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Research News

Persistent Photoinduced Effects in High-T_c Superconductors**

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1. Introduction

The field of superconductivity has gained much attention in recent years due to the discovery of the high temperature cuprate superconductors. Besides their high transition temperature ($T_{\rm cs}$ up to ≈ 160 K), they show a variety of physical properties that are remarkably different from those of conventional superconductors. Two of these are persistent photoconductivity (PPC) and persistent photoinduced superconductivity (PPS), which we review in this article.

The cuprate superconductors are layered materials that consist of CuO_2 planes sandwiched between "charge reservoirs" (see Fig. 1), e.g., the CuO chain layers in



Fig. 1. Structure of YBa₂Cu₃O₇. The material consists of CuO₂ planes and CuO chains separated by yttrium and barium. The charge carriers responsible for superconductivity are located within the CuO₂ planes, while the CuO chains act as a charge reservoir and their oxygen content determines the carrier concentration in the CuO₂ planes.

 $REBa_2Cu_3O_x$ (RE: rare earth or yttrium). The charge carriers responsible for superconductivity are located in the

 [*] Prof. I. K. Schuller, A. Hoffmann, Dr. D. Reznik Physics Department 0319 University of California at San Diego 9500 Gilman Drive, I.a Jolla, CA 92093-0319 (USA) CuO₂ planes and it is possible to change their concentration by modifying the charge reservoirs. For example, in REBa₂Cu₃O_x, as the oxygen content in the CuO chain layers is increased continuously from x = 6 to x = 7, the material changes from an antiferromagnetic insulator (x = 6) to a $T_c = 90$ K superconductor (x = 7).

Another way to vary the transport properties of REBa₂-Cu₃O_x is through illumination. In conventional superconductors (e.g., Pb), illumination is detrimental to the superconducting properties due to pair-breaking. In contrast, REBa₂Cu₃O_x thin films show an unexpected decrease in the normal state resistance^[1] and an increase of T_c upon illumination.^[2] These effects persist over a long time at low temperatures (≤ 100 K) and relax within days at room temperature.^[1,2]

2. Experimental Results

Because of the finite penetration depth of light (typically 1000 Å), all of the photoexcitation experiments were done on REBa₂Cu₃O_x thin films with thicknesses around 1000 Å. Persistent photoinduced changes were measured either before or after illumination or, for time-dependence measurements, the light intensities were reduced to avoid experimental artifacts such as thermal heating. Various light sources (Ar laser, halogen lamp, and Hg-Xe arc lamp) were used for the different experiments. To assure that there were no changes in oxygen stoichiometry, experiments were performed with the sample immersed in liquid nitrogen, in vacuum, or in an inert gas.

The basic effect of illumination on the temperature dependence of the resistance is shown in Figure 2b. After illumination the normal state resistance is reduced by a factor of two, and the T_c increases by more than 10 K. Notice that these effects are not due to simple heating of the sample, since this would increase the resistance and decrease the T_c . The original R(T) curve was recovered, after long time activated relaxation at room temperature, with an energy barrier of $0.9 \pm 0.1 \text{ eV}^{[3]}$

It was shown that PPC occurs in REBa₂Cu₃O_x only if the material is oxygen deficient (x < 7).^[5] Furthermore, the relative photoinduced conductivity enhancement increases

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Fig. 2. a) Doping dependence of PPC: Relative change in conductivity $\Delta a/\sigma_i$ at 95 K as a function of oxygen content x of REBa₂Cu₃O_x. Solid symbols refer to GdBa₂Cu₃O_x, while open symbols refer to YBa₂Cu₃O_x, b) R(T) curves before and after illumination for a GdBa₂Cu₃O_{6.45} sample. The data were obtained from [4].

with decreasing oxygen content x and reaches its maximum for completely deoxygenated samples $(x = 6)^{[4]}$ (see Fig. 2a).

The room temperature time dependence of the excitation and relaxation in YBa₂Cu₃O_{6.5} is shown in Figure 3. Clearly, the resistivity ρ_{xx} (Fig. 3a) and the Hall coefficient $R_{\rm H}$ (Fig. 3b) show the same time dependence. In a simple one-band model, $R_{\rm H}$ is inversely proportional to the carrier density. Thus the data in Figure 3 suggest that upon illumination the carrier density increases, which results in a decrease in resistivity.^[6] In addition, the Hall mobility $\mu = c(|R_{\rm H}| \rho_{xx})$ changes (Fig. 3c) and contributes to the variations in the resistivity ρ_{xx} .

A structural change accompanies the changes in the transport properties.^[5] Figure 3d shows the fractional change of the *c*-axis lattice parameter $\Delta c/c$, determined from X-ray diffraction, compared to the resistivity change $\Delta \rho/\rho$. The same time dependence is seen for $\Delta c/c$ as for ρ and indicates a contraction of the *c*-axis, contrary to what would be expected from thermal heating.

Raman scattering experiments on YBa₂Cu₃O_{6.4} showed, after prolonged illumination, an increase in intensity for several phonon modes located in the CuO₂ planes and the



Fig. 3. Time dependence of (a) the resistivity ρ_{xx} , (b) Hall coefficient $R_{\rm H}$, (c) Hall mobility $\mu = c(|\mathbf{R}_{\rm H}|/\rho_{xx})$ and (d) *c*-axis lattice parameter during excitation and relaxation measured at room temperature in a patterned YBa₂-Cu₃O_{6.5} film. The data were obtained from [5,6].

CuO chains, an increase in electronic Raman scattering at low frequencies, and a suppression of the two-magnon band.^[8] All these effects are probably caused by the increase in the carrier density due to photodoping.

All of the above mentioned experimental results were obtained either by broad band white light sources or with monochromatic light in the visible region. The spectral dependence of PPC in REBa₂Cu₃O_x shows an onset at $1.6 \text{ eV}^{[3,7]}$ and a pronounced peak at $4.1 \text{ eV}^{[9]}$ There is also a PPC effect observed in YBa₂Cu₃O_{6.0} upon irradiation with X-rays,^[10] which is very similar to the effects with visible light. Moreover, it is possible to partially quench the PPC at low temperatures with infrared radiation.^[11.12]

Recent experiments on overdoped high- T_c superconductors (Tl₂Ba₂CuO_{6+ δ}) also showed PPC at low temperatures upon illumination with visible light.^[12] Thus these photoinduced effects might be a generic feature of these materials and help to explain high- T_c superconductivity.

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Besides the PPC, there is also transient photoconductivity and photoinduced superconductivity, which are also connected to the photogeneration of additional carriers.^[13] In addition, there is a very fast photoresponse (≈ 1 ps) due to either non-equilibrium kinetic inductance or electron heating of the electronic subsystem in YBa₂Cu₃O_x.^[14]

It is interesting to note that all persistent photoinduced changes (T_c , resistivity, Hall coefficient, and structure) are similar to the effect of increased oxygen doping.^[15] However, absorption of oxygen can be excluded in all of the persistent photoexcitation experiments in REBa₂Cu₃O₃. This similarity suggests that there is an increase of the hole concentration in the planes and, as a consequence, an increased electrical conductivity. The relaxation is caused by electron-hole recombination.

3. Theoretical Models

Two different microscopic mechanisms for this process have been proposed: photoassisted oxygen ordering^[16] and photogeneration of mobile cartiers.^[3,4] It was found earlier that oxygen ordering in the CuO chains explains the change in transport properties during room temperature annealing of high temperature quenched YBa₂Cu₃O_x samples.^[17] Since this process and the relaxation of PPC show thermally activated behavior with a similar energy barrier ($E \approx 1 \text{ eV}$), it was proposed that the photoinduced effects could also be due to photoassisted oxygen ordering.^[16] However, this model fails to explain the observed PPC in almost completely deoxygenated ($x \rightarrow 6.0$) REBa₂Cu₃O_x films.

An alternative model is similar to that for PPC observed in semiconductors with defects such as DX centers in GaAs. In this model, the incoming photons create electron-hole pairs with some of the electrons being trapped in defects or oxygen vacancies. The spectral dependence points to the latter mechanism, since in GdBa₂Cu₃O_{6,3} there is a strong enhancement of the PPC at the photon energy of 4.1 eV. At this energy there is an electronic interband transition in the Cu–O chains at a Cu atom with two neighboring oxygen vacancies.^[9] The mechanism based on electron capture at oxygen vacancies is further supported by recent measurements of the photoluminescence in YBa₂Cu₃O_{6,4}.^[18]

In addition to studies related to the effect of light in high- T_c superconductors, the possibility of easily changing

the superconducting properties was used to modify the characteristics of grain boundary Josephson junctions.^[19] Furthermore, the occurrence of PPC implies that the grain boundary in these junctions is oxygen deficient.

4. Conclusion

In summary, oxygen-deficient REBa₂Cu₃O_x thin films show PPC, while photoinduced superconductivity has been observed in the underdoped REBa₂Cu₃O_x with oxygen contents $x \ge 6.4$. These effects appear to be a consequence of the layered structure of these materials and might exist in other high temperature oxide superconductors.

- V.I. Kudinov, A.I. Kirilyuk, N. M. Kreines, R. Laiho, F. Lähderanta, *Phys. Lett. A* 1990, 151, 358.
- [2] G. Nieva, E. Osquiguil, J. Guimpel, M. Macnhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple, I. K. Schuller, *Appl. Phys. Lett.* **1992**, 60, 2159.
- [3] V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk, N. M. Kreines, R. Laiho, E. Lähderanta, C. Ayache, *Phys. Rev. B* 1993, 47, 9017.
- [4] J. Hasen, D. Lederman, I. K. Schuller, V. Kudinov, M. Macnhoudt, Y. Bruynseraede, *Phys. Rev. B* 1995, 51, 1342. J. Hasen, Ph.D. Thesis, University of California, San Diego, CA 1995.
- [5] D. Lederman, J. Hasen, I. K. Schuller, E. Osquiguil, Y. Bruynseraede, Appl. Phys. Lett. 1994, 64, 652.
- [6] G. Nieva, E. Osquiguil, J. Guimpel, M. Macnhoudt, B. Wuyts, Y. Bruynseracde, M. B. Maple, I. K. Schuller, *Phys. Rev. B* 1992, 46, 14249.
- [7] S. L. Bud'ko, H. H. Feng, M. F. Davis, J. C. Wolfe, P. H. Hor, Phys. Rev. B 1993, 48, 16707.
- [8] J. Watte, G. Els, C. Andrzejak, G. Güntherodt, V. V. Moshalkov, B. Wuyts, M. Maenhoudt, E. Osquiguil, R. E. Silverans, Y. Bruynseraede, *J. Supercond.* 1994, 7, 131.
- [9] T. Endu, A. Hoffmann, J. Santamaria, I. K. Schuller, Phys. Rev. B 1996, 54, 3750.
- [10] M. Jiménez de Castro, J. L. Alvarez Rivas, Phys. Rev. B 1996, 53, 8614.
- [11] D. C. Chew, J. F. Federici, J. Guiticrrez-Solana, G. Mofina, W. Savin, W. Wilber, Appl. Phys. Lett., 1996, 69, 3260.
- [12] A. Hoffmann, D. Reznik, Z. F. Ren, J. Y. Lao, J. H. Wang, I. K. Schuler, unpublished.
- [13] G. Yu, C. H. Lee, A. J. Heeger, N. Herron, E. M. McCarron, L. Cong, G. C. Spalding, C. A. Nordman, A. M. Goldman, *Phys. Rev. B* 1992, 45, 4964.
- [14] M. Lindgren, M. Currie, C. Williams, T. Y. Hsiang, P. M. Fauchet, R. Sobolewski, S. H. Moffat, R. A. Hughes, J. S. Preston, F. A. Hegman, unpublished.
- [15] J. T. Markert, B. D. Dunlap, M. B. Maple, MRS Bull. 1989, 14(1), 37.
- [16] E. Osquiguil, M. Maenhoudt, B. Wuyts, Y. Bruynscraede, D. Lederman, I. K. Schuller, Phys. Rev. B 1994, 49, 3675.
- [17] B. W. Veal, H. You, A. P. Paulikas, H. Shi, Y. Fang, J. W. Downey, *Phys. Rev. B* 1990, 42, 4770.
- [18] J. F. Federici, D. Chew, B. Welker, W. Savin, J. Gutierrez-Solana, T. Fink, W. Wilber, Phys. Rev. B 1995, 52, 15 592.
- [19] K. Tanabe, F. Hosseini Teherani, S. Kubo, H. Asano, M. Suzuki, J. Appl. Phys. 1994, 76, 3679.