Paper presented at the *Second International Conference on Macroscopic Quantum Phenomena (ICMQP-2)*, August 31 - September 4, 1992, Smolenice (Czechoslovakia)

NEW PROPERTIES OF OXYGEN DEPLETED $YBa_2Cu_3O_x$ FILMS

Y. Bruynseraede, E. Osquiguil, M. Maenhoudt, and B. Wuyts
Laboratorium voor Vaste Stof-Fysika en Magnetisme
Katholieke Universiteit Leuven
B-3001 Leuven, Belgium.

G. Nieva†, J. Guimpel†, D. Lederman, and Ivan K. Schuller
Physics Department - 0319
University of California - San Diego
La Jolla, CA 92093 - 0319.

ABSTRACT

The possibility of preparing high quality oxygen deficient $YBa_2Cu_3O_x$ c-axis oriented films has revealed that the photoinduced phenomena observed in insulating YBCO are not directly related to the existence of the metal-insulator transition. Metallic films, with critical temperatures varying between 2 K and 50 K show a clear enhancement of the superconducting transition after illumination. The increase in T_c is correlated with an increase in carrier density as shown by photoinduced Hall effect measurements. Possible mechanisms which may explain these results are presented.

INTRODUCTION

It is well known that the structural, electrical and magnetic properties of $YBa_2Cu_3O_x$ (YBCO) are drastically changed when the oxygen content x decreases from x = 7 to x = 6 [1-3]. For instance, the crystalline structure of YBCO changes from orthorhombic to tetragonal [4], the critical temperature T_c is a decreasing function of x characterized by two plateaus at $T_c \sim 90$ K ($6.8 \leq x \leq 7$) and $T_c \sim 60$ K ($6.5 \leq x \leq 6.7$) [5,6], and a metal-insulator (M-I) transition occurs for $x \leq 6.5$.

The existence of a M-I transition makes YBCO particularly interesting for the study of photoexcitation phenomena. The first experiments in high T_c superconductors were

performed on insulating YBCO single crystals [7]. Transient photoinduced changes of more than ten orders of magnitude in the surface resistivity were reported. Later on, the effect of persistent photoconductivity in insulating ($x \leq 6.4$) YBCO films was discovered [8]. It was shown that photoexcitation reduces the resistivity of the material over the whole temperature range $0 < T < 300$ K with an abrupt decrease in the resistivity at low temperatures, and that *prolonged irradiation led to a seemingly complete loss of resistivity below 5 K*. These results indicated the possibility of a photoinduced enhancement of superconductivity in insulating YBCO due to an increase in carrier density produced by photoexcitation. The effect was attributed [7,8] to a property of the M-I transition, in close analogy with photoinduced phenomena in traditional semiconducting systems. Studies as a function of oxygen concentration were not reported.

Recently, a reliable technique was developed which allows the controlled, reproducible preparation of oxygen deficient YBCO thin films [9]. This opens the possibility to perform interesting studies related to phenomena in which the sample size plays a dominant role. In particular, the advantage of performing photoexcitation experiments in thin films is obvious [10,11]. Unlike single crystals, they can be manufactured with thicknesses d of the same order of magnitude as the light penetration depth, allowing a precise study of the changes in the "bulk" properties of the material.

In this paper we first review the preparation and characterization of oxygen deficient YBCO thin films. A simple well controlled, reproducible and reversible technique to obtain different oxygen contents ($6.4 \leq x \leq 7$) in c-axis oriented YBCO thin films (500 Å$\leq d \leq$ 5000 Å) is described. In the second part we show that illumination of oxygen deficient *metallic* $YBa_2Cu_3O_x$ films decreases the electrical resistivity $\rho(T)$, increases the critical temperature T_c and decreases the Hall coefficient. These changes relax back at room temperature to the equilibrium values, with characteristic times of the order of days. These experiments clearly show that photoexcitation increases the carrier density, thus inducing or enhancing superconductivity in oxygen depleted YBCO films, and that this effect is not related to the M-I transition. Finally, we show that the photoexcitation relaxation times are comparable to the relaxation times due to oxygen ordering measured

in quenched oxygen deficient films, indicating the possibility that the two processes are related.

EXPERIMENTAL

Preparation and Properties of Fully Oxidized Films

The YBCO films are prepared using a sputtering system with a base pressure of $\simeq 10^{-8}$ Torr, on heated substrates ($\simeq 900°C$) using a load-lock chamber which allows pre- or post heat treatments in oxygen. The MgO or $SrTiO_3$ substrate temperature T_S is calibrated using a thermocouple in contact with the substrate or by optical pyrometry. Disk shaped 38 mm diameter stoichiometric YBCO targets (prepared by classical solid state reaction) are vertically mounted on a magnetron sputtering cathode. The films are deposited in the 90° off-axis geometrical configuration in a mixed Ar/O_2 (80/20) sputtering gas with a total pressure of 400 mTorr and a substrate temperature $T_S = 740°C$ at a deposition rate close to 20 Å/min. After deposition the film is annealed in-situ during 15-30 minutes at $T_S = 500°C$ and $P_{O_2} = 1$ atm to allow full oxidation. These in-situ prepared films are c-axis oriented with $T_c(R = 0)$ between 84 and 89 K, transition widths ΔT_c between 0.5 and 2 K, and magnetically measured $J_c(5\ K)$ exceeding 10^7 A/cm^2. More details on the film preparation technique will be published elsewhere [12].

Preparation and Characterization of Oxygen Deficient Films

Oxygen deficient YBCO films [9], with a nominal oxygen content $6.4 < x_n < 7.0$ are prepared using the P_{O_2} - T phase diagram for bulk material [13]. The film is placed in a small stoichiometric YBCO ceramic box which in turn is introduced in a quartz tube, evacuated to $P = 10^{-6}$ Torr at room temperature. Although the role of the YBCO box is not clear at this time, it is thought to either provide a stable oxygen environment for the film or to prevent contamination of the film by the outgassing of the quartz tube [14]. Once the tube has been evacuated, it is filled with oxygen to $P_{O_2} = 10$ Torr and the temperature is increased to the desired T_{ann} (x_n) appropriate to obtain an oxygen content x_n (T_{ann} varies between 435°C for $x_n = 6.9$ and 695°C for $x_n = 6.4$). Once the pressure P_{O_2} inside the tube is stabilised (usually after 1 - 3 hrs at T_{ann}) the sample is slowly cooled (2 - 3°C/min) while the O_2 pressure is decreased so as to follow the corresponding

P_{O_2} - T phase line [13]. Finally, the samples are quenched to room temperature in $P_{O_2} \simeq$ 75 mTorr and from a quenching temperature T_Q (x_n) (T_Q = 360°C (x_n = 6.9) and T_Q = 549°C (x_n = 6.4)). Using this procedure, resistive transitions as shown in Fig. 1 for a 1000 Å thin YBCO film, are regularly obtained. The transitions are sharp, featureless, without shoulders or tails, moving in an almost uniform way to lower temperatures when x_n is reduced, illustrating that the process is highly controllable.

Figure 2 clearly shows the reproducibility and reversibility of this oxygen depletion method. The results for a 2000 Å thick YBCO film after the film is reoxidized for half an hour in P_{O_2} = 600 Torr and T = 450°C and again depleted are shown in the figure. The original R(T) curve (a) is closely recovered after this process (curve b) indicating good reproducibility of the method. Even after twelve treatments the T_c of the reoxidized sample is recovered, showing that oxygen removal and uptake are reversible. It should finally be noted that the T_c vs x_n of the oxygen deficient films does not show the two characteristic plateaus as in bulk material [9]. Wether this is due to the preparation method or to an intrinsic difference of $T_c(x_n)$ in thin films has still to be elucidated.

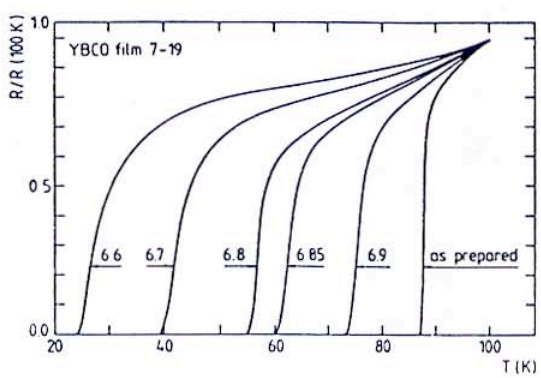

Figure 1 : Normalized resistance vs temperature for a 2000 Å thick YBCO film. The labels near each curve are nominal oxygen contents.

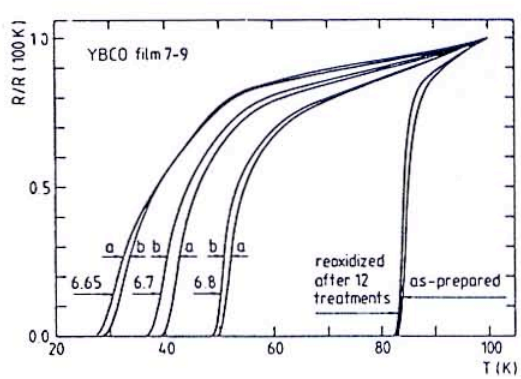

Figure 2 : Normalized resistance vs temperature for a 2000 Å thick YBCO film, after a first (curves "a") and a second (curves "b") oxygen depletion following a complete reoxidation of the film.

Photoexcitation Experiments

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. An Ar ion laser with a series of lines in the range 454.5 nm $< \lambda <$ 514.5 nm and a total output power of 6 W, or an ordinary halogen white light source were used. In order to avoid heating during the laser light illumination, the samples were immersed in liquid nitrogen. For the halogen lamp illumination, the samples were kept at room temperature. The negligible changes in resistivity detected immediately after turning off the light source indicate that in both cases (laser or halogen lamp illumination) the heating caused by the illumination is at most 3 K. Nominally 1000 Å thick YBCO films were patterned using a standard photolithographic technique into lines 0.5 mm wide and 5 mm long with appropriate voltage and current contacts. 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 with a current density of 20 A/cm^2 using a standard four-probe technique. The room temperature Hall constant R_H was measured with a current density of 2000 A/cm^2 in a 6 KGauss magnetic field. Spurious contributions to the Hall voltage from probe misalignment were avoided using the standard field inversion technique and by signal averaging over a large number of measurements for each direction of the applied field.

RESULTS

Figure 3 shows the resistivity as a function of temperature before and after laser illumination for four 1000 Å thick YBCO films with nominal oxygen stoichiometries (a) $x_n = 6.5$, (b) $x_n = 6.55$ and (c), (d) $x_n = 6.6$. The time evolution of the resistivity at 77 K was measured for samples a, b and c shown as an inset in Fig. 3a. Notice that the relative change in resistivity is smaller for the more "metallic" samples. For all samples, after illumination the resistivity decreases throughout the entire temperature range, the change being an almost T independent shift above $\sim$ 50 K. The insets in Figs. 3b - 3d, show in an expanded scale the superconducting transitions before and immediately after illumination. Notice that the higher the T_c, the smaller the relative change in superconducting transition. Moreover, all transitions are clearly shifted to higher temperatures

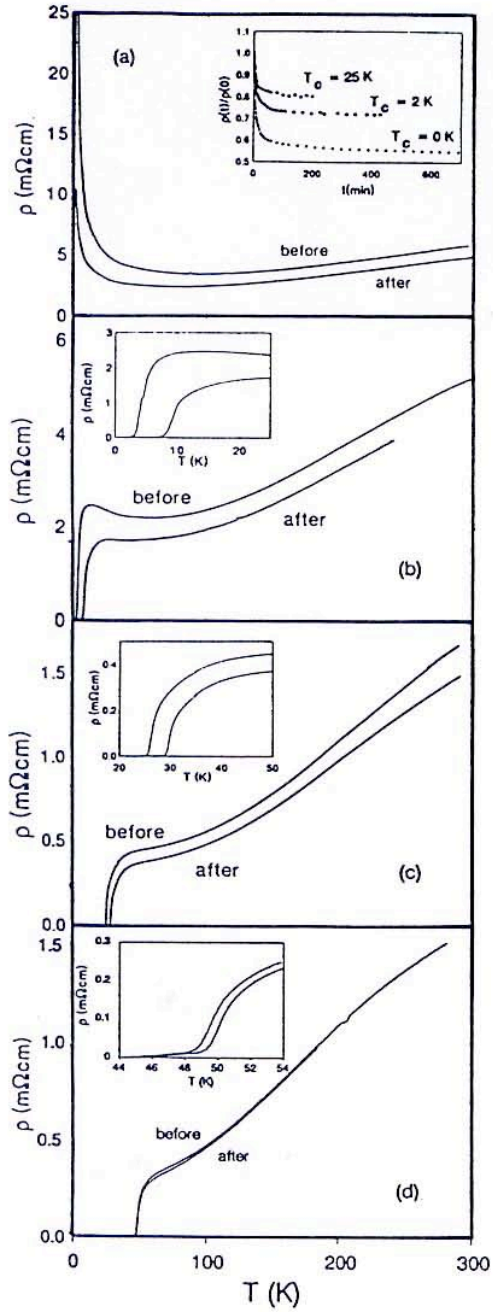

Figure 3 : Electrical resistivity vs temperature before and immediately after laser illumination for films with nominal oxygen stoichiometries (a) x_n = 6.5, (b) x_n = 6.55 and (c), (d) x_n = 6.6. The inset in (a) shows the time evolution of the resistivity at 77 K during illumination for samples a, b and c. The insets in (b), (c) and (d) show the region near T_c in expanded scale.

after illumination in a uniform way without a change in the shape of the normal to superconducting transition. In particular for the sample shown in Fig. 3b, *the change is well outside the transition width and consequently independent of the T_c definition.* 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.

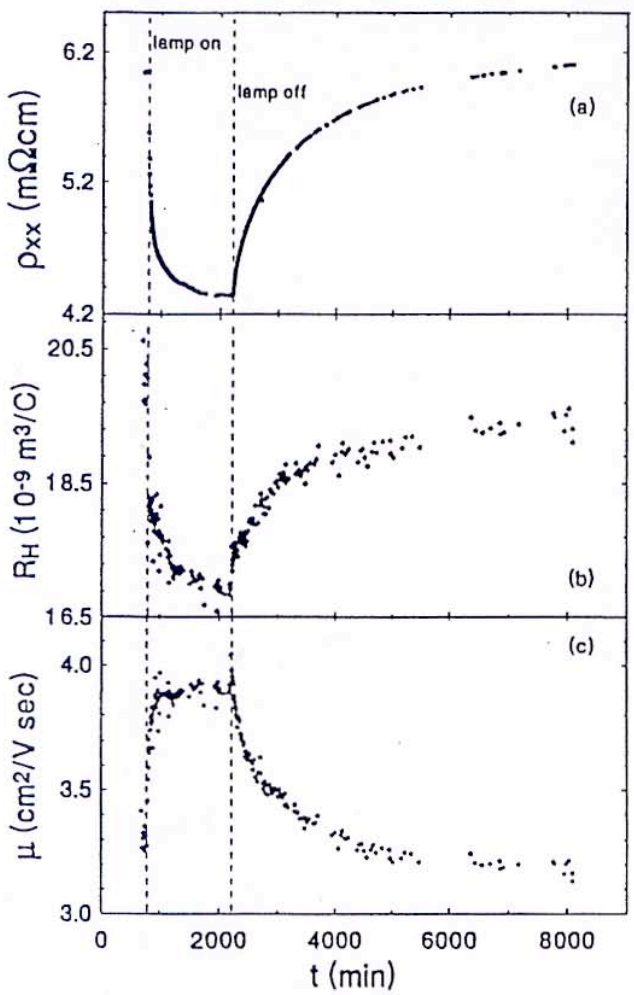

Figure 4 : Time dependence at room temperature during and after halogen white light illumination of (a) the electrical resistivity, ρ_{xx}, (b) Hall coefficient, R_H, and (c) Hall mobility, μ, for an x_n = 6.5 film.

In order to address this point, we have performed a series of experiments in which ρ_{xx} and R_H were simultaneously measured as a function of time during and after illumination by halogen white light, and after illumination by laser light. In Fig. 4 we present the results obtained during and after white light illumination at room temperature for an x_n = 6.5 film. Notice that both ρ_{xx} and R_H decrease during illumination ("lamp on" Fig. 4a, b). The calculated Hall mobility $\mu_H = \frac{c.|R_H|}{\rho_{xx}}$, shown in Fig. 4c, 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 the mobility is also affected by illumination and contributes to the variation in ρ_{xx}. This general trend is again observed during relaxation ("lamp off" in Fig. 2) (Notice the difference in time scale with the excitation. See also inset Fig. 3a).

The room temperature time evolution of μ_H normalized by its initial value, after laser illumination at 77 K, is shown in Fig. 5 for films with different nominal oxygen contents x_n. Within the absolute experimental accuracy (10 %) the Hall mobility at t = 0 is independent of x_n. However, there is a clear trend showing larger relative changes for smaller x_n. In general we may conclude that *all photoinduced changes decrease with increasing x_n. This includes relative changes in ρ_{xx}, R_H, T_c and μ_H.* Clearly, the observed changes are not uniquely related to the M-I transition and seem to be present for all $x_n < 7$.

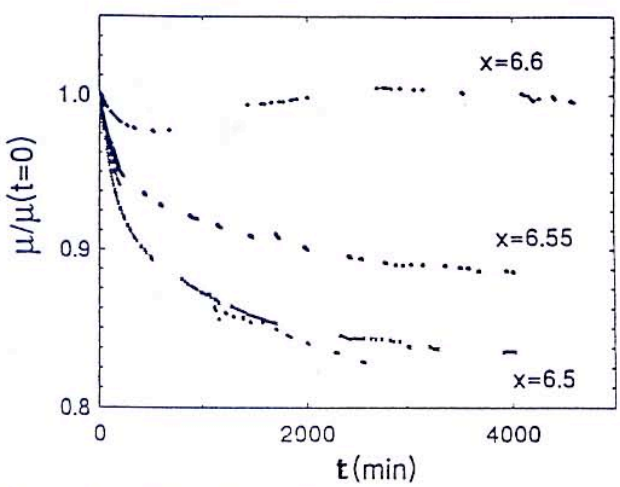

Figure 5 : Time dependence at room temperature after Ar ion laser light illumination at 77 K of the Hall mobility, $\mu = \frac{c.|R_H|}{\rho_{xx}}$ for films of different oxygen content x_n. Values have been normalized to the initial value, which for all samples is 4.2 ± .3 $cm^2/V.sec$.

The microscopic mechanism underlying the observed photoinduced phenomena is not clearly identified at the present time. One possible explanation, invoked to explain the photoexcitation phenomena in low T_c granular In-CdS [15] films and the enhancement of the Josephson effect in Sn-CdS-Sn junctions [16], 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. A second possibility is that the variations in ρ_{xx} and R_H are due to photogenerated electron-hole pairs in the $Cu2O_2$ planes. This mechanism is likely to be operational in insulating YBCO making plausible the analogy with the well- known phenomena in semiconductors. 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 T-x phase diagram and 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. It was shown that the ordering of oxygen vacancies increases T_c in quenched oxygen-deficient ($x < 6.9$) single crystals. Since oxygen diffusion in the basal $Cu1O_x$ plane is usually high in YBCO [17] and since the O1 activation energy ($\epsilon \sim 1.2$ eV) [18] is of the same order of magnitude as the supplied photon energies, photoassisted oxygen ordering could occur.

To address this issue we have performed a series or relaxation experiments in non-illuminated oxygen deficient films. Figure 6 shows the time dependence of ρ_{xx}, R_H and μ for an $x_n = 6.6$ film starting immediately after deoxygenation and quenching from $\sim$ 400°C to room temperature. During these room temperature relaxation experiments the sample remained isolated from any light source. 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

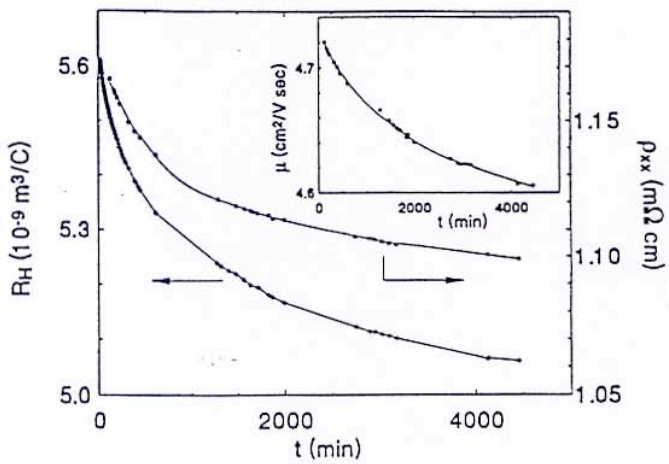

Figure 6 : Time dependence at room temperature starting immediately after deoxygenation of the electrical resistivity, ρ_{xx}, and Hall coefficient, R_H, for a non-illuminated $x_n = 6.6$ film. Inset shows the time dependence of the Hall mobility, μ. Solid lines are guides to the eye.

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 the photoinduced phenomena are observed even during room temperature illumination, raises 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.

CONCLUSIONS

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 illumina-

tion : i) for $x_n \leq 6.6$, 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 non-illuminated quenched oxygen deficient films.

We are grateful to D. Magde and K. Walda for use of the laser facility supported by NSF grant CHE91-14613. We thank D. Kelly and I.N. Chan 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 and M.B. Maple for collaboration in the original photoexcitation experiments. Work supported by ONR grant N00014-91J-1438 (GN,JG,DL,IKS), and the Belgian High Temperature Superconductivity Incentive (EO, MM) and Concerted Action Programs. International travel provided by NATO. GN is a researcher of CONICET, Argentina.

† Permanent address : Centro Atomico Bariloche, 8400 Bariloche, RN, Argentina.

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