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Persistent photoconductivity in insulating and superconducting $YBa_2Cu_3O_x$ thin films: Temperature and spectral dependence

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Temperature and spectral dependencies of photoinduced changes of resistance in $YBa_2Cu_3O_x$ thin films with oxygen content ranging as $6.35<x<6.75$ were measured on both sides of the metal-insulator transition (MIT). The absolute value of efficiency of initiation of photoinduced changes decreases with an increase of oxygen content, but the position of peaks in the spectral dependence does not change with a change of x. Temperature dependencies of efficiency have an anomaly at $T\sim220$ K, which is present in all the samples studied and correlates with anomalies observed by other experimental techniques. Qualitatively similar temperature and spectral dependencies of efficiency for the samples in both the insulating and metallic phases may be considered as an indication that the persistent photoconductivity effect in Y-Ba-Cu-O on both sides of the MIT has a common origin.

INTRODUCTION

It has been well established that the CuO_2 planes of high-T_c cuprates (HTSC) are the most essential structural unit, and that the concentration of carriers (holes for p-type HTSC) in these planes is one of the most important and universal parameters, which affects various properties of the cuprates both in the metallic (superconducting) and insulating phases. There are several techniques by which additional carriers may be added to the CuO_2 planes: variation of oxygen content or mixed-valence substitution (chemical doping), charge transfer to the CuO_2 planes through application of hydrostatic pressure, and carrier generation by photoexcitation (photodoping). Photodoping of partially doped HTSC, and in particular, of $YBa_2Cu_3O_x$ (YBCO), has been recently studied.[1] Apart from *transient* photoconductivity, the phenomenon of *persistent* photoconductivity (PPC) has been observed and examined in YBCO thin films near the metal-insulator transition (MIT),[2,3] both in the insulating and metallic states. Exposure to light creates a metastable PPC state with a long relaxation time. This metastable state can be annealed out at temperatures above $T\sim270$ K. Illumination of oxygen-deficient YBCO films by visible light leads to decrease in both resistivity and the Hall constant. For films close to the MIT, illumination can even induce superconductivity and cause an increase of the superconducting critical temperature (T_c).[2,3] The spectral dependence of relative changes in resistivity of semiconducting films (with oxygen content $x\sim6.4$) has been measured at 293 K; this dependence is correlated with the electronic structure of YBCO.[2]

Although the PPC effect in HTSC has been extensively studied, its mechanism has remained unclear. In this paper we intend to address several points which can give more information about the PPC effect in YBCO. We will present results of measurements of (a) the temperature dependence of the PPC effect for YBCO films on both sides of the MIT for white light and for different spectral regions of visible light; and (b) the spectral dependence of the PPC effect for both semiconducting and metallic (superconducting) oxygen-deficient YBCO films over a wide temperature range.

EXPERIMENTAL

Photoconductivity measurements were performed as a function of time at different fixed temperatures on oxygen-deficient c-oriented YBCO thin films on $SrTiO_3$ (sample S1) and $LaAlO_3$ (samples L1–L5) substrates. Superconducting YBCO films were prepared by pulsed laser ablation and were nominally 3000 Å (S1) and 1200 Å (L1–L5) thick with $T_c\sim88$–89 K. The oxygen content was adjusted to the desired value by controlled temperature and oxygen pressure annealing (following in general Refs. 4 and 5) with subsequent fast cooling down to room temperature. The annealing was performed in the ATS-3210 furnace specially modified for a fine tuning of gas pressure/flow. An estimation of the final oxygen content (x),[5] based on the values of c-axis parameter, obtained

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from x-ray-diffraction measurements and on T_c values for superconducting films, gives $6.35 < x < 6.75$ (hereafter we shall use the following notation of samples: sample L1, oxygen content $x = 6.35$; L2, $x = 6.45$; L3, $T_{c,\mathrm{offset}} = 30.2$ K, $x = 6.65$; L4, $T_{c,\mathrm{offset}} = 43.5$ K, $x = 6.72$; L5, $T_{c,\mathrm{offset}} = 48.8$ K, $x = 6.75$; S1, $x = 6.4$). The width of the superconducting transition ($0.9R_n - 0.1R_n$) for L3–L5 samples was $\Delta T_c \sim 3-5$K. Resistance was measured by a standard ac (LR-400 ac resistance bridge) or dc (with switching of the polarity of the current) four-probe technique. The measurements were performed in a Janis Research CCS-450 optical closed-cycle refrigerator system. A silicon diode sensor located in the vicinity of the sample was used to monitor the temperature. The samples were illuminated using a tungsten-quartz-halogen lamp (the light intensity on the surface of the sample was about 15 mW/cm^2 for "white light" measurements). Oriel Corporation interference filters (bandwidth 10 nm, range 400–1200 nm) were used for the spectral measurements (intensity on the surface of the sample was 0.2–2 mW/cm^2). A procedure of *in situ* heating of the film up to 375 K and "annealing" at this temperature for 10–15 min was used to return samples to the "initial" state after each illumination. This procedure, being repeated several times, caused a slight shift of the $R(T)$ curve to the higher R values (a similar phenomenon was observed in Ref. 3). However, this shift does not affect the relative changes of resistance during illumination.

Test measurements on a fully oxygenated YBCO film were carried out in order to estimate the contribution of sample heating during illumination to the measured quantities. A characteristic thermal time constant appears to be $\tau \sim 3-5$ min. All our results for a short-time ($t \sim 30$ min) illumination presented below are therefore based on the experimental data for $t > 10$ min to minimize any temperature drift contribution to the measured effect.

For short-time illumination with the light intensities mentioned above, resistance vs time curves were close to linear and the derivatives

$$\eta = \mathrm{abs}\{(1/I)d(\ln R)/dt|_T\} , \quad \text{for white light illumination} \tag{1a}$$

and

$$\eta_\lambda = \mathrm{abs}\{(E_{\mathrm{ph}}/I)d(\ln R)/dt|_T\} , \quad \text{for a given light wavelength} \tag{1b}$$

(where I is light intensity, E_{ph}, photon energy, R, resistance, t, time, and T, temperature) were taken as a measure of the efficiency of the initiation of PPC state in the film (for η and η_λ we shall use, hereafter, the term "efficiency").

Test measurements of efficiency for different light intensities (white light, $I = 15-0.15$ mW/cm^2) were carried out for sample L2. Efficiency was independent of intensity. This result indicates an absence of substantial nonlinear effects in the PPC phenomenon for given intensity range.

RESULTS

All six samples studied in this work demonstrate the PPC effect: exposure to light brings them to a metastable state with the resistivity lower than in the initial state and raises T_c in the case of superconducting samples (Fig. 1).

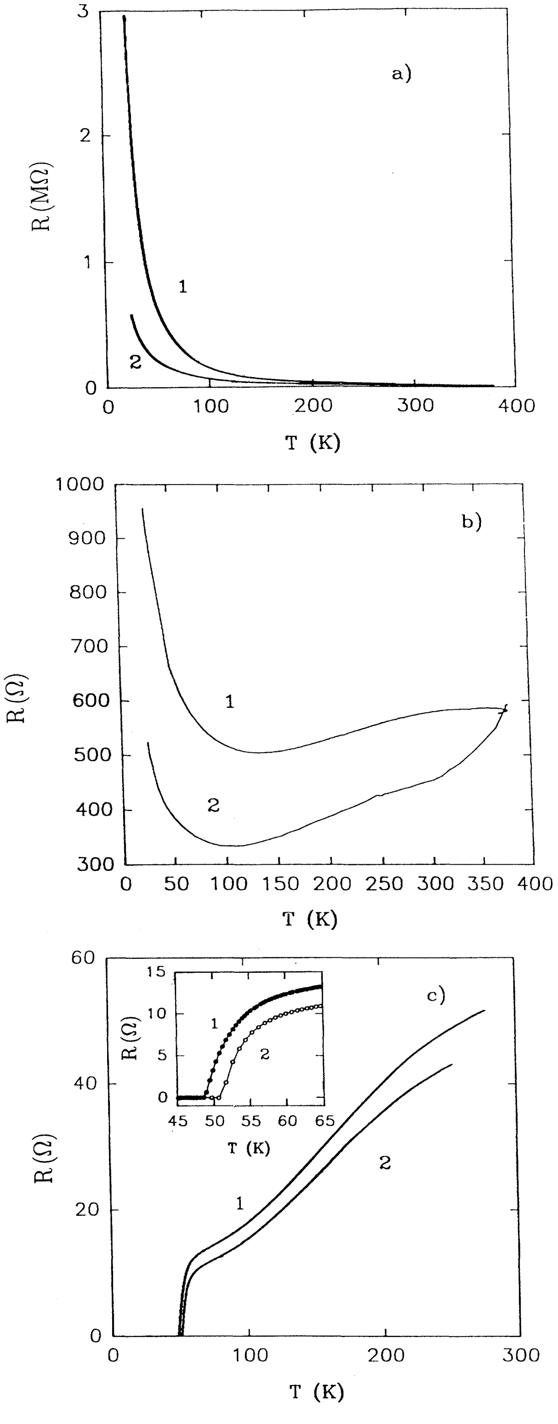

FIG. 1. $R(T)$ dependencies before (1) and after (2) illumination at $T = 250$ K. (a) Sample L1, (b) sample L2, (c) sample L5, inset: shift of superconducting transition.

The width of the superconducting transition does not change during illumination. The change of T_c caused by illumination is proportional to the change of resistivity (Fig. 2, inset), and both of them saturate after a long illumination time (Fig. 2).

The resistance of the films decreases during illumination. Experimental results can be well described by the empirical *fractional exponential function*,[6,7] which in the case of resistance can be written as

$$[R_0-R(t)]=(R_0-R_\infty)\exp[-(t/\tau)^{\beta}] \qquad (2)$$

where R_0 is initial resistance, R_∞, final resistance, τ, characteristic relaxation time, and β, dispersion parameter $(0<\beta<1)$. Fractional exponential behavior (2) has been observed in a wide variety of processes (decays) and for different classes of materials.[7] The current understanding of the microscopic mechanism of the PPC effect seems insufficient to unambiguously attribute Eq. (2) to the physics of the PPC effect in YBCO. However, it serves as a good approximation with enough adjustable parameters.

The temperature dependence of efficiency $\eta(T)$ for white light illumination (Fig. 3) shows several characteristic properties for the samples in an insulating phase (L1, L2, S1): (1) $\eta(T)$ dependence turns flat and then decreases for temperatures $T>260$ K; (2) efficiency decreases with the increase of oxygen content; (3) efficiency η has a pronounced minimum at temperatures around 200–220 K.

As it was shown in Ref. 2 the relaxation of PPC becomes significant and increases with temperature for $T>270$ K. It means that during illumination at temperatures higher than ~ 270 K we have a competition of two opposite effects: initiation of PPC and its relaxation. The total effect of these two processes results in observed $\eta(T)$ behavior for $T>260$ K.

However, for metallic samples together with a decrease of efficiency in the samples with higher oxygen content, a "flattening" of the low-temperature ($T<200$ K) part of $\eta(T)$ was observed.

It has been previously shown that efficiency is wavelength dependent.[2] We have thus studied the temperature dependence of efficiency $\eta_\lambda(T)$ for the wavelengths which correspond to maxima and minima in the $\eta_\lambda(E_{\rm ph})$. Several examples of $\eta_\lambda(T)$ curves are shown in Fig. 4.

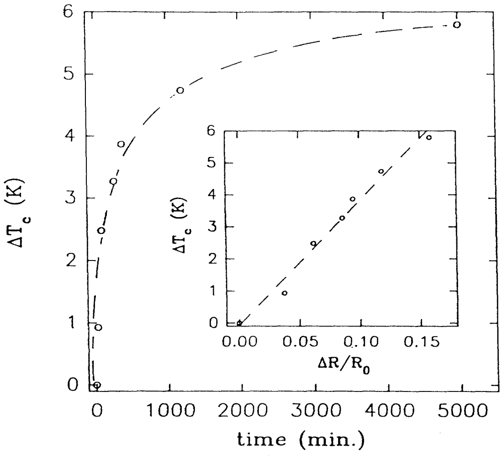

FIG. 2. Change of T_c caused by illumination (sample L4) (the line is a guide for the eye). Inset: correlation between the change of T_c and relative change of normal-state resistance (at $T=250$ K).

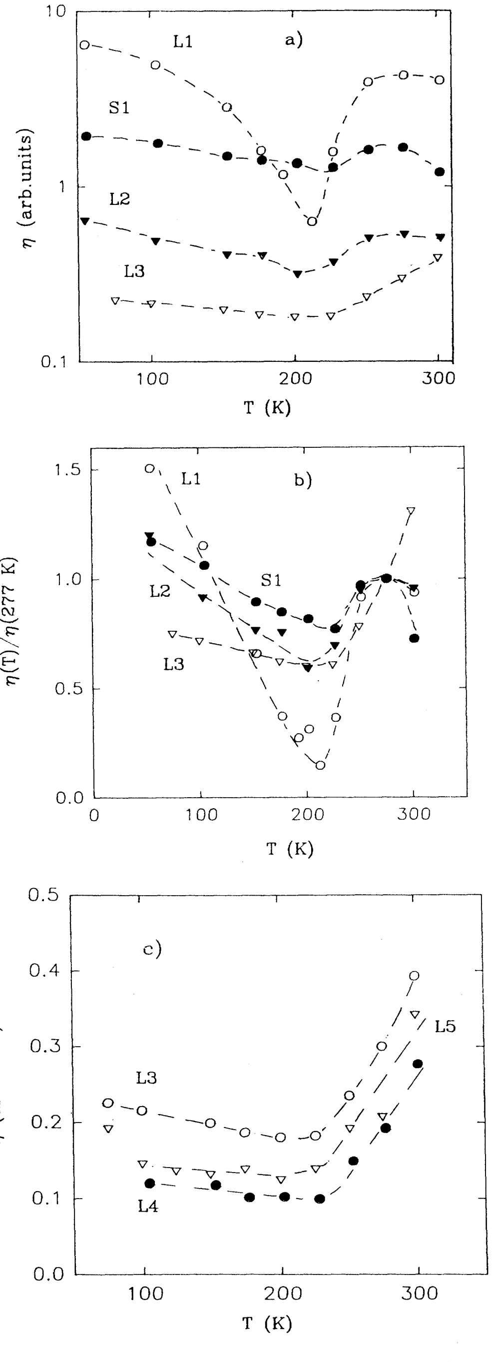

FIG. 3. Temperature dependence of efficiency (white light illumination). (a) Samples L1–L3 and S1 (b) the same as (a), normalized to efficiency at 277 K, (c) samples L3–L5. Lines are guides for the eye.

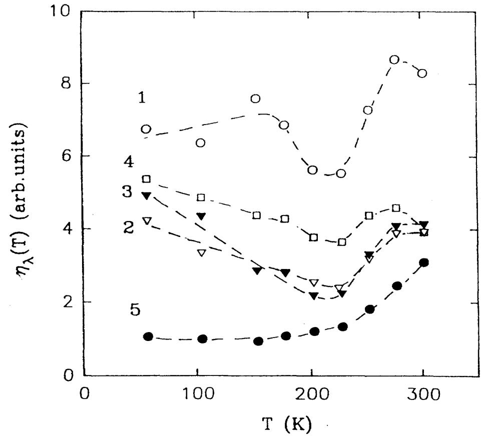

FIG. 4. Temperature dependence of efficiency for different parts of spectrum. 1, for peak 1 [see notation in Fig. 5(c)]; 2, for peak 2; 3, for peak 3; 4, for peaks 4+5 (unresolved); 5, for minimum. Lines are guides for the eye.

For every given sample the $\eta_\lambda(T)$ curves corresponding to the different maxima in $\eta_\lambda(E_{\rm ph})$ have qualitatively similar behavior, the shape of $\eta_\lambda(T)$ being close to that of $\eta(T)$ for white light illumination; the temperature dependencies for minima in $\eta_\lambda(E_{\rm ph})$ are more "shallow" and the absolute values of the efficiencies are smaller than in the case of the maxima.

Spectral dependencies of efficiency η_λ at 277 K for different samples are presented in Figs. 5(a) and 5(b). The positions of the maxima in $\eta_\lambda(E_{\rm ph})$ are consistent with the position of Lorentzian peaks in Ref. 2 [Fig. 5(c)]. Peaks 2 and 3 are better resolved in our measurements, however, the "density of points" in our spectral dependencies is not sufficient to distinguish between peaks 4 and 5. A difference in relative amplitudes of the peaks 1 and (4+5) (unresolved) of our data and the data of Ref. 2 could be caused not only by the films themselves, but also by the procedure of measurement: our annealing to the initial state after every measurement differs from the continuous measurements of Ref. 2. Oxygen content x does not affect noticeably the positions of the maxima in $\eta_\lambda(E_{\rm ph})$ at 277 K [Figs. 5(a) and 5(b)]. In general, only the absolute value of efficiency is sensitive to the oxygen content: it decreases with an increase of x, following the trend observed in Refs. 2 and 3 for white light illumination.

Spectral dependencies $\eta_\lambda(E_{\rm ph})$ for several samples measured at different temperatures are shown in Figs. 6(a)–6(c). The positions of the maxima are essentially temperature independent (with the exception of peak 3, which shows a trend to shift to higher photon energy with decreasing temperature). Additionally, the relative heights of peaks 2 and 3 change noticeably in the temperature range 100–270 K.

DISCUSSION

The effect of enhancement of the superconducting transition temperature by illumination has been seen in low-temperature granular superconductors, such as CdS-In films[8] and In-doped $Pb_{1-x}Sn_xTe$ films with Pb inclusions.[9] This effect was understood by considering that the coherence length of superconductivity in a semiconducting region is extended by the photoinduced carriers.

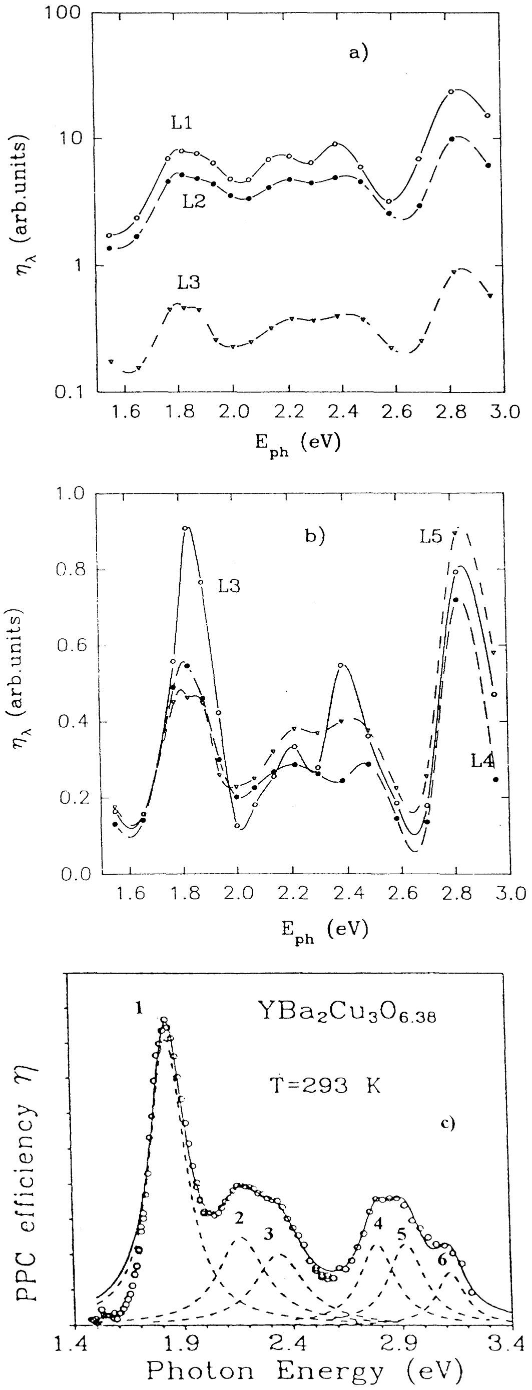

FIG. 5. Spectral dependence of efficiency at 277 K. (a) Samples L1–L3, (b) samples L3–L5 (lines are guides for eye), (c) Lorentzian fitting and notation of the peaks (figure was taken from Ref. 2).

However, in the case of granular superconductors, exposure to light causes a decrease of the width of the superconducting transition without an accompanying change in its onset.[8,9] Both in Ref. 3 and in the present work, a clear parallel shift of the superconducting transition without changes in its width was observed. This significant difference can probably rule out the enhancement of the Josephson effect in grain boundaries as a possible mechanism of the PPC effect in YBCO.

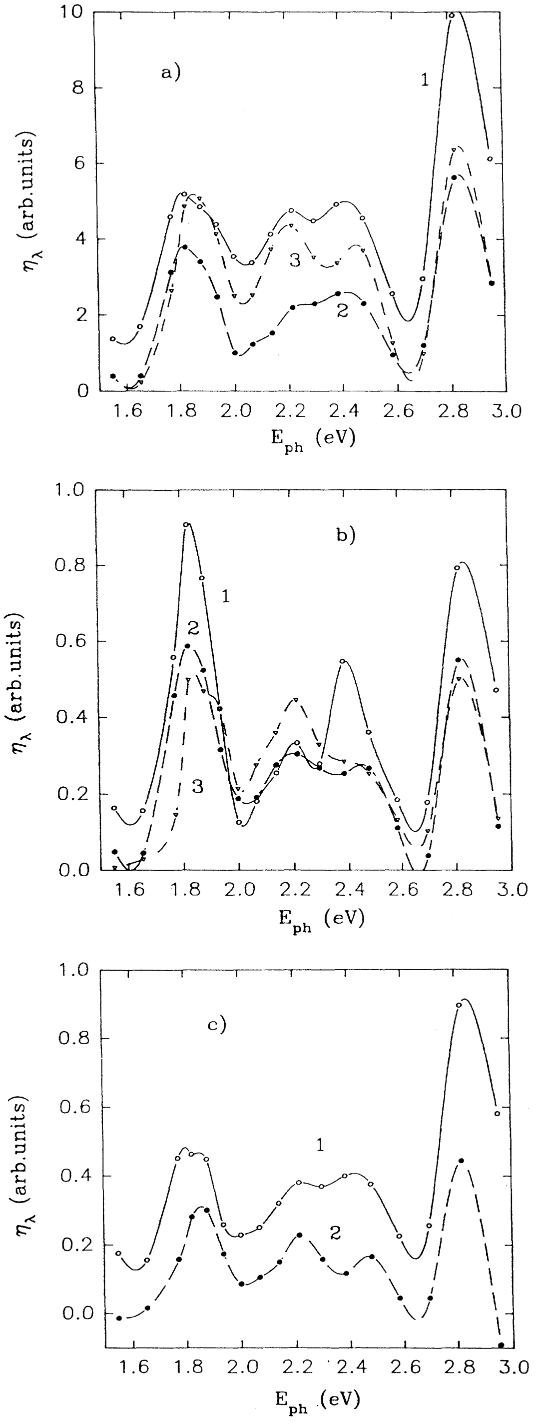

FIG. 6. Examples of spectral dependencies of efficiency at different temperatures. (a) sample L2: 1, 277 K; 2, 200 K; 3, 100 K; (b) sample L3: 1, 277 K; 2, 200 K, 3, 100 K; (c) sample L5: 1, 277 K; 2, 100 K. Lines are guides for the eye.

The concept of electronic phase separation in HTSC (Ref. 10) was used in Ref. 1 to explain the results of measurements of transient photoconductivity in YBCO in an insulating state. The signature of the superconducting transition [a kink in the $R(T)$ curve] in these measurements appears directly at $T \sim 90$ K (which corresponds to the optimum carrier concentration for YBCO) without anomalies at lower temperatures. The signature also becomes more pronounced at higher photoexcitation levels without any shift in temperature. In contrast to this, in the case of the PPC effect in the metallic state, T_c increases from some intermediate value [$T_{c0} < 50$ K, (Ref. 3 and this work)] and saturates at temperatures still substantially lower than 90 K (Fig. 2). In addition, a kink in the $R(T)$) curve, induced by illumination of an insulating film close to the MIT, appears in the long illumination time experiment at some temperature, substantially lower than optimum.[2] The temperature of this kink (which is considered as an onset of induced superconductivity) increases with increase of the illumination dose. These substantial differences lead to elimination of electronic phase separation as a causative mechanism of the PPC effect.

The most reasonable model to explain the PPC effect in YBCO is probably the photoinduced charge-transfer mechanism:[2,3] exposure to light creates electron-hole pairs, with a certain probability that electrons transfer to CuO (chain) layers, where they are trapped; the holes remain and increase the carrier density in the CuO_2 plane, which causes the decrease of resistivity and the increase of T_c.

In the present work, anomalies in $\eta_\lambda(T)$ dependencies, observed for the wavelengths corresponding to the different maxima in $\eta_\lambda(E_{ph})$ (i.e., following the interpretation in Ref. 2, to the different transitions to upper Hubbard sublevel formed by $3d_{x^2-y^2}$ orbitals of Cu^{2+} atoms in CuO_2 planes), all have a similar shape. There is additionally no qualitative change of the spectral dependence $\eta_\lambda(E_{ph})$ with a change of temperature from 100 to 277 K. We consider these to be an indication of the fact that the physical phenomena that cause the anomalies, are related to the state of the system of CuO_2 planes and CuO chains as a whole, and not to one particular transition.

The decrease of the efficiency with the increase of the oxygen content is in qualitative agreement with the charge-transfer model: the number of vacancies in Cu-O chains where the electron from the photoexcited weakly coupled electron-hole pair could be trapped decreases with the increase of the oxygen content. (However, it is possible to consider one more additional reason for S1 film to have smaller changes during illumination: its thickness is ~ 3000 Å and the penetration depth of visible light in the HTSC sample is about 2000 Å.[11] It means that in this case probably not the whole volume of the film is participating in the PPC effect.)

The minimum in $\eta(T)$ behavior was observed for films deposited on two different substrates and with different oxygen content. This allows us to rule out the effect of the substrate as a reason for the anomaly. The characteristic temperature of the minimum in $\eta(T)$ is far from the temperature of the "annealing of PPC" ($T_{\mathrm{ann}} > 270$ K), so these two effects are, also, not related.

Many experimental observations (measurements of elasticity, specific heat, neutron and x-ray diffraction, Raman, thermal expansion, piezoresistance, etc.) have pointed out the existence of anomalies in the physical properties of YBCO in the vicinity of 220 K;[12] attempts were made to correlate these anomalies with some kind of phase transition (order-disorder type). Recent calculations of the x-T phase diagram of the oxygen ordering at low temperatures[13,14] suggest an existence of a cell-triplicated O_{III} orthorhombic phase in addition to the well-established O_{I} and O_{II} (cell-duplicated) phases. (The results of electron microscopy studies in Ref. 15 may be considered as an experimental evidence of the existence of the O_{III} phase.)

The anomaly in the temperature dependence of efficiency may possibly be interpreted as an indication of a phase boundary in the oxygen concentration–temperature phase diagram. However, it is necessary to consider two different phase boundaries which exist on the phase diagram in Ref. 14: between the cell-duplicated (O_{II}) and a mixture of cell-duplicated and cell-triplicated ($O_{\mathrm{II}} + O_{\mathrm{III}}$) for the samples in the insulating state and between O_{I} or O_{III} and a mixture ($O_{\mathrm{I}} + O_{\mathrm{III}}$) for the samples in the metallic state.

The positions of the maxima and the relative intensity of the peaks in our measurements are similar for different temperatures and for samples with different oxygen contents. A purely electronic origin of the transitions may be the reason for an absence of strong temperature dependence in the position of the peaks.[2]

The peak at $E_{\mathrm{ph}} \sim 1.8$ eV (peak 1) is widely recognized[1,2] as being due to a charge-transfer transition between the $2p_{x,y}$ level of in-plane O^{2-} into the $3d_{x^2-x^2}$ upper Hubbard sublevel of Cu^{2+}. In other spectroscopic experiments, this peak was observable only in the semiconducting state of YBCO and not in the metallic state.[16] However, careful examination of recent results of measurements of optical conductivity[17] shows traces of this peak (together with the traces of other peaks, which exist in the semiconducting phase) even in samples with the oxygen content $x = 6.9$, although smeared by the presence of a significant background. Thus, our results for measurements of the spectral dependence of efficiency $\eta_\lambda(E_{\mathrm{ph}})$ are not at odds with optical measurements of Ref. 17 and our measurements have an advantage of being more sensitive because of practically the absence of background.

As discussed in Ref. 18, the electronic state of Cu^2 in the CuO_2 plane remains unchanged with hole doping, however, additional holes arise in the $2p_{x,y}$ level of in-plane O^{2-}. This may be an origin for the similar $\eta_\lambda(E_{\mathrm{ph}})$ dependencies for differing oxygen contents x. The decrease of the absolute value of efficiency with an increase in x is probably due to the decrease of the number of oxygen vacancies in the CuO chains. These vacancies should serve as traps for electrons in photogenerated electron-hole pairs in the photoinduced charge-transfer mechanism of the PPC effect.[2,3]

CONCLUSIONS

A photoinduced and persistent decrease of resistivity along with an increase of T_c (in superconducting samples) were observed in oxygen-deficient YBCO thin films with the oxygen content $6.35 < x < 6.75$. Temperature and spectral dependencies of efficiency of the PPC effect were measured on both sides of the MIT. The absolute value of efficiency decreases with an increase of oxygen content x, but the spectral dependence does not change qualitatively with a change of x. Temperature dependencies of efficiency have an anomaly at $T \sim 220$ K, which exists in all samples under consideration and correlates with anomalies observed by other experimental techniques. This anomaly relates to the system of CuO_2 planes and CuO chains as a whole and is probably an indication of phase boundaries on the oxygen concentration–temperature phase diagram. Qualitatively similar temperature and spectral dependencies of efficiency for samples in insulating and metallic phases may be considered as manifestations of the same originating mechanism of the PPC effect for YBCO on both sides of the MIT.

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