Scientific Session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (25 March 1992)

Usp. Fiz. Nauk **162**, 183–188 (August 1992)

V. I. Kudinov and N. M. Kreĭnes. *Metastable photoinduced superconductivity in* $YBa_2Cu_3O_{6.4}$ *films near the semiconductor–metal transition.*

It is well known that the phenomenon of high-temperature superconductivity appears when initially semiconductor metal-oxide compounds are doped. Superconductivity appears in the immediate vicinity of the metal-insulator transition. The phenomenon of photoconductivity, i.e., excitation of free carriers into the conduction band by light, can be considered as an alternative method for doping semiconductors, which does not involve a change in their chemical composition.[1–5] Recently,[1,2] *frozen photoconductivity* (FPC) was discovered in $YBa_2Cu_3O_{6.4}$ semiconductor films near the transition into the metallic phase: Under irradiation with visible light the resistance of the films dropped and the metallic properties were enhanced. Relaxation of FPC at temperatures $T < 270$ K was not observed. This phenomenon was explained by *photodoping*—the generation of additional mobile holes in conducting CuO_2 planes by light.

In this report the experimental investigations in which it is shown that irradiation of $YBa_2Cu_3O_{6.4}$ semiconductor films not only can enhance the metallic properties but it can also induce growth of a superconducting phase at low temperatures (the phenomenon of *photoinduced superconductivity*) are reviewed.

The initial material for preparing the experimental samples consisted of $YBa_2Cu_3O_7$ superconducting films ($T_c = 91$ K), prepared by the method of laser deposition on a $SrTiO_3$ substrate. The oxygen concentration in the films was reduced to 6.4 by low-temperature vacuum annealing of the initial samples for 6–8 h at 320 °C; this corresponded to a semiconductor-metal transition. After annealing, the superconducting transition in the film was completely suppressed, and the resistance of the film increased monotonically with decreasing temperature (curve *1* in Fig. 1). The annealed films were then irradiated with different doses of visible light using different lasers: argon, krypton, or helium-neon. The transport, magnetic, and relaxation properties of the irradiated samples were investigated in a wide range of temperatures.[1–7]

The study of the influence of irradiation on the transport properties of the annealed films led to the discovery of the following effects. Under the action of irradiation at temperatures $T < 270$ K the resistance of the samples drops significantly with time (or with increasing irradiation dose). At 77 K the decrease in the resistance for high irradiation doses reaches 30–40% at saturation. At the temperature of liquid helium (where the superconducting phase can, in principle, appear in the sample) the resistance of the film drops by at least four to five orders of magnitude and becomes less than the measurable limit ($R < 0.05\ \Omega/\square$). After the illumination is switched off, the new value of the resistance at any time remains (at the same temperature) without any indications of relaxation, i.e., the phenomenon of FPC is observed.[1–5]

The virtually complete absence of relaxation of the photoinduced increment to the conductivity at temperatures $T < 270$ K made it possible to conduct a series of measurements of the temperature dependences of the resistance with increasing total irradiation dose, after which the light was switched off and the temperature dependence of the resistance was measured. The R as a function of T curves were completely reproduced at temperatures $T < 270$ K. These measurements (Fig. 1) indicate unequivocally that as the irradiation dose increases the semiconductor increase of the film resistance at low temperatures is suppressed. Moreover, at some critical irradiation dose a section of decreasing resistance, indicating the appearance of small isolated nuclei of the superconducting phase, appears on the curves $R(T)$ below 20 K. For high irradiation doses the resistance drop becomes more significant and starts at higher temperatures. Prolonged irradiation causes the resistance of the film at $T < 5$ K to drop to zero, indicating the appearance of volume superconductivity in the sample. At the same time, the current-voltage characteristic of the film becomes significantly

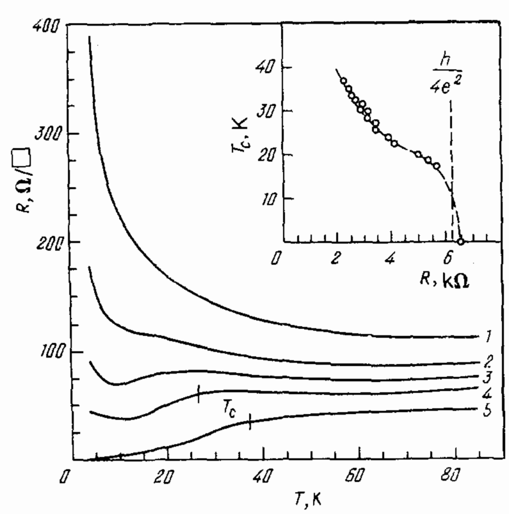

FIG. 1. Temperature dependences of the resistance of a $YBa_2Cu_3O_{6.4}$ film after irradiation with an argon laser with total absorbed photon dose Q (photons/cm^2) $= 0$ (*1*), $4.8\cdot10^{21}$ (*2*), $1.4\cdot10^{22}$ (*3*), $1.8\cdot10^{22}$ (*4*), and $5\cdot10^{23}$ (*5*). Inset: Onset of the superconducting transition T_c as a function of the resistance of the film in the normal state with $T = 60$ K, calculated per elementary layer.

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nonlinear and corresponds more to the characteristic of a system of weakly linked superconducting domains. The critical current of the observed photoinduced superconductivity can be roughly estimated as ≈ 100 Å/cm^2.[7]

The temperature shift of the superconducting transition with increasing irradiation dose can already be seen qualitatively in Fig. 1. As a quantitative measure of the increase in the onset temperature of the superconducting transition, the inset in Fig. 1 shows a plot of T_c as a function of the resistance of the film in the normal state at 60 K, calculated per layer of thickness 11.8 Å corresponding to one unit cell (per double CuO_2 layer). The maximum photoinduced-superconductivity onset temperature was 37 K. Superconductivity in the $YBa_2Cu_3O_{6.4}$ film appears at the resistance of a single CuO_2 layer close to the value $R = h/4e^2 = 6.45$ kΩ, corresponding to the localization limit for two-dimensional conducting systems. Thus changing the conductivity of the films by the method of photodoping has made it possible to check the hypothesis of localized suppression of superconductivity.[3]

In order to confirm the hypothesis that $YBa_2Cu_3O_{6.4}$ films become superconducting under irradiation and also to study the dynamics of growth of the photoinduced superconducting phase, the diamagnetic moment of the film was measured as a function of the irradiation dose (Fig. 2).[3] For low doses the diamagnetic moment remains practically unchanged. For high doses, however, a photoinduced diamagnetic moment appears in the film. The induced moment at first increases linearly with the irradiation time (dose) and approaches saturation at high doses. The maximum photoinduced diamagnetic moment under identical conditions is approximately 1% of the diamagnetic moment of the initial (from vacuum annealing) superconducting $YBa_2Cu_3O_7$ film with $T_c = 91$ K.

As noted above, relaxation of photoconductivity and of the induced diamagnetic moment is not observed at low temperature. At room temperature, however, relaxation does appear, and with time the equilibrium (existing prior to irradiation) value of the conductivity is restored in the sample.[2,4] The characteristic relaxation time, obtained from measurements of the photoconductivity, is approximately 10 h. As the temperature increases, the relaxation time decreases exponentially, and at 318 K it is less than 1 h.[4] Relaxation of photoconductivity in an illuminated film at room temperature leads to degradation: photoinduction gradually vanishes as the resistance relaxes to its equilibrium state. After the photoinduced conductivity has relaxed, the transport properties of the irradiated film are completely restored (curve *1* in Fig. 1).

The transport and magnetic data as a whole are described by the following scenario of photoinduced growth of the superconducting phase. Prior to irradiation the $YBa_2Cu_3O_{6.4}$ films are semiconductors. As a result of photoexcitation of additional mobile holes in CuO_2 planes, the conductivity of the medium increases and the semiconductor behavior is gradually replaced by metallic behavior. At high irradiation doses the free-carrier density reaches the critical value corresponding to the appearance of nuclei of the superconducting phase. As a result, a resistive transition appears on the curves $R(T)$, and the photoinduced diamagnetic moment starts to increase with the irradiation time. Further irradiation results in growth of the superconducting regions and an increase of the transition temperature T_c. Finally, the size of the superconducting domains reaches the percolation limit, at which the resistance of the sample drops to zero at a temperature below 5 K.

The phenomenon of FPC is well known in semiconductor physics.[8] It arises in systems in which the photoexcited electrons and holes are, for some reason, separated by an energy barrier that prevents their relaxation. Up to now, however, the FPC phenomenon has been observed in very weakly doped semiconductors. The discovery of the FPC effect in the compound $YBa_2Cu_3O_{6.4}$, which, according to its conducting properties, is more like a semimetal than a semiconductor (the resistivity of the films studied $\rho \sim 10^{-3}$ $\Omega \cdot$cm), was extremely unexpected. Such unique behavior is evidently connected with the characteristics of the crystal structure of the compounds $YBa_2Cu_3O_{6+x}$ and the two-dimensional character of conduction in it.

The most likely explanation of the FPC effect in $YBa_2Cu_3O_{6+x}$ films, which explains all experimental data, is the mechanism of *photoinduced charge transfer*—excitation by light of electrons in CuO_2 planes and transfer of the electrons in Cu–O–Cu–... chains in the CuO_x layers.

It is well known that as the oxygen content in the compound $YBa_2Cu_3O_{6+x}$ (for $x \geqslant 0.4$) increases a transition with charge transfer occurs: The electron density is "pulled" away from the CuO_2 planes toward the chains in the CuO_x layers. In the process, hole conductivity arises in the CuO_2 planes and the transport properties of the compound change from semiconductor to metallic (and at low temperatures, superconducting). In the semiconductor phase with $x \leqslant 0.4$ under equilibrium conditions the charge transfer between CuO_2 planes and chains does not occur. This process can occur, however, under the action of light. Indeed, let an absorbed photon excite in the CuO_2 planes an electron into the upper unfilled conduction band. The photoexcited electron

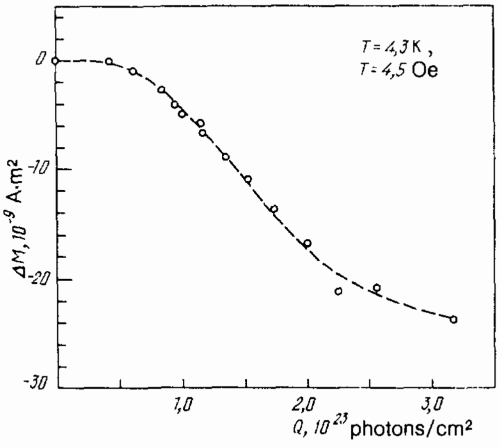

FIG. 2. Photoinduced diamagnetic moment versus the total absorbed photon dose in a $YBa_2Cu_3O_{6.4}$ film.

and hole are weakly bound with one another. With some probability the electron occupies neighboring CuO_x layers, in which for $x \leqslant 0.4$ oxygen forms with the copper ions chains of finite length Cu–O–Cu–... . The electron is then localized in CuO_x chains in unfilled electron orbitals of O^- (or Cu^{2+}) ions. The electron is then captured in a strongly localized level deep inside the energy gap and it is necessary to overcome an energy barrier of 1 eV, corresponding to the energy required to excite an electron into the upper unfilled conduction band. The photoexcited electron is thereby spatially separated from the hole. The photoexcited hole remains free and increases the total free-hole density in the CuO_2 planes. Under continuing irradiation the hole density increases and the semiconductor properties of the films gradually change into metallic properties. If prior to irradiation the free-carrier density corresponded to the onset of nucleation of the superconducting phase at low temperature, then photodoping not only increases the conductivity, but it also results in growth of the superconducting phase in the sample. At $T < 270$ K the photoexcited electron, captured on an oxygen vacancy, in practice cannot overcome the 1-eV barrier and recombines with the hole. For this reason, relaxation of photoconductivity and of the photoinduced superconductivity is not observed at these temperatures. Relaxation of photoconductivity, determined by the thermal excitation of an electron captured in unfilled levels of O^- through the barrier into the upper band, appears at room temperature.

In principle, besides the explanation considered above for the FPC effect in $YBa_2Cu_3O_{6+x}$, other microscopic mechanisms have been proposed,[7] for example, *photoinduced diffusion*, i.e., redistribution of oxygen-ion sites under the action of irradiation. It is known that the tetragonal phase of $YBa_2Cu_3O_{6+x}$ is semiconducting while the orthorhombic phase is metallic. Irradiation of $YBa_2Cu_3O_{6.4}$ films could initiate diffusion of excited oxygen ions in CuO_x layers even at low temperature, which would result in local nucleation of the orthorhombic phase. In this case, under irradiation, as the chains become longer and the number of local nuclei of the orthorhombic phase increases, the free-hole density in the conducting CuO_2 planes would also increase.

We believe that the discovery of the phenomena of frozen photoconductivity and metastable photoinduced superconductivity in $YBa_2Cu_3O_{6.4}$ films could be helpful both for investigating the mechanism of high-temperature superconductivity itself and for technical applications. Thus, the phenomenon of photoinduced superconductivity potentially carries completely new possibilities for development of superconducting devices (for example, optically tunable and controllable SQUIDs).

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Translated by M. E. Alferieff