

Enhancement of persistent photoconductivity in insulating high- T_c thin films

Joel Hasen, David Lederman, and Ivan K. Schuller

Department of Physics, University of California—San Diego, La Jolla, California 92093-0319

V. Kudinov

Institute of Physical Problems, Russian Academy of Sciences, 117973 Moscow, Russia

M. Maenhoudt and Y. Bruynseraede

Laboratorium voor Vaste Stof-Fysika en Magnetisme, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001, Leuven, Belgium

(Received 7 July 1994)

Persistent photoconductivity, characterized by a long-term increase in the conductivity due to illumination of oxygen-deficient high-temperature superconductors, is greatly enhanced in $\text{RBa}_2\text{Cu}_3\text{O}_x$ ($R = \text{Y}$ or Gd) films as x decreases to 6.1. These results are in qualitative agreement with a model similar to that used to explain the existence of DX centers in GaAs. However, they cast doubts over several models commonly used to explain the mechanism behind this phenomenon and that of photoinduced superconductivity.

Persistent photoconductivity¹ (PPC) and photoinduced superconductivity² (PSC) are remarkable discoveries in the field of high-temperature superconductivity. During the illumination of an oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_x$ film with a laser or an ordinary halogen lamp, the electrical conductivity (σ) (Ref. 1) and the superconducting critical temperature (T_c) (Ref. 2) increase substantially. After the light is turned off, the film remains in this excited state without decay at temperatures below 100 K. At room temperature, however, the film relaxes back to the original state over the period of several days.

Much additional work has been performed to characterize these simple but interesting phenomena. It is presently known that (a) the frequency necessary for the observation of the effect covers the whole visible spectrum,^{3–5} (b) an insulating film can be excited to become superconducting,^{2,4} (c) the magnitude of the effect increases as the sample approaches the metal-insulator transition,^{2–4} (d) oxygen vacancies are essential,⁶ (e) the c axis contracts,⁶ and (f) the excited state is correlated with a decrease in the Hall coefficient, i.e., presumably an increase in charge carriers.³

Several models have been proposed to explain these phenomena. In this paper, we focus on two of the most commonly invoked models. They are the photoinduced oxygen-diffusion mechanism⁷ and photoinduced charge-transfer mechanism.⁴ Both of these models seem to correctly describe the PPC dependence on oxygen concentration for *superconducting* oxygen-deficient samples. However, they fail to explain in a direct fashion the large enhanced PPC in *insulating* oxygen-deficient samples.

The experiments were performed independently in two laboratories at UCSD and KUL. Using standard magnetron sputtering, c -axis-oriented $\text{RBa}_2\text{Cu}_3\text{O}_7$ films were grown on (100) SrTiO_3 substrates. $\text{GdBa}_2\text{Cu}_3\text{O}_7$ was used at UCSD and $\text{YBa}_2\text{Cu}_3\text{O}_7$ was used at KUL. The films

ranged in thickness from 1000 to 2000 Å. During growth, the substrates were placed off to the side of the glow discharge to avoid resputtering effects.⁸ The transition temperatures of films grown in this manner, defined by the 50% point of the resistive transition, are reproducibly above 88 K. The orientation and lattice parameters were measured using high-resolution x-ray diffraction.

Oxygen can be removed from $\text{RBa}_2\text{Cu}_3\text{O}_7$ samples by treatment along the pressure-temperature phase diagram.⁹ However, a major concern during oxygen treatment is adverse reactions with contaminants or film decomposition. These adverse reactions may result in changes in transport and structural properties which mimic changes obtained as a function of oxygen deficiency. Therefore, we took special precautions to minimize this type of contamination. After every transport measurement, glass bead abrasion was used to remove indium electrical and thermal contacts. Rinses in organic solvents were used to remove surface contaminants on the film. The quartz tube used to contain the sample during oxygen treatment had a base pressure less than 10^{-3} Torr.

Oxygen was removed from the films by following the pressure-temperature curves, which are known to produce reproducibly and repeatedly oxygen-deficient films with sharp resistive transitions.¹⁰ The sample temperature was slowly raised from room temperature to 500°C (2°C/min), while continuously controlling the oxygen partial pressure.⁹ The sample was left at 500°C for 5 h in order to complete the reaction and then slowly cooled to room temperature (1°C/min) still controlling the pressure. The motivation for this slow-cool technique is to maintain thermodynamic equilibrium at all times and thereby minimize any disorder. The oxygen content was determined by comparing the relative c -axis expansion to measurements on bulk samples.¹¹

The four-lead electrical conductivity was measured in a closed-cycle refrigerator or a cryostat with optical windows. In order to check for contamination, some unpatterned films were measured using a modified Montgomery technique.¹² The films were excited at 95 K with a halogen lamp or an Ar laser for more than 8 h with a surface power density of about 1 W/cm². Due to losses at the cryostat windows the exact power impinging on the sample is difficult to ascertain.

Figure 1 shows the conductivity as a function of temperature for a GdBa₂Cu₃O_{6.15} film before and after illumination. The conductivity has increased by more than two orders of magnitude over the entire temperature range. We define σ_i and σ_f as the conductivity at 95 K before and after illumination, respectively. The absolute increase in conductivity, $\Delta\sigma = \sigma_f - \sigma_i$, is shown in Fig. 2. The agreement between samples prepared and measured in two different laboratories is considered excellent. At low oxygen concentrations, for all temperatures σ_i is negligibly small compared to σ_f and therefore, $\Delta\sigma$ is dominated by σ_f . Under the assumption that σ_f is proportional to σ_i , the low-temperature behavior reflects the characteristic decrease in conductivity as the samples become insulating.

The magnitude of the PPC effect in insulating films is best characterized by the increase in conductivity by illumination, normalized by the conductivity before illumination ($\Delta\sigma/\sigma_i$). The normalization removes the inherent decrease in conductivity as oxygen concentration is decreased. The results for illumination at 95 K are shown in Fig. 3. The PPC effect is greatly enhanced at low oxygen concentrations and seems to increase faster than exponentially.

An important check on these results was done by fully reoxygenating various samples to assure that the initial high-temperature superconducting film is recovered. Therefore, any suppression of the conductivity and T_c is due to reversible changes in the oxygen concentration and not adverse chemical reactions during processing.

These experiments are similar to an experiment reported earlier by Kudinov *et al.* (Ref. 4, Fig. 11) which showed an enhancement of the PPC effect down to $x=6.4$. However, for $x<6.4$ the effect continuously decreased to zero in complete disagreement with the present results. The origin of these differences may arise

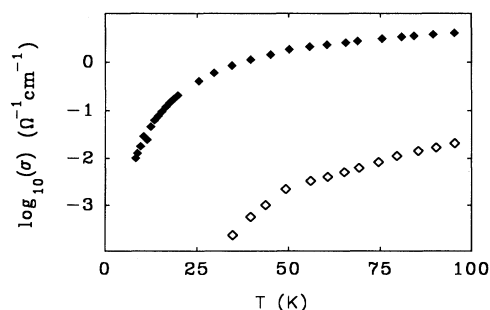


FIG. 1. The conductivity vs temperature for a GdBa₂Cu₃O_{6.15} film before (◇) and after (◆) illumination. The films were excited to saturation for 8–12 h at 95 K.

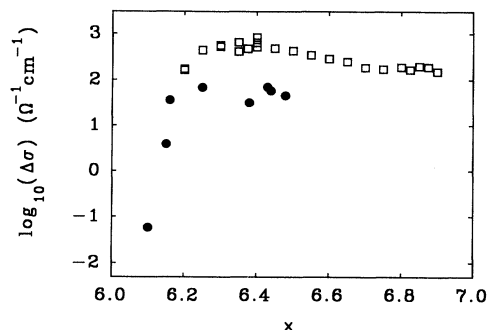


FIG. 2. Absolute increase in conductivity vs oxygen concentration of RBa₂Cu₃O_x films at 95 K, where R=Y (□) or Gd (●).

from the differences between the two experiments. Kudinov *et al.* performed their experiments at 300 K,⁴ while the present results were done at 95 K. Although most of our experiments were performed at 95 K, a measured PPC effect of $\Delta\sigma/\sigma_i=2.9$ at 300 K for a sample with $x=6.10$ is in complete disagreement with the earlier results of Kudinov *et al.*⁴ Kudinov *et al.* quenched their samples from high temperature during oxygen treatment instead of maintaining thermodynamic equilibrium. This quench might suppress the PPC effect in some unknown way. Finally, Kudinov *et al.* did not reoxygenate their samples to check for adverse chemical reactions. We therefore conclude that either their samples may have been contaminated during oxygen treatment or the effect is suppressed in quenched samples in an unknown fashion.

CuO_x chains are believed to play an important role in the high-temperature superconductivity of RBa₂Cu₃O_x compounds. Long chain fragments are able to inject holes into the CuO₂ planes.¹³ Oxygen ordering in the CuO_x chains of RBa₂Cu₃O_x, which may allow the chain fragments to grow, has been extensively studied since its discovery.¹⁴ Experiments have focused on quenching oxygen-deficient bulk samples from high temperatures and measuring the changes in transport and structural properties during room-temperature annealing.^{15,16} Similar to PPC, there is a long term increase in conductivity, increase in T_c , and contraction of the c axis. It is only natural to assume that the underlying mechanism

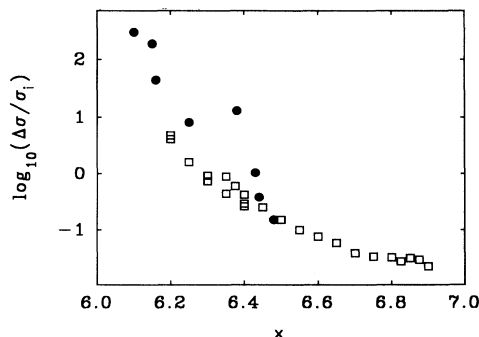


FIG. 3. Magnitude of the PPC effect vs oxygen concentration of RBa₂Cu₃O_x films at 95 K, where R=Y (□) or Gd (●).

for both of these effects must be similar. This assumption forms the basis of the photoinduced oxygen-diffusion mechanism.⁷ The mechanism proposes that photons assist the diffusion of oxygen by inducing local electric fields in the chains; this in turn increases chain length, thereby enhancing the superconductivity. We would expect this model to be sensitive to the chains lengths in the sample.

In order to understand the environment in the CuO_x chains for an oxygen-deficient film, we have performed a statistical calculation for the "chain fragment length," n , defined as the number of consecutive oxygen atoms in a chain fragment (Fig. 4). The oxygen atoms are assumed to be randomly distributed in the CuO_x chains and the $\text{RBa}_2\text{Cu}_3\text{O}_x$ to be in the tetragonal phase, where the a and b axes are identical.¹³ As the oxygen concentration decreases below $x=6.3$, most of the oxygen atoms are located on short chain fragments. For $x=6.1$ over 90% of the oxygen atoms are located in single unit chain fragments. In order for a chain fragment to inject holes into the CuO_2 plane it must be greater than a critical length, $n=3$ or 4.¹⁵ As the oxygen concentration decreases, it will be less likely for oxygen movement to produce chains greater than this critical length. Therefore, photoinduced oxygen-diffusion mechanism predicts a decrease in PPC as the oxygen concentration is decreased, in disagreement with the experimental results shown here.

Furthermore, there is a fundamental difference between oxygen ordering in quenched samples as compared to the photoinduced oxygen-diffusion mechanism. A quenched sample in a disordered metastable state orders at room temperature. In contrast, the photoinduced oxygen-diffusion mechanism predicts that a sample in an ordered metastable state disorders at room temperature.

The second model used to explain PPC and PSC also involves the CuO_x chain fragments, but in a very different way. The basis of the photoinduced charge transfer mechanism is that the holes in chain fragments can trap electrons.⁴ A chain fragment of length n may consist of one oxygen atom in the divalent state and $n-1$ in the monovalent state.¹³ Consequently, there are $n-1$ p holes in the chain fragments.¹³ During illumination, the photons produce electron-hole pairs. The electrons can be trapped in the chain fragments while the holes remain as carriers in the conduction band. The hole doping results in an enhancement of the superconducting properties.¹³ However, according to this model, there are electron traps only in chain fragments of length 2 or greater. Therefore, this model also predicts a decrease in the PPC effect as the oxygen concentration decreases.

It is clear that a simple interpretation of the two leading models for the PPC effect does not explain our results. However, we propose a model which is similar to an older work by Kreines and Kudinov¹⁷ and was used earlier to explain DX centers in GaAs.¹⁸ During illumination a photon creates an electron-hole pair. The electron can be trapped in an oxygen vacancy in the CuO_x chains layer where normally an O^- ion would be located in a fully oxygenated sample. The trapping of the electron causes a lattice distortion which results in a large energy barrier impeding the reverse recombination with

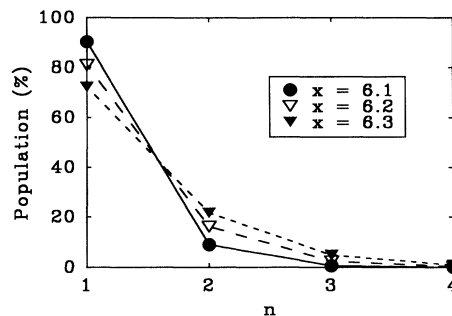


FIG. 4. Distribution of oxygen atoms in chain fragments of length n for various oxygen concentrations. The statistical calculation assumes a random distribution of oxygen atoms in the CuO_x chains and the $\text{RBa}_2\text{Cu}_3\text{O}_x$ is in the tetragonal phase.

the hole. The hole in turn is transferred into an extended state in the CuO_2 plane, thus enhancing the conductivity. As a result, the electron-hole pairs are only able to recombine at a high enough temperature for the electron to be thermally activated out of this self-trapped well. The photoinduced vacancy capture mechanism is then enhanced as the oxygen concentration decreases and the number of oxygen vacancies increase. It should vanish when the chain fragments lengthen and the oxygen vacancies disappear.

We emphasize that the PPC effect cannot be explained exclusively with a long lived photodoping model. According to a single band model, the magnitude of the PPC effect, for small values, is

$$\Delta\sigma/\sigma_i = \Delta p/p_i + \Delta\mu/\mu_i,$$

where p is the hole density and μ is the hole mobility. Clearly, hole doping is only part of the effect. In fact, it has been recently shown, using Hall and conductivity measurements, that the increase in μ dominates the PPC effect at $x=6.35$.¹⁹ Perhaps the observed changes in the lattice are a reflection of the changes in mobility.

It has been suggested that this type of model is invalid because if every oxygen vacancy trapped an electron, there would be enough donated holes to raise the T_c of the material to its maximum value of 92 K.⁷ Inhomogeneities in the film such as grain boundaries and defects may play an important role in the trapping mechanism and limit the number of trapping sites. Additionally, there are other changes such as a contraction in the c axis and a change in the mobility which are being completely ignored. Consequently, without further experimental and theoretical evidence, the photoinduced vacancy capture mechanism is a valid model.

In conclusion, the PPC effect is greatly enhanced at very low oxygen concentrations in $\text{RBa}_2\text{Cu}_3\text{O}_x$ films. The two leading models used to explain the PPC effect predict the opposite behavior. The data is in qualitative agreement with a model used to explain photoconductivity

ty in *DX* centers in GaAs.

We wish to thank R. C. Dynes and L. J. Sham for useful discussions and comments. We gratefully acknowl-

edge the support of Office of Naval Research at UCSD (Grant No. N00019-91J-1438) and the Belgian High Temperature Superconductivity Incentive and Concerted Action Programs at KUL.

-
- ¹V. I. Kudinov, A. I. Kirilyuk, N. M. Kreines, R. Laiho, and E. Lähderanta, *Phys. Lett. A* **151**, 358 (1990).
- ²G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple, and I. K. Schuller, *Appl. Phys. Lett.* **60**, 2159 (1992).
- ³G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple, and I. K. Schuller, *Phys. Rev. B* **46**, 14 249 (1992).
- ⁴See V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk, N. M. Kreines, R. Laiho, E. Lähderanta, and C. Ayache, *Phys. Rev. B* **47**, 9017 (1993), and references cited therein.
- ⁵S. L. Bud'ko, H. H. Feng, M. F. Davis, J. C. Wolfe, and P. H. Hor, *Phys. Rev. B* **48**, 16 707 (1993).
- ⁶D. Lederman, J. Hasen, I. K. Schuller, E. Osquiguil, and Y. Bruynseraede, *Appl. Phys. Lett.* **64**, 652 (1994).
- ⁷E. Osquiguil, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, D. Lederman, and I. K. Schuller, *Phys. Rev. B* **49**, 3675 (1994).
- ⁸O. Nakamura, E. E. Fullerton, J. Guimpel, and I. K. Schuller, *Appl. Phys. Lett.* **60**, 120 (1992); B. Wuyts, Z. X. Gao, S. Libbrecht, M. Maenhoudt, E. Osquiguil, and Y. Bruynseraede, *Physica C* **203**, 235 (1992).
- ⁹P. K. Gallagher, *Adv. Ceram. Mater.* **2**, 632 (1987); M. Tetenbaum, B. Tani, B. Czech, and M. Blander, *Physica C* **158**, 377 (1989).
- ¹⁰E. Osquiguil, M. Maenhoudt, B. Wuyts, and Y. Bruynseraede, *Appl. Phys. Lett.* **60**, 1627 (1992).
- ¹¹R. J. Cava, B. Batlogg, K. M. Rabe, E. A. Rietman, P. K. Gallagher, and L. W. Rupp, *Physica C* **156**, 523 (1988).
- ¹²H. C. Montgomery, *J. Appl. Phys.* **42**, 2971 (1971).
- ¹³G. V. Uimin, V. F. Gantmakher, A. M. Neminsky, L. A. Novomlinsky, D. V. Shovkum, and P. Brüll, *Physica C* **192**, 481 (1992).
- ¹⁴I. K. Schuller, D. G. Hinks, J. D. Jorgensen, L. Soderholm, M. A. Beno, K. Zhang, C. U. Segre, Y. Bruynseraede, and J.-P. Locquet, in *Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 647.
- ¹⁵J. D. Jorgensen, S. Pei, P. Lightfoot, H. Shi, A. P. Paulikas, and B. W. Veal, *Physica C* **167**, 571 (1990).
- ¹⁶B. W. Veal, A. P. Paulikas, H. You, H. Shi, Y. Fang, and J. W. Downey, *Phys. Rev. B* **42**, 6305 (1990).
- ¹⁷N. M. Kreines and V. I. Kudinov, *Mod. Phys. Lett. B* **6**, 289 (1992).
- ¹⁸See P. M. Mooney, *J. Appl. Phys.* **67**, R1 (1990), and references cited therein.
- ¹⁹K. Tanabe, S. Kubo, F. H. Teherani, H. Asano, and M. Suzuki, *Phys. Rev. Lett.* **72**, 1537 (1994).