PHYSICAL REVIEW B VOLUME 46, NUMBER 21 1 DECEMBER 1992-I

Photoinduced changes in the transport properties of oxygen-deficient $YBa_2Cu_3O_x$

G. Nieva
Physics Department, University of California–San Diego, La Jolla, California 92093-0319

E. Osquiguil
Laboratory for Solid State Physics and Magnetism, University of Leuven, B3001, Leuven, Belgium

J. Guimpel*
Physics Department, University of California–San Diego, La Jolla, California 92093-0319

M. Maenhoudt, B. Wuyts, and Y. Bruynseraede
Laboratory for Solid State Physics and Magnetism, University of Leuven, B3001, Leuven, Belgium

M. B. Maple and Ivan K. Schuller
Physics Department, University of California–San Diego, La Jolla, California 92093-0319
(Received 12 August 1992)

We show that illumination of oxygen-deficient metallic $YBa_2Cu_3O_x$ films produces a change in the Hall coefficient, an increase in the critical temperature, and a decrease in the electrical resistivity. These changes relax to equilibrium with characteristic times of the order of days, and are due to variations in both the carrier density and mobility. The relaxation times are of the same order of magnitude as the ones measured in nonilluminated oxygen-deficient films immediately after quenching.

Photoconductivity has a long history and occurs in a variety of insulating and semiconducting materials.[1] The existence of a metal-insulator (M-I) transition in high-T_c superconductors make these materials attractive systems for photoexcitation experiments. Raman scattering measurements indicate the appearance of normally forbidden modes in fully oxygenated photoexcited samples.[2] Transient photoinduced changes of more than ten orders of magnitude in the surface resistivity of $YBa_2Cu_3O_x$ (YBCO) single crystals have been reported earlier.[3] Later on, persistent photoconductivity in insulating YBCO films was observed.[4,5] It was shown that laser illumination induces a systematic decrease with long relaxation times in the electrical resistivity $\rho_{xx}(T)$ of oxygen-deficient YBCO films. These experimental findings opened up the possibility for the existence of photoinduced superconductivity. Recently we have unambiguously shown[6] that the decrease in resistivity in superconducting YBCO films is accompanied by a simultaneous increase in T_c. This confirmed the expectations of a photoinduced transition to the metallic state and of photoinduced superconductivity in high-T_c oxides.

In this letter, we explicitly show that under laser or halogen lamp illumination the nonequilibrium carrier density is *indeed* increased and that changes in the carrier mobility are also induced. These conclusions are reached through photoinduced Hall coefficient R_H and electrical resistivity ρ_{xx} measurements in oxygen-deficient YBCO films. A comparison of these results with those obtained as a function of time in nonilluminated quenched YBCO films indicates that the relaxation towards equilibrium occurs with similar relaxation times. These measurements allow precise comparisons between changes in resistivity and the Hall coefficient which may give a clue to the origin of the puzzling normal transport properties in high-T_c superconductors.

Photoconductivity and photoinduced Hall effect measurements were performed as a function of time on oxygen-deficient YBCO films on both sides of the M-I transition. Superconducting YBCO films were prepared as described earlier by off-axis sputtering on MgO substrates.[7,8] The oxygen content of the films was adjusted to the desired value by controlled temperature T and oxygen partial pressure P_{O_2} annealing,[7] following a constant oxygen content line in the P_{O_2}-T phase diagram.[9] The nominally 1100-Å-thick films were patterned (see schematic drawing in Fig. 1) using standard photolithographic techniques into lines 0.5 mm wide and 5 mm long allowing reliable measurement of the electrical resistivity and Hall coefficient. Care was taken to place the Au voltage contact pads outside the current flow in order to avoid any possible spurious photoconducting contribution from the metal-YBCO contact. The ρ_{xx} component of the resistivity was measured using a standard four probe technique with a current density of 20 A/cm^2. The room-temperature Hall constant R_H was measured with a current density of 2000 A/cm^2 in a field of 6 kG. In order to avoid spurious contributions to the Hall effect from probe misalignment, the standard field inversion technique was used. The measurements presented here are obtained from the difference of the voltages acquired by reversing the magnetic field and the current, and by signal averaging over a large number of measurements.

The photoconductivity experiments were performed

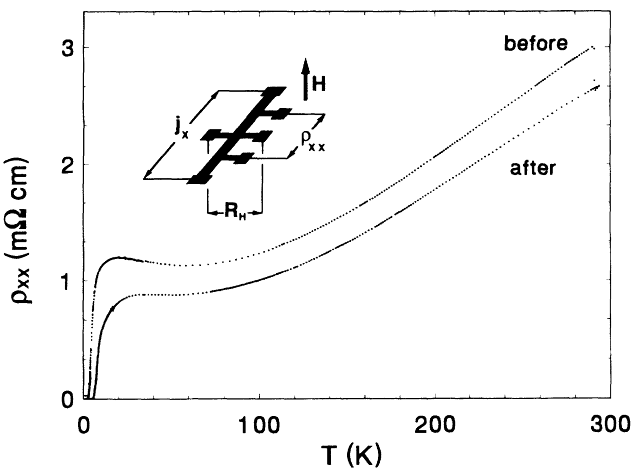

FIG. 1. Temperature dependence of the electrical resistivity ρ_{xx} for a metallic $YBa_2Cu_3O_{6.55}$ film before and after 10 h illumination by Ar ion laser light at 77 K. Schematic drawing shows the sample and contacts geometry, and the field configuration for the Hall effect measurements. The increase of T_c is ~5 K.

using either an Ar ion laser with a series of lines in the range 454.4 nm $<\lambda<$ 514.5 nm and a total output power of 6 W, or an ordinary halogen white light source. The laser spot covered the sample between the voltage contacts. In order to avoid heating during high-power laser light illumination, the samples were immersed in liquid nitrogen. The experiments using white light were performed at room temperature under nitrogen gas flow. The negligible changes in resistivity detected immediately after turning off the light source indicate that in both cases the heating caused by the illumination is at most 3 K. Moreover, given the positive slope of ρ_{xx} (T) at 77 K and at room temperature for all studied samples, the changes due to heating are in the opposite direction to those measured for photoexcitation. During some of the experiments we noticed an apparent degradation of the film properties which was later identified as relaxation of the photoinduced conductivity by illumination under an optical microscope during inspection of the films. Because of this, extreme care was exercised in assuring that the samples were not exposed to large amounts of light before the measurements were presented here.

Figure 1 shows ρ_{xx} as a function of temperature for a superconducting YBCO sample with $x=6.55$ and zero resistance $T_c=2$ K, before and after laser light illumination with the sample immersed in liquid nitrogen. The resistivity of the sample decreases, a photoinduced phenomenon apparently common to YBCO films with reduced oxygen content. On the metallic side of the M-I transition, a clear increase of T_c is observed after illumination as shown in Fig. 1.[6] The temperature-dependent ρ_{xx} of the illuminated sample relaxes back to the initial ρ_{xx} of the virgin sample after four days at room temperature in dry air. The simultaneous decrease in resistivity and increase in T_c indicates that a possible source for these changes may be an increase in the nonequilibrium carrier density during photoexcitation.

In order to address this point, we have performed a series of experiments in which we simultaneously measured ρ_{xx} and R_H as a function of time during and after illumination by halogen white light, and after illumination by laser light. Figures 2(a) and 2(b) show the time evolution of ρ_{xx} and R_H during and after halogen white light illumination at room temperature, for an $x=6.5$ film. In this experiment R_H measured in two different parts of the same film, reproduced both in absolute value and time dependence, indicating uniformity of illumination and film properties. During the excitation ("lamp on" in Fig. 2) both quantities show a decrease as a function of time. A computation of the Hall mobility $\mu=c(|R_H|/\rho_{xx})$ shown in Fig. 2(c), indicates that the decrease in ρ_{xx} is not simply related to the corresponding decrease in R_H, i.e., an increase in carrier density, but that mobility changes also contribute to the variations in ρ_{xx}. This general trend is also observed during the relaxation ("lamp off" in Fig. 2). The particular behavior of R_H, ρ_{xx}, and μ has also been observed in ion-damaged YBCO films, in which the M-I transition was interpreted as a result of a reduction in carrier mobility rather than a drop in carrier density.[10]

Figure 3 shows the room-temperature time evolution of μ normalized by its initial value, after laser light illumination, for films with different oxygen content x. Within the absolute experimental accuracy (10%) the Hall mobility at $t=0$ in Fig. 3 is independent of x. However, there is a clear trend showing larger relative changes for smaller x. *In general all photoinduced changes increase substantially with decreasing x. This in-*

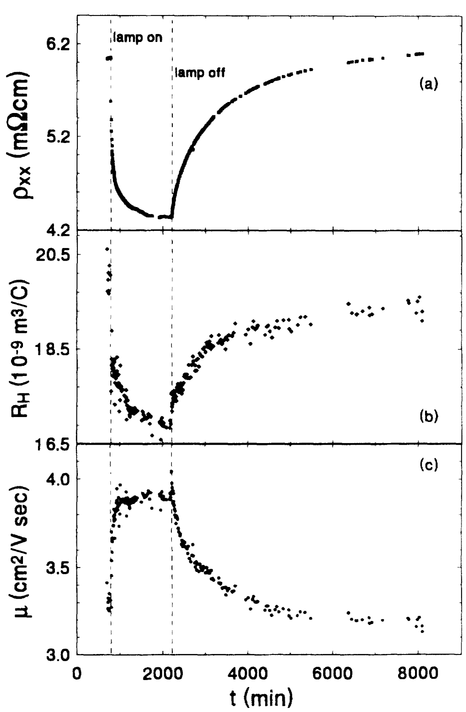

FIG. 2. Time dependence at room temperature during and after halogen white light illumination of the electrical resistivity ρ_{xx}, Hall coefficient R_H, and Hall mobility $\mu=c(|R_H|/\rho_{xx})$, for an insulating $YBa_2Cu_3O_{6.5}$ film.

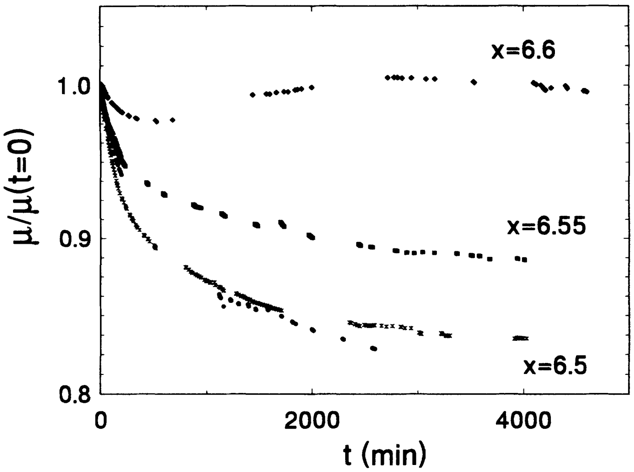

FIG. 3. Time dependence at room temperature after Ar ion laser light illumination at 77 K of the Hall mobility, $\mu=c(|R_H|/\rho_{xx})$, for $YBa_2Cu_3O_x$ films of different oxygen content x. Values have been normalized to the initial value, which for all samples is 4.2 ± 0.3 cm^2/V s.

cludes relative changes in ρ_{xx}, R_H, T_c, and μ.

Two natural sources of relaxation times may be present for laser illumination; direct decay of photoinduced carriers and lateral diffusion of these carriers into the unilluminated parts of the sample. Whether these two sources of relaxation might influence the measurements shown in Fig. 3 is not clear at the present time. We should point out that although the laser spot covers the area between the voltage leads, the possible nonuniform laser beam intensity profile implies that the changes in ρ_{xx} represent a lower limit for this value. However, independent measurements using the more uniform halogen white light source show that the laser beam intensity profile is unlikely to be a source of error here. The R_H is much less affected by this problem since the Hall electrodes are spatially closer.

The microscopic mechanism underlying the observed photoinduced phenomena is not clearly identified at the present time. One possible explanation, invoked to explain photoexcitation results in low-T_c granular In-CdS films[11] or enhancements of the Josephson effect in Sn-CdS-Sn junctions,[12] i.e., changes in the conductivity of the photosensitive (CdS) intergranular material, seems to be ruled out by the present experiments. Granular In-CdS films exhibit a decrease in the width of the normal to superconducting transition but no change in the onset temperature. In contrast, the present experiments show after illumination a parallel shift of the $R(T)$ curves and a clear increase in T_c. An alternate possibility is that the variations in ρ_{xx} and R_H are due to photogenerated electron-hole pairs in the Cu_2O_2 planes.[3-6] This mechanism is likely to be operational in insulating YBCO, where a semiconducting gap has been inferred from measurements of the conductivity,[13] making plausible the analogy with the well-known phenomena in semiconductors.[14] Our experiments show, however, that the photoinduced changes in ρ_{xx} and R_H are also present in YBCO films *well inside the metallic region* of the phase diagrams for which *a substantial increase of T_c is observed.* A third possibility is the occurrence of photoassisted oxygen ordering, since it is well known that oxygen orders in the basal $Cu1O_x$ planes after oxygen vacancies ($x<7$) are created. Various phases corresponding to different vacancy ordering have been theoretically proposed[15] and experimentally observed.[16] It was also shown[17] that the ordering of oxygen vacancies increases T_c in quenched oxygen-deficient single crystals for $x<6.9$. Since oxygen diffusion in the basal $Cu1O_x$ plane is very high in YBCO (Ref. 18) and since the O1 activation energy ($\varepsilon\sim1.2$ eV) (Ref. 19) is of the same order of magnitude as the photon energies, photoassisted oxygen ordering could occur.

To address this issue we have performed a series of relaxation experiments in nonilluminated oxygen-deficient films. Figure 4 shows the time dependence of ρ_{xx}, R_H, and μ for an $x=6.6$ film starting immediately after deoxygenation and quenching from $\sim400\,°C$ to room temperature. During this room-temperature relaxation experiment the sample was carefully isolated from any light source to avoid distortions of the results by spurious illumination. Clearly, the relaxation time is of the same order of magnitude as the ones measured after photoexcitation. Note, however, that the changes are opposite, i.e., both ρ_{xx} and R_H decrease with time during relaxation. The fact that during relaxation ρ_{xx} and R_H evolve in an opposite way compared to illuminated samples indicates that the metastable states obtained by photoexcitation and quenching are different. However, in both cases the Hall mobility has the same qualitative time dependence, i.e., it decreases with time. The comparison between the photoexcitation and quenching experiments seems to rule out oxygen ordering as a possible explanation of the photoexcitation results. The enhancement of T_c in the quenching experiments is associated with increased oxygen ordering due to annealing at room temperature. On the other hand, the fact that enhancements of T_c are observed even by room-temperature illumination raises

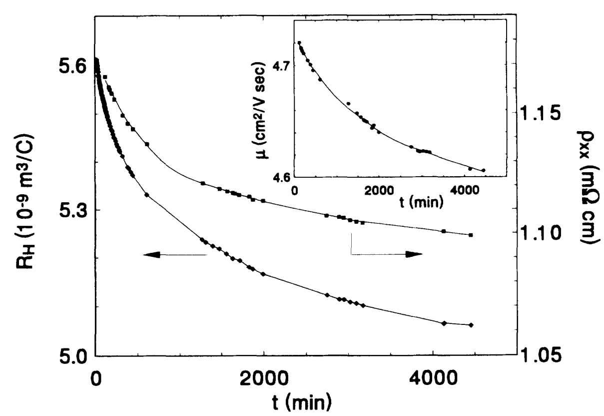

FIG. 4. Time dependence at room temperature of the electrical resistivity ρ_{xx} and Hall coefficient R_H for a nonilluminated metallic $YBa_2Cu_3O_{6.6}$ film, starting immediately after deoxygenation and quenching. The inset shows the time dependence of the Hall mobility, $\mu=c(|R_H|/\rho_{xx})$. Solid lines are guides to the eye.

doubts about photoassisted oxygen ordering as the operating mechanism. However, the similarity in relaxation times suggests the possibility of oxygen movement in the basal plane assisting the recombination of photoinduced carriers.

Clearly more work is necessary to get a deeper understanding of the photoexcitation effect. Currently experiments on films driven near the metal-insulator transition by mechanisms other than oxygen doping, as well as measurements of the critical currents, micro-Raman, and temperature and wavelength dependence of the relaxation time are under way.

In summary, we have found large measurable photoinduced changes in the resistivity (ρ_{xx}), Hall coefficient (R_H), and critical temperature (T_c) with long relaxation times in oxygen-deficient YBCO thin films. Our measurements clearly show that after illumination (i) for $x < 6.6$, T_c increases and ρ_{xx} decreases; (ii) the changes in ρ_{xx} and R_H are different indicating a change in the carrier mobility μ; (iii) the observed relative changes of ρ_{xx} and R_H decrease with increasing oxygen content; (iv) the relaxation times of ρ_{xx} and R_H after illumination are comparable to the ones measured in nonilluminated quenched oxygen deficient films.

We are grateful to D. Magde and K. Walda for use of the laser facility supported by NSF Grant No. CHE91-14613. We thank D. Kelly, I. N. Chan, and D. Lederman for experimental assistance. We thank R. C. Dynes, F. Hellman, V. Kresin, J. Hirsch, N. Conell, P. V. Santos, and Z. Fisk for useful conversations. This work was supported by ONR Grant No. N00014-91J-1438 (G.N., J.G., I.K.S.), U.S. Department of Energy Grant No DE-FG03-86ER45230 (M.B.M.), and the Belgian High Temperature Superconductivity Incentive (E.O., M.M.) and Concerted Action Programs. We also acknowledge support from NATO and from CONICET, Argentina.

---

*On leave from Centro Atómico Bariloche, 8400 Bariloche, Argentina.

[1]A. Rose, in *Interscience Tracts on Physics and Astronomy,* Vol. 19, edited by R. E. Marshak (Interscience, New York, 1963).

[2]D. R. Wake, F. Slakey, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. Lett. **67**, 3728 (1991).

[3]G. Yu, A. J. Heeger, G. Stucky, N. Herron, and E. M. McCarron, Solid State Commun. **72**, 345 (1989).

[4]V. I. Kudinov, A. I. Kirilyuk, N. M. Kreines, R. Laiho, and E. Lähderanta, Phys. Lett. A **151**, 358 (1990).

[5]V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk, N. M. Kreines, R. Laiho, and E. Lähderanta, Phys. Lett. A **157**, 290 (1991).

[6]G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple, and I. K. Schuller, Appl. Phys. Lett. **60**, 2159 (1992).

[7]E. Osquiguil, M. Maenhoudt, B. Wuyts, and Y. Bruynseraede, Appl. Phys. Lett. **60**, 1627 (1992).

[8]O. Nakamura, E. E. Fullerton, J. Guimpel, and I. K. Schuller, Appl. Phys. Lett. **60**, 120 (1992).

[9]P. K. Gallagher, Adv. Ceramic Mater. **2**, 632 (1987).

[10]J. M. Valles, Jr., A. E. White, K. T. Short, R. C. Dynes, J. P. Garno, A. F. J. Levi, M. Anzlowar, and K. Baldwin, Phys. Rev. B **39**, 11599 (1989).

[11]G. Deutcher and M. L. Rappaport, Phys. Lett. **71A**, 471 (1979).

[12]I. Giaver, Phys. Rev. Lett. **20**, 1286 (1986); R. C. Dynes and T. A. Fulton, Phys. Rev. B **3**, 3015 (1971).

[13]A. Levy, J. P. Falck, M. A. Kastner, R. J. Brigeneau, A. T. Fiory, A. F. Hebard, W. J. Gallagher, A. W. Kleinsasser, and A. C. Anderson (unpublished).

[14]P. V. Santos, N. M. Johnson, and R. A. Street, Phys. Rev. Lett. **67**, 2686 (1991).

[15]For an early report see, for instance, A. G. Khachaturyan and J. W. Morris, Phys. Rev. Lett. **59**, 2776 (1987).

[16]For an early report see, for instance, M. Alario-Franco and C. Chaillout, Physica C **153-155**, 956 (1988).

[17]B. W. Veal, A. P. Paulikas, H. You, H. Shi, Y. Tang, and J. W. Downey, Phys. Rev. B **42**, 6305 (1990).

[18]X. M. Xie, T. G. Chen, and Z. L. Wu, Phys. Rev. B **40**, 4549 (1989).

[19]J.-P. Locquet, J. Vanacken, B. Wuyts, Y. Bruynseraede, K. Zhang, and I. K. Schuller, Europhys. Lett. **7**, 469 (1988).