ENHANCEMENT OF SUPERCONDUCTIVITY BY PHOTOEXCITATION

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ABSTRACT. We report on extensive investigations of photoinduced phenomena in oxygen deficient YBCO films. It is clearly shown that persistent photoinduced phenomena are present for all oxygen contents $x < 7$, but are absent in films with an optimum doping level (i.e. maximum T_c). The illumination of fully oxidized Pr doped YBCO films does not produce persistent photoinduced effects at any doping level. However, by deoxidizing these films, persistent photoconductivity and photoinduced enhanced superconductivity are clearly observed. On the other hand, we could not observe persistent photoinduced phenomena after the illumination of underdoped, overdoped and/or optimum doped $Bi_2Sr_2CaCu_2O_{8+y}$ and $La_{2-x}Sr_xCuO_{4\pm\delta}$ films. Detailed x-ray diffraction studies show that light causes a large contraction of the c-axis lattice parameter in oxygen depleted YBCO films, which is similar to the change observed when oxygen deficient YBCO is annealed at room temperature after quenching from high temperatures. These observations not only indicate that oxygen vacancies are essential for the existence of persistent photoinduced phenomena, but they also strongly suggest that the chain planes play a crucial role in the microscopic mechanism responsible for the persistent photoinduced effects.

1. Introduction

It is well known that the photoexcitation of insulating and semiconducting materials gives rise to changes in their transport properties which are caused by the photoproduction of excess carriers. The existence of an insulating phase in high T_c superconductors triggered the search, a few years ago, for such effects in these copper-oxide materials [1].

It has been shown that the pulsed laser illumination of $YBa_2Cu_3O_x$ (YBCO) insulating single crystals induces an increase in the non-equilibrium carrier density for short periods of time [2]. These experiments opened the possibility to dope this material through the insulator-metal (I-M) transition without changing its oxygen concentration [1, 2]. On the

other hand, the work initiated by Kudinov et al. [3] with continuous wave laser illumination experiments performed in insulating YBCO thin films, led to the discovery of a persistent photoinduced enhancement of the conductivity [3, 4]. Both type of experiments indicated that photodoping is indeed an alternate way to induce superconductivity in YBCO insulating samples.

Motivated by these results, we demonstrated recently the existence of an interesting effect which only occurs in high temperature superconductors: the persistent photoinduced enhancement of superconductivity in metallic- oxygen-deficient YBCO thin films [5]. We also showed that the enhancement of superconductivity is accompanied by a corresponding decrease in the resistivity and Hall coefficient during photoexcitation, indicating a persistent increase in the carrier density [6].

In this paper we give a brief review and address important questions concerning the photoexcitation mechanism in YBCO films. In particular we discuss its dependence on the I-M transition, oxygen deficiency and the resulting structural changes. We show that although the proximity of the I-M transition enhances the photoinduced effects, the photoinduced enhancement of superconductivity can still be observed up to oxygen contents just below $x = 7$. In addition we show that the persistent photoinduced changes in the normal state and superconducting state, as well as in the structure of YBCO films, are strikingly similar to those changes induced by the ordering of oxygen ions in the basal planes.

2. Experimental

Fully oxidized c-axis oriented YBCO films were deposited on MgO(100) substrates using planar magnetron sputtering system in the 90° off- axis configuration. A detailed description of the film production and their properties has been published elsewhere [7]. Oxygen deficient YBCO films, with a nominal oxygen content $6.4 \leq x \leq 7$, are prepared using a method based on the oxygen partial pressure-temperature phase diagram for bulk material [8]. We adopted for this work the phase diagram reported in [9]. One 1000 Å thick YBCO film was patterned using conventional photolithography and wet etching, into a four point pattern with dimensions 35 μm x 1 mm. The illumination of the oxygen deficient YBCO film was performed during 8 hours using an Ar-ion laser (λ = 514 nm). The measured power density at the surface of the film was 1.83 W/cm^2 corresponding to a total photon density $Q \cong 1.4 \times 10^{23}$ ph/cm^2. The resistance versus temperature curves, R(T), were measured before and after illumination during the warming up cycle and up to temperatures not exceeding 250 K, in a He flow cryostat with optical access.

3. Results

The normalized resistive transitions before illumination measured in one YBCO film with different oxygen contents is shown in Fig. 1a. As x is reduced, the transitions move uniformly to lower temperatures but show a pronounced rounding near the normal state. Since the anisotropy of YBCO increases as oxygen is removed from the basal planes [10], this rounding might be due to an increased contribution of two-dimensional fluctuations at low x. The critical temperature T_c, defined as the temperature at which dR/dT is maximal, is plotted in Fig. 2b as a function of the oxygen content.

Fig. 2 shows the transitions to the superconducting state measured before and after the laser illumination, for several oxygen contents: near the metal-insulator transition (Fig. 2a and 2b); in the 60 K plateau region (Fig. 2c), and in the 90 K plateau region (Fig. 2d and 2e). In contrast to the results of ref. [11], persistent photoinduced changes in T_c and ρ_{ab}

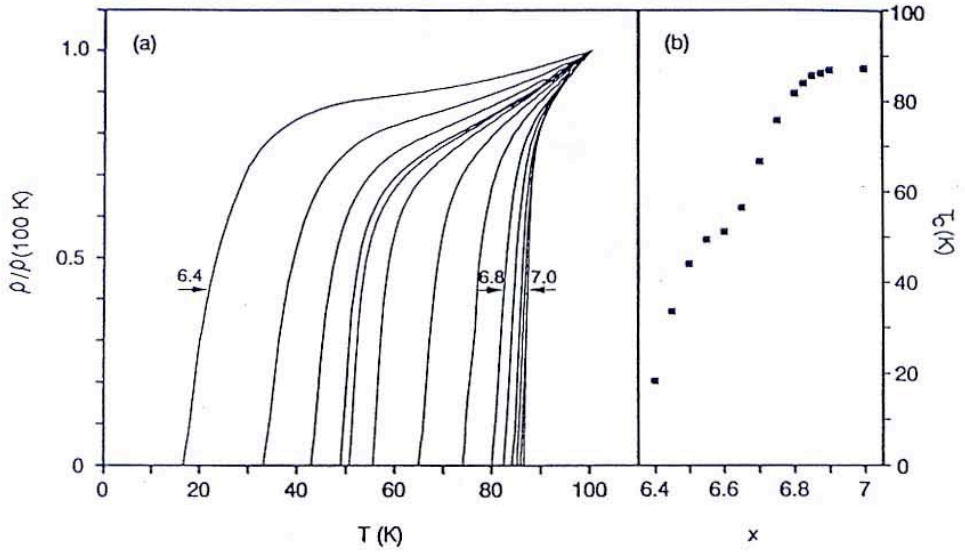

Figure 1: a) Normalized resistive transitions for a 1000 Å thick YBCO film with different oxygen contents x. Between x = 6.4 and x = 6.8 the oxygen content has been varied in steps of 0.05, while between x = 6.8 and x = 6.9 the step is 0.025.
b) Critical temperature as a function of the oxygen content.

are evident, for all oxygen concentrations. Clearly, the illumination produces a decrease of the resistivity throughout the entire temperature range for all $x < 7$. Note also that due to the parallel shift of the transition towards higher temperatures the same absolute shift of T_c (i.e. δT_c = T_c(after illumination) - T_c(before illumination)) is obtained irrespective of the definition of T_c. After 3 days of annealing at room temperature, the T_c and ρ(T) values measured before the illumination are recovered.

In Fig. 3 we plotted the *total* photoinduced shifts of respectively the critical temperature, δT_c, and the in-plane conductivity, $\delta\sigma_{ab}$ (see inset), as a function of x obtained after the illumination of the same YBCO film. The results (δT_c) are compared to the enhancement of T_c, ΔT_c, produced by room temperature annealing of quenched oxygen deficient YBCO single crystals as reported by Veal et al. [12]. *Clearly both quantities, δT_c and ΔT_c, display a similar functional dependence on x.* Three different regions can be recognized: i) for $x < 6.6$, there is a fast increase in ΔT_c and δT_c as the I-M transition is approached, ii) for $6.6 \leq x \leq 6.75$ the total increase in T_c is almost independent of the oxygen content giving rise to a plateau in both the $\delta T_c(x)$ and $\Delta T_c(x)$ curves, and iii) for $x > 6.75$, δT_c and ΔT_c decrease continuously as x is increased and extrapolate to zero at $x = 7$, where neither persistent photoinduced effects nor oxygen ordering effects are observed. Since an increase in the orthorhombicity [12], which is also reflected in a contraction of the c-axis lattice parameter [13], has also been observed during the room temperature annealing, we monitored eventual changes in the c-axis lattice parameter from $\Theta - 2\Theta$ x-ray scans of the [00 10] peak. These measurements were performed before, during, and after illumination

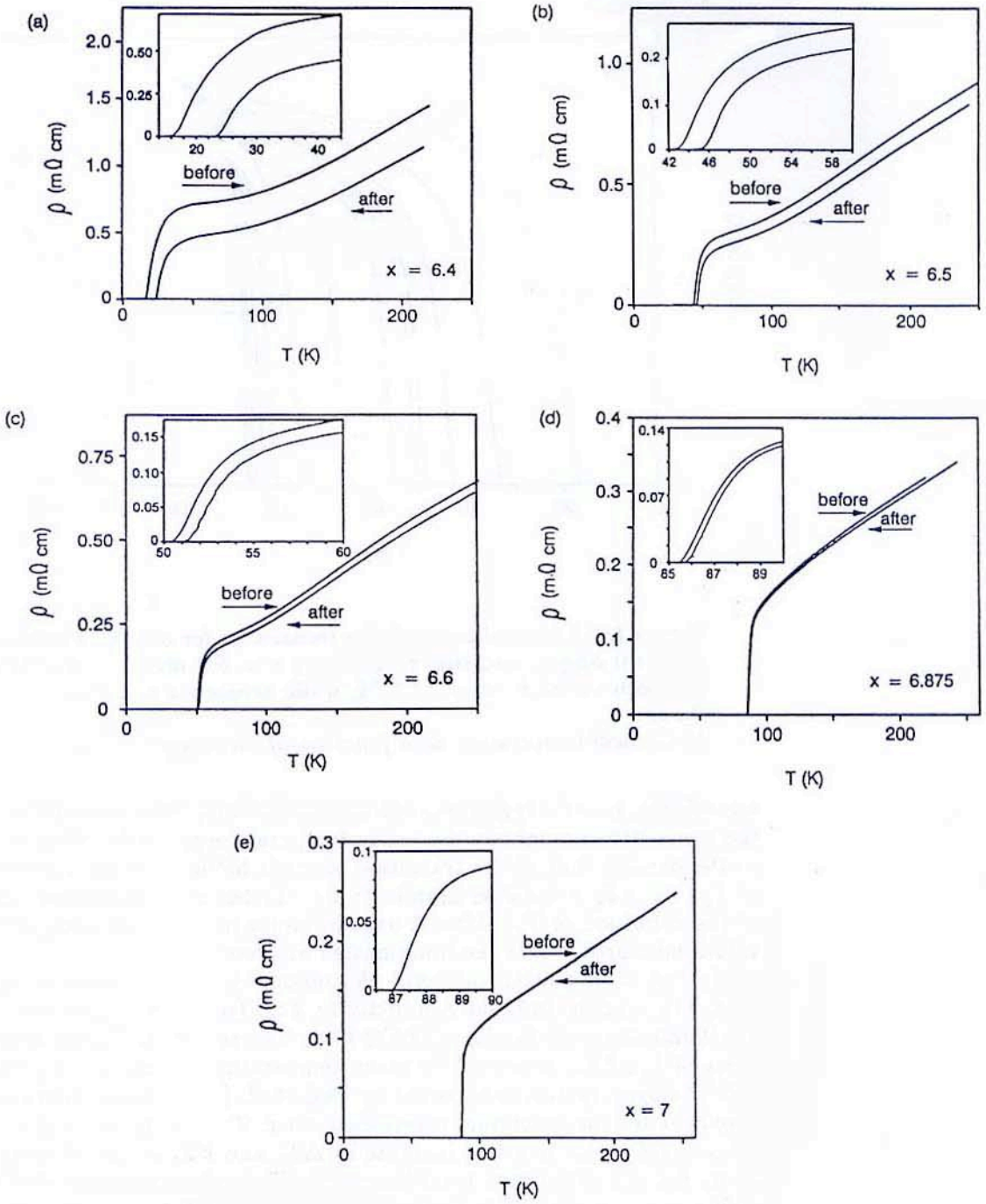

Figure 2: Electrical resistivity ρ vs temperature before and immediately after laser illumination for one YBCO film with different oxygen stoichiometries, a) $x = 6.4$, b) $x = 6.5$, c) $x = 6.6$, d) $x = 6.875$ and e) $x = 7$. The insets show the region near T_c in an expanded scale.

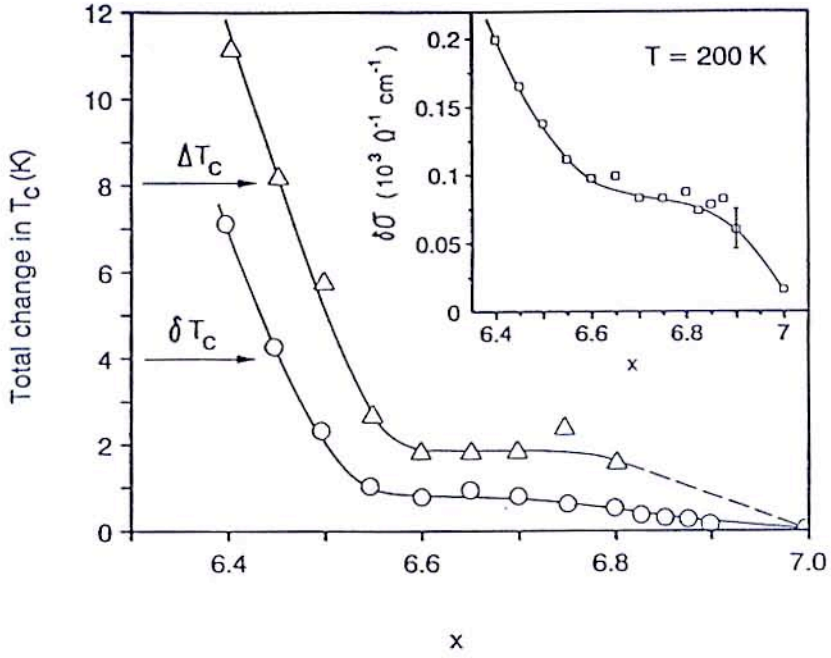

Figure 3: Total enhancement of the critical temperature after the illumination, δT_c, as a function of the oxygen content. The data are compared to the total increase of T_c due to oxygen ordering effects, ΔT_c, in YBCO single crystals (ref. 12). The inset shows the total increase of the conductivity at $T = 200$ K after the illumination. All the solid lines are guides to the eye.

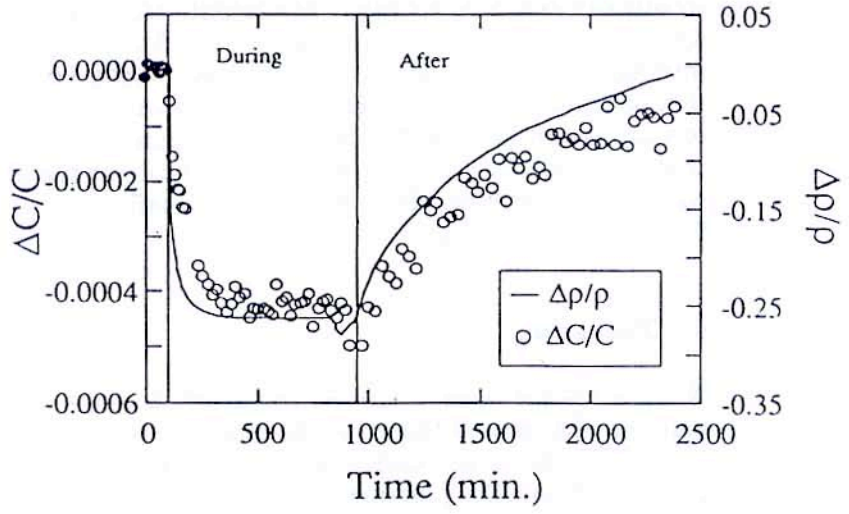

Figure 4: Fractional changes $\Delta c/c$ of the c-axis lattice parameter (o) and resistivity $\Delta\rho/\rho$ (solid line) versus time in a semiconducting ($x = 6.5$) 1000 Å thick YBCO film, before, during and after illumination.

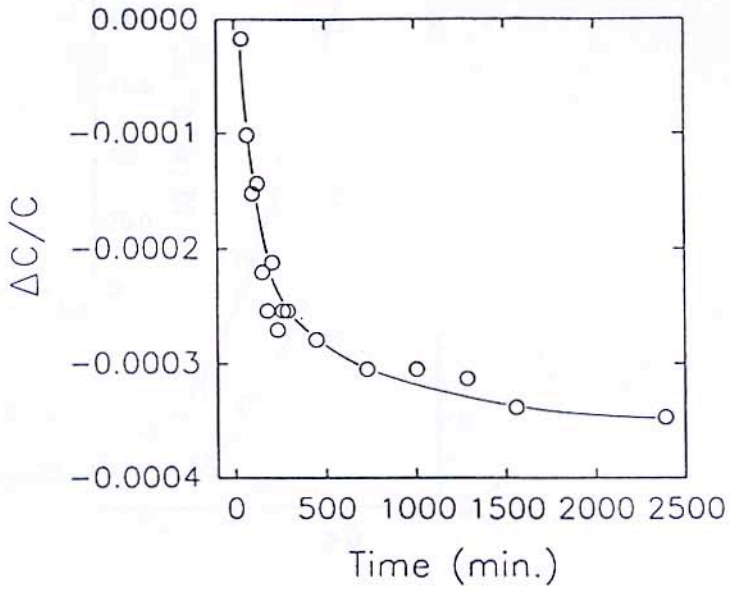

Figure 5: Fractional change $\Delta c/c$ of the c-axis lattice parameter as a function of annealing time at room temperature after quenching an $x = 6.55$ YBCO film (after ref. 13). The solid line is a guide to the eye.

with a halogen lamp at room temperature of an YBCO film with x = 6.5. The position of the peak was determined by fitting it to two Gaussians, corresponding to the $K_{\alpha 1}$ and $K_{\alpha 2}$ Cu x-ray wavelengths. Dry nitrogen gas was sprayed on the sample during the experiment to prevent excessive heating. The sample resistivity was simultaneously measured with a 4-point method. The resulting structural changes are displayed in Fig. 4, which shows the fractional changes in the c-axis lattice parameter ($\Delta c/c$) and resistivity ($\Delta\rho/\rho$) as a function of time, during and after the illumination. Notice that $\Delta c/c < 0$, which is the opposite of what would be expected from simple thermal expansion effects. This clearly indicates a contraction of the c-axis lattice parameter during the illumination, which can be compared with the contraction observed during annealing at room temperature of a quenched x = 6.55 film [13] (see Fig. 5).

4. Discussion

We now discuss several possible explanations of the observed persistent photoinduced phenomena. The first is related to the photoexcitation phenomena observed in low T_c granular In-CdS [14] films and in Sn-Cds-Sn junctions [15], i.e. changes in the conductivity of the photosensitive (CdS) intergranular material. Assuming that the superconductivity in the YBCO films is granular in character, an analogous effect might be present during the laser irradiation. It should be noted, however, that granular In-CdS films exhibit a decrease in the width of the normal to superconducting transition, but no change in the onset critical temperature after illumination. In contrast, our results show a parallel shift of the R(T)

curves and a clear increase in T_c after illumination. Moreover, a rather peculiar behaviour of the intergranular material must be assumed in order to explain the oxygen content dependence of the photoinduced phenomena using this granular model.

Another possibility comes from the analogy with the well known photoinduced phenomena in semiconductors. According to this model an electron- hole pair is photoinduced by absorption of one photon in the CuO_2 planes. While the hole increases the carrier density in these planes, the electron is transferred via some mechanism to the CuO chain planes, *where it is trapped by an oxygen vacancy* [11, 16]. Experimentally we find that at each oxygen content, T_c and σ_{ab} saturate at different values, T_c^{sat} and σ_{ab}^{sat} respectively. This seems to contradict the assumption that oxygen vacancies may act as effective traps for the photogenerated electrons during the long time photoexcitation. Indeed, the number of oxygen vacancies per unit cell in oxygen deficient $YBa_2Cu_3O_x$ is δ = 7-x ($0 \leq \delta \leq 1$) and the number of holes per unit cell necessary to increase T_c from zero ($\delta \geq 0.6$) to 90 K ($\delta = 0$) is approximately 0.15 [17]. It follows that the number of oxygen vacancies per unit cell for any oxygen content is large enough to trap all the electrons needed to raise the T_c of the material to 90 K, an effect that has never been observed in the continuous wave laser experiments. Nevertheless, the possibility might exist that there is an oxygen dependent distribution of trapping energies, which together with the recombination dynamics could give rise to the saturation of the photoenhancement of T_c and σ_{ab}.

The third possibility is based on the similarities shown in Figs. 3, 4 and 5, which suggest that during the long time laser illuminations a rearrangement of oxygen ions in the basal plane of YBCO may occur [18]. In general, the photoproduction of electron-hole pairs can give rise to local redistributions of charge inside the material with a consequent modification of the local electric fields, which in turn can induce the movement or diffusion of atoms. The occurence of ***photoassisted oxygen ordering*** may be described as follows. It has been shown [19] that the ordering of oxygen atoms decreases the fraction of three fold coordinated Cu1 and increases the fraction of two and four fold coordinated Cu1. It has also been shown [20] that the most probable oxidation state for Cu1 ions is 2+ when it is three fold (chain end) or four fold (Cu in a chain) coordinated, while it is 1+ when the Cu1 is two fold coordinated (empty chain). Therefore, we assume that in YBCO the produced photoelectrons change the valence state of three fold coordinated Cu1 from Cu^{2+} to Cu^{+} through the reaction $e^- + Cu^{2+} \longrightarrow Cu^{+}$, while the hole contributes to increase the carrier density. After the capture of the photoelectron the three fold coordination for a Cu^{+} ion is energetically unfavorable [20] (see Fig. 6.a), and therefore the system will locally relax to a new configuration in which longer chains are produced at the expense of shorter chains or wrongly positioned oxygen atoms (Fig. 6.b). The new ordered configuration does not correspond to an equilibrium state since it involves an increase in the lattice elastic strain energy. However, in the absence of enough thermal energy this new situation persists in time preventing the recombination of the electron-hole pair. The system disorders again when the temperature is raised (Fig. 6.c), with characteristic times equal to the ones observed in phenomena related to the oxygen ordering process and following the same time dependence [11].

This simple physical picture accounts, in a natural way, for i) the existence of persistent photoinduced phenomena for all $x < 7$; ii) the saturation of the persistent photoinduced phenomena; iii) the peculiar behaviour of δT_c as a function of the oxygen content (Fig. 3); iv) the contraction of the c-axis lattice parameter observed during the illumination of an insulating YBCO film (Fig. 4); and v) the non-exponential decay of the photoinduced phenomena.

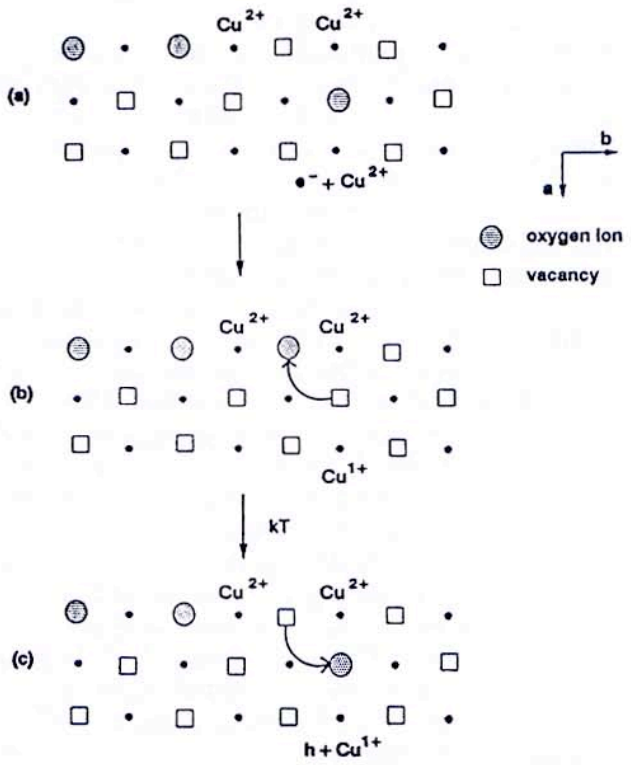

Figure 6: Schematic representation of the photoassisted growth of chains: (a) a photoelectron is captured at the end of a short chain; (b) the oxygen ion in the short chain finds a more stable environment in a longer chain; (c) when the temperature is raised the oxygen ion comes back to its original position and a hole is removed from the $Cu2O_2$ layers.

We note here that in ref. [6] we raised some arguments against the occurence of photoassisted oxygen ordering. Our arguments were based on the observation at room temperature of an *increase* in the Hall mobility μ during the illumination in an x = 6.5 film, while a *decrease* was seen during the annealing at room temperature of a different quenched (non-illuminated) film with a different x = 6.6. In Fig. 7 we show that the function μ(x) has a maximum at $x_{max} \simeq 6.55$ measured at T= 300 K. Note that an increase in n for $x < x_{max}$ gives rise to an increase in μ (since to increase n is equivalent to increase x), while the opposite is true for $x > x_{max}$. Aging and illumination experiments carried out in this film with x = 6.7, show indeed that μ *decreases in both cases*, while during the illumination of the same film with x = 6.5 the mobility *increased*. In view of this new experimental facts, the argument used in ref. [6] is not longer valid.

Finally, if this photoassisted oxygen ordering mechanism is correct, persistent photoinduced phenomena should only be present in high T_c materials containing chain planes in their crystalline structure. So far, we could not observe persistent photoinduced phenomena after the illumination of underdoped, overdoped and optimally doped $Bi_2Sr_2Ca_1Cu_2O_{8\pm y}$ [21] and $La_{2-x}Sr_xCuO_{4\pm\delta}$ [22] films, nor in fully oxidized Pr doped YBCO phase spread alloy films [23] for any Pr doping level [24].

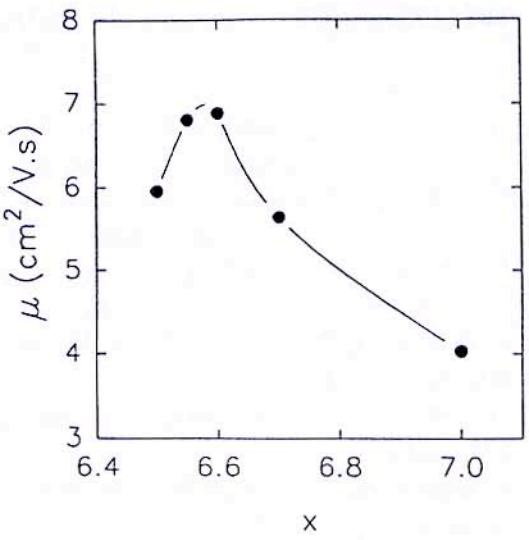

Figure 7: The Hall mobility $\mu = \frac{R_H}{\rho_{ab}}$ as a function of the oxygen content in an YBCO film. The solid line is a guide to the eye.

5. Summary and conclusions

In summary, we have shown the existence of measurable persistent photoinduced effects in YBCO films for all oxygen contents below x = 7. We have also shown that the total enhancement of T_c after illumination depends on x in a similar way as that observed for the T_c enhancement due to ordering effects in oxygen deficient YBCO single crystals. This, together with the similarity between the photoinduced structural changes and those caused by room temperature annealing of quenched samples, indicate that during the long time photoexcitation a rearrangement of oxygen ions in the basal plane of YBCO is likely to occur.

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