appear to be more relevant to our case.

The photon energy dependence of the FOR for oxygen-depleted and Zn-doped YBCO is shown in Fig. 3. Again three sharp resonance peaks are seen for both cases. While the locations and the separations of the peaks for oxygen-depleted YBCO are almost identical to the optimally doped YBCO, the peaks for the Zn-doped sample are seen to be

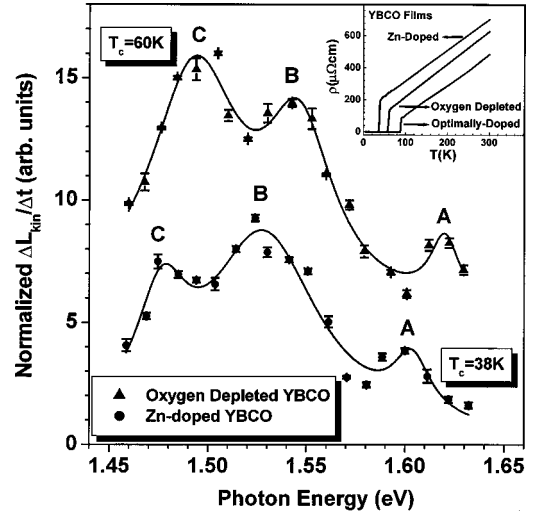


FIG. 3. Fast optical response as a function of photon energy for oxygen depleted YBCO ($T = 40$ K, $P = 0.8$ mW) and Zn-doped YBCO ($T = 20$ K, $P = 0.125$ mW) films. The data for oxygen depleted YBCO is shifted up by five units for clarity. The inset shows the ρ - T measurements for optimally doped, oxygen-depleted, and Zn-doped YBCO films.

uniformly redshifted by ~ 20 meV. It is well established that upon slow vacuum annealing, the removal of oxygen atoms occurs first from the Cu-O chains, and not from the Cu-O planes.²⁶ The fact that the main features of the triplet in oxygen-depleted YBCO are the same as in optimally doped YBCO confirms that these features originate in the Cu-O plane, which is crucial to high- T_C superconductivity. On the other hand, since Zn is known to substitute for Cu atoms in the plane sites,²⁷ one may expect Zn doping to modify the electronic band filling of the Cu-O plane. The ~ 20 -meV redshift of the triplet could arise due to this effect. With Zn doping, the superconducting carrier density is found to decrease due to the exclusion of charge carriers from the superfluid within an area of $\pi\xi^2$ around each Zn atom, ξ being the in-plane coherence length.²⁸ If we assume that for each doped Zn atom one charge carrier is excluded from the superfluid, then the change in Fermi energy E_F for the two-dimensional (2D) Cu-O plane system can be obtained from $\Delta E_F = (\Delta n/n)E_F$. Taking E_F to be ~ 0.25 eV,²⁹ the estimated value for ΔE_F in our case is ~ 19 meV, in close agreement with the experimentally observed shift of ~ 20 meV. Separately, the expected shift in the Fermi energy has also been calculated to be ~ 80 meV for $\text{YBa}_2\text{Cu}_2\text{ZnO}_{7-\delta}$ (i.e., 33% Zn) in a calculation based on the semiempirical tight-binding model.³⁰ If we assume that the shift in E_F is linearly dependent on the doping level of Zn, which is the case for a 2D electronic system, for our doping level this corresponds to $\Delta E_F \sim 15$ meV. Remembering that the carriers in YBCO are holes, this change in E_F should cause an effective decrease in the charge-transfer (CT) gap: a redshift, as observed.

Carrier dynamics on subpicosecond and picosecond time scales in high- T_C cuprates has been extensively studied over the years using time-resolved pump-probe techniques.^{12,21} A

model regarding Cooper pair (CP) breaking and quasiparticle (QP) recombination processes initiated by incoming photons was discussed in detail by Bluzer.³¹ According to this model, initially, photons will break CP's into QP's directly. Each absorbed photon with energy E creates two QP's with energy $E - \Delta$ and Δ , where Δ is the superconducting gap energy. Typically $E \gg \Delta$, and the thermalization of high-energy (hot) QP's first occurs by electron-electron ($e-e$) interactions. During each $e-e$ scattering, one hot QP with energy $E - \Delta$ will break a CP and generate two QP's with energies $E/2 - \Delta$ and a third QP with energy Δ . This avalanche process repeats itself until the energy of hot QP's reaches about 0.1 eV in the case of YBCO.³¹ The $e-e$ interaction time τ_{e-e} has been determined to be on the order of 100 fs for cuprates,²¹ and is comparable to the duration of the femtosecond laser pulses. After this fast $e-e$ process, it becomes more favorable for the relaxation to occur by phonon emission rather than cascading. The emitted phonons have large enough energy to break more CP's. In addition, two more processes become important at this stage of relaxation: QP recombination by phonon emission and escape of phonons into the substrates. The CP breaking by phonons and QP recombination processes have time scales of \sim ps,²¹ while the phonon escape time is much slower.³² Once enough phonons have escaped, net QP recombination follows until equilibrium is established. In the entire relaxation process, the most rapid CP breaking, which determines the FOR signal in our case, occurs during the cascading, since the $e-e$ interaction time is the shortest. If we simply consider the problem from an energy conservation point of view, in the first approximation, the maximum number of CP's that can be broken by a single laser pulse can be given by EN/Δ where E is the energy of one photon, N is the total number of photons in a single laser pulse, and Δ is the superconducting gap energy. If we assume τ_{e-e} to be roughly a constant over the photon energy range in this experiment (1.45–1.65 eV), since the laser power is equal to EN times the repetition rate (10 kHz), the maximum CP breaking rate, which determines the FOR, should remain nearly unchanged as the photon energy is tuned and the laser power is kept as constant. Clearly this is not what has been observed in this experiment, and a more sophisticated model than this simple energy consideration is needed.

The most striking feature of these results is the extremely sharp spectral width of the resonance, \sim 100 meV overall and \sim 20–50 meV for the fine structures. This is at least a factor of 5–10 smaller than the minimum width expected for an electronically homogeneous conventional metallic or superconducting state, where the electronic bandwidths are several hundred meV. On the other hand, such sharp linewidths are reported for excitonic transitions in semiconductors and insulators. These two factors together imply that the femtosecond pulse appears to encounter some insulating regions in the superconducting state in the YBCO films, and that the absorption in these regions influences the pair-breaking process. Recall that in our experiment, we ultimately and selectively record only the pair-breaking processes. This understanding is completely consistent with a scenario, which suggests a self-organization of doped holes in the form of conducting stripes or domains, separated by insulating anti-

ferromagnetic (AFM) regions. Although such regions are suggested to be highly dynamic in YBCO and therefore invisible for slow probes, the femtosecond pulse should see a snapshot of the dynamics, and therefore the insulating regions.

If we are indeed looking at a frozen picture of an electronically phase-separated system, we recognize that the insulating regions are not simply important from their electronic property perspective, but also from the magnetic one. In fact they support an AFM order, which is considered to be responsible for expelling the holes in the first place. Thus, any perturbation to the attendant driving forces leading to self-organization, electrical or magnetic, can be expected to have consequences for pair breaking. In light of this expectation it is heartening to see that our spectral features exhibit energy separations which have been identified in the literature with magnetic and phonon excitations in the system: \sim 40 meV corresponding to the magnetic resonance peak observed in neutron scattering experiments on YBCO,²³ and \sim 75 meV, the LO-phonon energy scale observed in both neutron-scattering measurements²⁴ and high-resolution angle-resolved photoemission measurements.³³ It has been suggested^{24,33} that LO phonons couple strongly with doped charges, and therefore contribute significantly to the pairing process.

It is now important to discuss the origin of the feature near 1.62 eV (peak *A*), with respect to which the peaks *B* and *C* are placed at -75 and $-(75+40)$ meV, respectively. The fact that this energy (1.62 eV) is close to, but slightly below, the charge-transfer gap (\sim 1.7 eV) (Ref. 34), strongly suggests that it may be of excitonic origin. The sharpness of peak *A* further supports this picture. The CuO_2 planes in insulating cuprates have indeed been shown to support excitonlike excitations of considerable complexity.³⁵ Among these, those of significance to our optical absorption based study are the dipole active ones, such as the excitons of E_u symmetry. Interestingly, Simón *et al.*³⁶ calculated the location of E_u excitonic states to be \sim 0.1 eV or less below the CT gap of 1.7 eV, which is clearly close to 1.62 eV (peak *A*). Here it is useful to point out that a similar experiment performed on epitaxial, optimally doped superconducting $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (LSCO) thin films did not show any resonance in the FOR.³⁷ This is indeed as per our expectation, since the CT excitation in LSCO is near 2 eV, which is out of the energy range of our experiment. This reaffirms that the behavior seen in YBCO is intrinsic to the system, and reinforces our assignment of peak *A* to a CT exciton. The assignment of peak *A* as a bound state of the excited electron with hole states near E_F also helps explain its close connection to peaks *B* and *C* through quasiparticle excitations near E_F and the attendant Cooper pair breaking. We recall that the contribution of peak *C* involving the important \sim 40-meV magnetic excitation and the \sim 75-meV LO phonon grows with decreasing temperature, with respect to peaks *B* and *A*. Given that our measurement probes only the pair breaking processes, the spectral intensity distribution and its evolution with temperature suggests a rather strong connection of the pairing to the magnetic excitations and phonons. According to the stripe phase model of HTS,⁴ the mobile holes are

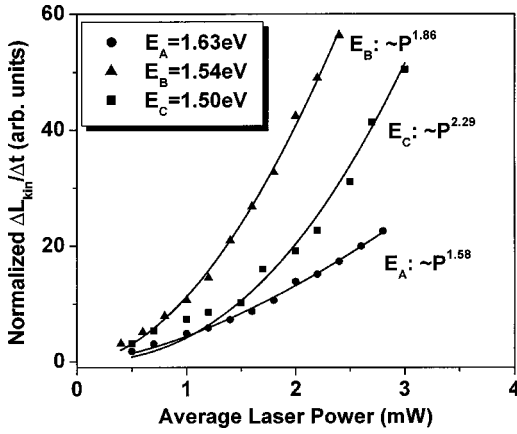


FIG. 4. Fast optical response as a function of the average laser power for the three individual contributions to the multiplet of optimally doped YBCO films.

confined in conducting stripes and exhibit a quasi-one-dimensional electronic character since the electronic coupling between the conducting stripes falls exponentially with the distance between them. Pairing, in this model, is simply the formation of a spin gap. Between the conducting stripes are hole-free AFM insulating regions. In these regions, a spin gap can be generated naturally through the spatial confinement by the conducting stripes.³⁸ By pair hopping between the conducting stripes and the AFM insulating environment, the mobile holes acquire a spin gap, which corresponds to pairing. The most important feature of this model is that pairing originates in the insulating regions and is simply transferred to the mobile holes by their excursions into the insulating environment. Therefore, any perturbation to the AFM insulating regions such as a CT exciton could result in dramatic pair breaking. For example, the CT exciton can itself break pairs by generating a ferromagnetic fluctuation in the AFM insulating background and thus locally suppressing the spin gap, or by influencing the effective mass of the conducting stripes and therefore the superfluid phase stiffness.⁴ Indeed, the notion of the change of kinetic inductance could have an entirely new microscopic interpretation in this electronic phase separation scenario.

Figure 4 shows the laser power dependence of the FOR at 80 K for optimally doped YBCO at photon energies corresponding to peaks A, B, and C. A fit (solid lines) to a simple power law (the FOR is asymptotically equal P^b where P is the average laser power) gives the exponents $b = 1.58 \pm 0.04$, 1.86 ± 0.05 , and 2.29 ± 0.14 for peak features A, B, and C, respectively. Before we discuss the origin of the differences in these exponents, one important factor must be considered, that is, the possible contribution of bolometric signal to the FOR due to laser heating. The maximum temperature increase of the superconducting device due to one laser pulse can be estimated as $\Delta T_{\max} = F(1-R)[1 - \exp(-d/\delta)]/(cd)$, where F is the laser fluence; c , d , and R are the specific heat, the thickness, and the reflectivity of the superconducting film, respectively, and δ is the penetration depth of the light. This is clearly an overestimation, since the superconducting device has been assumed to be thermally iso-

lated and the absorption at the window of the dewar has been ignored. For YBCO, $R \sim 0.1$,¹⁸ $\delta \sim 100$ nm,¹⁴ $c \sim 1$ J/cm³K,¹⁸ and $d \sim 100$ nm. For a spot size of ~ 5 mm \times 200 μ m, a laser power of 1 mW gives $F \sim 10$ μ J/cm² for each pulse. Therefore, $\Delta T_{\max} \sim 0.57$ K, which is certainly small enough to rule out any bolometric effect. A nonlinear laser power dependence of the FOR signal was also observed earlier using an electro-optic sampling technique with subpicosecond resolution for optimally doped YBCO.³⁹ There, a quasiquadratic dependence was found for an excitation photon wavelength of 390 nm at 77 K for low laser power, and was seen to change into a linear dependence for high laser power, when the bolometric response was also observed at the same time. The nonlinear power dependence of the FOR signal is not surprising considering the complexity of the Cooper pair breaking and quasiparticle recombination processes, as discussed earlier in this paper. It was shown⁴⁰ that the nonequilibrium kinetic inductive optical response due to femtosecond laser excitations can be fitted rather nicely by the Rothwarf-Taylor (RT) equations.⁴¹ The RT equations describe the deviations of the quasiparticle and phonon systems away from the equilibrium, and are nonlinear coupled rate equations themselves. However, the differences in the nonlinearity, as observed in our power dependence measurements for the three-photon energies, cannot be accounted for by this model alone. To this end, it is useful to recall that several electronic processes in solids, identified with the coupling of charges with the lattice and spin systems, are known to be characteristically nonlinear.⁴² The interactivity of extended or nonlocal fluctuations in the system heightens the nonlinearity. Thus, based on the assignments of features A, B, and C to different excitations in the system, one can expect a nonlinear dependence of these contributions on photon density. Moreover, since B and C involve couplings of two and three excitations, respectively, they should, in fact, be increasingly nonlinear. This is precisely what is observed. The strong coupling among spin, charge, and lattice degrees of freedom is a signature in the excitation spectrum of high- T_C cuprates. Recently, based on linear optical-absorption measurements of SrCuO₂Cl₂, Löwenich *et al.*⁴³ proposed a theory for charge-transfer excitation in the Cu-O plane. The theory explicitly includes the coupling of the CT exciton to LO phonons and to an additional low-energy electronic continuum of states. Further investigations are needed to make a possible connection of this theory to the data discussed in this paper, but it does provide further support to our assignment of features A, B, and C.

In conclusion, a pair-breaking spectroscopy study using 100-fs laser pulses, performed on optimally doped, oxygen-depleted, and Zn-doped epitaxial YBCO thin films in their superconducting state, reveals a sharp triplet fine structure near 1.5 eV. A comparison of the triplet features for the three sample types suggests that Cu-O planes are responsible for their occurrence. The narrowness of the linewidths, the appearance of CT exciton, and the specificity of peak separations attributable to the reported magnetic excitation and phonon energies suggest the existence of insulating AFM domains in the superconducting state of YBCO over the picosecond time scale.

The authors would like to thank C. Lobb and D. Drew for reading the manuscript and for suggestions. This work was supported by the Office of Naval Research under Grant No.

ONR-N000149611026 (Program Monitor: Dr. Deborah Van Vechten) and the University of Maryland (NSF-MRSEC) under Grant No. DMR 00-80008.

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