Relaxation of frozen photoconductivity in $YBa_2Cu_2O_{6+x}$ ($0<x<1$) films

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The magnitude of the frozen photoconductivity and its relaxation characteristics have been studied as a function of the oxygen content in $YBa_2Cu_3O_{6+x}$ films. The photoconductivity relaxation can be described by a "glass" law $\exp[-(t/\tau)^{\beta}]$ with $\tau=\tau(T)$ and $0<\beta(T)\leqslant 1$. The experimental data are explained by a model of a photoinduced charge transport.

A frozen photoconductivity has been observed[1] previously near the insulator–metal transition (at $x\approx 0.4$) in $YBa_2Cu_3O_{6+x}$ films. Illumination of the films with visible light resulted in a significant decrease in the resistance of the samples. When the light was turned off at $T<270$ K, the new value of the resistance was completely stable over time. Only at $T>270$ K did a very slow, nonexponential relaxation of the photoinduced increment in the conductivity appear.[1–3] The relaxation time at room temperature was ~ 10 h. After the relaxation was complete, all the transport properties of the illumination films were completely restored. The frozen photoconductivity which was observed was attributed to a light-induced generation of additional mobile

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holes in CuO_2 planes: a photodoping.[2,4] Various microscopic mechanisms for the frozen photoconductivity were proposed in Refs. 2–5. Further studies showed that the photodoping not only amplifies the metallic properties of the illuminated $YBa_2Cu_3O_{6+x}$ films but can lead to a photoinduced superconductivity at low temperatures.[2–4,6]

In this letter we are reporting a study of the efficiency with which the frozen-photoconductivity signal appears and of the relaxation of this signal in $YBa_2Cu_3O_{6+x}$ films as a function of the oxygen content $(0<x<1)$.

The starting material in these experiments consisted of superconducting $YBa_2Cu_3O_7$ films ($T_c = 91$ K) on a $SrTiO_3$ substrate. The films were grown by laser deposition. Their c axis was oriented perpendicular to the surface of the substrate. Their thickness was 70–90 nm. The oxygen content was reduced by annealing the films in vacuum at 320 °C for several hours. The oxygen concentration in the $YBa_2Cu_3O_{6+x}$ films was determined from x-ray measurements (from the lattice constant $\mathbf{c}$), with experimental results[13] on $\mathbf{c}(x)$ used as a reference. We carried out experiments on two films. In film 1, the oxygen concentration was reduced to $x = 0.38$ in a single annealing step. After the annealing, the temperature dependence of the resistance of film 1 was semiconducting, with $R_{4.2K}/R_{293K} \simeq 3$. This film was used for a detailed study of the time and temperature dependence of the relaxation of the frozen photoconductivity. In film 2, the oxygen was removed in 11 successive annealing steps. Film 2 was used for a study of the concentration dependence of the frozen photoconductivity. The films were illuminated with the beam from an argon laser ($\lambda = 511.4$ nm) with an intensity of 0.5 W/cm^2. All the measurements were carried out over the temperature range 273–330 K in an optical cryostat with a temperature regulation system.

In film 1 the frozen conductivity was observed over the entire temperature range $T<330$ K. The conductivity σ of the sample increased significantly during the illumination, reaching a value $\sigma_{max} \simeq 1.5\sigma_0$ at saturation (see the inset in Fig. 1). When the light was turned off, the conductivity relaxed slowly to its equilibrium value σ_0. Figure 1 shows curves of the relaxation of the photoinduced increment in the conductivity after prolonged illumination for certain intermediate temperatures. We see that (a) the relaxation is not exponential and (b) the relaxation time falls off rapidly with increasing temperature. Analysis of the experimental data revealed that the relaxation curves of the frozen conductivity can be described well by the time dependence

$$\Delta\sigma(t) = (\sigma(t) - \sigma_0) = \Delta\sigma(0)\times\exp[-(t/\tau)^{\beta}], \tag{1}$$

where $\tau(T)$ is the typical relaxation time, and $0<\beta\leqslant 1$ is a dispersion parameter. A similar relaxation law has been seen previously in numerous disordered systems.[7–12] The solid lines in Fig. 1 show the results of a fit of expression (1) to the experimental data. It was found that the relaxation time $\tau(T)$ decreases with increasing temperature, in accordance with the usual law for thermal relaxation across an energy barrier Δ (Fig. 2a):

$$\tau(T) = \tau_0\times exp(\Delta/kT). \tag{2}$$

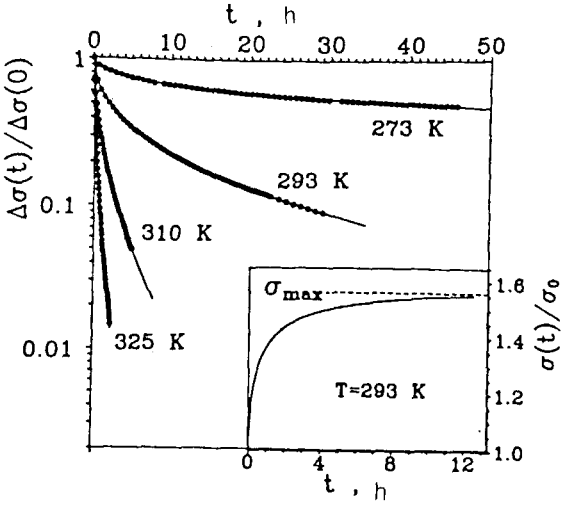

FIG. 1. Relaxation of the photoinduced increment in the conductivity of a $YBa_2Cu_3O_{6.38}$ film at several temperatures. The solid lines are fits of expression (1) to the experimental data. The inset shows a $\sigma(t)$ illumination curve measured at $T = 293$ K (the light intensity was 0.5 W/cm^2, and the wavelength was $\lambda = 511.4$ nm). Here σ_{max} is the maximum conductivity of the film, found after prolonged illumination at the given temperature.

For film $1(x = 0.38)$, the parameters in (2) were found to be $\Delta = 0.935$ eV and $\tau_0 = 1.4 \times 10^{-12}$ s. Over the temperature interval 270–330 K the parameter β is a linear function of the temperature: $\beta(T) = -0.63 + T/(264.6\ \text{K})$ (Fig. 2b).

The apparent reason for the nonexponential relaxation law in (1) is that there is a certain distribution of the barriers Δ in the film ($\delta\Delta \sim 0.1$ eV). The temporal param-

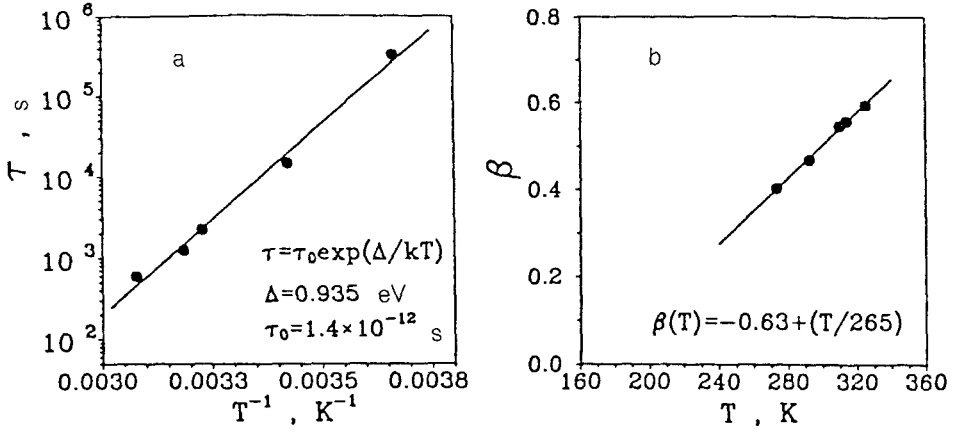

FIG. 2. Temperature dependence of (a) the relaxation time of the frozen photoconductivity, $\tau(T)$, and (b) the dispersion parameter, $\beta(T)$, for a $YBa_2Cu_3O_{6.38}$ film. The solid line in frame *a* is the result of a fit of Eq. (2) to the data on $\tau(T)$, with the parameter values $\Delta = 0.935$ eV and $\tau_0 = 1.4 \times 10^{-12}$. The straight line in frame *b* was calculated from the formula $\beta(T) = -0.63 + T/(264.6\ \text{K})$.

eter τ is the average relaxation time in the system, while the quantity $(1-\beta)$ characterizes the width of the distribution of these times. The preexponential factor τ_0^{-1} is a measure of the width of the level in which the photoexcited electron is captured (more on this below).

We turn now to the measurements of the efficiency at which the frozen photoconductivity arises and of the relaxation of this conductivity as a function of the oxygen concentration, carried out on film 2. In these experiments, film 2 was subjected to prolonged illumination at $T = 273$ K for each oxygen concentration obtained over the range $0 < x < 1$. We adopt the maximum induced conductivity σ_{max} as a measure of the effect (see the inset in Fig. 1). In the metallic phase, at $x > 0.45$, the frozen photoconductivity is not observed. The first indications of the photoconductivity arise at $x = 0.45$. The frozen-photoconductivity signal then rises rapidly to its maximum value at the point of the transition from the metallic phase to the semiconducting phase, $x = 0.4$. As x is lowered further, the signal decreases smoothly; it vanishes at $x = 0.1$. Figure 3a shows the absolute value σ_{max} and the relative value σ_{max}/σ_0 of the photoinduced conductivity as a function of the oxygen concentration according to measurements at $T = 273$ K after prolonged illumination. Also shown in this figure is the behavior of the equilibrium conductivity, $\sigma_0(x)$, at $T = 273$ K. On this curve we can clearly see the metal–insulator transition at $x \approx 0.4$.

To study the concentration dependence $(0 < x < 1)$ of the relaxation characteristics $\Delta(x)$ and $\tau_0(x)$ [see (2)] in film 2, we measured curves of the relaxation of the frozen conductivity, $\Delta\sigma(T)$, at three temperatures (273, 298, and 318 K) after illumination for 30 min. The relaxation time $\tau(T)$ was found by fitting expression (1) to the

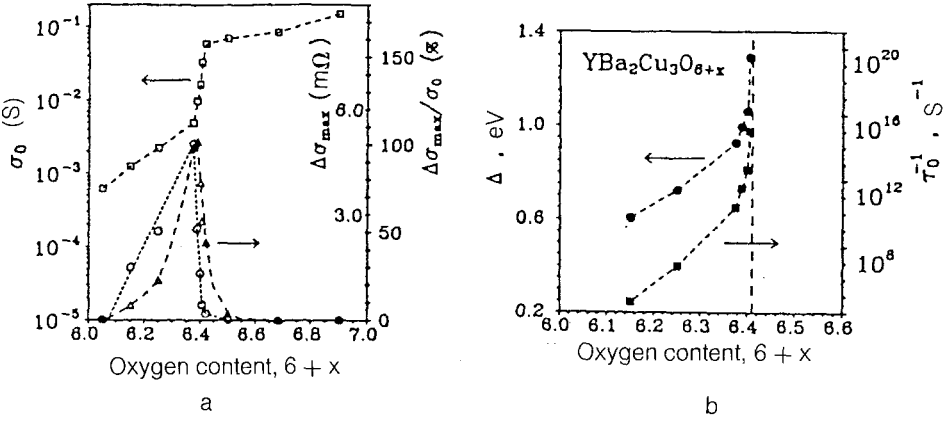

FIG. 3. a: △—Absolute value of the frozen photoconductivity, $\Delta\sigma_{max}$, as a function of x in a $YBa_2Cu_3O_{6+x}$ film, measured after prolonged illumination at 273 K; ○—the same, as the relative value $\Delta\sigma_{max}/\sigma_0$; □—$\sigma_0$, the equilibrium value of the conductivity of film 2 at 273 K, measured before the illumination. b: Relaxation parameters of the frozen photoconductivity in a $YBa_2Cu_3O_{6+x}$ film: the barrier height $\Delta(x)$ and the preexponential factor $\tau_0^{-1}(x)$.

$\Delta\sigma(T)$ curves. From the curves of $\tau(T)$ which we found, we calculated the barrier height $\Delta(x)$ and the temporal preexponential parameter $\tau_0(x)$ in accordance with expression (2), for each oxygen concentration x (Fig. 3b). We can clearly see the following tendency: As the semiconductor–metal transition ($x \simeq 0.4$) is approached along the oxygen concentration scale, the height of the relaxation barrier, Δ, increases, while the time τ_0 decreases by many orders of magnitude.

We believe that the microscopic mechanism for the frozen photoconductivity in the compound $YBa_2Cu_3O_{6+x}$ is associated with particular features of the crystal structure of this compound and the 2D nature of the conductivity in it. We think that the most probable explanation, which describes the entire set of experimental data, is a mechanism of a photoinduced charge transport: an excitation of electrons in CuO_2 planes by the light and a transport of these electrons to Cu–O–Cu–... chains in CuO_x layers.

As the oxygen content is raised in the compound $YBa_2Cu_3O_{6+x}$, a charge-transport transition arises at $x \approx 0.4$ (Refs. 14 and 15): Electron density "withdraws" from the CuO_2 planes and goes into chains in CuO_x layers. A p-type conductivity arises in the CuO_2 planes, and the transport properties of the compound change from semiconducting to metallic (and, at low temperatures, superconducting). In the semiconductor phase, with $x \leqslant 0.4$, there is no charge transport between the CuO_2 planes and chains under equilibrium conditions. This process can, however, be stimulated by light. Let us assume that an absorbed photon excites an electron into the unfilled upper conduction band in CuO_2 planes. There is a certain probability that the electron will move into neighboring CuO_x layers, in which, at $x \leqslant 0.4$, the oxygen forms Cu–O–Cu–... chains of finite length with copper ions. The electron then localizes in the CuO_x chains in vacant electron orbitals of O^- ions (or oxygen vacancies[2]). In this case the electron is captured at a highly localized level deep in the bandgap, at 1.8 eV, between the valence band and the upper excited band. For this electron to recombine with a hole, it would have to overcome an energy barrier $\Delta \sim 1$ eV, corresponding to the excitation energy of an electron in the unfilled upper conduction band. The photoexcited electron and the hole are thus spatially separated. A photoexcited hole remains free and causes an increase in the overall density of free holes in CuO_2 planes. In the course of the illumination, the density of holes increases, and the conductivity of the medium increases. At $T < 270$ K, a photoexcited electron captured by an oxygen vacancy is essentially unable to overcome the barrier of $\Delta \sim 1$ eV and to recombine with a hole. The relaxation of the photoconductivity and of the photoinduced superconductivity is thus not observed at these temperatures. At room temperature, a relaxation of the photoconductivity arises. It is governed by a thermal excitation of electrons captured by O^- levels across the barrier into the upper band.

In light of these arguments, the experimental results might be interpreted in the following way. The position of the acceptor levels (vacant orbitals of O^- ions in chains) and their width are highly dependent on the oxygen content in the film. At $x \simeq 0.1$, the chains have not yet formed, and there are no vacant levels of O^- ions in CuO_x layers. In the absence of acceptor levels, the frozen photoconductivity is not observed in the CuO_x layers. At $x > 0.1$, short (two-unit) Cu–O–Cu–O–Cu chains begin to appear; they may acquire an additional electron.[15] At this point the frozen-

photoconductivity signal appears in the films (Fig. 3). At $x = 0.15$, the acceptor levels lie in the gap between the valence and conducting bands, at a distance $\Delta = 0.6$ eV below the edge of the upper excited band in $YBa_2Cu_3O_{6+x}$. Their width, $h\tau_0^{-1}$, is exceedingly small ($\tau_0^{-1} \sim 10^{-6}$ s^{-1}). With increasing x in $YBa_2Cu_3O_{6+x}$, the number of chains (and the length of the chains) increases. Correspondingly, the frozen-photoconductivity effect increases, up to $x = 0.38$ (Fig. 3a). The acceptor levels move progressively closer to the valence band formed by the CuO_2 planes. This shift corresponds to an increase in the energy barrier Δ in Fig. 3b. Simultaneously, the localized O^- levels undergo a catastrophic broadening (to $h\tau \sim 1$ eV) as the semiconductor–metal transition ($x = 0.4$) is approached, because of a hybridization with the CuO_2 valence band (Fig. 3b). At $x = 0.4$, there is a transition to the metallic phase in the system, and the excited electron states in the chains are no longer isolated from the states in the conducting CuO_2 planes. Under these conditions, there can be no quasi-equilibrium states, and the frozen photoconductivity disappears rapidly at $x > 0.4$.

In principle, the explanation offered above for the frozen photoconductivity in $YBa_2Cu_3O_{6+x}$ is not the only possibility. Other microscopic mechanisms have been proposed.[2,4] For example, there is the mechanism of a photoinduced diffusion,[4] i.e., a light-induced redistribution of the positions of the oxygen ions. In our opinion, however, that mechanism could not explain the observed increase in the relaxation barrier Δ and the exceedingly sharp increase in the "frequency of attempts" τ_0^{-1} in (2) as the oxygen concentration approaches $x = 0.4$. The results of recent measurements of the Hall effect[6] in $YBa_2Cu_3O_{6+x}$ film exposed to visible light provide further evidence that the frozen photoconductivity and the diffusion of oxygen differ in nature.

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