

# SPECTROSCOPY OF THE IRRADIATED YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> SUPERCONDUCTORS

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*(Received January 4, 1993; revised version June 29, 1993)*

Complex investigations of the photoinduced changes in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> single crystals were performed. As laser sources the low-power He-Ne, He-Cd, He-Se, N<sub>2</sub> lasers and YAG:Nd, XeCl pulsed lasers were used. For the investigations the crystalline samples both in super- and semiconducting phases were chosen. A considerably strong dependence of a defectiveness parameter  $x$  on the laser power, wavelength and external conditions was observed. The oxygen parameter  $x$  shows a tendency to increase for the initially semiconducting phase and to decrease for superconductors. The most interesting results were obtained using XeCl excimer laser, where corresponding changes were observed only under applied hydrostatic pressure (up to 200 MPa) in oxygen atmosphere. In all the cases the penetration depth of the new induced superconducting phase was within 5.5–6.5  $\mu\text{m}$ .

PACS numbers: 74.10.+v

## 1. Introduction

Since the discovery of high- $T_c$  superconductors only few experiments have been done on the photostimulated effects [1–4]. Therefore very little is known about the mechanism of photoinduced changes in high- $T_c$  superconductors. On the other hand, photoinduced changes can be used for creation of finely dispersed defects which form the pinning centers of the magnetic flux in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> materials.

Recently some reports have appeared which are devoted to the measurement of the transient photoinduced conductivity in high- $T_c$  superconductors at different light levels [5–9]. Photodoping in high- $T_c$  crystals and films was clearly shown. A phase separation and metallic-droplet formation subsequent to photoexcitation with disconnected superconducting regions was revealed. Photodoping tends to increase the free electron concentration at fixed  $x$  and the Fermi level is moved through the mobility edge.

In this report we have presented our experimental investigations of the photoinduced phenomena caused by laser sources at different light power, wavelength and irradiation time in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> single crystals. The investigations were performed for both the initially semiconducting and superconducting phases.

## 2. Experimental

For growth of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  samples the flux technique was employed.  $\text{BaCO}_3$  and  $\text{CuO}$  in molar ratio 6:17 were used as flux materials. The mixture of flux and Y-Ba-Cu-O compound in weight ratio of 3.5:1 was melted at 1290 K and slowly cooled to 1095 K at rates 2–4 K/hour employing vertical furnace couple with a programmed controller. The size of crystal surface was  $2 \times 2 \text{ mm}^2$ . The parameter  $x$  was checked employing X-ray diffraction technique. Superconducting behaviour was estimated also using resistance-temperature measurement. The samples were placed in the thermoregulated helium cryostat. They were irradiated using different laser sources. Critical current was measured by the standard four-probe method.

Optical spectra, including the Raman, IR- and visible reflection spectra were measured simultaneously. The Raman spectra were obtained using Ar lasers. Reflection spectra were measured by spectrophotometers Specord-M40 and SF-26.

To check the surface structure changes the method of the X-ray photoelectron spectroscopy (XPS) was used. XPS measurements were performed on a Perkin Elmer Phi ESCA 5000 with pass energies at 17.7, 8.96 eV Mg X-rays. Sputter depth profiling using three-point differentiation and peak-to-peak measurements was conducted simultaneously on a Perkin Elmer Phi 660 Scanning Auger electron multiprobe (SAM) with the electron beam energy 9.6 keV.

## 3. Results and discussion

Figure 1 represents the change of the parameter  $x$  as a function of irradiation time. All measurements were performed in oxygen atmosphere under hydrostatic pressure because there were no significant effects in normal conditions. It can be seen that  $x$  has a tendency (Fig. 1a) to saturation both for the initially semi- and superconducting specimens (Fig. 1b). But in the first case the parameter  $x$  reached its maxima after 12–15 minutes of irradiation. The reversible processes occurred very slowly. The change of  $x$  which appeared after the irradiation was

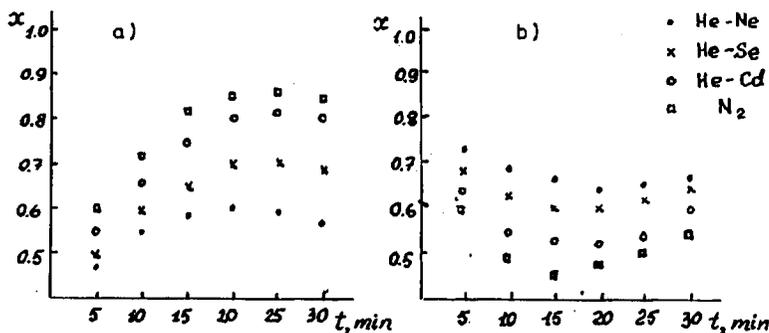


Fig. 1. The change of the parameter  $x$  as a function of the irradiation time (a) for the sample in initial semiconducting phase, (b) in initial superconducting phase.

observed only in the vicinity of sample surface ( $5-8 \mu\text{m}$ ). The small depth of this layer complicated its investigations. The measurements of critical current demonstrated the absence of significant effects. From Fig. 1 one can see that with the decrease in wavelength the corresponding changes are greater. In the case of the initial superconducting phase, essential changes are observed also without oxygen atmosphere. The temperature of the illuminated samples was unchanged because they were placed in liquid helium medium ( $T = 4.2 \text{ K}$ ).

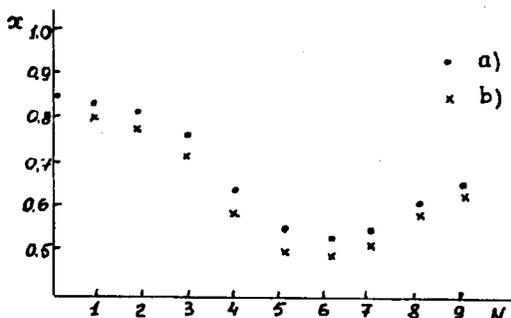


Fig. 2. The dependence of the parameter  $x$  on the number of laser pulses  $N$ : a) for the YAG:Nd laser, b) for the XeCl excimer laser in the case of starting superconducting phase.

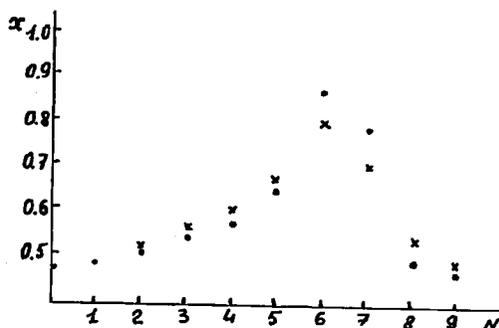


Fig. 3. The same as in Fig. 2 in the case of starting semiconducting phase.

Quite different features were observed under the influence of pulsed lasers. Figure 2 shows the dependence of the parameter  $x$  on the number of pulses of YAG:Nd (power density  $70-75 \text{ W/cm}^2$ ,  $\lambda = 1.06 \mu\text{m}$ ) and XeCl excimer laser (power density  $80-85 \text{ W/cm}^2$ ,  $\lambda = 308 \text{ nm}$ ). All the measurements were performed in oxygen atmosphere under the hydrostatic pressure near 20 kbar.

In Fig. 3 the corresponding dependence for the semiconducting samples is plotted. As in the previous case one can clearly see the saturation of  $x$  after the irradiation with 5-7 pulses. Afterwards, the parameters  $x$  has a tendency to a sharp decrease. This testifies to the possibility of operation by high- $T_c$  parameters.

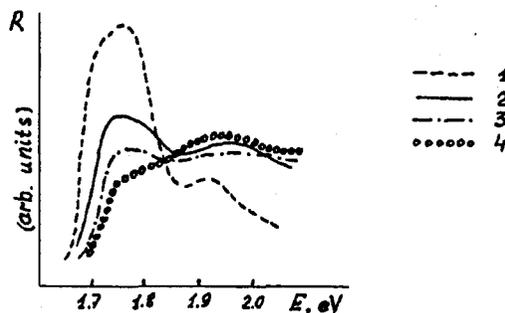


Fig. 4. Fragment of reflection spectra as a function of pulses for XeCl-laser irradiation: 1 — before irradiation; 2 — after 3; 3 — 5; 4 — 7 laser pulses.

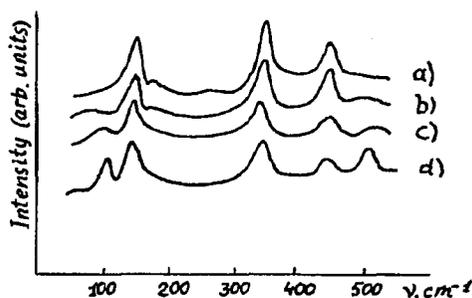


Fig. 5. The changes in the Raman spectra under influence of the XeCl-laser irradiation: a) before the irradiation, b) duration of irradiation 2 hours, c) 4 hours, d) 8 hours.

In Fig. 4 the reflection  $R(\lambda)$  spectra as a function of the number of laser pulses  $N$  are plotted. The measurements were performed in the vicinity of excitonic resonances ( $E = 1.77$  eV), which are sensitive to oxygen deficiency [4]. The increase in  $N$  tends to the decrease in excitonic maxima, e.g. to the appearance of superconducting phase.

For more detailed investigation of their origin, analogous study using the Raman spectra for different scattering geometry was performed. These spectra are very similar. Therefore we consider only  $Z(XX)Z$  geometry. From Fig. 5 one can note that the peaks at  $115$  and  $405$   $\text{cm}^{-1}$  are the most sensitive to irradiation in the superconducting phase. Using group theory, these peaks can be assigned to the translational vibrations Cu(2) (or Ba) and symmetric Cu(1)–O(2) stretching ones, respectively. With the increase in the parameter  $x$  under the XeCl-laser irradiation, the marked peaks increase.

Besides, our results indicate that more oxygen vacancies are produced along Cu(1)–O(1) chain and the Cu(1)–O(1) bonds are partly broken by irradiation. A reasonable explanation for the change in the Raman spectra is that the bond of Cu(1)–O(1) may be partly broken through the electron produced by laser light

illumination. On the other hand, the breaking bonds are so dispersed that they may play the role of pinning centers. Some evidence was also shown that illumination might cause an increase in electrical resistivity of weak bonds which will lead a decrease in the critical current  $I_c$ .

When we used the nonlaser sources, particularly the mercury vapour lamp, the corresponding changes were negligible. It is interesting that we did not observe any photostimulated changes in Y-Ba-Cu-O single crystals at room temperature. The most convenient mechanism is the one based on breaking of the Cu-O chemical bonds which tends to the appearance of great amounts of additional free carriers. Thermally induced changes were weaker.

To explain the obtained results one can use a theoretical approach proposed in [10, 11]. It was shown that the hole mobility is inhibited by the phase-separated droplets. This approach was based on a two-dimensional antiferromagnetical approach. Dilute holes are unstable during phase separation into a hole-rich phase and a pure antiferromagnetic insulating phase. Moreover, it was argued that dynamic phase separation (fluctuations in the carrier density at intermediate scales) can lead to BCS pairing. This causes a diffusion-limited carrier mobility and thereby the photoconductance. The competition between this effect and charge-carrier recombination results in the photocurrent peak observed in [5-9].

XPS checking of irradiated and nonirradiated sample surfaces showed relative changes in Ba and Cu concentrations for various conditions of laser irradiation.

The concentration profiles of Cu, Ba, Y, and O were measured as a function of distance from the surface obtained both by XPS and SAM measurements (Fig. 6).

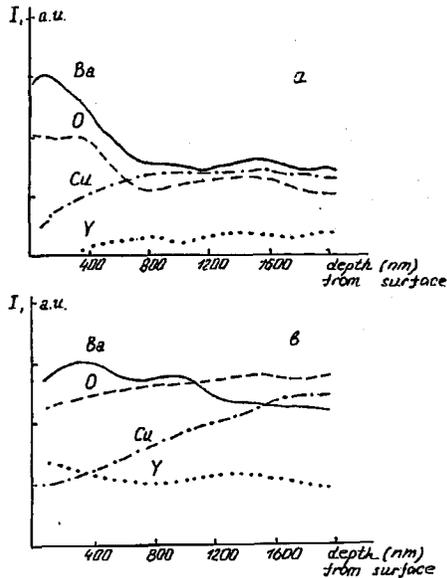


Fig. 6. Depth profile of  $YBa_2Cu_3O_x$  (a) before the irradiation, (b) after XeCl-laser irradiation.

Different behaviour of the chemical element concentration before and after XeCl-laser irradiation was clearly shown. Analogous behaviour was observed also for the surfaces under other laser sources irradiation. It is necessary to note that the width of the corresponding transitions is not smaller than 4–5 K, which is twice greater than for the starting superconducting specimens.

#### 4. Conclusions

The performed investigations indicate the possibility of operation by high- $T_c$  parameters using different kinds of lasers. Besides the application aspects, the obtained results can be important for better understanding of superconducting features, including its origin.

From the obtained results it is clear that the high- $T_c$  parameters can be changed in desirable directions. But it is difficult to build up the final picture of the observed phenomena. This requires performing of the additional experimental and theoretical work and will be the goal of the special report.

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