

Enhancement of persistent photoconductivity by uv excitation in $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$

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(Received 28 February 1996; revised manuscript received 16 May 1996)

The spectral dependence of the persistent photoconductivity in $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$ was measured in the near-infrared to the ultraviolet energy range. The excitation efficiency is strongly enhanced for a photon energy of 4.1 eV. Photons with this energy create electron-hole pairs close to oxygen vacancies in the Cu-O chain layers. Therefore, the probability for the excited electron to be trapped at an oxygen vacancy is very high, which leads to the strong enhancement of the excitation efficiency of persistent photoconductivity. [S0163-1829(96)50130-X]

Shortly after the discovery of high-temperature superconductivity, it was found that under illumination with visible light, oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films show persistent photoconductivity¹ and photoinduced superconductivity.² After the illumination with visible light of an oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film, its normal-state resistivity decreases and its superconducting transition temperature increases substantially. This effect is persistent at temperatures below 100 K and relaxes within several days at room temperature. In addition to the resistivity change, there is a Hall coefficient change, which implies that the carrier density increases through illumination.³ Furthermore, there is a structural change upon illumination, similar to the structural changes observed with increased oxygen doping of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁴ Moreover, persistent photoinduced effects can only be observed when oxygen vacancies are present,⁴ the magnitude increasing with decreasing oxygen content,^{2,3,5} and reaching its maximum for fully deoxygenated, insulating $\text{YBa}_2\text{Cu}_3\text{O}_6$ thin films.⁶

A theoretical model which explains qualitatively all photoinduced effects, is based on the trapping of electrons at oxygen vacancies in the Cu-O chain layer.⁶ In this scenario an incoming photon produces an electron-hole pair. Subsequently the electron is trapped at an oxygen vacancy in the Cu-O chain layer (see Fig. 1). The trapped electron causes a lattice distortion, which gives rise to a large energy barrier for the reverse recombination with the hole. The hole is transferred to the CuO_2 plane layer which increases the number of carriers and enhances the conductivity. This model is supported by recent photoluminescence measurements, which show that under illumination with visible light the decrease in resistivity is correlated with a decreasing number of available oxygen vacancies in the Cu-O chain layers.⁷

The spectral dependence of the photoinduced effects has been investigated in the visible light range (1.6–3.4 eV).^{5,8} The spectral efficiency of persistent photoconductivity shows several pronounced peaks, which according to Kudinov *et al.* can be attributed to electronic transitions within the CuO_2 plane layers.⁵ In this work, we extended the measurements of the spectral efficiency into the ultraviolet energy region. Compared with excitations in the visible light region, there is a strong enhancement of the excitation efficiency of persis-

tent photoconductivity at the 4.1 eV photon energy. This can be directly attributed to electronic excitations in the Cu-O chain layers.

The experiments were performed on a *c*-axis-oriented $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$ thin film, with a thickness of 1000 Å and a surface area of $4 \times 7 \text{ mm}^2$. A $\text{GdBa}_2\text{Cu}_3\text{O}_7$ film was grown using magnetron sputtering on a (100) SrTiO_3 substrate.⁹ Initially the film was fully oxygenated with a T_c above 88 K. To reduce the oxygen content, the film was annealed in oxygen gas, following the pressure-temperature curve for the corresponding oxygen content.¹⁰ The sample was slowly heated from room temperature to 500°C (2°C/min), while the oxygen pressure was continuously adjusted.¹¹ To decrease the oxygen content the sample was maintained for 5 h at 500°C. Afterwards it was slowly cooled to room temperature (1°C/min), while controlling the oxygen pressure. After this annealing process, the oxygen content was determined from the expansion of the *c*-axis parameter using high-resolution x-ray diffraction.¹² We choose for our experiments a $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$ thin film, since with this oxygen content it is close to the metal-insulator transition, and exhibits large persistent photoconductivity.^{2,3,5}

To reduce contact resistance, small silver pads were sputtered through a contact mask on the film surface. The four point resistance was measured in a He-flow cryostat

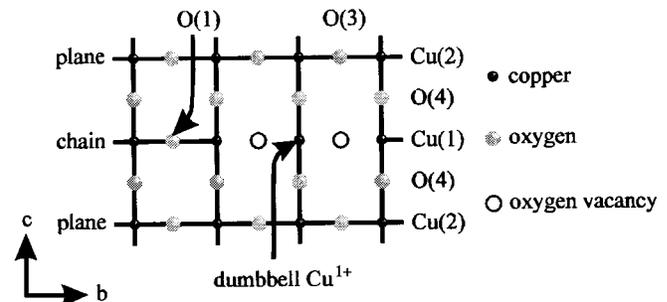


FIG. 1. Schematic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the *bc* plane. Cu(1) and O(1) denote copper and oxygen atoms in the Cu-O chain, O(4) is the apical oxygen between the chains and the planes, and Cu(2), O(2), and O(3) are atomic sites in the CuO_2 planes. Note that the Cu^{1+} (1) atom in an O(4)-Cu(1)-O(4) dumbbell has an oxygen vacancy on both sides. The notation used here is taken from Ref. 19.

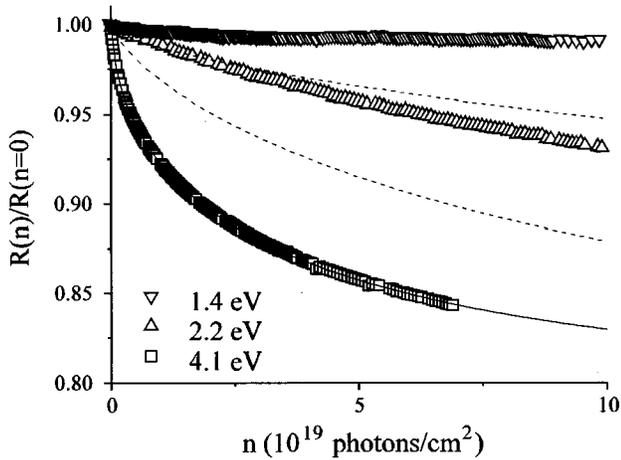


FIG. 2. Excitation of the persistent photoconductivity for different photon energies $\hbar\omega$. The resistance is normalized to the resistance in the relaxed state $R(0)$. The solid line is a stretched exponential fit to the data at $\hbar\omega=4.1$ eV. The dashed lines indicate the region in which the plot of the resistance vs photon number varies for photon energies between 2.1 and 3.3 eV.

equipped with optical quartz windows. A 1000 W mercury-xenon arc lamp was used for the optical excitation. To protect other optical elements from excessive heat, far infrared wavelengths were eliminated using a liquid water filter. For the excitation, a specific wavelength in the range 250–900 nm (4.8–1.4 eV) was selected using interference bandpass filters with a bandwidth of 10 nm. The monochromatic light passed through a beam splitter; part of the beam was focused on the sample, while the intensity of the other part was monitored to check the stability of the mercury-xenon arc lamp. Before the measurements, the light intensity for each wavelength and the absorption of the optical windows in the cryostat were carefully measured. The light intensity at the sample varied, depending on the wavelength, between 0.04 and 5 mW/cm². During excitation the sample was kept at a temperature of 95 K. For relaxation the sample was taken out of the cryostat, so that the sample was at room temperature in air. After several repetitions of the relaxations a small increase in the resistance of the film was observed. This could indicate that the film might have degraded somewhat, while in contact with air. However, this did not affect our measurements.

For a given wavelength the excitation of the photoinduced effects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films depends only on the number of photons per surface area exciting the sample.⁵ Therefore, for the excitation the measurement time t was converted into photon numbers per surface area n [photons/cm²] using

$$n = \frac{I \times t}{\hbar\omega}, \quad (1)$$

where I [W/cm²] is the light intensity at the sample surface and $\hbar\omega$ the photon energy. Figure 2 shows the resistance change versus photon number for a few representative photon energies. Below 1.5 eV there is essentially no change in resistance, while in the 1.5 to 4.8 eV range the changes are pronounced. The small differences observed for excitations

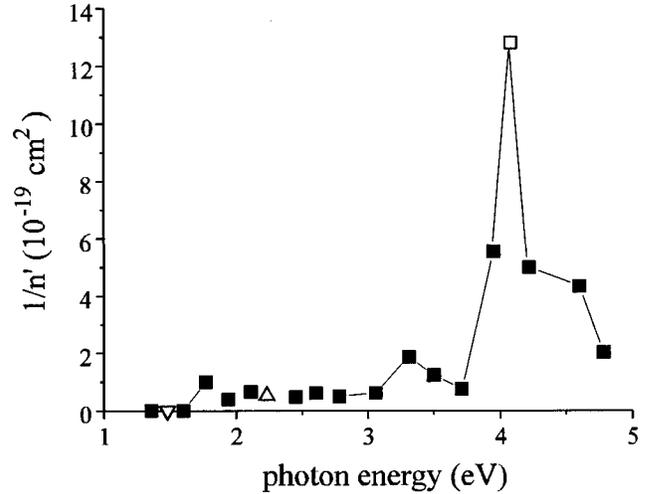


FIG. 3. Spectral efficiency of the persistent photoconductivity excitation: $1/n'$ vs photon energy. n' is the number of photons per unit area necessary for a 2% change in the resistance. The data at 4.1, 2.2, and 1.4 eV is indicated by the same symbol as in Fig. 2.

in the 1.5 to 3.2 eV range are consistent with earlier measurements of the spectral dependence of persistent photoconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.^{5,8} The change of resistance $R(n)$ during the excitation can be fitted phenomenologically to a stretched exponential.⁵ Figure 2 shows as an example a fit for the resistance data at 4.1 eV. A possible reason for the stretched exponential behavior of the excitation might be a distribution of excitation times due to inequivalent trapping sites or disorder.¹³

For photon energies larger than 3.2 eV, the photon number n' necessary for a given change in resistance (e.g., 2%) drops steeply, and reaches its minimum at 4.1 eV. In order to show more clearly the strong enhancement of the excitation of the persistent photoconductivity, we plot the inverse of the photon number necessary for a 2% reduction of the resistance of the film ($1/n'$) against the energy of the exciting photons. This can be seen in Fig. 3. Clearly, the excitation is enhanced by an order of magnitude at 4.1 eV compared with excitations in the visible range (1.5–3.2 eV). Notice, that since $\Delta R/R=2\%$ is constant, $1/n'$ is proportional to the spectral efficiency for the persistent photoconductivity as defined by Kudinov *et al.*,⁵

$$\eta(\hbar\omega) = \frac{1}{R(0)} \left. \frac{dR(n)}{dn} \right|_{(n=0)}. \quad (2)$$

Also the main features in Fig. 3 are independent of the choice of $\Delta R/R=2\%$. A graph with $\Delta R/R=5\%$ looks identical.

It is very interesting to compare the spectral dependence of persistent photoconductivity with the optical conductivity and the dielectric function of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ determined from optical measurements. These measurements show a large absorption peak at 4.1 eV, which depends strongly on the oxygen content of the sample.^{14,15} Its intensity is maximum for completely deoxygenated samples ($\delta=1$) and vanishes for fully oxygenated ones ($\delta=0$).^{15–17} This behavior is reminiscent of the dependence of persistent photoconductivity on oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁶ However, the en-

hanced absorption alone is not sufficient to explain the strong enhancement of excitation of the persistent photoconductivity at 4.1 eV. For samples with a similar oxygen content like our $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$ thin film, the intensity of the absorption peak at 4.1 eV is at most a factor of two higher than in the visible region.¹⁷ On the other hand, the persistent photoconductivity shows an enhancement of an order of magnitude.

The key to understand this strong enhancement, is the origin of the absorption peak at 4.1 eV. This peak has been assigned to a $3d_{3z^2-1}$ to $4p_x$ electronic transition of $\text{Cu}^{1+}(1)$ atoms in an O(4)-Cu(1)-O(4) dumbbell.^{14,17,18} These $\text{Cu}^{1+}(1)$ atoms are located in the Cu-O chain layers and have an oxygen vacancy on both sides, as shown in Fig. 1. On the other hand, the excitations with photons in the visible light region have been all attributed to O(2,3) $2p$ -Cu(2) $3d$ charge transfer excitations.^{5,15} These electronic transitions are therefore located within the CuO_2 plane layers (see Fig. 1). This implies that the persistent photoconductivity is enhanced as soon as an electron-hole pair is created in close proximity to an oxygen vacancy.

This observation supports and is consistent with a recent model of persistent photoconductivity.⁶ In this model, the incoming photon excites an electron-hole pair, and the electron is trapped at an oxygen vacancy in the Cu-O chain layer. The trapped electron then causes a lattice distortion, which prevents reverse recombination. Since the top of the Cu-O chain valence band is located below the top of the CuO_2 plane valence band,²⁰ the hole may then be transferred to the CuO_2 plane layer and thus enhance the conductivity.

When an electron-hole pair is created with visible light (1.5–3.2 eV), they are both in the CuO_2 plane layer. For the electron to become trapped at an oxygen vacancy, it needs to

be transferred into the Cu-O chain layer before it recombines with a hole.²¹ Therefore, the probability for an excitation with visible light to contribute to the persistent photoconductivity is rather small. This is also supported by the rapid decay of transient photoconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ using visible light.²² On the other hand, when the electron-hole pair is created with 4.1 eV photons, the electron is already close to the oxygen vacancy and therefore has a much higher probability to become trapped and thus to contribute to the persistent photoconductivity. This easily explains the strong enhancement of the excitation of persistent photoconductivity at 4.1 eV.

In conclusion, we measured the spectral dependence of persistent photoconductivity in $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$ from the near infrared into the ultraviolet energy region. The efficiency of the excitation is enhanced by an order of magnitude for 4.1-eV light compared with light in the visible region (1.5–3.2 eV). Comparison with optical measurements suggests that this enhancement is due to the fact that at 4.1 eV an electron-hole pair is created in the Cu-O chain layer next to two oxygen vacancies, while in the visible region the electron-hole pair is created in the CuO_2 plane layer. This results in higher probability for the electron to become trapped at an oxygen vacancy, if excited with 4.1 eV photons.

We gratefully acknowledge the support of Office of Naval Research. We thank J. Hasen for growing the samples used in this study, J. Price for loaning us some of his equipment, and A. A. Abrikosov, L. Gorkov, and D. Reznik for useful conversations. One of us (J.S.) would like to thank the Spanish CICYT for financial support through Grant No. MAT94-0604-c02-01-4715.

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