Photoinduced superconductivity and structural changes in high temperature superconducting films

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(Received 23 September 1993; accepted for publication 24 November 1993)

The illumination of $Pr_yGd_{1-y}Ba_2Cu_3O_x$ semiconducting and superconducting thin films increases their critical temperatures and decreases their normal state resistivities *if and only if* the films are oxygen deficient. Moreover, these changes are enhanced near the Pr-induced metal-insulator transition. Light also causes a contraction of the c-axis in $YBa_2Cu_3O_x$ which is correlated with the observed photoinduced resistivity changes. These changes are similar to those observed when oxygen-deficient $YBa_2Cu_3O_x$ is enriched with oxygen or annealed at room temperature after quenching from high temperatures.

The persistent photoinduced enhancement of superconductivity is an unexpected effect which may be the basis for a variety of superconducting devices. Motivated by the initial work of Kudinov *et al.*,[1] we recently showed that illumination of $YBa_2Cu_3O_x$ (YBCO) oxygen-deficient films causes their superconducting critical temperatures (T_c) to increase by as much as 5.5 K,[2] and their Hall coefficients and normal state resistivities to decrease significantly.[3] These changes become more pronounced as the metal/superconductor to insulator (M-I) transition, due to oxygen deficiency, is approached.[2,4] Furthermore, illuminating, enriching with oxygen,[5] or annealing at room temperature after quenching from high temperatures[6] oxygen-deficient RBCO (R=rare earth or Y), as well as lowering the Pr concentration of $Pr_yR_{1-y}Ba_2Cu_3O_{7.0}$ (Pr/RBCO),[7] all have qualitatively similar effects on the transport properties. This raises a number of important experimental issues regarding the photoexcitation mechanism, such as its dependence on the M-I transition, oxygen deficiency, and the possible resulting structural changes.

In this letter, we show that persistent photoinduced effects are absent in *fully oxygenated* Pr/GdBCO films, even in semiconducting samples. On the other hand, significant increases in T_c's and decreases in normal state resistivities are observed in *oxygen-deficient* Pr/GdBCO films. Therefore, oxygen vacancies are crucial for the existence of persistent photoinduced superconductivity. In addition, the effects are enhanced as the Pr-induced M-I transition is approached. Structural studies in oxygen deficient YBCO indicate that the c-axis *contracts* upon illumination. The structural changes are qualitatively similar to those observed when oxygen-deficient films are enriched with oxygen or quenched from high temperatures to room temperature.

Several c-axis oriented Pr/GdBCO films with different Pr concentrations were simultaneously sputtered on the *same* MgO substrate and characterized as described elsewhere.[8] Their oxygen content was decreased by annealing in an Ar atmosphere at 270 °C for 30 min. From a similar treatment of a fully oxygenated GdBCO film, we estimate their oxygen concentrations to be $x\approx6.7$.[8] For the YBCO sample, this was accomplished by a technique described earlier.[9]

Temperature-dependent resisitivities [$\rho(T)$] were measured under vacuum between 8 K and room temperature. Prior to illumination, measurements were carried out during an initial cooldown. Then the samples were illuminated *in situ* with a ~1 W/cm^2 halogen lamp for up to ~12 h at 95 K. Subsequently $\rho(T)$'s were again measured while cooling the samples from 95 K to 8 K.

Structural measurements were carried out on a 1000 Å $YBa_2Cu_3O_{6.5}$ semiconducting film. Changes in the c-axis lattice parameter were determined from Θ-2Θ, room temperature x-ray scans of the [00 10] peak, performed before, during, and after the halogen lamp illumination. The data were fit to two Gaussians, corresponding to the $K_{\alpha1}$ and $K_{\alpha2}$ Cu x-ray wavelengths. Dry nitrogen gas was sprayed on the sample during the experiment to prevent film degradation and excessive heating. The sample resistivity was simultaneously measured with a four-point method. In a separate run, Θ-2Θ scans were performed between 2Θ=5° and 70°, before and after illumination. Changes in the [002] MgO substrate peak position, used as an internal thermometer, determined that the sample warmed up ~10 K during illumination, and that its temperature relaxed to the preillumination value within 30 min after turning off the halogen lamp.

Typical $\rho(T)$'s, before and after illumination, are shown in Fig. 1 for two of five simultaneously grown 2200 Å *fully oxygenated* ($x=7$) thin films with Pr concentrations $y=0.35$ and 0.55. No significant changes in the resistivities or T_c's of these films are detected, even for the semiconducting film. In contrast, a semiconducting, *oxygen-deficient* YBCO film with a similar $\rho(T)$ exhibits a 40% photoinduced decrease in resistivity throughout the entire temperature range.[2] This result can be compared with Fig. 2, which shows the effect of illumination on four *oxygen-deficient* 2500 Å ($x\approx6.7$) Pr/GdBCO thin films with $0.05<y<0.23$. All films exhibit a clear enhancement of superconductivity, characterized by an increase of the T_c and a decrease in $\rho(T)$. Furthermore, the proximity to the M-I transition, driven by increased Pr dop-

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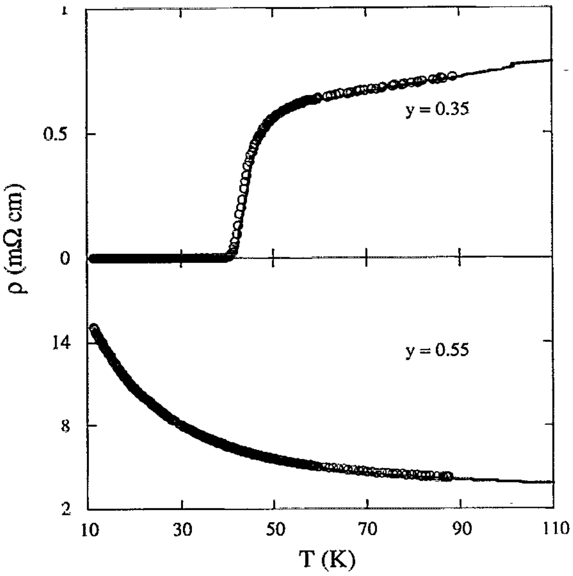

FIG. 1. Resistivities of two fully oxygenated $Pr_yGd_{1-y}Ba_2Cu_3O_x$ films simultaneously grown on the same substrate before (circles) and after illumination (solid lines) at 95 K for ~12 h.

ing at a fixed oxygen stoichiometry, enhances these effects. In all cases, oxygen vacancies are crucial for the existence of photoinduced superconductivity.

Figure 3 shows the fractional changes in the c-axis lattice parameter ($\Delta c/c$) and their correlation with the fractional resistivity changes ($\Delta\rho/\rho$) as functions of time, during and after illumination of an x=6.5, 1000 Å YBCO film. Notice that $\Delta c/c<0$, the opposite of what would be expected from simple thermal expansion effects.

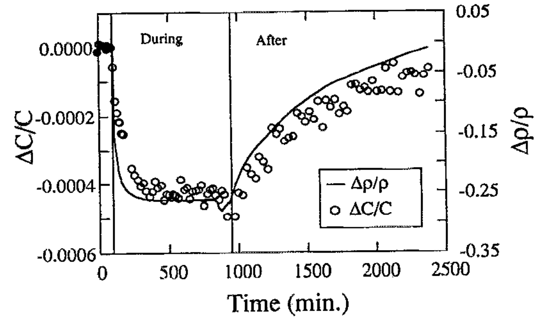

FIG. 3. Fractional changes $\Delta c/c$ of the c-axis lattice parameter (O) and resistivity $\Delta\rho/\rho$ (solid line) vs time in a semiconducting 1000 Å $YBa_2Cu_3O_{6.5}$ film, before, during, and after illumination.

Further structural information was obtained by refining[10] Θ-2Θ scans performed before and immediately after illumination, as shown in Fig. 4(a) and 4(b). At first glance the two scans seem identical; however, Fig. 4(c) shows their difference, where it is easy to see that after illumination all of the peaks have moved to larger angles and therefore the c-axis has contracted. Qualitatively, Table I shows the changes in various interplanar distances determined from the fits. As oxygen is added to oxygen-deficient YBCO single crystals, neutron diffraction studies show that c-axis contracts, with most of this contraction occuring precisely in the Ba-Cu1 interplanar distance, while the R-Cu2 and Cu2-Ba distances expand.[11,12] Similar structural effects are observed after oxygen-deficient YBCO is quenched to room temperature, without oxygen absorption.[6] Our data indicate that illumination induces a contraction of the Ba-Cu1 distance; however,

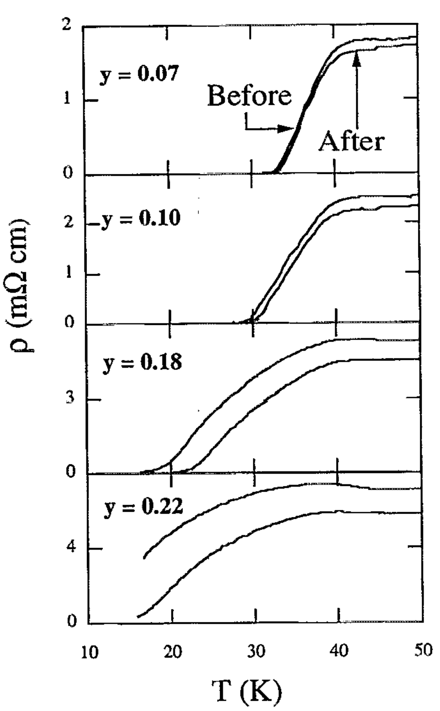

FIG. 2. Resistivities of a set of deoxygenated $Pr_yGd_{1-y}Ba_2Cu_3O_x$ films (with x~6.7) before and after illumination.

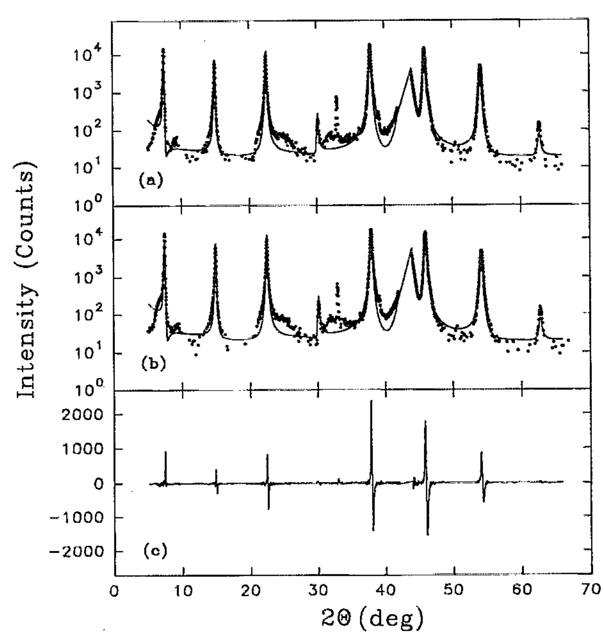

FIG. 4. Data (0) and simulation (solid line) of scans performed (a) before and (b) 9 min after 12 h of illumination of a semiconducting 1000 Å $YBa_2Cu_3O_{6.5}$ film. The peak near 2Θ=33° corresponds to In used for electrical contacts. The large peak at 2Θ=42.9° (cutoff) corresponds to the [002] MgO substrate. (c) is the subtraction of the data in (b) from (a).

TABLE I. Rare-earth CuO_2 (R-Cu2), CuO_2-BaO (Cu2-Ba), and Ba-CuO_x (Ba-Cu1) interplanar distances as functions of time after illumination of a 1000-Å-thick $YBa_2Cu_3O_{6.5}$ film, determined from Θ-2Θ scans (Fig. 4) and the model in Ref. 10. The changes were calculated with respect to scans performed prior to illumination. The $t=0$ data correspond to a scan performed with the light on after 12 h of illumination, immediately before turning off the light. The uncertainties are ±0.002 Å, as determined from fits to different scans taken in the unexcited state.

	R-Cu2		Cu2-Ba		Ba-Cu1	
Time	Value (Å)	Change (Å)	Value (Å)	Change (Å)	Value (Å)	Change (Å)
Off	1.681	···	2.000	···	2.245	···
0	1.682	0.001	2.004	0.004	2.238	−0.007
9 min	1.682	0.001	2.001	0.001	2.239	−0.006
60 min	1.681	0.000	2.002	0.002	2.240	−0.005
2.5 days	1.681	0.000	2.002	0.002	2.243	−0.002

the changes in the R-Cu2 and Cu2-Ba distances are within experimental errors. The shift in T_c obtained by scaling the contraction of the Ba-Cu1 distance (~0.007 Å) with the expected change in T_c from bulk crystal data[12] is ~10 K. This shift is of the same order of magnitude as the shift previously observed in a $T_c=2$ K sample (~5.5 K).[2]

In summary, photoinduced effects in Pr/GdBCO films occur only when the films are oxygen deficient. Consequently, in RBCO the oxygen vacancies are crucial for the existence of photoinduced superconductivity. Photoinduced structural changes in oxygen-deficient YBCO are similar to those observed when oxygen-deficient YBCO is enriched with oxygen or after quenching to room temperature from high temperatures. However, the photoinduced transport changes are enhanced with increasing Pr concentration and a fixed oxygen stoichiometry. Hence, although the structural effects may be explained by oxygen ordering, the enhancement of photoinduced superconductivity with increased Pr doping cannot be easily explained in the same way. Therefore, the mechanism responsible for these effects remains an open question.

We thank G. Nieva, J. Guimpel, M. Maenhoudt, B. Wuyts, and I. Chan for initial assistance, and I. Felner for useful discussions. The supports of the ONR at UCSD (Grant No. N00014-91J-1438) and the Belgian High Temperature Superconductivity Incentive and Concerted Action Programs at K. U. L. are gratefully acknowledged. International travel provided by NATO.

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