

Persistent photoinduced superconductivity

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Abstract

We review work done at UCSD on persistent photoconductivity and photoinduced superconductivity in REBa₂Cu₃O_x thin films. It is shown that the resistivity, Hall coefficient and *c*-axis parameter change significantly upon illumination. All these effects require the presence of oxygen vacancies. The maximum enhancement of the conductivity with illumination occurs for fully deoxygenated samples (*x*=6.0). The spectral dependence of the persistent photoconductivity has a pronounced peak in the UV region at ≈4.1 eV. All these observations can be understood qualitatively with a model based on the trapping of photoexcited electrons at oxygen vacancies in the Cu–O chains of REBa₂Cu₃O_x.

Keywords: High-*T_c* superconductors; Photoconductivity; Thin film

1. Introduction

Illumination of standard superconductors (e.g., Pb) is normally detrimental to the superconducting properties due to pairbreaking [1]. However, granular systems, which are Josephson coupled through a photosensitive barrier, show an enhancement of their superconducting properties [2]. In these granular systems the transition width ΔT_c is reduced upon illumination, while the critical temperature onset remains constant.

The observation of photoinduced superconductivity in REBa₂Cu₃O_x thin films (RE=rare earth or yttrium) is very different. After illumination, in contrast, not only does the zero resistance temperature increase, but the *T_c* onset increases as well [3]. This effect is accompanied by a significant reduction of the normal state resistance, which can also be observed for non-superconducting YBa₂Cu₃O_x [4]. The photoinduced superconductivity and photoconductivity are persistent at low temperatures and relax within days at room temperature [3,4].

In this paper, we review work done at UCSD on the

persistent photoconductivity and photoinduced superconductivity in REBa₂Cu₃O_x thin films. We first discuss the basic effect and show the dependence of the persistent photoconductivity on oxygen stoichiometry *x* and light wavelength. Then, we present related photoinduced effects on the magnetotransport and structure of REBa₂Cu₃O_x. These experimental results are then discussed in relation to various possible theoretical models.

2. Experimental results

2.1. Persistent photoconductivity and photoinduced superconductivity

2.1.1. Film preparation

The experiments were performed on a variety of REBa₂Cu₃O_x thin films (typically 1000 Å thick). Using magnetron sputtering, *c*-axis oriented REBa₂Cu₃O_x thin films (with RE either Y or Gd) were grown on (100) MgO and (100) SrTiO₃ substrates [5]. After growth these films are fully oxygenated (*x*≈7) with a *T_c* above 88 K. In order to prepare REBa₂Cu₃O_x films with a specific oxygen content *x*<7, they were annealed at 500 °C at an oxygen pressure given by the pressure–temperature phase diagram [6]. During the initial heating and the final cool down, the oxygen pressure was controlled in order to follow the pressure–temperature curves [7].

After the annealing process, the oxygen content was

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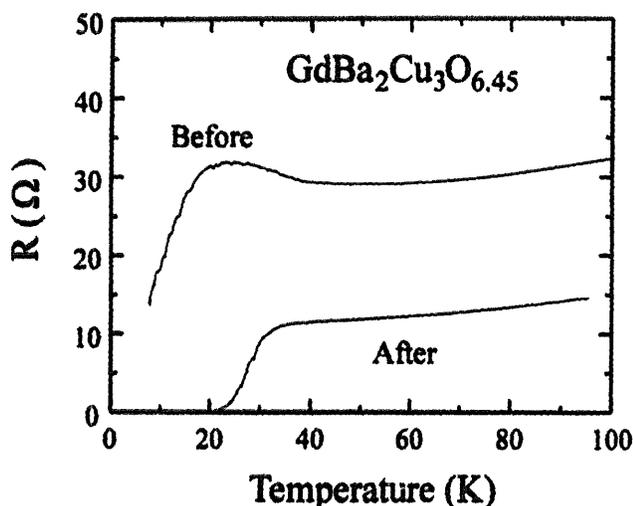


Fig. 1. Temperature dependence of the resistance for a $\text{GdBa}_2\text{Cu}_3\text{O}_{6.45}$ film. Measurements are shown before and after illumination. There is a decrease of the normal state resistance and an increase of T_c . The data were obtained from Ref. [10].

determined by measuring the expansion of the c -axis parameter using high resolution X-ray diffraction [8]. In addition, for the superconducting $\text{REBa}_2\text{Cu}_3\text{O}_x$ films, we also used the T_c to determine the oxygen content x [9].

2.1.2. Illumination setup

The resistivity measurements were done with a four probe technique either directly immersed into liquid nitrogen, in a closed cycle refrigerator, or in a He-flow cryostat,

each equipped with optical quartz windows. For the illumination we used several different light sources. For most of the excitation measurements a halogen lamp or an Ar laser ($\lambda=514$ nm) was used with a typical power density at the sample surface of 1 W cm^{-2} . In order to measure the spectral dependence, we used a 1000 W Hg–Xe arc lamp with an infrared water filter to protect the sample and the optics from excessive heating. Specific wavelengths in the range from 250 to 900 nm were chosen with interference band-pass-filters having a bandwidth of 10 nm. Using this setup the power density of monochromatic light ranged between 0.04 and 5 mW cm^{-2} .

After each light excitation the sample was relaxed at room temperature while monitoring the resistivity to determine when the sample was fully relaxed.

2.1.3. Photoinduced superconductivity

The basic effect is shown in Fig. 1. Before illumination the $\text{GdBa}_2\text{Cu}_3\text{O}_{6.45}$ film shows a resistivity minimum with a superconducting onset temperature at roughly 20 K. After illumination for 8 h at 95 K, the lamp is turned off and the resistance is measured as a function of temperature. The resistance changes such that the normal state resistance is metallic, decreases substantially and the T_c increases by more than 10 K.

The time dependence of the excitation and the relaxation is shown in Fig. 2. Both the excitation and the relaxation show a stretched exponential time dependence [11]. After switching the light off, the sample maintains its reduced resistance, if kept at temperatures below approximately

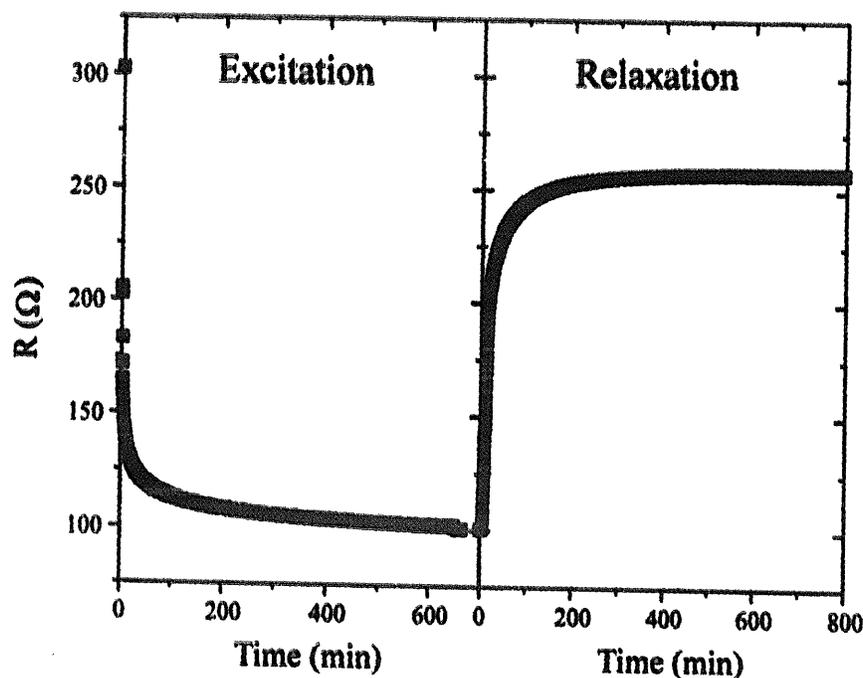


Fig. 2. Time dependence of the excitation and relaxation of persistent photoconductivity in a $\text{GdBa}_2\text{Cu}_3\text{O}_{6.45}$ film. For the excitation, the light source was switched on at $t=0$, while the sample was kept at 95 K. For the relaxation, the temperature was raised from 95 to 300 K in about 12 min near $t=0$. The data were obtained from Ref. [10].

100 K. Notice that the relative change in resistance at 95 K is larger in Fig. 2 than for the film with a slightly higher oxygen concentration in Fig. 1. This effect will be discussed further in Section 2.2.

2.1.4. Effect of oxygen vacancies

The measurements shown in Figs. 1 and 2 were made on oxygen deficient films with a decreased T_c compared to optimally doped films. Besides changing the T_c with oxygen doping, it is also possible to decrease T_c by doping Pr on the Y site [12]. Therefore, we measured the persistent photoconductivity on $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_x$ phase spread alloy films [13]. A phase spread alloy is a thin film with a continuously varying stoichiometry on a single substrate [14]. Fig. 3 shows the temperature dependence of the resistivity of a fully oxygenated $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7.0}$ phase spread alloy for different Pr concentrations y before and after illumination. There is only a slight change of the resistivity upon illumination within the experimental error.

On the other hand, Fig. 4 shows the temperature dependence of the resistivity of an oxygen deficient $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6.7}$ phase spread alloy. In this case, after illumination there is a large decrease of the resistivity and an increase of T_c . This shows that oxygen vacancies play a major role in the mechanism responsible for the persistent photoconductivity and photoinduced superconductivity [13].

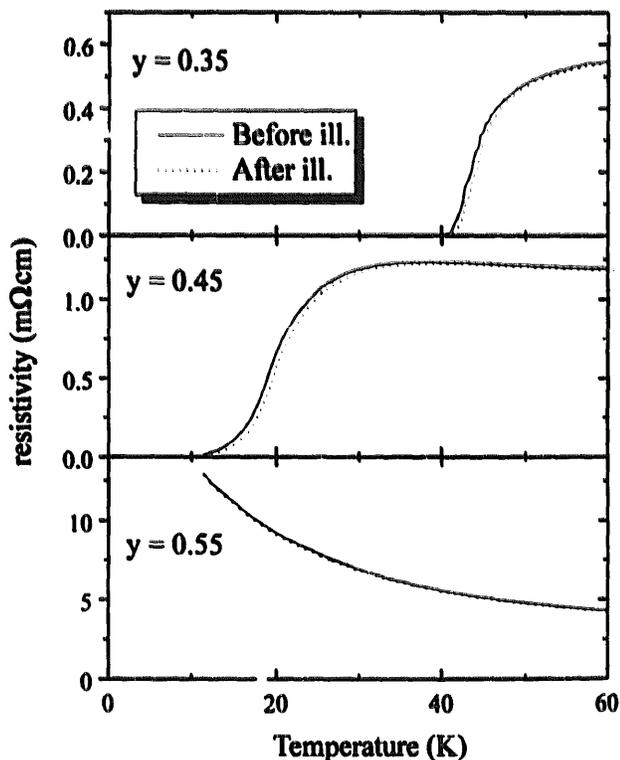


Fig. 3. Temperature dependence of the resistivity of fully oxygenated $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7.0}$ for various Pr content y before (solid line) and after (dotted line) illumination. The data were obtained from Ref. [13].

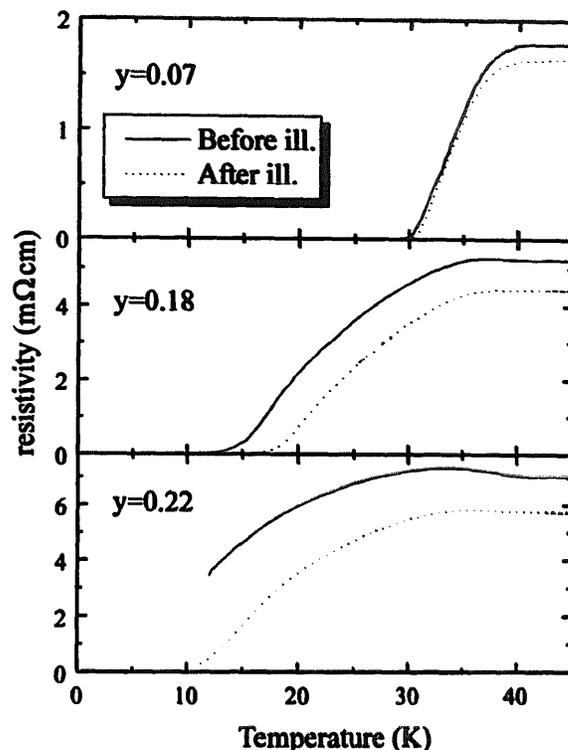


Fig. 4. Temperature dependence of the resistivity of oxygen deficient $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6.7}$ for various Pr content y before (solid line) and after (dotted line) illumination. The data were obtained from Ref. [13].

2.2. Influence of oxygen stoichiometry

Since oxygen vacancies are crucial for the persistent photoconductivity in $\text{REBa}_2\text{Cu}_3\text{O}_x$ (see Section 2.1.4), it is interesting to study the oxygen dependence of this effect. Fig. 5 shows the change of relative conductivity at 95 K as a function of oxygen content x . The data is normalized to the conductivity before illumination, since the conductivity decreases strongly with decreasing oxygen content x . From Fig. 5 it is clear that the photoinduced effect is strongly enhanced at low oxygen contents x [15].

2.3. Spectral dependence

We investigated the spectral dependence of the persistent photoconductivity in a $\text{GdBa}_2\text{Cu}_3\text{O}_{6.3}$ thin film, since for this oxygen content ($x=6.3$) the change in resistance upon illumination is large (see Section 2.2). For a given wavelength, the magnitude of the photoinduced effects in $\text{REBa}_2\text{Cu}_3\text{O}_x$ depends only on the number of photons per surface area exciting the sample [11]. In order to compare the excitations at different wavelengths, we converted the measurement time t into number of photons per surface area n [photons cm^{-2}] using

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

where I [W cm^{-2}] is the light intensity at the sample

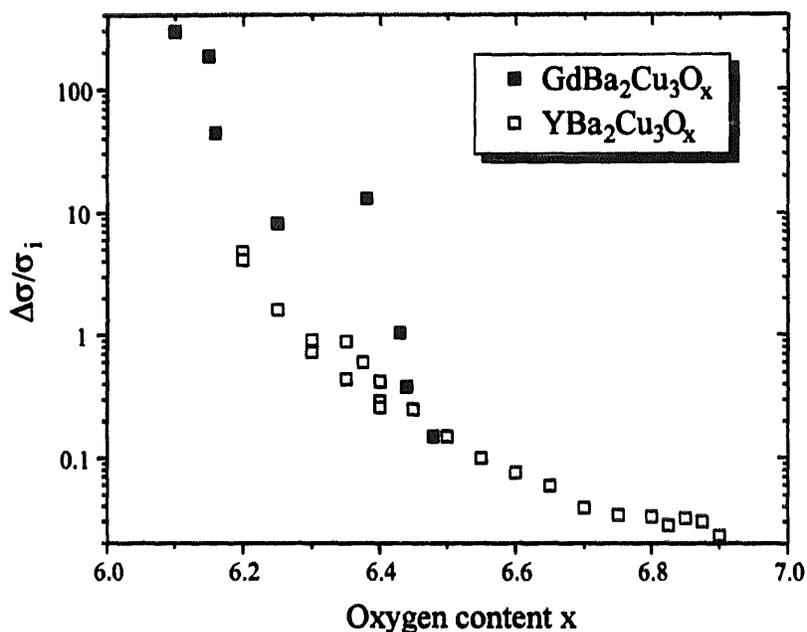


Fig. 5. Relative change in conductivity $\Delta\sigma/\sigma_i$ at 95 K as a function of oxygen content x of $REBa_2Cu_3O_x$. Solid symbols refer to $GdBa_2Cu_3O_x$, while open symbols refer to $YBa_2Cu_3O_x$. The data were obtained from Ref. [15].

surface and $\hbar\omega$ the photon energy. Fig. 6 shows the resistance change vs. photon number for a few different characteristic photon energies. For 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 in the 1.5 to 3.2

eV range are consistent with earlier measurements of the spectral dependence of persistent photoconductivity in $YBa_2Cu_3O_{7-\delta}$ [11,17].

A strong enhancement of persistent photoconductivity is observed for certain frequencies as shown in Fig. 7. Here we plot the inverse of the photon number necessary for a

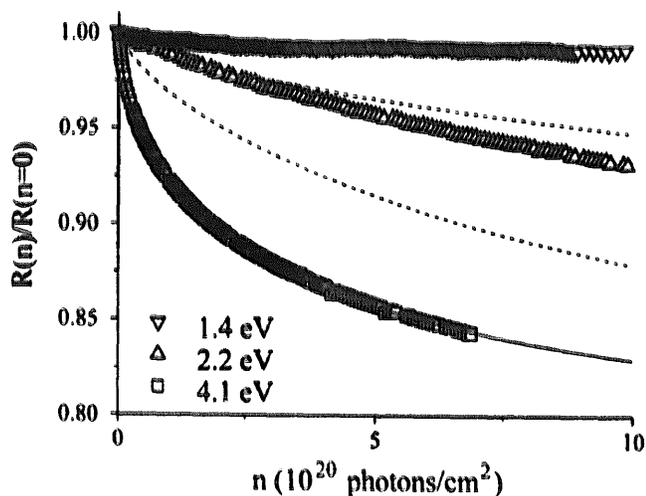


Fig. 6. Excitation of the persistent photoconductivity for different photon energies $\hbar\omega$. The measurements were taken on a $GdBa_2Cu_3O_{6.5}$ film. The resistance is normalized to the resistance in the relaxed state $R(0)$. The solid line is a stretched exponential fit to the data at $\hbar\omega=4.1$ eV. The dashed lines indicate the range of resistance vs. photon number variation at photon energies between 2.1 and 3.3 eV. The data were obtained from Ref. [16].

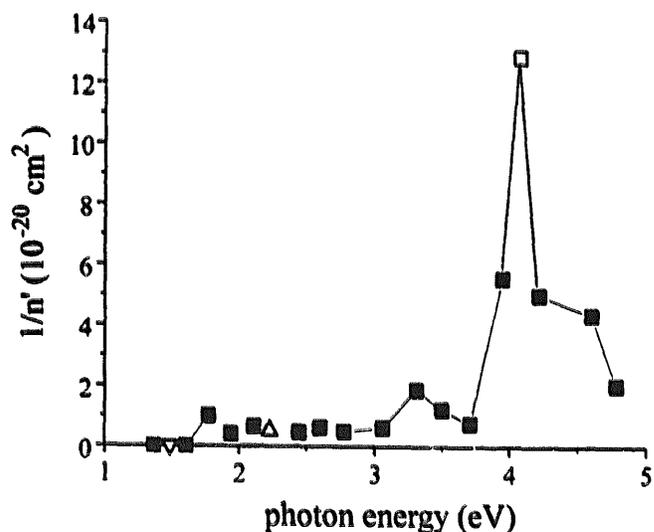


Fig. 7. Spectral efficiency of the persistent photoconductivity excitation: $1/n'$ vs. photon energy. n' is the number of photons per unit area necessary for a 2% change in the resistance. The data at 4.1, 2.2 and 1.4 eV is indicated by the same symbol as in Fig. 6. The data were obtained from Ref. [16].

2% reduction of the film resistance ($1/n'$) against the exciting photons energy. Clearly, the excitation is enhanced by an order of magnitude at 4.1 eV compared with excitations in the visible range (1.5 to 3.2 eV) [16].

2.4. Change of magnetotransport properties with illumination

So far, we have only discussed the changes in resistivity ρ_{xx} due to illumination. The Hall coefficient, R_H and the Hall mobility $\mu = c(|R_H|/\rho_{xx})$ also show measurable changes [18], as shown in Fig. 8. In a simple one band model, the Hall coefficient R_H is inversely proportional to the carrier density. Thus the data in Fig. 8 suggest that the carrier density increases, which results in a decrease in resistivity. In addition, the Hall mobility μ changes and also contributes to the variations in the resistivity ρ_{xx} described in earlier sections [18].

2.5. Structural effects

The photoinduced effects described so far are similar to the observed changes with increased oxygen doping in $YBa_2Cu_3O_x$. Increasing the oxygen concentration x leads

to a lower normal state resistance ρ_{xx} , a higher T_c , and a lower Hall coefficient R_H [19]. However, in none of our experiments could the samples absorb oxygen during illumination, since they were immersed either in liquid helium, liquid nitrogen, inert gas, or vacuum.

It is well known that increasing the oxygen concentration x in $YBa_2Cu_3O_x$ leads to structural changes, such as a contraction of the c -axis [8]. Therefore, we measured the c -axis lattice parameter during illumination at room temperature, using Θ - 2Θ X-ray scans of the [00 10] peak. The fractional change $\Delta c/c$ is compared to the resistivity change $\Delta\rho/\rho$ during and after illumination in Fig. 9. Interestingly, during illumination $\Delta c/c < 0$, contrary to the thermal expansion due to heating. In fact, after the lamp is switched off, both the c -axis length and the resistivity ρ decrease slightly (0.05%) due to cooling of the sample. As shown, the change in resistivity is directly correlated to the change of the c -axis lattice parameter. A more careful structural refinement [20–22] of the Θ - 2Θ X-ray scans reveals that the contraction of the c -axis is due to a reduced Ba–Cu1 interplanar distance [13].

3. Theoretical models

3.1. Photoassisted oxygen diffusion

The experimental results presented in Section 2 show that photoinduced superconductivity and persistent photoconductivity depend strongly on the oxygen content x of the $REBa_2Cu_3O_x$ films. Most of the effects during illumination are similar to resistivity and structural changes observed during room temperature annealing of oxygen deficient $REBa_2Cu_3O_x$ samples rapidly quenched from higher temperatures [23,24]. The effect of room temperature annealing of quenched samples may result from oxygen ordering in the Cu–O chain layers [23,24]. The relaxation of the photoinduced effects is thermally activated with an energy barrier of 0.9 ± 0.1 eV [11], close to the oxygen diffusion activation energy of 1.3 eV [26]. This suggests that the photoinduced effects could be due to photoassisted oxygen ordering [25].

There is an important difference between oxygen ordering in quenched samples and the photoinduced effects. While in quenched samples the oxygen in the Cu–O chains orders during room temperature annealing, in the photoexcited samples the oxygen has to disorder from a metastable ordered state during room temperature relaxation [15]. Furthermore, the oxygen ordering should be zero in completely deoxygenated ($x \approx 6.0$) $REBa_2Cu_3O_x$ samples, and thus cannot explain the observed dependence of the persistent photoconductivity on the oxygen stoichiometry (see Section 2.2). Therefore it is doubtful that the photoassisted oxygen ordering model explains the persistent photoconductivity in $REBa_2Cu_3O_x$.

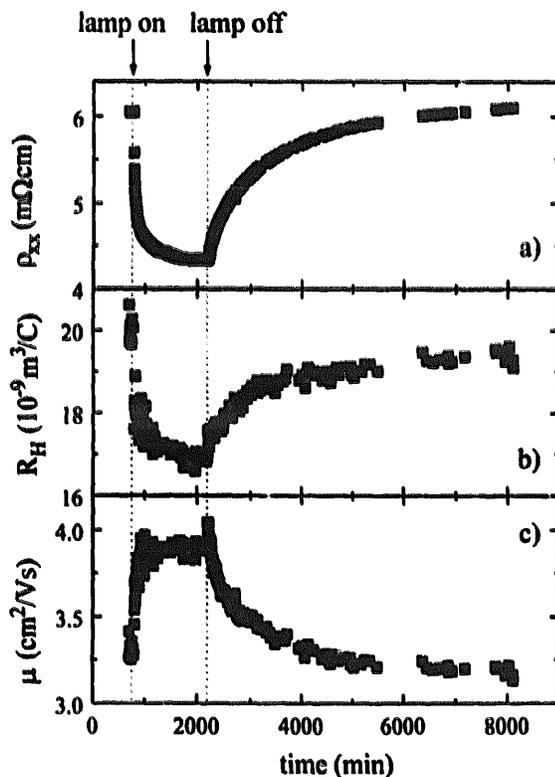


Fig. 8. Time dependence of the resistivity ρ_{xx} , Hall coefficient R_H and Hall mobility $\mu = c(|R_H|/\rho_{xx})$ during excitation and relaxation measured at room temperature in a patterned $YBa_2Cu_3O_x$ film. The data were obtained from Ref. [18].

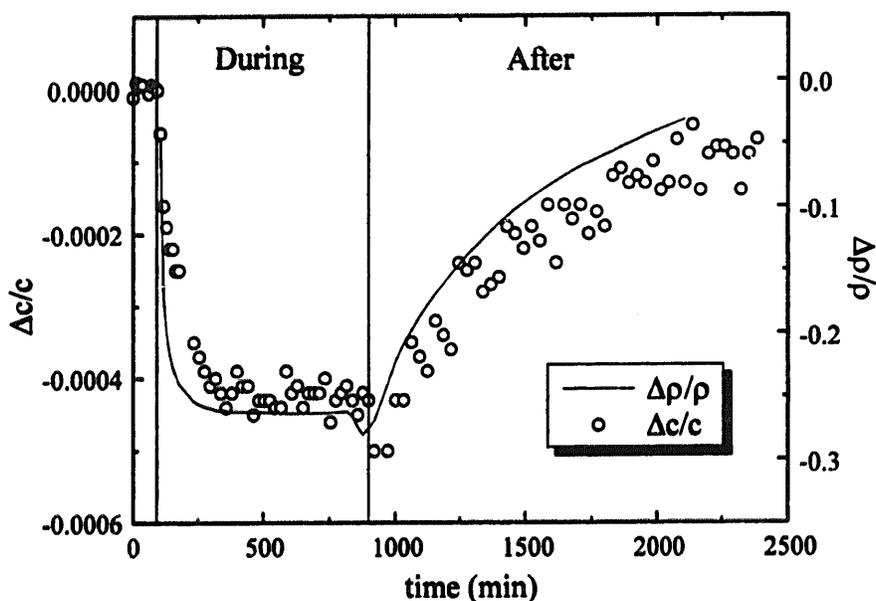


Fig. 9. Time dependence of the fractional change $\Delta c/c$ of the *c*-axis lattice parameter and resistivity $\Delta \rho/\rho$. The measurements were done on a $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ film at room temperature, during, and after illumination. The data were obtained from Ref. [13].

3.2. Electron trapping

An alternate model is similar to persistent photoconductivity observed in semiconductors with defects, which can trap some of the carriers [27]. In this model, the incoming photons create electron-hole pairs. Subsequently, the electron is trapped at an oxygen vacancy in the Cu-O chain, while the hole is transferred to an extended state in the CuO_2 planes and thus enhances the conductivity [15]. As the number of vacancies increases for lower oxygen contents *x*, the photoinduced effects are expected to increase. This model naturally explains the observed dependence on oxygen stoichiometry (Section 2.2).

The spectral dependence (Section 2.3) can also be understood within this model. From optical measurements it is known that there is strong absorption at 4.1 eV in oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_x$ due to a transition in the Cu-O chains at a Cu-atom with two neighboring oxygen vacancies [28–30]. The strong enhancement of persistent photoconductivity at 4.1 eV could be caused by the generation of photoexcited electrons in close proximity to the oxygen vacancies, which act as traps [16]. The mechanism based on electron capture at oxygen vacancies is further supported by recent measurements of the photoluminescence in oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_x$ [31].

The structural changes (see Section 2.5) can be understood by a lattice distortion caused by the trapped electrons. This lattice distortion gives rise to an energy barrier, which inhibits the recombination of the trapped electron with a hole [15]. However, it is not presently clear how the proposed models can explain photoinduced changes in the mobility (see Section 2.4). One possibility is that the

photoinduced structural modification causes the change in the mobility.

4. Conclusion

In summary, oxygen deficient $\text{REBa}_2\text{Cu}_3\text{O}_x$ thin films show persistent photoconductivity, and for high enough oxygen contents ($x > 6.4$) photoinduced superconductivity. The presence of oxygen vacancies is crucial and controls the magnitude of the conductivity enhancement. Furthermore, the spectral dependence shows a pronounced peak at a photon energy of 4.1 eV. In addition to the photoinduced changes in the magnetotransport, there are also measurable structural changes.

Two models have been used to describe the experimental observations. The photoassisted oxygen diffusion mechanism fails to explain the observed dependence on the oxygen content *x* in the $\text{REBa}_2\text{Cu}_3\text{O}_x$ films, while a model based on photoexcited electrons at oxygen vacancies is consistent with all current observations.

Acknowledgments

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