RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 5 1 FEBRUARY 1994-I

Photoexcitation and oxygen ordering in $YBa_2Cu_3O_x$ films

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(Received 23 August 1993; revised manuscript received 26 October 1993)

We report on the photoinduced enhancement of the critical temperature δT_c and the in-plane conductivity $\delta\sigma_{ab}$ measured in a *c*-axis-oriented $YBa_2Cu_3O_x$ film as a function of oxygen concentration ($6.4 \leq x \leq 7$). Both δT_c and $\delta\sigma_{ab}$ decrease with the oxygen content, display a plateaulike behavior for $6.6 \leq x \leq 6.75$, and become zero at $x = 7$. This dependence of δT_c on x is similar to that observed for the T_c enhancement due to ordering effects in oxygen-deficient $YBa_2Cu_3O_x$ single crystals. We propose that the *persistent* photoinduced changes in $YBa_2Cu_3O_x$ films are due to photoassisted oxygen ordering.

Recently, various experiments clearly indicated that the illumination with visible light of oxygen-depleted $YBa_2Cu_3O_x$ (YBCO) with nominal oxygen concentration, x, causes an increase in the nonequilibrium carrier density.[1-7] Two different time regimes have been explored experimentally. The first involves the photoexcitation of the sample with very short laser pulses (~ 0.6 ns) with a rather low photon density in each pulse ($Q \cong 10^{13}-10^{16}$ photons/cm^2).[1,2] In these experiments, the excess carriers are photogenerated during short periods of time, giving rise to transient photoconductivity changes (~ 1 ns) in insulating YBCO single crystals of more than 10 orders of magnitude.[2] Moreover, a deep minimum in the temperature dependence of the photoinduced resistivity has been observed near 90 K, indicative of transient photoinduced superconductivity.[2] In the second type of experiments, a continuous-wave laser is used to irradiate thin films during long periods of time (5–40 h) with total doses $Q \cong 10^{18}-10^{23}$ photons/cm^2.[3] In contrast to the pulsed excitation experiments, the excess photoconductivity is persistent in time at low temperatures and it saturates as a function of increasing photon dose.[3,4] Using this method we showed that the critical temperature T_c of oxygen-deficient YBCO films is enhanced by several degrees in a persistent manner below room temperature,[6] and that this is accompanied by an increase of the carrier density.[7] All the photoinduced changes relax back at room temperature to their equilibrium values with characteristic times of the order of days following a Kohlrausch law.[4] The results from the pulsed laser experiments have been interpreted in terms of a model in which electron-hole pairs are created in the Cu2O_2 planes[8] during illumination. The photoelectrons are trapped in localized energy states which belong to the basal planes while the holes increase the carrier density in the Cu2O_2 planes.[2] Essentially the same mechanism was used to explain the persistent photoinduced effects in the long-time illumination experiments.[4,5] In both cases it has also been suggested that oxygen vacancies may act as the trapping centers for the photogenerated electrons.[2,5] The differences between the very short- and long-time illuminations may indicate the existence of different trapping mechanisms governing both types of photoinduced effects.

In this paper, we studied the oxygen content dependence of the persistent photoinduced phenomena (PPP). Continuous-wave laser-illumination experiments, performed in the same YBCO film in which the oxygen content x has been varied between 6.4 and 7 atoms per unit cell, show that persistent photoinduced effects clearly occur for all $x < 7$. In particular, we show that the variation with oxygen content of the total photoinduced enhancement of T_c and of the T_c enhancement due to oxygen ordering are similar. This result suggests that during the long-time photoexcitation a rearrangement of oxygen atoms occurs in the basal plane of YBCO. This experimental insight in the nature of the PPP may give clues to understand the differences between the very short- and long-time illuminations.

Fully oxidized *c*-axis-oriented YBCO films were deposited on MgO(100) substrates using a planar magnetron sputtering system in the 90° off-axis configuration. A detailed description of the film production has been published elsewhere.[9] Oxygen-deficient YBCO films, with a nominal oxygen content $6.4 \leq x \leq 7$, are prepared using a method[10] based on the oxygen partial pressure-temperature phase diagram for bulk material. We adopted for this work the phase diagram reported in Ref. 11. One 1000-Å-thick YBCO film was patterned using conventional photolithography and wet etching, into a four point pattern with dimensions 35 μm × 1 mm. After each oxygen depletion treatment the sample was kept at room temperature for at least three days in order to allow a complete relaxation.[12] The illumination was performed at $T = 100$ K during 8 h using an Ar-ion laser ($\lambda = 514$ 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. During the illumination the sample temperature increased by approximately 5–6 K. The resistance versus temperature curves were mea-

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sured 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.

Figure 1(a) shows the normalized resistive transitions before illumination for the same YBCO film with different oxygen contents. As x is reduced, the transitions move uniformly to lower temperatures and show a pronounced rounding near the normal state. This effect hinders the determination of the normal-state resistance R_N at the onset of the superconducting transition, and makes it difficult to define T_c. Since for $x \geq 6.8$ the temperature at which dR/dT is a maximum coincides with $T_c(R=50\% R_N)$, we adopted this criterion to define T_c, which is plotted in Fig. 1(b) as a function of the oxygen content.

Figure 2 shows the transitions to the superconducting state measured before and after the illumination, for three characteristic oxygen contents: (a) near the metal-insulator transition, (b) in the 60-K plateau region, and (c) in the 90-K plateau region. In contrast to the results of Ref. 4, persistent photoinduced changes in T_c and ρ_{ab} are evident, for all oxygen concentrations. Note that due to the parallel shift of the transition towards higher temperatures the same absolute shift of T_c [i.e., $\delta T_c = T_c$ (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 $\rho(T)$ values measured before the illumination are recovered.

Figure 3 summarizes the main experimental results obtained after illumination of the YBCO film with different oxygen contents. The *total* photoinduced shifts of the critical temperature δT_c and the in-plane conductivity $\delta\sigma_{ab}$ (see inset) are respectively plotted as a function of x. Our results (δT_c) are compared to the enhancement of T_c, ΔT_c, produced by oxygen ordering effects in oxygen deficient YBCO single crystals as reported by Veal *et al.*[13] *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 metal-insulator transition is approached, (ii) for $6.6 \leq x \leq 6.75$ the total increase in T_c

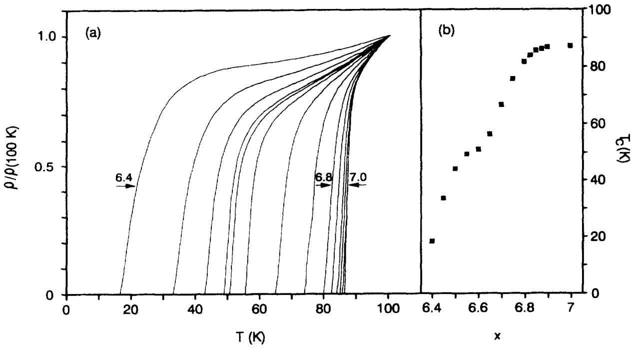

FIG. 1. (a) Normalized resistive transitions for a 1000-Å-thick YBCO film with different oxygen contents x. Between $x=6.4$ and 6.8 the oxygen content has been varied in steps of 0.05, while between $x=6.8$ and 6.9 the step is 0.025. (b) Critical temperature as a function of the oxygen content.

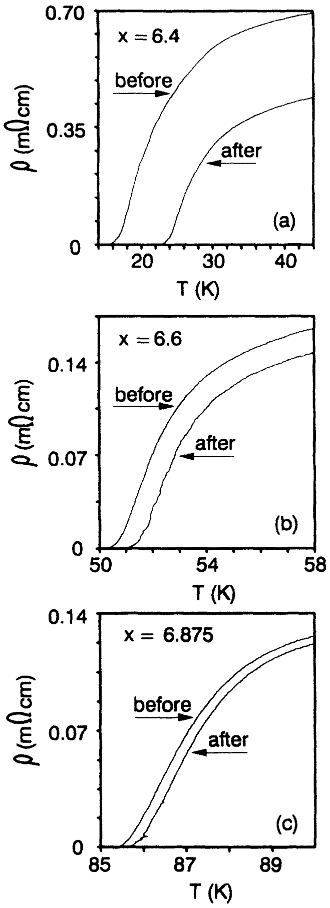

FIG. 2. Resistive transitions for the YBCO film of Fig. 1(a) before and after the laser illumination and for different oxygen contents x. Notice the parallel shift of the transitions towards higher temperatures after the illumination.

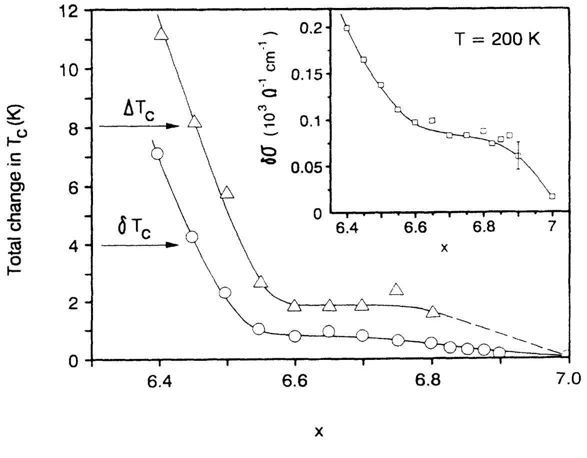

FIG. 3. Total enhancement of the critical temperature after the illumination δT_c as a function of the oxygen content. The data are compared to the total increase of T_c due to oxygen ordering effects ΔT_c in YBCO single crystals (Ref. 13). The inset shows the total increase of the conductivity at $T=200$ K after the illumination. All the solid lines are guides to the eye.

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. 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[5] during the long-time photoexcitation. Indeed, the number of oxygen vacancies per unit cell in oxygen deficient $YBa_2Cu_3O_x$ is $\delta = 7 - x$ $(0 \leq \delta \leq 1)$ 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.[14] 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}. On the other hand, the remarkable similarity between $\delta T_c(x)$ and $\Delta T_c(x)$ shown in Fig. 3, strongly indicates that the mechanism limiting the excess photoinduced carriers in the long-time illumination experiments may be identical to the one which controls the charge transfer to the $Cu2O_2$ planes during room-temperature annealing, i.e., the ordering of oxygen atoms. This ordering produces an increase in the orthorhombicity[13] which is also reflected in a contraction of the c-axis lattice parameter.[12] Interestingly enough, it has recently been observed that the c-axis also contracts during the illumination of an insulating YBCO film.[15]

Although a detailed microscopic model has not yet been developed so far, a possible scenario for the occurrence of photoassisted oxygen ordering may be as follows. The photoproduction of electron-hole pairs gives 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 of atoms. This process is different from thermally induced diffusion in which the bond breaking is produced by the enhanced movement of the ions due to the energy provided by the thermal bath. An example of indirect photoassisted diffusion is the photodissolution of metals inside amorphous chalcogenides.[16] On the other hand, it is known[17] that the oxygen ordering gives rise to a decrease on the fraction of threefold coordinated Cu1 (chain end) together with an increase in the fractions of two (empty chain) and fourfold coordinated Cu1 (Cu in a chain). It has also been shown[18] that the most probable oxidation state for twofold coordinated Cu1 is +1, while it is +2 when three- or fourfold coordinated. It has been pointed out that chains shorter than a critical length are unable to inject holes into the $Cu2O_2$ planes, while longer chains transfer holes in proportion to their length.[19] Conversely, the injection of electrons in any chain fragment longer than the critical length will tend to increase its length and this will occur at the expense of chains shorter than this critical length. A possible way in which this could happen is through the reaction $e^- + Cu^{2+} \rightarrow Cu^{1+}$, where e^- is the produced photoelectron. In order to account for the above-mentioned changes in the fractions of two-, three-, and fourfold coordinated Cu1 ions, the injected photoelectrons should be trapped at the chain ends. Notice that since a threefold coordination for a Cu^{1+} ion is energetically unfavorable,[18] this reaction will cause a local instability which may allow, in principle, the growth of the chain leading to a new ordered configuration.

It should be noted that the new ordered configuration after the illumination does not correspond to an equilibrium state. This has been clearly illustrated by the existence of photoinduced phenomena at room temperature in insulating YBCO films, which were equilibrated at that temperature prior to the illumination.[7] Nevertheless, 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, with characteristic times equal to the ones observed in phenomena related to the oxygen ordering process and following the same time dependence.[12,13]

It is worth noticing that the photoassisted oxygen ordering is distinctly different from the photoinduced diffusion mechanism proposed by Kudinov and coworkers.[4,5] 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 PPP; (iii) the peculiar behavior 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;[15] and (v) the nonexponential decay of the photoinduced phenomena.[4-7] We note here that in Ref. 7 we raised some arguments against the occurrence 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 (nonilluminated) film with a different $x = 6.6$. Recent aging and illumination experiments,[20] carried out in the *same* film with $x = 6.7$, show that μ *decreases in both cases,* while during the illumination of the same film with $x = 6.5$ the mobility *increased.* The photoinduced changes in μ are smaller than those induced by the annealing of the quenched film (both for $x = 6.7$), an effect that seems to be in agreement with the results shown in Fig. 3 for the total increase in T_c. In view of these experimental facts, the argument used in Ref. 7 is no longer valid.

Finally, this photoassisted oxygen ordering might help to understand the differences observed between the short- and long-time illumination experiments. The time needed for an oxygen ion to jump between two different positions is the characteristic time τ associated with the proposed trapping mechanism. If the illumination time is much shorter than τ, it will not be possible to trigger the mechanism and persistent effects will be absent. In this regime $(t \ll \tau)$ the decay time $(\sim 1$ ns) observed for the photocurrent in single crystals may be due to *transient* trapping of the photoelectrons in oxygen vacancies or other defects, as has been suggested by Yu and coworkers.[2] Nevertheless, the alternate possibility might exist that the transient relaxation times are related to bulk diffusion of photoexcited carriers.

It is important to note that a direct consequence of our model is *the absence of persistent photoinduced effects in any high-T_c* material without chain planes. So far, we could not observe persistent photoinduced phenomena after the illumination of underdoped, overdoped, and optimum-doped $Bi_2Sr_2Ca_1Cu_2O_{8\pm y}$ and $La_{2-x}Sr_xCuO_{4\pm\delta}$ films.

In summary, we have presented experimental results which clearly show the existence of persistent photoinduced effects in YBCO materials for all oxygen contents below $x = 7$. The experimental results are consistent with a photoassisted rearrangement of the oxygen ions in the chain planes being the mechanism responsible for the observed persistent photoinduced phenomena.

We are indebted to P. Wagner and H. Adrian for providing us with the Bi-2:2:1:2 films, to J.-P. Locquet for providing the La-Sr-Cu-O films and for active collaboration, to C. Van Haesendonck for a critical reading of the manuscript, and to V. V. Moshchalkov for many useful conversations. One of us (E.O.) acknowledges very interesting discussions with A. Robledo and R. Griessen. This work was supported by the Belgian High Temperature Superconductivity Incentive (E.O. and M.M.) and Concerted Action Programs at KUL and ONR Grant No. N00014-91J-1438 at UCSD.

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