Transient Photoinduced Conductivity in Single Crystals of $YBa_2Cu_3O_{7-\delta}$: "Photodoping" to the Metallic State

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The temperature dependences of the transient photoinduced conductivity in $YBa_2Cu_3O_{7-\delta}$ at different light intensities (I_L) and of the doping-induced conductivity at different δ are similar, indicative of "photodoping." For $\delta \approx 0.7$, signatures of the photoinduced transition to metallic behavior are observed at $I_L > 5\times10^{15}$ photons/cm^2; the deep resistivity minimum below 100 K, reminiscent of the onset of superconductivity in granular superconductors and in inhomogeneously doped samples, is interpreted in terms of phase separation and metallic-droplet formation. For $\delta \approx 0.6$, the lifetime of the photoexcited state is enhanced by nearly 3 orders of magnitude at high excitation levels, indicative of metastability.

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The transition from the insulating and antiferromagnetic phase to the metallic and superconducting phase as a function of oxygen content (δ) in $YBa_2Cu_3O_{7-\delta}$ is correlated with the density of charge carriers (n_c) in the CuO_2 layers. Photoexcitation offers an alternative method to vary n_c with a number of advantages; n_c can be increased without the complication of a change in composition or crystal structure, and the transient n_c can be increased to high levels with subnanosecond resolution using pulsed laser excitation.

The initial results of transient photoinduced conductivity (TPIC) in crystals of $YBa_2Cu_3O_{6.3}$ indicated that the peak photocurrent changes dramatically as a function of I_L: The initially linear dependence at low light intensity becomes first sublinear and then superlinear [1]. The TPIC is delayed by 300–500 ps relative to the absorption, demonstrating that time is required for the photogenerated carriers to acquire the relatively high mobility implied by the peak photoconductive response.

In this Letter, we show that the temperature (T) dependences of the transient *photoinduced conductivity in $YBa_2Cu_3O_{7-\delta}$ (with $\delta \approx 0.7$) at different I_L* and the *doping-induced conductivity in $YBa_2Cu_3O_{7-\delta}$ at different δ* are similar, indicative of "photodoping." The (transient) photoinduced transition to metallic behavior is observed at $I_L > 5\times10^{15}$ photons/cm^2. A resistivity (ρ) minimum is observed below 100 K reminiscent of the onset of superconductivity in granular superconductors and in inhomogeneously doped samples. This borderline metallic behavior is interpreted in terms of phase separation of the photogenerated carriers in the antiferromagnetic (AF) insulator. For $\delta \approx 0.6$, the lifetime of the photoexcited state is enhanced by nearly 3 orders of magnitude at high excitation levels, indicative of metastability. A longitudinal magnetic field (≤ 0.5 T) suppresses both the minimum in $\rho(T)$ and the associated superlinear contribution to the TPIC.

The TPIC measurements use the Auston switch configuration [2]. The sample is mounted across a gap (0.2 mm) in a 50-Ω strip-line transmission line (both the upper strip and the ground plane are Au evaporated onto the alumina substrate). A dc bias (typically 0–100 V) is applied. After absorption of a light pulse, the sample acts as a current source; the current pulse propagates down the transmission line into the detector. The 50-Ω impedance matches into the input of the sampling head (Tektronix S-4) and boxcar (PARC 4400 system), thereby avoiding spurious reflections; the transmission line configuration enables picosecond temporal resolution (since the configuration is essentially a microwave strip line with >200-GHz frequency response). The excitation source was either a nitrogen laser ($\hbar\omega = 3.7$ eV, 600-ps pulse width) or a pumped dye laser ($\hbar\omega = 2.6$ eV, 30-ps pulse width).

The a-b plane resistivity (ρ) of the $YBa_2Cu_3O_{6.3}$ crystals is about 5×10^2 Ω cm at 300 K; $\rho(T) \approx \rho_0 \times \exp(-E_a/k_BT)$, with $E_a = 0.18 \pm 0.1$ eV. For the $YBa_2Cu_3O_{6.4}$ crystals, $\rho \approx 10$ Ω cm at 300 K and E_a is nearly an order of magnitude smaller ($E_a = 0.03$ eV). After storing the $YBa_2Cu_3O_{6.3}$ crystals in a desiccator for more than a year, E_a increased to 0.22 eV, indicating a slight loss of oxygen; the TPIC did not change significantly over this period. All aspects of the TPIC were reproducible from sample to sample.

The T dependences of the photoresistivity at several levels of 3.7-eV photoexcitation are compared with the dark resistivity in the same sample in Fig. 1. The photoinduced resistivity was calculated from the reciprocal of the peak transient photoinduced conductivity by dividing the surface resistance by the optical absorption depth [3] ($\alpha^{-1} \approx 300$ Å). The transient decrease in ρ with $I_L = 10^{16}$ photons/cm^2 ($\approx 3\times10^{21}$ photons/cm^3 in the absorption depth) is more than 10 orders of magnitude at 80 K. More importantly, the T dependence of $\rho(T)$ changes dramatically; the activation energy decreases with $E_a \rightarrow 0$ at high I_L, and a deep minimum in $\rho(T)$ ap-

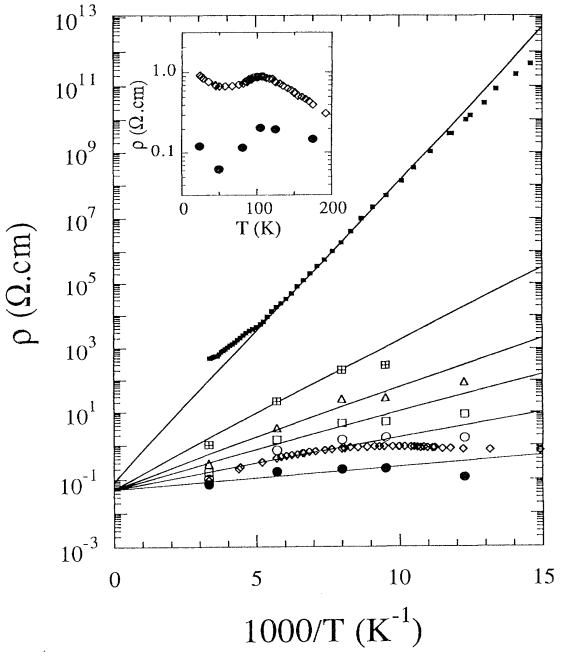

FIG. 1. Temperature dependences of the photoresistivity at different I_L are compared with the dark resistivity (■) in the same sample; (⊞) $I_L=1\times10^{13}$, (△) $I_L=1\times10^{14}$, (□) $I_L=1\times10^{15}$, (○) $I_L=7\times10^{15}$, (◇) $I_L=1.1\times10^{16}$, and (●) $I_L=2.3\times10^{16}$ photons/cm^2. Inset: $\rho(T)$ at low T in greater detail for the two highest light intensities.

pears below 100 K. The latter is shown in greater detail in the inset to Fig. 1; for $I_L=2.3\times10^{16}$ photons/cm^2, the minimum value is a factor of 10 below the value extrapolated from $\rho(T)$ above 100 K.

$YBa_2Cu_3O_6$ is an AF insulator; decreasing δ introduces carriers in the CuO_2 layers, destroys AF order, and results in the transition from insulator to metal and superconductor. Chemical doping of AF insulators has been used for many years to study the transition to the metallic state in highly correlated systems [4]. Such systems show behavior characteristic of a metal-insulator (M-I) transition which can be understood in the context of disorder-induced localization. The disorder from random mixed-valence substitution and partial oxygenation leads to the formation of a mobility edge at an energy E_c; hole states at $E>E_c$ are localized. The M-I transition occurs when E_F is moved through E_c by doping.

A characteristic of the disorder-induced M-I transition is the existence of a minimum metallic conductivity [5,6]. For the anisotropic layered high-temperature superconductivity materials, a two-dimensional (2D) model is appropriate, and the minimum metallic conductivity is universal [6],

$$\Sigma_{\min}\approx e^2/h \qquad (1)$$

($e^2/h=3.9\times10^{-5}\ \Omega^{-1}$). In the strict 2D limit, $\Sigma_{\min}=\sigma_{\min}c$, where c is the spacing between successive pairs of CuO_2 planes ($c\approx12$ Å). In the "insulating" regime, transport is activated by thermal excitation of carriers from E_F to E_c; $E_a=|E_c-E_F|$. At lower T, variable-range hopping through localized states near E_F is the dominant mechanism [5].

The effects of chemical doping are consistent with the predictions of localization theory. From the dark conductivity of $DyBa_2Cu_3O_{7-\delta}$ [7], $\sigma_{\min}\sim100$ S/cm corresponding to a conductance per layer, $\Sigma\approx0.5e^2/h$. The data separate into two categories: When $\rho<1/\sigma_{\min}$, the material is metallic and superconducting, and $\rho(T)$ extrapolates to a relatively low value as $T\to0$; when $\rho>1/\sigma_{\min}$, the material shows thermally activated behavior, and $\rho(T)\to\infty$ as $T\to0$. Comparison of the photoconductive response [1] and the infrared absorption [3] of $YBa_2Cu_3O_{6.3}$ also implies localization of the low-energy states; the absorption observed throughout the infrared does not lead to generation of mobile carriers.

Precisely the same features, indicating a M-I transition as E_F is moved through E_c, are observed from *photogenerated* carriers as shown in Fig. 1. From E_a of the dark conductivity, we conclude that E_F lies above E_c by about 0.2 eV in $YBa_2Cu_3O_{6.3}$. Photodoping increases n_c and shifts E_F toward E_c as indicated by $E_a\to0$ at high I_L. The extrapolation to $1/T\to0$ determines $\sigma_{\min}\approx35$ S/cm so that $\Sigma\approx0.2e^2/h$. In order to get precise agreement between the measured $\sigma_{\min}$ and Eq. (1), one would have to assume that the 2D transport is restricted to a few atomic layers, rather than one; however, since the Auston switch is a two-probe measurement, such precision is beyond that of the experiment.

Thus, a sufficient carrier density can be generated by transient photodoping $YBa_2Cu_3O_{6.3}$ to raise E_F to E_c and thereby induce borderline metallic behavior. The obvious question is whether such a transient borderline metal can condense to the superconducting phase. The observation of the minimum in $\rho(T)$ at high excitation levels is suggestive of the onset of photoinduced transient superconductivity. Curves similar to that in Fig. 1 were seen frequently following the discovery of high-temperature superconductivity in $\rho(T)$ for samples with multiphase composition [8]. Such behavior is indicative of *phase separation* with disconnected superconducting regions separated by insulating regions: The decrease in $\rho(T)$ near 100 K is due to the onset of superconductivity, and the increase in $\rho(T)$ at lower temperatures is due to the "series resistance" of the insulating regions. Similar results are observed in granular superconducting films which exhibit local superconductivity with tunneling between grains [8].

Theoretical studies of the two-dimensional AF conclude that dilute holes are unstable against phase separation into a hole-rich phase and a pure AF insulating phase [9]. Since no region in the phase diagram was found in which a dilute gas of holes is stable, phase sepa-

ration might be intrinsic in $YBa_2Cu_3O_{7-\delta}$ whether carriers are injected through changes in δ or through photodoping. Phase separation following photoexcitation is consistent with several aspects of the TPIC and the related photoinduced absorption data.

The onset of superconductivity (as indicated by the onset of the resistivity decrease) is approximately that of the highest doped material, $YBa_2Cu_3O_7$—i.e., the droplets appear to be well into the metallic regime. The observation of a resistivity minimum with onset equal to the bulk T_c is typical of granular or inhomogeneous superconducting materials which exhibit local superconductivity [8].

During photoexcitation the absorbed photons create electron-hole pairs in the CuO_2 planes. The electrons will be quickly trapped at oxygen vacancies on adjacent partially oxidized CuO chains and would tend to locally enhance the orthorhombic distortion, as observed in the photoinduced absorption experiments [10,11].

Although the holes are initially photogenerated uniformly within the optical absorption depth, hole mobility is inhibited by the AF spin correlations. Diffusion to form phase-separated droplets results in hole-rich regions with relatively high mobility causing a diffusion-limited increase in the photocurrent, consistent with the time delay of the peak photocurrent. As I_L increases, the hole density is sufficient to shift E_F through E_c in the hole-rich regions, resulting in metal-like $\rho(T)$ for the (partially) phase-separated system.

The frequencies of the infrared-active vibrational (IRAV) modes observed in photoinduced absorption do not correlate with the Raman modes of the insulating phase, but they do correlate with the Raman modes of the metallic phase [11]. This is true even in $Tl_2Ba_2Ca_{1-x}Gd_xCu_2O_8$ where the semiconductor ($x=0.02$) and the metal ($x=0$) have the same structure [11]. These results imply that photodoping leads to metallic screening and associated shifts in the phonon frequencies characteristic of the metallic phase, consistent with droplet formation. Isolated holes would not give IRAV correlated with the metallic phase, especially when the crystal structure is the same in both cases. Moreover, in spite of the relatively large shifts ($\Delta\omega \sim 50$–100 cm^{-1}), the IRAV are narrow and well defined indicating a long range for the metallic phase consistent with phase separation; otherwise a broad featureless band covering the entire $\Delta\omega$ would be observed.

Motivated by the interpretation of the minimum in $\rho(T)$ at high I_L as indicative of the onset of photoinduced transient superconductivity, we carried out a series of TPIC measurements in a magnetic field ($B \leq 0.5$ T). The magnetic field was parallel to the applied electric field so that any effects due to the Lorentz force would be eliminated. In Fig. 2, we compare the peak photoconductance (G_{ph}) as a function of I_L for $B=0$ and $B=0.5$ T for $YBa_2Cu_3O_{6.3}$ at 60 K. The data were taken with field

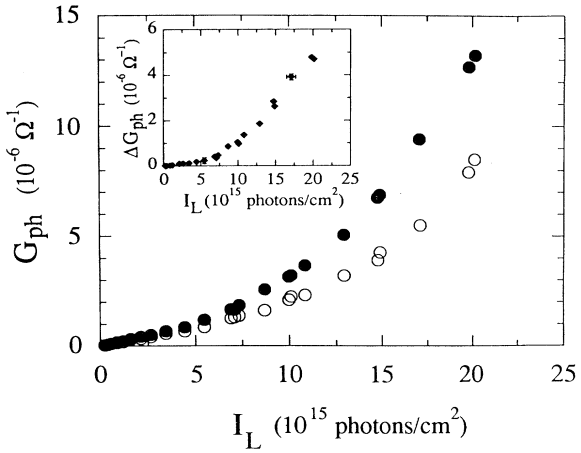

FIG. 2. The peak photoconductance (G_{ph}) vs excitation intensity (I_L) for $B=0$ (●) and $B=0.5$ T (○) for $YBa_2Cu_3O_{6.3}$ at 60 K; $\Delta G_{ph}=G_{ph}(B=0)-G_{ph}(B=0.5\text{ T})$ is plotted vs I_L in the inset.

on and off, alternately, at each I_L. The differential conductance, $\Delta G_{ph}=G_{ph}(B=0)-G_{ph}(B=0.5\text{ T})$, is plotted versus I_L in the inset. A magnetic-field dependence is observed at excitation levels above a critical I_L, which is coincident with the onset of the superlinear dependence, coincident with the onset of metallic behavior, and coincident with the onset of the minimum in $\rho(T)$. The dependence of $\Delta G_{ph}(B)$ is approximately $\Delta G_{ph}/G_{ph} \sim B^{1/2}$. We checked carefully for magnetic-field dependence of the dark resistivity; none was detected ($\Delta G/G < 10^{-4}$). Examination of the time evolution of the transient photoconductance for $B=0$ and for $B=0.5$ T shows that the peak of the *differential* photoconductance is time delayed with respect to the peak in G_{ph} at $B=0.5$ T, demonstrating that the time delay associated with the growth of carrier mobility is magnetic-field dependent, with a longer time delay at zero field. Although it is tempting to associate the magnetic-field suppression with the onset of transient photoinduced superconductivity (e.g., by magnetic-field suppression of Josephson coupling between droplets), the magnetic-field effect is observed even at T well above the resistivity minimum. Thus, the magnetic-field suppression of the TPIC is a more general feature of the M-I border.

Figure 3 shows a series of transient decay curves following different levels of excitation for a sample with oxygen content even closer to the M-I transition, $YBa_2Cu_3O_{6.4}$; the data were taken at 35 K. Since for this sample $E_a \approx 0.03$ eV, experiments for $T > 50$ K were not possible because of the low resistivity. At low excitation levels, the power-law ($\approx t^{-\alpha}$) decay occurs on the ns time scale, indicative of dispersive transport in a disordered system [12]. At higher excitation levels, the photoinduced conductivity persists at $\sigma \approx \sigma_{min}$ to times in excess of 100 ns. The remarkable persistence of the pho-

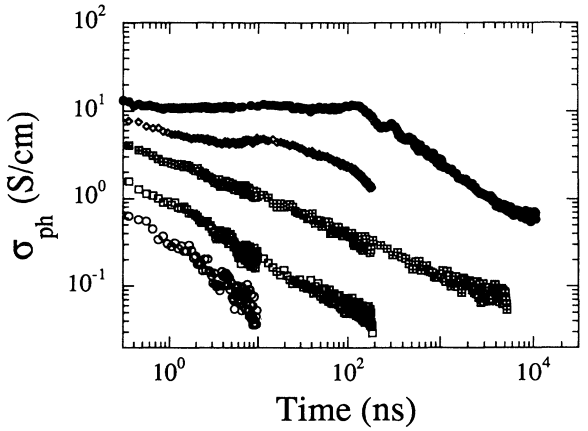

FIG. 3. Decay of the photoinduced conductivity for $YBa_2Cu_3O_{6.4}$ at 35 K; $I_L = 4.5\times10^{14}$ (○), $I_L = 8.6\times10^{14}$ (□), $I_L = 2.1\times10^{15}$ (⊞), $I_L = 4.5\times10^{15}$ (◇), and $I_L = 1\times10^{16}$ (●) photons/cm^2.

toinduced conductivity at $\sigma \approx \sigma_{min}$ suggests metastability at high levels of excitation, consistent with phase separation and the formation of metallic regions.

The most obvious potential artifact in photoexcitation experiments is resistance changes which result from surface heating (ΔT), caused by the light absorption, rather than genuine TPIC. The importance of sample heating was carefully examined; heating is not a dominating factor in our TPIC experiments as indicated by the following: (i) To obtain the observed change in ρ from heating, ΔT would have to exceed the melting temperature (see Fig. 1). However, even after thousands of laser shots, there is no indication of surface damage. (ii) In contrast to the behavior expected from heating ($\Delta T \sim \tau^{1/2}$, where τ is the laser pulse width) [13], neither the magnitude of the peak photocurrent nor the time delay are dependent on the width of the excitation pulse which has been varied from 30 to 600 ps. (iii) The nonmonotonic T dependence observed at high I_L is not consistent with heating. (iv) Similar measurements were carried out on ultrathin (40 Å) epitaxial films [14] of $DyBa_2Cu_3O_{7-\delta}$ which absorbed only ~10% of the incident photons. For δ near 0.7, the photoinduced changes in $\rho(T)$ are essentially identical to those shown in Fig. 1. Since the latter absorb only ~10% of I_L, ΔT would be smaller than in the crystals by an order of magnitude; one would expect several orders of magnitude reduction in the signal if it were caused by surface heating. (v) Finally, the remarkable enhancement of the lifetime (Fig. 3) with $\sigma \approx \sigma_{min}$ to times in excess of 100 ns is not consistent with heating.

In conclusion, we have demonstrated photodoping of $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.6$–0.7) to borderline metallic levels. The data are consistent with disorder-induced localization as the origin of the M-I transition. At high excitation levels, a deep minimum in $\rho(T)$ is observed for $\delta \approx 0.7$ below 100 K, reminiscent of the onset of superconductivity in granular superconductors and in inhomogeneously doped samples. For $\delta \approx 0.6$, the lifetime of the photoexcited state is enhanced by nearly 3 orders of magnitude at high excitation levels. The results are interpreted in terms of phase separation and metallic-droplet formation. A longitudinal magnetic field (≤ 5 kG) reduces both the resistivity minimum and the superlinear contribution to the transient photocurrent.

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