SUBTHRESHOLD DEFECT FORMATION IN $YBa_2Cu_3O_{7-\delta}$ AT NONUNIFORM HEATING OF ELECTRON GAS IN ELECTROMAGNETIC FIELD

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Abstract

In $YBa_2Cu_3O_{7-\delta}$ high temperature superconductors with $\delta<0.3$ the irradiation by super high-frequency electromagnetic field with impulse power 10^4-10^6 W gives rise to a decrease of the rates of annihilation and capture of positrons, a growth of resistance, residual resistance, thermopower and the block of diffusive transitions of Au atoms, which are caused by the subthreshold defect formation in the intermediate layers. The irradiation effect is enhanced with rise of the number of defects in samples and does not depend on an impulse power. The defect formation is related to the excitation of low-frequency weakly damped collective excitations under irradiation, whose propagation through the crystal is accompanied by the Coulomb ejection of atoms from the lattice sites and the transformation and transport of defects.

Introduction

In high temperature superconductors the plasmon mechanism of superconductivity may be realized at presence of the low-frequency collective excitations [1, 2]. The subthreshold defect formation in the intermediate layers is the feature of such excitations and may indicate the exhibition of the low-frequency plasmons [3]. The low-energy subthreshold defect formation in the field of plasmons, when the energy of excitations $E \ll E_d$ and the time of atomic displacement $\tau \geq \varpi_D^{-1} \gg \tau_d$ (E_d, τ_d are the threshold energy and time of atomic displacement for the impact defect formation due to elastic collisions with particles having the overthreshold energy, ω_D is the Debye frequency) [4], is possible if the antinodes of the charge density of excitations is strongly localized on atoms and the localization time for charge antinodes on the lattice ions $\tau \leq T$ (T is the period of collective excitations) is sufficient to push out them into interstices to the distance, excluding the defect recombination, or when the frequency of excitations is

$$\Omega_{\mathbf{q}} = \mathbf{qu} \leq \omega_D \qquad (1),$$

where **q, u** are the wave vector and velocity of excitations. Since the energy of collective vibrations of the carriers in the cuprate layers (the light l-carriers), in the bands *B1* built *dp*-orbitals of Cu2, O2, O3 atoms [5, 6], is $\hbar\Omega_l$=1.3-2.8 eV [7], the plasma frequency is $\Omega_l \gg \omega_D$ ($\hbar\omega_D \approx 0.05$ eV [8]), and the subthreshold defect formation with participation of the l-carriers is improbable. In $YBa_2Cu_3O_{7-\delta}$ the energy of plasmons moving along the **c** axis is 10-40 meV [9], hence the condition for the subthreshold creation of defects is correct for such excitations. Along the **c** axis it is possible the propagation of carriers (the heavy h-carriers) localized in the band formed by *dp*-orbitals of Cu1, O1, O4 and Cu2 atoms (*B2* band). The propagation along the **c** axis of carriers localized in *B1* and *B3* band which is created by *dp*-orbitals of Cu1, O4, O1 atoms and has the vacant character is improbable [5, 6].

In normal conditions the low-frequency collective excitations are created owing to effects of the local field [1, 2], however the subthreshold defect formation is not realized due to the Landau damping of plasmons on l and h-carriers and the low number of weakly damped plasmons. To increase the number of weakly damped excitations and to enhance the subthreshold defect formation the external super high-frequency (SHF) electromagnetic field can be used. Under action of the SHF electric field $\mathbf{E} = \mathbf{E_o} \sin \varpi_o t$, when $\varpi_o << \upsilon_{h,l}$ ($\upsilon_{h,l}$ are the collision frequencies of l and h-carriers) the l and h-carriers localized in the quasi-two-dimension bands with the different dispersion laws and effective masses $m_h^* >> m_l^*$ acquire the various velocities

$$\tilde{\mathbf{v}}_{h,l}(t) = -\frac{e\mathbf{E_o}}{m_{h,l}^* \varpi_o \upsilon_{h,l}} \cos \varpi_o t \,. \qquad (2)$$

The Landau damping on the l-carriers weakens as the field amplitude and the velocities of carriers rise. When the Fermi velocities of h and l-carriers is $\tilde{\mathbf{v}}_{\mathbf{F}h}(t) << \tilde{\mathbf{v}}_{\mathbf{F}l}(t)$, the collective excitations with modes having the phase velocity

$$\tilde{\mathbf{v}}_{\mathbf{F}h}(t) << \mathbf{u} << \tilde{\mathbf{v}}_{\mathbf{F}l}(t) \qquad (3),$$

may propagate without dissipation through the crystal with creation of defects. Note that the effect of SHF irradiation can not directly give rise to the formation, transport and transformation of defects, since the quantum energy of SHF field is neglectly low in contrast to the displacement energy E_d>20 eV for Y, Ba, Cu atoms, E_d≥4.5 eV for O1, O2, O3 atoms [10-12] or their migration energy.

In the present work the subthreshold defect formation under action of SHF irradiation was investigated in $YBa_2Cu_3O_{7-\delta}$ superconductors. The investigations were performed by positron lifetime spectroscopy, X-ray structural analysis, dc resistivity, thermopower and diffusion of radioactive tracers. Positron spectroscopy was used for determination of the electron density in the intermediate layers, where in$YBa_2Cu_3O_{7-\delta}$ positrons annihilate [13]. To control the lattice parameters **a**, **b, c** and parameter η= (CO1-CO5)/(CO1+CO5), where CO1, CO5 are the concentrations of oxygen atoms in O1 and O5 sites [14], X-ray diffraction was used. The influence was studied of defect formation in the Ba-O, Cu1-O layers on dc resistivity, thermopower and diffusive transitions of gold atoms.

Samples and experimental details

The $YBa_2Cu_3O_{7-\delta}$ X-ray single-phase polycrystalline samples with δ≤ 0.3 and density 5.5 g/cm^3 were investigated. Sintered samples were prepared by solid-phase synthesis [3]. The nonstoichiometric compounds with δ>0 were obtained by annealing of samples with δ=0 in vacuum. The amount of oxygen was determined using Q-1500 derivatograph and X-ray diffraction. Samples for investigations were prepared from the same polycrystalline block.

Samples were irradiated by impulsive SHF electromagnetic emission with impulse powers P=10^6 W, frequency 3.0 GHz, duration 2.5 μs, repetition frequency 350-400 Hz and P=10^4 W, frequency 9.4 GHz, duration 2.5 μs, repetition frequency 400 Hz at room and nitrogen temperatures T_r. Samples were situated in the antinode of SHF electrical field in the reentrant resonator.

The positron lifetime annihilation spectra were measured using “ORTEC” spectrometer at room temperature. The positron annihilation rate λ_f and capture rate υ were determined from expressions

$$\lambda_f = I_1/\tau_1 + I_2/\tau_2, \quad \upsilon = I_2(1/\tau_1 - 1/\tau_2), \qquad (4)$$

where I_1, I_2 and τ_2, τ_1 are the intensities and positron lifetimes in the quasi-free and bound states.

X-ray structural analysis was done on DRON-2 and ADP-1 diffractometers. The parameter η was determined from ratio of structure amplitudes of the 102 and 012 reflections [14]. The measurements of annihilation and lattice parameters were carried out on the same samples.

Resistance was measured by four-probe method. Thermopower was measured with copper contacts when the temperature gradient on sample was 0.5-1.5 K.

The diffusion coefficient of gold atoms was measured by the layer removal method using radioactive tracers ^{195}Au. The diffusion profiles development in an air environment in the temperature interval 200-500^{o}C for 5-45 h and were determined with a step size of 3-5 μm to a depth of 150-250 μm.

Experimental results and discussions

The positron lifetimes and the lattice parameters of $YBa_2Cu_3O_{7-\delta}$ samples prior and after SHF irradiation with P=10^6 W, ω_o=3.0 GHz are listed in the Table. At 293 and 77 K the SHF irradiation gives rise to a growth of τ_1 and τ_2; moreover after irradiation the τ_2 exceeds the value 500 ps which is typical for annihilation in the large vacancy clusters or on the surface [15]. The irradiation effect is distinctly manifested in behavior of the rates of annihilation and capture of positrons (Fig. 1). The dependencies of $\lambda_f(t)$ and $\upsilon(t)$ are similar. In both compounds λ_f and υ abrupt lower after irradiation for 1 min. With rise of irradiation time the changes in λ_f and υ weaken and for t>5 min parameters are insignificantly varied.

Table. Parameters of positron annihilation, crystal lattice and vacancy clusters

Samples	T_r, K	t, min	τ_1, ps	I_1,%	τ_2, ps	I_2, %	c, Å	η	$N_+\times 10^{-15}$, cm^{-3}	r_+, Å
$YBa_2Cu_3O_7$	293	0	169±2	83±1	331±27	17±1	11.667	0.09	13	3.0
		1	195±1	97±1	540±39	3±1	11.668	0.36	2.7	3.4
		5	188±2	96±2	510±31	4±2	11.645	0.35	3.4	3.0
		30	186±2	92±1	385±31	8±1	11.645	0.05	5.5	3,2
	77	0	169±2	83±1	331±27	17±1	11.667	0.09	13	3.0
		1	184±3	91±1	360±37	9±1	11.660	0.15	6.2	3.1
		5	183±3	92±1	363±51	8±1	11.642	0.46	5.8	3.0
		10	180±2	90±2	366±24	10±2	-	-	7.0	3.2
		30	179±1	84±3	302±26	16±3	-	-	10	2.7
$YBa_2Cu_3O_{6.7}$	293	0	180±2	86±2	341±24	14±2	11.715	0.35	11	2.7
		1	197±1	97±1	593±57	3±1	11.677	0.60	2.3	3.3
		5	199±2	95±1	438±67	5±1	11.677	0.60	3.4	3.2
		30	194±2	96±1	469±47	4±1	11.705	0.44	3.6	2.9
	77	0	180±2	86±2	341±24	14±2	11.715	0.35	11	2.7
		1	196±2	96±1	491±69	4±1	11.660	0.03	3.3	2.8
		5	198±2	96±1	476±55	4±1	11.660	0.03	2.6	3.2

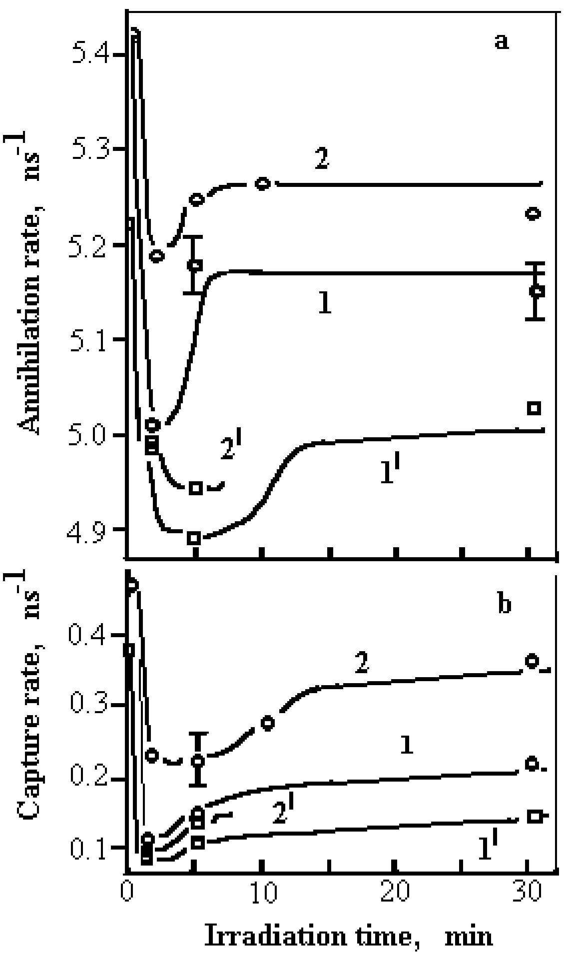

Fig. 1. The rates of annihilation (*a*) and capture (*b*) of positrons as function of SHF irradiation time with impulse power 10^6 W at 293 and 77 K in $YBa_2Cu_3O_{7-\delta}$ with δ=0 (*1, 1*^{1}) and 0.3 (*2, 2*^{1}).

Note that in $YBa_2Cu_3O_7$ irradiated samples the annihilation rate corresponds to value of λ_f in compounds with oxygen deficit $0.3 \le \delta \le 0.45$ and T_c=45-60 K [16]. However, the SHF irradiation does not change the oxygen content in $YBa_2Cu_3O_{7-\delta}$ samples, since in irradiated and unirradiated samples the curves of mass variation due to loss or absorption of oxygen upon heating are identical. Besides, in $YBa_2Cu_3O_7$ irradiated samples the reduction in T_c and transformation of resistance behavior in the R(T) run, which are typical for compounds with oxygen deficit $0.3 \le \delta \le 0.45$, are not observed. After SHF irradiation of $YBa_2Cu_3O_7$ superconductors the T_c is not shifted, though at $T_c < T \le 150$ K in the R(T) dependence a growth of resistance is revealed as T lowers (Fig. 2), which is also observed in samples with the high number of radiation defects [17]. The effect of SHF irradiation does not depend on the impulse power, while that is determined by the number of defects in samples and is enhanced as the amount of defects arises. The multiple irradiation by impulses with P=10^4 W for 5-15 min leads to the increase in T_c on 0.5-1 K without change in the run of R(T) for shot times and the reduction in T_c on about 4.5 K, broadening of superconducting transition, transformation of the R(T) run, when R rises as temperature lowers for t>30-45 min (Fig. 2, insert a). The enhancement of the SHF irradiation effect is distinctly manifested in samples with the uncompleted superconducting transition, where the single irradiation for 15 min essentially arises R in the normal state and the residual resistance at $T<T_c$, while T_c is not

shifted (Fig. 2, insert b).

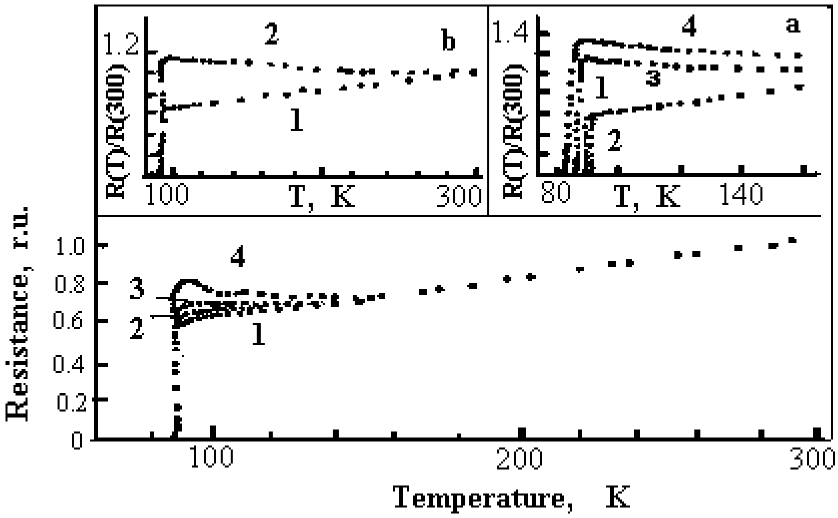

Fig. 2. Temperature dependencies of resistance in $YBa_2Cu_3O_7$ prior (*1*) and after SHF irradiation with impulse power 10^6 W for 1 (*4*), 5 (*3*), 10 (*2*) min at 77K. The insets show temperature variations in the resistance of $YBa_2Cu_3O_7$ prior (*1*) and after irradiation at 293 K with impulse power 10^4 W under multiple action (*a*) for 30 (*2*), 240 (*3*), 720 (*4*) min and single action (*b*) on samples with uncompleted superconducting transition for 15 min.

The drop in λ_f and υ accompanied by a decrease of the lattice parameter **c,** while parameters **a**=3.821Å, **b**=3.889Å for $YBa_2Cu_3O_7$ and **a**=3.828Å, **b**=3.889Å for $YBa_2Cu_3O_{6.7}$ are not varied, and the random changes of η in the interval 0.05-0.46, which corresponds to transitions of 10^{21} cm^{-3} oxygen atoms between O1 and O5 sites in the basal plane. The reduction in **c** indicates that the possible lattice defects are the metal atoms, whose exit into interstices or drains decreases the repulsion among lattice layers and may result in compression of the lattice. The displacement of oxygen atoms from O1, O5 sites is apparently caused by the subthreshold mechanism, since the energy which carriers acquire in the SHF field is essentially less than the energy of impact displacement of O1 atoms or the energy of O1→O5 migration [18].

Thus, under action of SHF irradiation the positron annihilation rate reduces when in the intermediate layers the oxygen content is constant. The reduction in λ_f may be ascribed to the formation of Ba and Cu1 defects and the exit of atoms from the annihilation volume. The annihilation rate is related to the charge density of electrons $n^-(\mathbf{r})$ and positron $n^+(\mathbf{r})$ by expression [19]

$$\lambda_f = \frac{\pi r_0^2 c}{e^2}\int d^3r\ n^+(\mathbf{r})\, n^-(\mathbf{r})\varepsilon[n^-(\mathbf{r})], \qquad (5)$$

where $n^-(\mathbf{r}) = e\sum_{\mathbf{k},l}\Psi^*_{\mathbf{k},l}(\mathbf{r})\Psi_{\mathbf{k},l}(\mathbf{r})$, $n^+(\mathbf{r}) = \sum_n \Psi^{*+}_n(\mathbf{r})\Psi^+_n(\mathbf{r})$, $\Psi_{\mathbf{k},l}(\mathbf{r})$, $\Psi_n^{\ +}(\mathbf{r})$ are the electron and positron wave functions, **k** is the wave vector ($\mathbf{k}\le\mathbf{k_F}$ is the Fermi wave vector), l, n are the band and positron numbers, r_0, c are the classical radius of electron and light speed, $\varepsilon[n^-(\mathbf{r})]$ is the enhancement factor. The electron density in intermediate layers ρ includes the density of core electrons of Cu1, Ba, O1, O5, O4 ρ_{core} atoms, the electron density in the *B2* ρ_{B2} and *B3* ρ_{B3} bands. When the carriers are strongly localized in *B2* and the *B3* band has a vacant character, we can write

$\lambda_f = \pi r_0^2 c \varepsilon \rho \approx \pi r_0^2 c \varepsilon(\rho_{core} + \rho_{B2} + \rho_{B3})$, (6)

where the enhancement factor is given [20]

$\varepsilon(r_s) = 1 + 0.1512 r_s + 2.414 r_s^{3/2} - 2.01 r_s^2 + 0.4466 r_s^{5/2} + 0.1667 r_s^3$, (7)

and ε=2.3 for $r_s=(3/4\pi\rho)^{1./3}=1$ ($\rho=1.6\times10^{24}$ cm^{-3}).

After UHF irradiation during 1-30 min the changes $\Delta\lambda_f = \lambda_f(0) - \lambda_f(t)$ are in the interval $0.18 \le \Delta\lambda_f \le 0.40$ ns^{-1}, which corresponds the reduction in the electron density $\Delta\rho \approx (1.1\text{-}2.4)\cdot10^{22}$ cm^{-3}. The $\Delta\rho$ value exceeds the density of free carriers $\rho_{B1+}\rho_{B2+}\rho_{B3} \approx 5\cdot10^{21}$ cm^{-3} [16], (ρ_{B1} is the density of carriers in the *B1* band), i.e. $\Delta\rho > \rho_{B1+}\rho_{B2+}\rho_{B3}$ and $\Delta\rho > \rho_{B2+}\rho_{B3}$. Since $\rho_{B2} \gg \rho_{B3}$, we have $\Delta\rho \approx \Delta\rho_{core}$ and

$\Delta\lambda_f = \pi r_0^2 \varepsilon \Delta\rho \approx \pi r_0^2 \varepsilon \Delta\rho_{core}$. (8)

Thus, the reduction in λ_f is caused by the exit of core electrons of atoms from annihilation process. In $YBa_2Cu_3O_{7-\delta}$ when $\delta \rightarrow 0.3$ the λ_f drops as the number of O1 vacancies arises in Cu-O1 layers. Under SHF irradiation when the oxygen content is unchanged the vacancies and interstitial atoms of Ba and Cu1 may be by defects whose electrons do not participate in annihilation. In the interstices the charge of cations repels positrons, decreases the overlap of $\Psi_{\mathbf{k},l}(\mathbf{r})$ and $\Psi_n^+(\mathbf{r})$, prevents to the annihilation with core electrons and reduces ρ.

The influence of O4, O1 interstitial defects on λ_f is improbable. The exit of O4, O1 atoms in interstices may reduce the overlap of $\Psi_{\mathbf{k},l}(\mathbf{r})$ and $\Psi_n^+(\mathbf{r})$ wave functions and λ_f magnitude. However, if the defects have a negative charge, the noninvolvement of the core electrons in annihilation is improbable. The oxygen transitions from O1 in O5 sites do not apparently affect on λ_f, since oxygen atoms remain in the annihilation volume.

The appearance of Ba and Cu1 vacancies is consistent with reduction of **c** parameter. The number of defects of Ba and Cu1 atoms $n_d \approx \Delta\rho/n_e$ can be estimated assuming that the average number of core electrons which does not participate in the annihilation is n_e=45. Then n_d equals ~$(2.4\text{-}5.3)\cdot10^{20}$ cm^{-3}. The obtained values of n_d are probably understated, since the deep core electrons of defects are not involved in the annihilation. However, the subthreshold mechanism of defect formation is evident, since the displacement energy of Ba and Cu1 atoms from the lattice sites is 20-25 eV that excludes the defect formation directly under action of SHF irradiation. Besides, the ejection of atoms is caused by the collective excitations of h-holes, because the SHF irradiation cannot create the long-lived holes on the deep levels of atoms, in whose field the defect formation may take place, due to the low energy of quantum. Note that the subthreshold defect formation is not apparently realized in the cuprate layers, where the modulate field of collective excitations of h-carriers is screened by the l-carriers.

The lifetime of positrons captured by defects essentially exceeds the values τ_2=160-280 ps, which characterize the positron annihilation with the single defects or Cu1-O1 bivacancies in $YBa_2Cu_3O_{7-\delta}$ [21], and indicates that the vacancy clusters are the positron traps. The $\upsilon(t)$ behavior shows that transformation of clusters takes simultaneously place with formation of the single defects. Since the capture rate [22]

$$\upsilon = 4\pi r_+ D_+ \int_r^\infty R P_+(R)\,dR \approx 4\pi r_+ D_+ N_+, \quad (9)$$

where r_+ , $N_+ = \int_r^\infty P_+(R)\,dR$ are the radius and concentration of vacancy clusters, $P_+(R)$ is the function of defect distribution in radius, r is the minimum radius when positrons are captured by traps, D_+ is the diffusion coefficient of positrons and in approximation of the spherical symmetry the trap radius is [23]

$r_+ = [x^2 (1+y)^2 /(2mU/\hbar^2)]^{1/2}$, (10)

where m is the electron mass, U is the depth of the potential well of defects, $\hbar$ is Plank's constant, $x=1/y[\lambda_f\tau_2/((1+y^2)-1)]$, $x=\pi$-arctg1/y. Assuming that U=2 eV [21], $D_+=0.1$ cm^2/s [24] in the initial samples we can get $r_+ = 2.7\text{-}3$ Å, $N_+=(1.1\text{-}1.3)\cdot 10^{16}$ cm^{-3} (see the Table), i.e. the traps are vacancy clusters consisting of 6-10 point vacancies. The SHF irradiation enhances the association and dissociation reactions of clusters in normal and superconducting states of $YBa_2Cu_3O_{7-\delta}$ superconductors. For shot irradiation time t≤5 min the number of clusters reduces in ~2.4-5.3 times, while the radius of clusters, as rule, arises. The rise of r_+ indicates the association of single vacancies and clusters, and the reduction in N_+ may be caused by the partial healing of clusters, their dissociation or recombination on the surface. Since the changes in N_+ and r_+ are accompanied by reduction in ρ, the formation of Ba and Cu1 vacancies simultaneously occurs with transformation of clusters. Note that the recombination of clusters on the surface is improbable due to high activation energy of cluster migration.

When t>5 min the N_+ and ρ arise, r_+ is altered with increase of irradiation time. This may be ascribed to the association of Ba, Cu1, O5, O1 single vacancies in clusters. From the other side, the changes in N_+ and r_+ may be evidence that SHF irradiation enhances the defect migration in the crystal bulk.

Since n_d»N_+, the changes in R(T) is apparently caused by the Ba, Cu single defects created in the intermediate layers. The transformation of R(T) run, growth of residual resistance, width of superconducting transition show a formation of the high number of defects under action of the SHF field. The appearance of defects leads to a decrease of the relaxation time of l-carriers on defects τ_d and if in the interval $T>T_c$ [2]

$$R(T)=\frac{4\pi}{\Omega_l^2}\left[r_d^{-1}+r_{ph}^{-1}(T)+\gamma_{\mathbf{q}}(T)\right], \qquad (11)$$

where τ_{ph} is the relaxation time on phonons, the R growth with decreasing temperature is caused by the predominant dissipation on defects in the range $T_c<T<240$ K, where $r_d^{-1} > [\tau_{ph}^{-1}(T)+\gamma_{\mathbf{q}}(T)\}$, when the dissipation time on phonons τ_{ph}^{-1}~T and the Landau damping of collective excitations on h-carriers (γ_q~T and γ_q~T^2 for the nondegenerate and degenerate carriers) are reduced.

The non-monotonous shift of the critical temperature in $YBa_2Cu_3O_7$ is apparently caused by a rise of the number of holes in the cuprate layers responsible for high temperature superconductivity, since T_c is related to the hole concentration p by relation [25]

$T_c(p)= T_{cm}[1-82.6(p-0.16)^2]$, (12)

where T_{cm} is the maximum value of T_c. Under SHF irradiation the smooth entering of holes in the CuO_2 layers caused by the hole redistribution among layers when the electron density lowers and p arises in the intermediate layers may result in the increase of T_c to T_{cm} for shot t, and the reduction in T_c with growth of t and p in the intermediate layers.

From the other side, when the hole redistribution among the *B1*, *B2* bands occurs the behavior of the critical temperature [2]

$$T_c=\tilde{\Omega}\exp[-(1+\lambda)/(\lambda-\mu_c^*(1+\lambda))], \qquad (13)$$

where $\tilde{\Omega}$ is the average frequency of plasmons, μ_c^* is the Coulomb potential

$$\mu_c^* = \mu_c^0[1+\mu_c^0\ln(E_F/\tilde{\Omega})]^{-1},$$

λ is the coupling constant

$$\lambda = \frac{2}{\pi} N(0)\int_0^{\infty} \frac{d\omega}{\omega} \left\langle V_c(\mathbf{q}) \mathrm{Im}\,\varepsilon^{-1}(\mathbf{q},\omega)\right\rangle = \mu_c^{\infty} - \mu_c^{0} \ ,$$

μ_c^{∞} =N(0)<4πe^2/$\mathbf{q}^2$>, $V_c(\mathbf{q})=4\pi e^2/\varepsilon(\mathbf{q},\omega)\mathbf{q}^2$,

E_F is the Fermi energy, N (0) is the density of l-carriers at the Fermi level, may be ascribed to the reduction in $\tilde{\Omega}$ frequency with weakening of the Coulomb repulsion and pseudopotential μ_c^*, whose competition leads to the non-monotonous behavior of T_c due to a decrease of the plasma frequency of h-carriers $\Omega^2 = 4\pi e^2 n_h / m_h^*$ as the number of carriers n_h in the *B2* band lowers after formation of Ba and Cu1 vacancies. Note, the slight shift of T_c when the number of defects in the cation sublattice is anomalously high may be evidence that the reduction in ρ is caused by exit of the core electrons of Ba and Cu1 atoms from the annihilation when in the oxygen sublattice the defect formation, excluding O1↔O5 transitions, is absent, since the influence of cation defects on T_c is essentially less than the effect of oxygen defects [26].

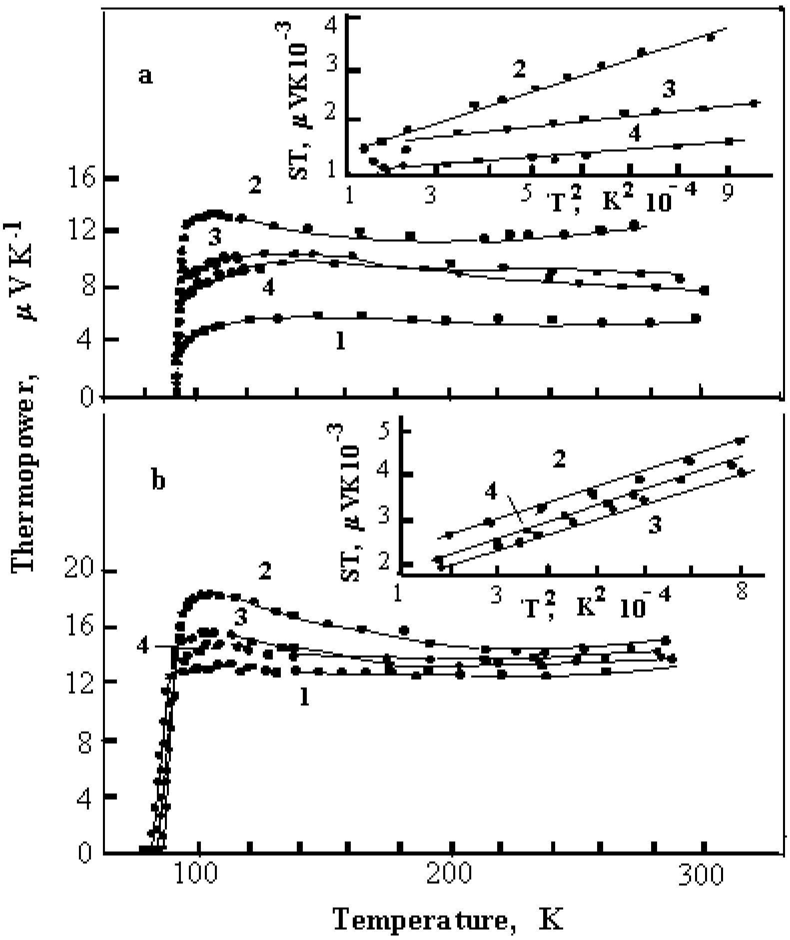

Fig. 3. Thermopower as function of temperature in $YBa_2Cu_3O_{7-\delta}$ samples with δ=0 (*a*) and δ=0.2 (*b*) prior (*1*) and after single SHF irradiation with impulse power 10^4 W at 293 K for 5 (*2*), 15 (*3*), and 45 (*4*) min. The inserts show the run of ST as a function of T^2.

The creation of high defect concentration under action of SHF irradiation is manifested in temperature dependencies of thermopower and diffusion coefficient of gold atoms. SHF irradiation of $YBa_2Cu_3O_{7-\delta}$ samples with $\delta=0$ (Fig. 3, a) and $\delta=0.2$ (Fig. 3, b) gives rise to an increase of S and maximum of S(T) in the interval 100<T<160 K, which is spread and shifted in side of high temperatures with t growth. Besides, in $YBa_2Cu_3O_{6.8}$ samples T_c arises with increasing time to 82 K (t=15 min) and then lowers to 80 K (t=45 min). The rise of thermopower is related to the growth of an amount of defects, since the analogous run of S(T) is observed upon introduction of radiation defects [27]. The maximum of S(T) is probably caused by the phonon drag effect [27,28]. In the cuprate superconductors [29]

$$S(T)= S_d(T)+ S_{ph}(T)=\frac{\pi^2 k^2 T}{3e}\left(\frac{\partial \ln \sigma}{\partial \varepsilon}\right)_{E_F} + \frac{-2|e|}{(\sigma/\tau)V}\sum\left(\frac{\partial N}{\partial T}\right)\alpha_{qj}\langle\Delta v\rangle u, \quad (14),$$

where S_d, S_{ph} are the diffusive and related to the phonon drag components of S, σ, V are the tensor of conductivity and the volume of material, *N* is the density of phonon states with momentum q in j branch, *u* is the phonon velocity, τ is the phonon-electron relaxation time, *Δv is* the change of electron velocity due to the phonon adsorption. Since $\sigma \sim T^{-1}$, $\frac{dN}{dT} \approx (\frac{k}{\hbar\omega})(X^2/\sin X)$, here $X= \hbar\omega/2kT$, we have $S_{ph} = bT^{-1}$ (b is the constant). Assuming $S_d=\alpha T$ (α is the constant) we get $S \sim aT + bT^{-1}$. The dependencies $ST(T^2)$ are linear in the range T≥150 K (insert in Fig. 3) that is consistent with a phonon contribution in thermopower. In accordance with relation (14), the rise of S and the S(T) maximum are caused by reduction in the σ, τ and growth of the S_{ph} contribution due to formation of the high number of defects under SHF irradiation. The free path of carriers and phonons reduces with increasing irradiation time that results in the less contribution of S_{ph} and spreading of the S(T) maximum.

Temperature dependencies of the diffusion coefficient of gold atoms are shown in Fig. 4. In initial samples the diffusion is characterized by slow and rapid components of the surface diffusion (in cm^2/s) in the temperature interval 200-410 ^oC

$D_s^s=2.8\times10^{-11}\exp(-0.072/kT)$ and $D_{sr}^r=1.9\times10^9\exp(0.13/kT)$, (15)

and by a volume component [30], which is observed at thermodesorption of O1 atoms when T≥ 410 ^oC

$D_v^s=6.6\exp(-1.24/kT)$ and $D_v^r=1.9\times10^{-2}\exp(-1.08/kT)$. (16)

The action of SHF irradiation gives rise to the blocking of volume transitions of Au atoms and the suppression of both components of $D_v^{s,r}$, though the irradiation does not effect on the oxygen desorption. The activation energy and preexponential factor of surface diffusion coefficients rise, and in the temperature range 200-305 ^oC the surface diffusion is described by expressions

$D_s^{s1}=8.0\times10^{-10}\exp(-0.17/kT)$ and $D_s^{r1}=1.8\times10^{-7}\exp(-0.18/kT)$, (17)

while at T≥305 ^oC that is

$D_s^{s2}=2.3\times10^{-7}\exp(-0.45/kT)$ and $D_s^{r2}=2.0\times10^{-6}\exp(-0.30/kT)$, (18)

(Fig. 4, curves 2, 2'). The components of surface diffusion D_s^s and D_{sr}^r have the close values of activation energy which are essentially less than the values of activation energy in D_v and do not depend on the number of oxygen in Cu1-O layers. The block of volume diffusive transitions indicates the enhancement of defect formation in the bulk and the accumulation of a high amount of defects in the surface layer of crystals under UHF irradiation.

The suppression of volume diffusion, which may be described by expression $D_v=D_o(1-q)\exp(-E/kT)$, where $q=m/M$, *m* is the number of occupied interstices, *M* is the total number of interstices, is caused by a rise of factor q and the blocking of volume transitions as in the surface layer of crystallites the interstices are occupied by defects, i.e. $D_v \to 0$ when $q \to 1$.

The increase of preexponential factor of $D_s^{r,s}$ may be ascribed to occupation of the interstices by defects.

In the case of diffusion with two types of interstices, when [31]

$$D_s^{r,s} = \alpha l^2 \omega \left(\frac{\lambda + q\mu - K}{q\mu^2} \right) \exp(-E/kT), \qquad (19)$$

where α is a geometrical factor, *l* is the jump length, ω is the vibration frequency of atom in an interstices, $\mu=1-\varepsilon$, $\lambda=1+2\varepsilon$, $K=\sqrt{(\lambda+31\mu)^2 - 12q\mu}$, $\varepsilon = \exp[(u_o - u_T)/kT)$, u_o, u_T are the potential energy of an atom in various interstices, the increase of pre-exponential barriers u_o and u_T.

In case of diffusion transitions from a node at an interstice when [32]

$$D_s^{r,s} = \frac{1}{6} l^2 (g\tau_g \tau_z)^{-1/2} \exp(-E/kT), \qquad (20)$$

where g is the number of vacant nodes, τ_g, τ_z are the residence time at a node and at an interstices, the behavior of D_s^s and D_s^r can be related to a decrease of τ_g and τ_z when defects occupy interstices and a rise of g due to formation of defects under irradiation.

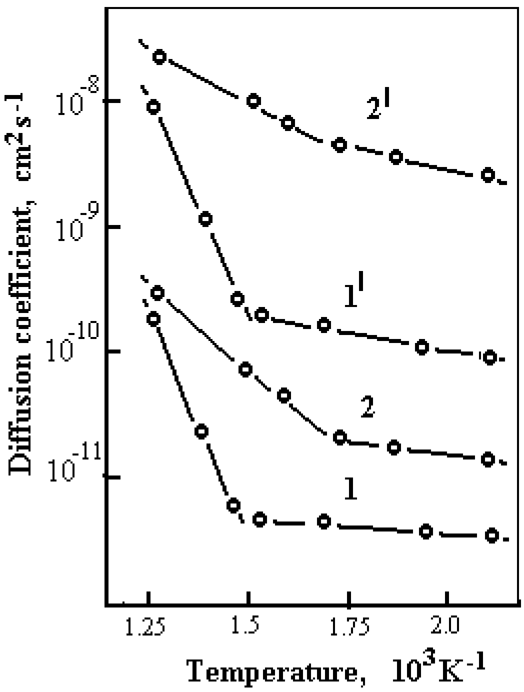

Fig. 4. Diffusion coefficient of Au atoms as function of temperature in $YBa_2Cu_3O_7$ samples prior (*1,1*[1]) and after 10 (*2, 2*[1]) min of SHF irradiation with impulse power 10^4 W at 293 K.

The blocking of volume diffusive transitions indicates the accumulation of the high number of defects within the surface layer of crystals. Such defect distribution in the crystals testifies to the defect transport in the crystal bulk under SHF irradiation. Besides, the defect accumulation within the thick surface layer may give rise to reduction in λ_f. If the layer thickness is less than the diffusion length of positrons the major part of positrons annihilate in the crystal bulk where after irradiation the number of Ba and Cu atoms and the electron density are lower than in the initial samples.

Thus, the SHF irradiation of $YBa_2Cu_3O_{7-\delta}$ high temperature superconductors with $\delta \leq 0.3$ in normal and superconducting states enhances the subthreshold formation of defects in the intermediate layers, such as vacancies and interstitial atoms of Ba, Cu1 and O1↔O5 transitions, that leads to lowering of the electron density in the intermediate layers, a redistribution of holes among the cuprate and intermediate layers, a rise of resistance and thermopower in the normal phase and residual resistance, width of the superconducting transition. The defect formation is apparently accompanied by the defect transport, which results in the transformation of vacancy clusters and blocking of the volume and surface diffusion transitions of Au atoms due to the atomic accumulation within the surface layer of crystals. Besides, an intensity of the subthreshold defect formation does not depend on the irradiation power and is enhanced with growth of the number of defects in samples.

The independence of irradiation effect from impulse power may be ascribed to the realization of condition of the non-dissipation propagation of excitations [1, 2]

$$\frac{\gamma_{\mathbf{q}}}{\Omega_{\mathbf{q}}} = \frac{\pi}{4\sqrt{3}}\left(\frac{m_l^* n_h}{m_h^* n_l}\right)^{1/2} << 1, \tag{21}$$

where n_l is the concentration of l-carriers, in the interval of impulse power 10^4-10^6 W, where $\tilde{\mathbf{v}}_{\mathbf{F}h}(t) << \tilde{\mathbf{v}}_{\mathbf{F}l}(t)$, and the Landau damping on l-carriers $\gamma_{\mathbf{q}}$ is low. The enhancement of defect formation with growth of the number of defects in $YBa_2Cu_3O_7$ samples may be ascribed to a rise of the Drude dissipation and a decrease of plasmon mobility that leads to an increase of the time interval for interaction of the charge antinodes of collective excitations with atoms and pushing out them into interstices.

The subthreshold pushing out of Ba, Cu, O1 atoms indicates an existence of the low-frequency hole collective excitations in the *B2* band, whose localization time on atoms is about ω_D^{-1}. Such excitations are enhanced under action of SHF field due to the nonuniform heating of carriers in the *B1* and *B3* bands and weakening of the Landau damping on carriers in the *B1* band. The SHF irradiation weakens the Landau damping and enhances the propagation of weakly damped collective excitations through the $YBa_2Cu_3O_{7-\delta}$ crystals. The positive charged Ba and Cu atoms are pushed out into interstices by moving holes, which are predominantly localized at oxygen atoms, whose *p*-orbitals make the major contribution to *pd*-hybrid orbitals of the *B2* band, due to the interaction of antinodes of the hole density with atoms. The oxygen O1↔O5 transitions and their random character are probably caused by the mutual repulsion of charge antinodes on the neighboring oxygen atoms. The transformation of vacancy clusters and the defect accumulation near the surface apparently is a result of the defect transport in the field of moving excitations through the crystal, when the association and dissociation of defects and their accumulation near the surface, where plasmons are scattered, are possible.

Conclusions

In $YBa_2Cu_3O_{7-\delta}$ high temperature superconductors with $\delta \leq 0.3$ the SHF irradiation, which does not directly create the lattice defects or the local hole excitations on the deep levels of atoms, enhances the subthreshold defect formation in the intermediate layers which is accompanied by the defect transport through the crystals and the defect accumulation near the crystal surface. The defect formation and atomic transport may be realized in the modulated field of low-frequency collective excitations propagating along the **c** axis. The enhancement of excitations is probably caused by non-uniform heating of carriers in the various bands.

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