Interrelation between persistent photoconductivity and oxygen order in GdBa$_2$Cu$_3$O$_x$ thin films

J. Guimpel, B. Maiorov, E. Osquiguil, G. Nieva, and F. Pardo

Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 S. C. de Bariloche, R. N., Argentina

(Received 10 March 1997)

We study the metastable states induced by photoexcitation, oxygen disorder, and both effects combined, in superconducting GdBa$_2$Cu$_3$O$_x$ thin films. The states are identified by the temperature dependence of the resistivity. The relaxation dynamics is characterized through the time evolution of the conductivity. The results show that photoexcitation and oxygen disorder behave as noninteracting and do not cancel each other out. However, in both cases the relaxation dynamics is related to oxygen movement. [S0163-1829(97)09131-5]

Since the existence of persistent photoconductivity[1] (PPC) and photoinduced superconductivity[2,3] in high-T_c superconductors was established, these phenomena have attracted attention. The experiments show that illumination with visible[1–3] or UV light[4] produces an increase in the conductivity, σ, and the superconducting critical temperature, T_c, of the material. These changes are persistent[1–3,5] in the experimental time scale if the sample is kept at temperatures below 250 K, but relax back to the equilibrium state at higher temperatures.

Although from the beginning it was clear that the phenomena were due to the trapping of photoinduced electrons with the consequent pumping of photoexcited holes to the conduction band,[1] the trapping mechanism remains elusive until now. Several models have been proposed like photoassisted oxygen ordering,[6] trapping at oxygen vacancies,[4,7] and photoinduced oxygen diffusion.[8] Experimental evidence has been presented supporting all the models. For example, the similarity between time scales for oxygen ordering and PPC relaxation,[3] and the similar oxygen content dependence of the maximum induced change in T_c by photoexcitation and by oxygen disorder,[6] have been used as arguments in favor of photoassisted oxygen ordering. On the other hand, the existence of a monotonic behavior for the $\Delta\sigma/\sigma$ vs oxygen content curve,[9] the existence of a peak in the photoexcitation efficiency for UV illumination,[4] and the correlation between the efficiency curve and the photoluminescence spectra[10] have been used as arguments in favor of electron trapping in oxygen vacancies.

Recently,[11] results have been presented in which the effect of oxygen disorder at constant oxygen content is studied. This type of experiments are very important since they offer a chance to separate between those effects due to oxygen disorder and those effects related to the number of oxygen vacancies. The results presented there seem to support the photoassisted oxygen order model.[6] However, in analyzing the data the authors assume that the photoexcitation and oxygen ordering effects are linearly additive, a point that will be proved in this paper.

In this work we study the metastable states induced by photoexcitation and by oxygen disorder at constant oxygen content, and their relaxation dynamics. In this way we are able to directly compare the oxygen ordering and PPC relaxation processes towards the same equilibrium state, differently from Müller *et al.*[11] where oxygen disorder relaxation

is compared to PPC excitation. Starting from the equilibrium state at a temperature T_{eq} we induce different metastable states by oxygen disorder, photoexcitation, or both combined. If the PPC and the oxygen disorder effects could be explained solely by a charge transfer process, i.e., by a one free parameter process, then a photoexcitation simultaneous to an oxygen disorder of adequate magnitudes should cancel each other out, leaving the sample in the equilibrium state. The results presented here show that this is not the case and that the combined metastable state is not the equilibrium one. Also, the relaxation dynamics of the PPC and the oxygen disordered states relax independently with different time scales. In both cases the dynamics is described by a stretched exponential. The exponents of these stretched exponentials and the activation energies of the thermally activated characteristic times are very similar, indicating that both processes involve oxygen movement.

The GdBa$_2$Cu$_3$O$_x$ (GdBCO$_x$) thin films were grown by dc magnetron sputtering from a stoichiometric target in the parallel off-axis configuration.[12] Film deposition was done in an Ar(90%)/O$_2$(10%) mixture at a total pressure of 300 mTorr. The substrate temperature was controlled[13] at 760 °C during this stage. After deposition, the film was cooled down to 450 °C where it was oxygenated for 1 h at 100 Torr of pure O$_2$. The film thickness was 3000 Å for a 2 h deposition period. The x-ray diffraction spectra show (001) oriented growth over the single crystalline (100) MgO substrates. Typical rocking curve widths indicate a mosaic spread of 0.5 °. Scanning electron microscopy micrographs show a smooth surface with no inclusions and energy dispersive spectroscopy analysis indicates that the chemical composition is correct within the resolution achievable in thin film samples. The as-grown films show linear metallic behavior for the resistivity, $\rho(T)$, and T_c of 88–90 K with transition widths, ΔT_c, of 2 K. The oxygen content of the samples was adjusted in a controlled fashion using the isostoichiometry line annealing method.[14] All measured samples were patterned into a four probe geometry by wet photolithography.

The experiments were carried out in a closed cycle refrigerator equipped with an optical window. The maximum cooling rate of the system was 3 K/min. All temperature dependencies were measured at a controlled rate of 1 K/min at which no thermal lag was detected. A halogen lamp was used as the illumination source. The light beam was guided to the sample through an optical fiber, which cuts off the IR
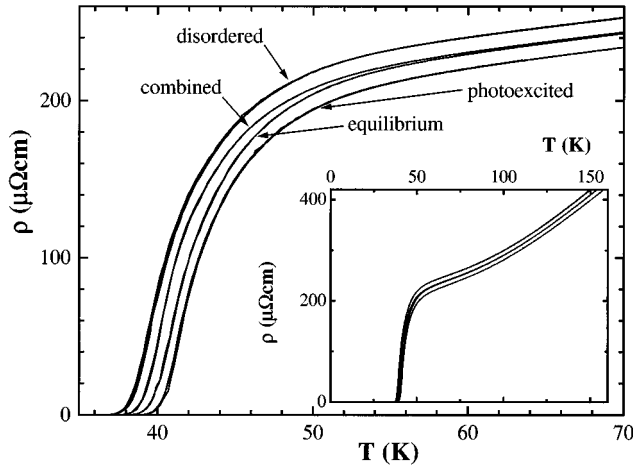
FIG. 1. Temperature dependence of the resistivity of a $GdBa_2Cu_3O_{6.625}$ thin film. Curves for the equilibrium and metastable states described in the text are shown for the case $T_{eq} = 310$ K. The inset shows the same curves in an extended temperature range.

part of the spectrum. This avoided the IR quenching effect.[15] For most of the illuminations an interference filter of 644 nm central wavelength and 10 nm bandwidth was used to render a monochromatic beam of $1 \, mW/cm^2$ over the sample. Where indicated we also illuminated without filtering, i.e., with the full spectrum of the lamp at an intensity of $160 \, mW/cm^2$.

As a starting point in the experiments, thermodynamic equilibrium was achieved at a temperature T_{eq} in the range of room temperature or above. From this equilibrium state three different metastable states were induced: (i) an oxygen disordered state, obtained by achieving thermodynamic equilibrium at $350 \, K > T_{eq}$ and cooling down at the maximum cooling rate to 200 K. (ii) A photoexcited state, induced by quenching the T_{eq} equilibrium state down to 150 K and illuminating with monochromatic light. The amount of illumination was selected such that the photoinduced change in resistivity was equal to that produced by the oxygen disordered state (i), i.e., $\rho_{dis}(150 \, K) - \rho_{eq}(150 \, K) = \rho_{eq}(150 \, K) - \rho_{ph}(150 \, K)$. (iii) a combined metastable state, in which the same illumination as in (ii) was applied to the disordered state (i). In this way, a metastable state was achieved that had the same resistivity as the equilibrium one at 150 K, $\rho_{comb}(150 \, K) = \rho_{eq}(150 \, K)$.

The reproducibility of the induced metastable states was determined to be of the order of $\delta\sigma = 4 \, S \, cm^{-1}$

Figure 1 shows the metastable and equilibrium $\rho(T)$ curves of a $GdBCO_{6.625}$ film for $T_{eq} = 310$ K. An interesting feature is that the critical temperature of the combined state is not the same as that of the equilibrium state, clearly indicating that they are not equivalent. It should be noted however that adjusting the combined state to have equal resistivity to the equilibrium state at 150 K, produces $\rho_{comb}(T) = \rho_{eq}(T)$ in the whole temperature range of the normal state. This result is not consistent with an explanation of photoexcitation based only on the basis of charge transfer. The simultaneous cancellation of effects on ρ and noncancellation on T_c implies that charge transfer is not the only parameter being affected by either the photoexcitation or the
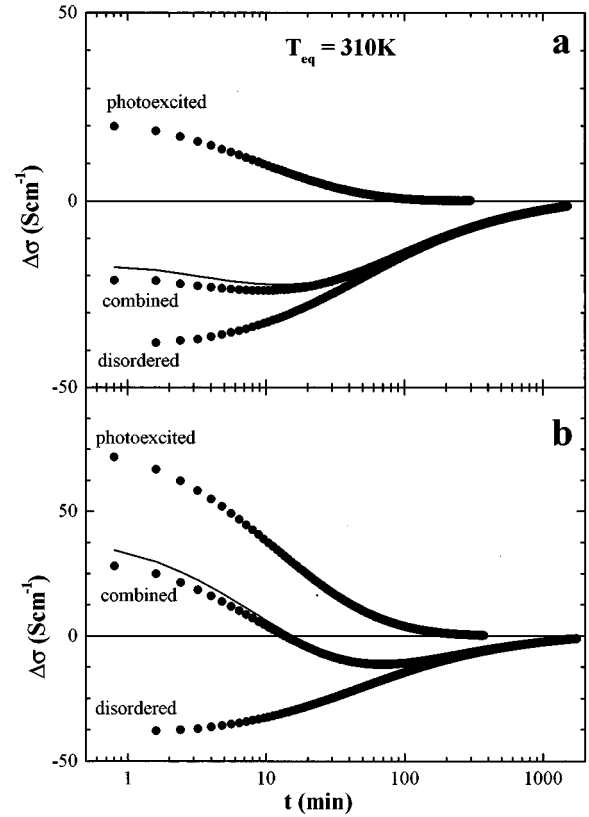

FIG. 2. Relaxation dynamics of $\Delta\sigma(t) = \sigma(t) - \sigma_{eq}$ for a $GdBa_2Cu_3O_{6.625}$ thin film at $T_{eq} = 310$ K. (a) Photoexcitation dose to compensate the oxygen disorder effect at 150 K; (b) Photoexcitation dose to achieve a nearly saturated PPC state. The solid line is the addition of the relaxations for the oxygen disordered and the photoexcited states.

oxygen disorder. The behavior shown in this figure is typical and has been observed also in a $GdBCO_{6.5}$ sample and for different T_{eq} temperatures.

After measuring each $\rho(T)$ curve, the relaxation dynamics of the metastable state was studied by increasing the temperature to T_{eq} at the maximum achievable rate (6 K/min), and measuring σ as a function of time. Figure 2(a) shows the time dependence of $\Delta\sigma = \sigma - \sigma_{eq}$ after the temperature is stabilized for the three metastable states of Fig. 1.

The oxygen disordered state and the photoexcited state relax to the equilibrium state with time dependencies that can be adjusted by stretched exponentials. This behavior will be discussed later, but it is already noticeable that the time scales in which both relaxations occur are significantly different, the one for PPC relaxation being shorter than the one for oxygen ordering. The relaxation of the combined state shows a nonmonotonic behavior with an initial decrease in σ, a minimum and a final increase towards the equilibrium state. This again indicates that the combined state is not equivalent to the equilibrium one, both having the same conductivity only due to the way in which the combined state was constructed. An experimental detail worth mentioning is that the initial value of the combined state $\Delta\sigma_{comb}$ is not zero at the initial time in Fig. 2 because $t = 0$ was defined as the time at which T stabilizes at T_{eq}. This means that there has already been a small amount of relaxation by the time the temperature has stabilized.
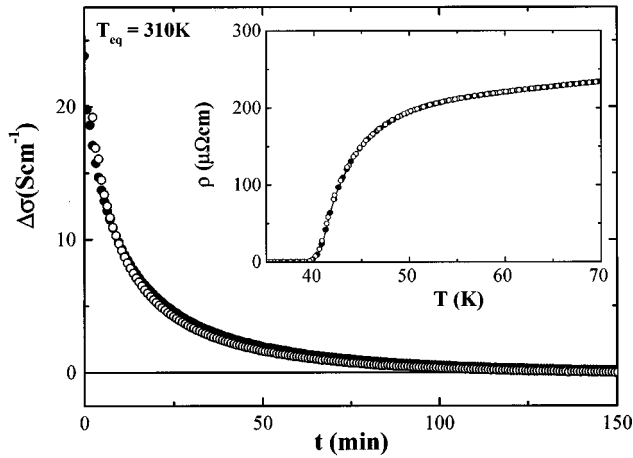
FIG. 3. Comparison of the relaxation of $\Delta\sigma(t)=\sigma(t)-\sigma_{\mathrm{eq}}$ for the metastable states induced in a $\mathrm{GdBa_2Cu_3O_{6.625}}$ thin film, by illumination with monochromatic light, $\lambda=644$ nm (full circles), and with the full spectrum of the lamp (open circles). The inset shows the temperature dependence of the resistivity for both states.

The striking point in these data is the relation between the three time dependencies. The solid line included in the figure is the sum of the oxygen ordering and PPC relaxation dependencies. Within the experimental reproducibility of the metastable states the relaxation of the combined state is the linear addition of the PPC and oxygen disorder relaxations,

$$\Delta\sigma_{\mathrm{comb}}(t)=\Delta\sigma_{\mathrm{ph}}(t)+\Delta\sigma_{\mathrm{dis}}(t). \qquad (1)$$

This result shows that the effects of photoexcitation and oxygen disorder behave as noninteracting.

The photoexcited metastable state constructed in this experiment was far from saturation. In order to check if the different time scales are due to this, we repeated the experiment on the same sample and at the same T_{eq}, but with a nearly saturated PPC state instead of cancelling the oxygen disorder effects. Figure 2(b) shows the relaxation dynamics for the metastable states in which the PPC was saturated. The same qualitative features as in Fig. 2(a) are observed and the same conclusions can be drawn, plus the fact that the relaxation time of the PPC is shorter than that of oxygen ordering for all values of PPC excitation.

In performing this last experiment, and to avoid the very long illumination times due to the low intensity of the monochromatic light, we illuminated with the whole lamp spectrum. In all the scenarios proposed for PPC (Refs. 4 and 6) it is assumed that the role of the incident photon is to generate a photoinduced electron-hole pair but that it has no direct relation to the trapping mechanism. In this sense the illumination process would be dependent on the photon energy[4,8,16,17] only through the photopair generation efficiency, but the final state is only dependent on the integrated dose received, convoluted with the spectral efficiency. This point, to our knowledge, has not been experimentally checked. Figure 3 shows the $\rho(T)$ curve and the relaxation towards equilibrium for the states achieved by illuminating with 644 nm monochromatic light and with the whole spectrum. The whole spectrum illumination dose was selected as to produce the same $\Delta\rho$ as the monochromatic dose. Obvi-
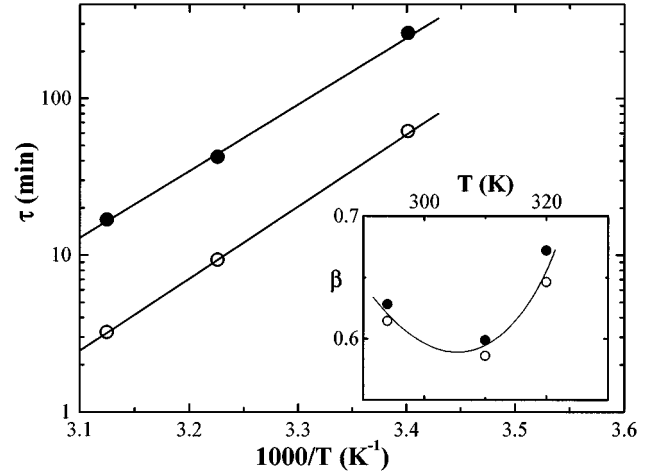

FIG. 4. Temperature dependence of the characteristic time, τ, and the exponent, β, in expression (2) for a $\mathrm{GdBa_2Cu_3O_{6.5}}$ thin film. The τ values are shown in an Arrhenius plot with linear fits to the data, $\tau=\tau_0 e^{\Delta/kT}$, as solid lines. The line in the β vs T inset is a guide to the eye. Values for PPC relaxation (open circles) and for oxygen order dynamics (full circles) are shown.

ously the metastable state and the relaxation are the same, implying that, indeed, the trapping process is not dependent on the incident wavelength.

The stretched exponential behavior was studied adjusting the functional form

$$\Delta\sigma=\Delta\sigma_0 e^{-[(t-t_0)/\tau]^\beta} \qquad (2)$$

to the relaxation data at different temperatures. In expression (2) t is the time after T_{eq} is stabilized, and t_0 is the time at which relaxation is activated, not zero in our case but finite and negative due to the finite warm up time, as was previously discussed. The stretched exponential behavior can be understood in terms of a microscopic distribution of characteristic times. Expression (2) is not invariant with respect to t_0, i.e., the adjusted τ and β will depend on the value of t_0. This is not a mathematical artifact, and reflects the fact that if the measurement is started a time t after the relaxation is activated, all the microscopic systems with characteristic times smaller than t will be already at equilibrium. These experiments provide a natural way to select the correct t_0 since its value should be such that $\Delta\sigma_{\mathrm{comb}}(t_0)=0$.

Figure 4 shows the temperature dependence of τ and β for oxygen disorder and PPC relaxation for a $\mathrm{GdBCO_{6.5}}$ sample. Two facts are remarkable. First, although the time scales are different, the activation energies are comparable, 0.85 eV for oxygen ordering and 0.91 eV for the PPC relaxation. Similar values for both have been found in the literature.[5,8,18] Second, the exponent values are the same for both processes. The nonmonotonic behavior of $\beta(T)$ observed in the inset reflects the fact that in metallic samples at low temperatures[5] β decreases with increasing T, while at high T, β should approach unity.

These facts allow us to draw an obvious conclusion, the microscopic mechanism that induces the relaxation for PPC and oxygen ordering is the same. Since it is known that this mechanism for oxygen ordering is the hopping of an oxygen

ion to a neighboring vacancy, then the electron detrapping in PPC should involve an oxygen ion movement.

The noninteraction of the photoexcited metastable state and the oxygen disordered metastable state could be explained under two different scenarios. The first and naive one is to simply state that PPC and oxygen disorder affect the electronic system at different locations in the structure. This hypothesis would favor the oxygen vacancy trapping model,[4] where the oxygen ordering processes happen at the chain fragments and the electron trapping at the oxygen vacancies. However it is expected that a certain amount of interaction is present, since oxygen movement occurs through the vacancy sites. This would be more evident at higher oxygen contents, where the number of vacancies is smaller.

The second possibility is more elaborate and is based on the stretched exponential dynamics of oxygen ordering.[18] As was already mentioned this behavior can be understood in terms of a microscopic distribution of characteristic times. The system response will be determined by a convolution of this distribution with the excitation mechanism. Under the hypothesis that the temperature disorder affects more effectively the longer characteristic times, while PPC affects the shorter ones, then a response qualitatively like the one observed could be expected.

The fact that the electron detrapping involves oxygen movement could also be explained in both models. In the photoassisted oxygen ordering model,[6] this is straightforward since the electron trapping is due to oxygen rearrangement. In the oxygen vacancy trapping model[4] this fact could be taken into account under the hypothesis that the lifetime of the trapped electron is much longer than the measured τ and that the energy barrier for oxygen hopping is not considerably changed by the trapped electron. In this scenario the detrapping would occur when an oxygen ion hops into the trapping vacancy.

In conclusion, we have demonstrated that the effects of photoexcitation and oxygen disorder are noninteracting and do not cancel each other out. The relaxations for both effects evolve independently, following the same dynamics with different time scales. The characteristic times, however, are intimately related since they have the same activation energy, showing that oxygen movement is involved in both. These results introduce new constraints that should be accounted for by the models.

[1] A. I. Kirilyuk, N. M. Kreines, and V. I. Kudinov, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 696 (1990) [JETP Lett. **52**, 49 (1990)].

[2] 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).

[3] G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple, and I. K. Schuller, Phys. Rev. B **46**, 14 249 (1992).

[4] T. Endo, A. Hoffmann, J. Santamaría, and I. K. Schuller, Phys. Rev. B **54**, 3750 (1996).

[5] W. Markowitsch, C. Stockinger, W. Göb, W. Lang, W. Kula, and Roman Sobolewski, Physica C **265**, 187 (1996).

[6] E. Osquiguil, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, D. Lederman, and I. K. Schuller, Phys. Rev. B **49**, 3675 (1994).

[7] I. P. Krylov, Pis'ma Zh. Éksp. Teor. Fiz. **52**, 1049 (1990) [JETP Lett. **52**, 443 (1990)].

[8] V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk, N. M. Kreines, R. Laiho, E. Lähderanta, and C. Ayache, Phys. Rev. B **47**, 9017 (1993).

[9] J. Hasen, D. Lederman, I. K. Schuller, V. Kudinov, M. Maenhoudt, and Y. Bruynseraede, Phys. Rev. B **51**, 1342 (1995).

[10] J. F. Federici, D. Chew, B. Welker, W. Savin, J. Gutierrez-Solana, T. Fink, and W. Wilber, Phys. Rev. B **52**, 15 592 (1995).

[11] J.-P. Müller, A. Schmalstieg, B. Güttler, A. Schönhals, J. Schubert, W. Zander, and H.-U. Müller, Physica C **261**, 269 (1996).

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

[13] F. Pardo, G. Burmeister, and J. Guimpel, Rev. Sci. Instrum. **67**, 2370 (1996).

[14] E. Osquiguil, M. Maenhoudt, B. Wuyts, and Y. Bruynseraede, Appl. Phys. Lett. **60**, 2159 (1992).

[15] D. C. Chew, J. F. Federici, J. Gutierrez-Solana, G. Molina, W. Savin, and W. Wilber, Appl. Phys. Lett. **69**, 3260 (1996).

[16] C. Ayache, I. L. Chaplygin, A. I. Kirilyuk, N. M. Kreines, and V. I. Kudinov, Solid State Commun. **81**, 41 (1992).

[17] S. L. Bud'ko, H. H. Feng, M. F. Davis, J. C. Wolfe, and P. H. Hor, Phys. Rev. B **48**, 16 707 (1993).

[18] B. W. Veal, H. You, A. P. Paulikas, H. Shi, Y. Fang, and J. W. Downey, Phys. Rev. B **42**, 4770 (1990).