DEFECT FORMATION IN THE INTERMEDIATE LAYERS OF $YBa_2Cu_3O_{7-\delta}$ SUPERCONDUCTORS DEPENDING ON OXYGEN CONTENTS

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Abstract

In $YBa_2Cu_3O_{7-\delta}$ superconductors with $0\leq\delta<0.6$ the defect formation in the intermediate layers depending on oxygen content was revealed under γ-irradiation with doses 8-250 kGy. In $YBa_2Cu_3O_7$ the subthreshold creation of Ba, Cu1, O1 defects, which give rise to lowering of the annihilation rate of positrons and lattice parameter **c,** disorder of Cu-O chains, dominates. The defect formation is weakened with δ growth. In $YBa_2Cu_3O_{6.7}$ superconductor the subthreshold pushing out of atoms occurs at low temperatures and in O1→O5 transitions, while in compounds with $\delta>0.3$ the subthreshold defect formation in the intermediate layers is not observed. The subthreshold defect formation is related to the Coulomb ejection of atoms from the lattice sites in the field of the weakly damped low-frequency collective excitations enhanced by irradiation in $YBa_2Cu_3O_{7-\delta}$ superconductors with $\delta\leq0.3$.

Introduction

The $YBa_2Cu_3O_{7-\delta}$ compounds are superconductors in the $0\leq\delta<0.6$ region of oxygen content, whose critical temperature T_c step like arises when $\delta\to0$ [1]. The abrupt increase of T_c to ~90K takes place in the narrow interval of oxygen content $0.25\leq\delta\leq0.3$ that is related to a switching on of the plasmon mechanism of high temperature superconductivity [2]. If this is true, the $YBa_2Cu_3O_{7-\delta}$ superconductors with $\delta\leq0.25$-0.3 are differed from compounds with $\delta>0.3$ by a presence of the low-frequency collective excitations or the acoustic plasmons. The propagation of the weakly damped excitations can give rise to the low-energy subthreshold defect formation in the Ba-O and Cu1-O intermediate layers when an energy of atomic displacement from lattice sites is $E_s\ll E_d$ and a time of displacement $\tau_s\gg\tau_d$, (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). The subthreshold creation of defects [3] is caused by pushing out atoms from lattice sites to the distance, which excludes the recombination of defects, during the time when the antinodes of the plasmon charge density is located on the atom, i.e. $\tau_s\leq T$ (T is the period of vibrations) or 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, ω_D is the Debye frequency. Therefore, if to excite the weakly damped plasmons, for instance under γ-irradiation, in the superconductors of $YBa_2Cu_3O_{7-\delta}$ with $\delta\leq0.25$-0.3 the defect formation can be enhanced due to the subthreshold creation of defects in the field of low-frequency plasmons, in contrast to superconductors with $\delta>0.3$, where such plasmons are improbable and the impact atomic displacement takes place. Note that the other type of subthreshold creation of defects occurs during the relaxation on atoms of the strongly localized electronic excitations whose lifetime is $\tau \geq 1/\omega_D$ [4]. In $YBa_2Cu_3O_{7-\delta}$ compounds such states may be formed when the band spectrum is changed as $\delta \rightarrow 1$. However, in compounds with $0 \leq \delta \leq 0.6$, where the number of free carriers is high, the existence of the charged local excitations is improbable (the polaron states were probably observed in the semiconductor of $YBa_2Cu_3O_{6.3}$ [5], though coexistence of the spin excitations and band electrons is possible [6-8].

In present work the influence of oxygen content on the defect formation in the intermediate layers of $YBa_2Cu_3O_{7-\delta}$ superconductors with $0 \leq \delta \leq 0.55$ was investigated under irradiation with low doses of γ-quanta. Samples of three compositions with $\delta=0$ and 0.55 which corresponded to the high temperature superconductor, where the low-frequency plasmons may be realized, and the superconductor, where the existence of such plasmons is improbable, as well as samples of the intermediate composition with $\delta=0.3$ were studied. To excite the weakly damped plasmons, samples were irradiated with low doses of γ-quanta, which create a low number of radiation defects N_d, but enhance a rise of the number of plasmons, since the screening of perturbations in the charge density δZe_i (δZ is the effective charge of perturbations, i is the defect number) in the vicinity of defects leads to the rise of the spectral density of plasmon states [9]:

$$S(\omega,T) = -\frac{1}{\pi}\sum_{i,q} V_i(\mathbf{q}) \operatorname{Im} \varepsilon^{-1}(\mathbf{q},\omega) \qquad (2),$$

where $\varepsilon(\mathbf{q},\omega)$ is the dielectric permeability, $V_i(\mathbf{q})=4\pi\delta Ze_i^2/\mathbf{q}^2$, ω is the frequency, and the number of plasmons $N(\omega) \sim \int S(\omega,T) f(\omega,T) d\omega$ ($f(\omega,T)$ is Bose function). The rise of $N(\omega)$ increases the number of defects n_d, created due to the subthreshold mechanism, and $n_d \gg N_d$ in the interval of low doses. It was used the dose interval $8 \leq D \leq 250$ kGy, where $D \ll D_n = 4$ MGy, since when $D \geq D_n$ the irradiation creates the high number of radiation defects in $YBa_2Cu_3O_7$ which results in the reduction of T_c [10]. The defect formation was studied using the lifetime positron spectroscopy which admits to evaluate the number of defects in Cu1-O and Ba-O layers, since positrons annihilate in the intermediate layers of $YBa_2Cu_3O_{7-\delta}$ compounds [11], X-ray diffraction was used to control the occupancy of O1, O5 oxygen positions in the basal plane.

Samples and experimental details

The objects of investigations were X-ray single phase polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ with density 5.5 g/cm^3. The $YBa_2Cu_3O_7$ compound was prepared from a mixture of Y_2O_3, $BaCO_3$ and CuO powders by solid-phase synthesis [3]. The nonstoichiometric compounds with $\delta>0$ were obtained by annealing samples with $\delta=0$ in vacuum. The amount of oxygen was determined using Q-1500 derivatograph and X-ray structural analysis. Samples for investigations were prepared from the same polycrystalline block.

The samples were singly irradiated by γ-quanta from ^{60}Co source with doses 8, 30, 100, 250 kGy at room and nitrogen temperatures T_r.

The positron lifetime annihilation spectra were measured using "ORTEC" spectrometer with full width at half maximum of resolution function 220 ps at room temperature. More 10^6 counts were accumulated for each spectrum. The ^{22}Na positron source with activity 20 μCi was mounted between two samples with sizes $10\times10\times1.5$ mm^3. The annihilation spectra were analyzed using "POSITRONFIT" program with correction of the positron annihilation in source material and the resolution function parameters. The positron annihilation rate λ_f and capture rate υ were determined from expressions:

$$\lambda_f = I_1/\tau_1 + I_2/\tau_2, \quad \upsilon = I_2(1/\tau_1 - 1/\tau_2), \qquad (3),$$

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= (CO1-CO5)/(CO1+CO5), where CO1, CO5 are the concentrations of oxygen atoms in O1 and O5 positions, was determined from ratio of structure amplitudes of the 102 and 012 reflections [12]. The measurements of annihilation and lattice parameters were carried out on the same samples.

Experimental results and discussions

The lifetimes of positron and the corresponding intensities in $YBa_2Cu_3O_{7-\delta}$ samples prior and after γ-irradiation are listed in the Table.

Table. Parameters of positron annihilation, concentration and radius of vacancy clusters.

Samples	T_r K	D, kGy	τ_1, ps	I_1, %	τ_2, ps	I_2, %	N_+, 10^{-15} cm^{-3}	r_+, Å
$YBa_2Cu_3O_7$	300	0	170±2	84±2	331±27	16±2	13	2.8
		8	165±4	73±3	286±19	27±3	20	2.6
		30	176±2	89±2	410±21	11±2	9.5	3.0
		100	184±2	93±2	492±41	7±2	5.7	3.2
		250	179±3	92±2	443±35	8±2	6.4	3.1
	77	0	170±2	84±2	331±27	16±2	13	2.8
		8	163±7	53±3	271±19	47±3	37	2.6
		30	170±4	66±3	290±17	34±3	26	2.5
		100	186±3	86±2	386±29	14±2	11	2.8
		250	175±3	80±2	340±27	20±2	16	2.8
	300	0	180±3	86±2	341±24	14±2	8.6	3.5
		8	176±5	80±4	290±29	20±4	12	3.1
$YBa_2Cu_3O_{6,7}$		30	180±3	84±2	323±30	16±2	9.2	3.3
		100	184±5	89±4	363±39	11±4	6.6	3.6
		250	173±7	80±5	291±30	20±5	12	3.1
	77	0	180±3	86±2	341±24	14±2	8.6	3.5
		8	183±3	91±2	397±37	9±2	5.7	3.8
		30	187±3	91±2	363±43	9±3	5.3	3.6
		100	185±3	90±3	336±49	10±3	6.1	3.4
		250	179±5	85±4	347±29	15±4	9.3	3.5
	300	0	189±2	77±5	300±30	23±5	12	3.1
		8	202±5	88±5	365±44	12±5	5.8	3.4
$YBa_2Cu_3O_{6.45}$		30	210±3	94±2	440±51	6±2	3.9	3.3
		100	179±5	62±7	268±25	38±7	20	2.8
		250	191±2	71±5	295±32	30±5	15	2.9
	77	0	189±2	77±5	300±30	23±5	12	3.1
		8	204±5	90±5	366±53	9±5	4.9	3.4
		30	198±7	85±7	327±45	15±7	7.5	3.2
		100	189±7	78±7	315±25	22±7	12	3.1
		250	197±6	85±6	343±38	15±6	7.7	3.3

In the samples with various oxygen content the effect of equal irradiation doses is distinctly manifested in the behavior of the rates of positron annihilation and capture (Fig.1). In initial samples $\lambda_f(\delta)$ smooth reduces as the number of atoms lowers in the intermediate layers. In $YBa_2Cu_3O_7$ high temperature superconductors γ-irradiation lowers the λ_f , and the changes in λ_f are enhanced with decreasing irradiation temperature. After irradiation the smooth reduction in $\lambda_f(\delta)$ is transformed in the non-monotone behavior of λ_f in the irradiated samples, where in the interval $0 \le \delta < 0.3$ the λ_f arises with reduction of oxygen content while at $\delta \ge 0.3$ the behavior of λ_f is not changed. The capture rate slightly depends on D and T_r when $\delta=0.3$.

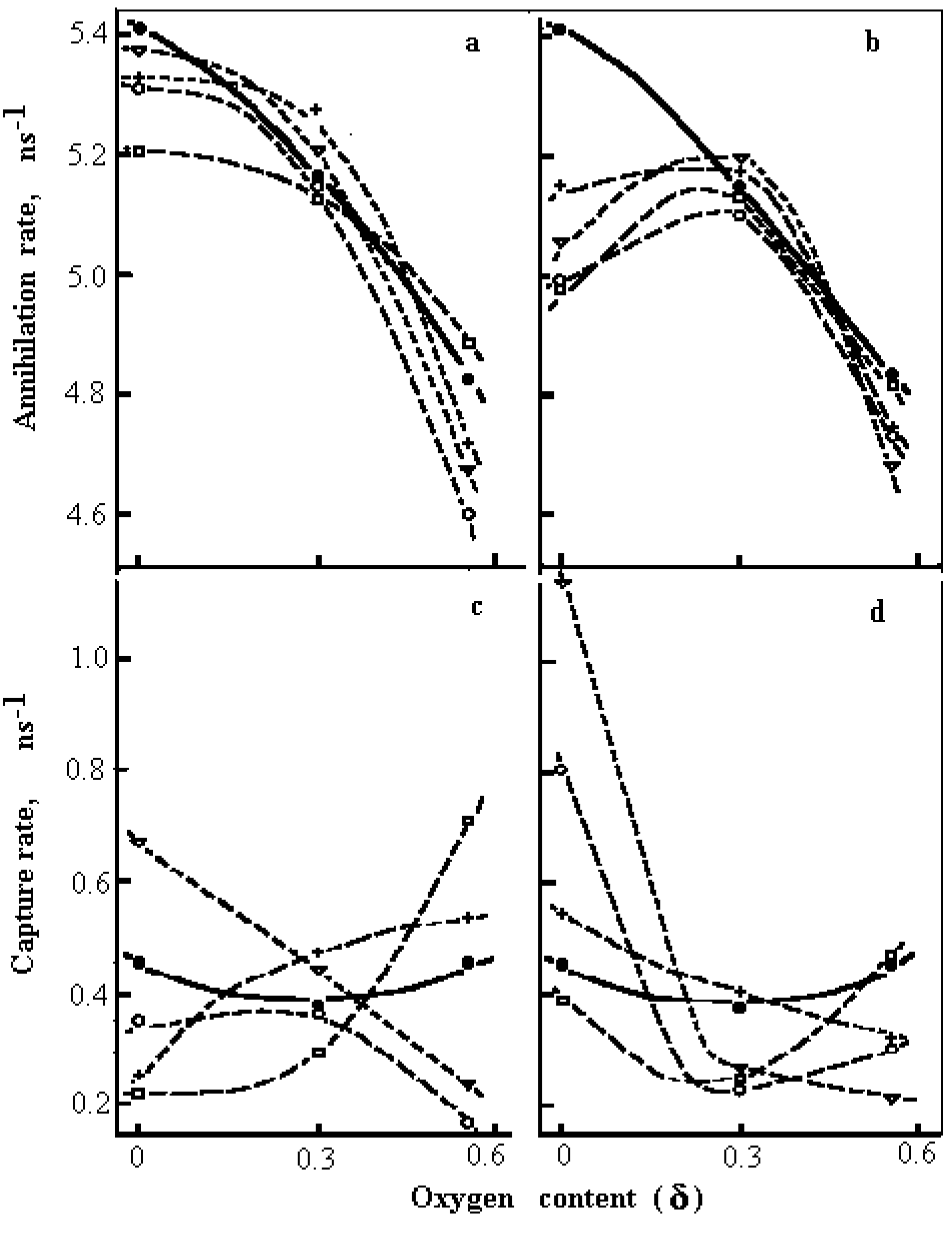

Fig. 1. Dependencies of annihilation rate and capture rate of positrons on oxygen contents in $YBa_2Cu_3O_{7-\delta}$ before (•) and after irradiation at 300 (*a*, *c*) and 77 K (*b*, *d*) with doses 8 (▼), 30 (○), 100 (□) and 250 (+) kGy.

In compounds with $\delta=0$ and 0.55 at T_r=300 K the changes in υ are similar, while as temperature lowers these are enhanced in the first system and are weakened in the second system. Thus, the principal irradiation effect is manifested in $YBa_2Cu_3O_7$ high temperature superconductors, where λ_f lowers under irradiation and the variations of λ_f and υ are enhanced with decreasing temperature. With growth of δ the changes in λ_f and υ weaken and in $YBa_2Cu_3O_{7-\delta}$ superconductors with $\delta\geq0.3$ these have the random character and decrease as T lowers.

In $YBa_2Cu_3O_7$ high temperature superconductors the annihilation rate non monotonously reduces with D growth (fig. 2). After irradiation at T_r=300 K the maximum change is $\Delta\lambda_f$ (D)=$\lambda_f(0)$-λ_f(D)≈0.21 ns^{-1}, while at T_r=77 K λ_f slightly arises with D growth. Such behavior of λ_f(D) does not correlate with smooth rise of the number of radiation defects as D arises.

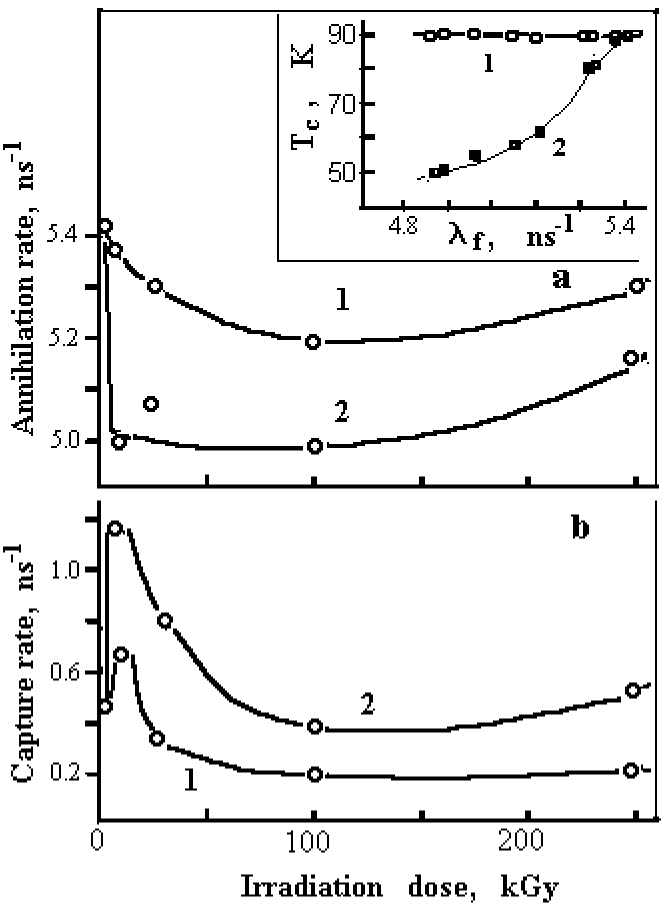

Fig. 2. The rates of annihilation (*a*) and capture (*b*) of positrons in $YBa_2Cu_3O_7$ as function of irradiation doses at temperatures 300 (*1*) and 77 K (*2*). The insert shows the critical temperature as function of annihilation rate in $YBa_2Cu_3O_7$ after γ-irradiation (*1*) and after oxygen desorption from the intermediate layers (*2*).

Note that the effects of irradiation and desorption of oxygen atoms from the Cu1-O layers on λ_f are analogous in $YBa_2Cu_3O_7$. The maximum of $\Delta\lambda_f$(D) equals the change in $\lambda_f(\delta)$ caused by removal 0f ~$2.5\cdot10^{21}$ cm^{-3} atoms when δ increases from 0 to 0.46. However, in $YBa_2Cu_3O_7$ samples the irradiation does not vary an amount of oxygen, since the curves of mass loss due to oxygen desorption are identical in the initial and irradiated samples. Besides, the drop in λ_f caused by irradiation does not influence on T_c and temperature dependence of resistance in $YBa_2Cu_3O_7$ samples, while the analogous drop in λ_f due to removal of O1 atoms leads to the drop in T_c more than 40 K [1] (insert in Fig. 2, a).

The capture rate of positrons by defects is non-monotonously changed with D growth and has the maximum at D=8 kGy. The dependence of υ(D) does not correlate with λ_f(D) and a smooth rise of the number of radiation defects as D increases (Fig. 2, b).

In $YBa_2Cu_3O_{7-\delta}$ superconductors with $\delta \geq 0.3$ under irradiation the changes in λ_f are essentially less than in the system with δ=0 and have the random character. The λ_f value may exceed the initial magnitude (Fig. 3, a, c). In samples with δ=0.3 the λ_f(D) and υ(D) dependencies are similar, while in the system with δ=0.55 their behavior are practically the same and do not correlate with smooth rise of the number of radiation defects as D increases. Note that in $YBa_2Cu_3O_{6.45}$ the weakening of variations in λ_f and υ with temperature is more noticeable (Fig. 3, b, d).

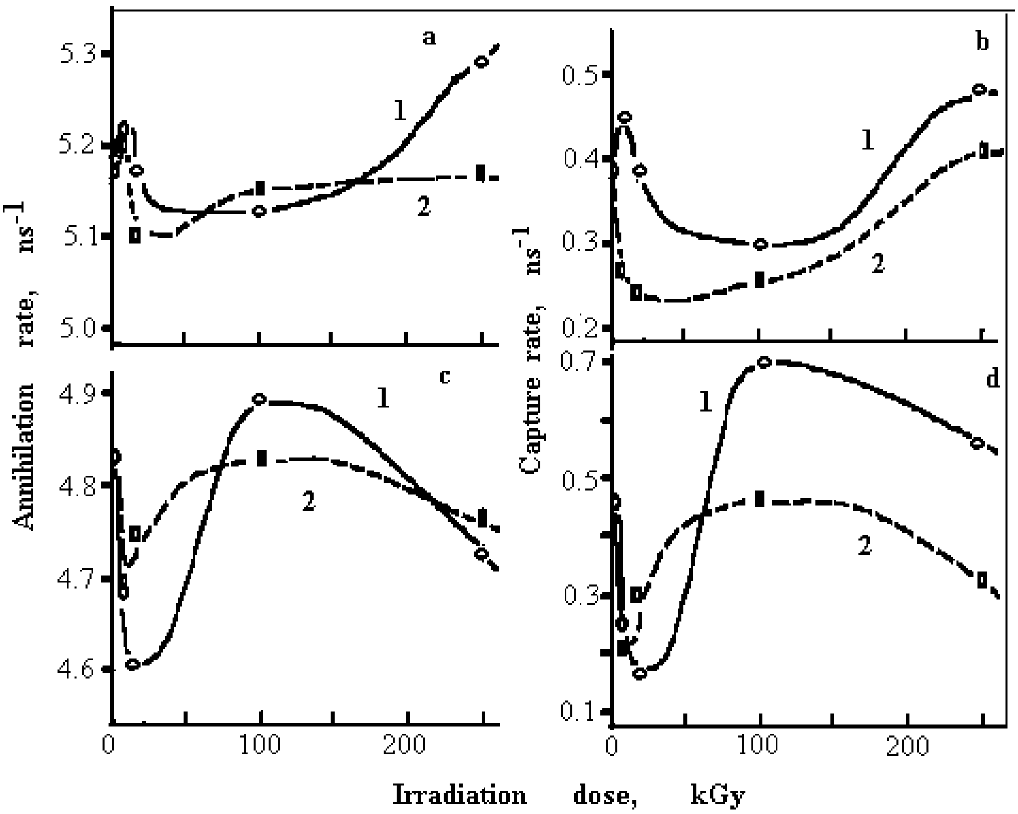

Fig. 3. The rates of annihilation and capture of positrons in $YBa_2Cu_3O_{7-\delta}$ with δ=0.3 (*a*, *b*) and δ=0.55 (*c*, *d*) as function of irradiation doses at temperatures 300 (*1*) and 77 K (*2*).

The behavior of η and **c** parameters of the crystal lattice in $YBa_2Cu_3O_{7-\delta}$ superconductors under irradiation is shown in Fig. 4. The **a** and **b** lattice parameters are not varied after irradiation. In $YBa_2Cu_3O_7$ the reduction in λ_f is usually accompanied by a decrease of **c** parameter and the drop in η which indicates the disorder of Cu1-O chains. In the basal plane the transitions of ~$5 \cdot 10^{20}$ and $1.3 \cdot 10^{21}$ cm^{-3} oxygen atoms from O1 in O5 sites take place at T_r= 300 and 77 K, and the number of transitions does not practically depends on D (Fig. 4, a, b). In $YBa_2Cu_3O_7$ a similarity of the η(D) and λ_f(D) dependencies, a rise of the number of O1→O5 transitions and the changes in λ_f, υ with decreasing temperature indicate the common mechanism of defect formation and oxygen transitions in the intermediate layers. Besides, the decrease of **c** parameter shows that the probable defects are the Y, Ba, Cu vacancies, since the exit of cations in interstices may weaken the Coulomb repulsion among layers and gives rise to compression of the lattice.

In $YBa_2Cu_3O_{6.7}$ samples the behavior of c(D) and λ_f(D) dependencies does not correlate. The parameter ή drops when D≥8 kGy and its behavior does not practically depend on T_c (Fig. 4, c, d). The drop in η corresponds to O1→O5 transitions of ~$7.1\cdot10^{20}$ cm^{-3} oxygen atoms. Note that at T_r=77 K the λ_f(D) and η(D) dependencies are similar. This may indicate the common mechanism of their behavior.

In $YBa_2Cu_3O_{6.45}$ compound the **c**(D) and λ_f(D) dependencies do not correlate, namely, the annihilation rate lowers when the **c** increases and vice versa. The parameter η arises with increasing D, and the number of O5→O1 transitions does not depend on T_r (Fig. 4, e, f). Such behavior of η may be related to the impact mechanism of transitions of oxygen atoms in Cu1-O layers, as well as the correlation of **c**(D), λ_f(D), υ(D) dependencies may be caused by the common impact defect formation in the intermediate and CuO_2 layers.

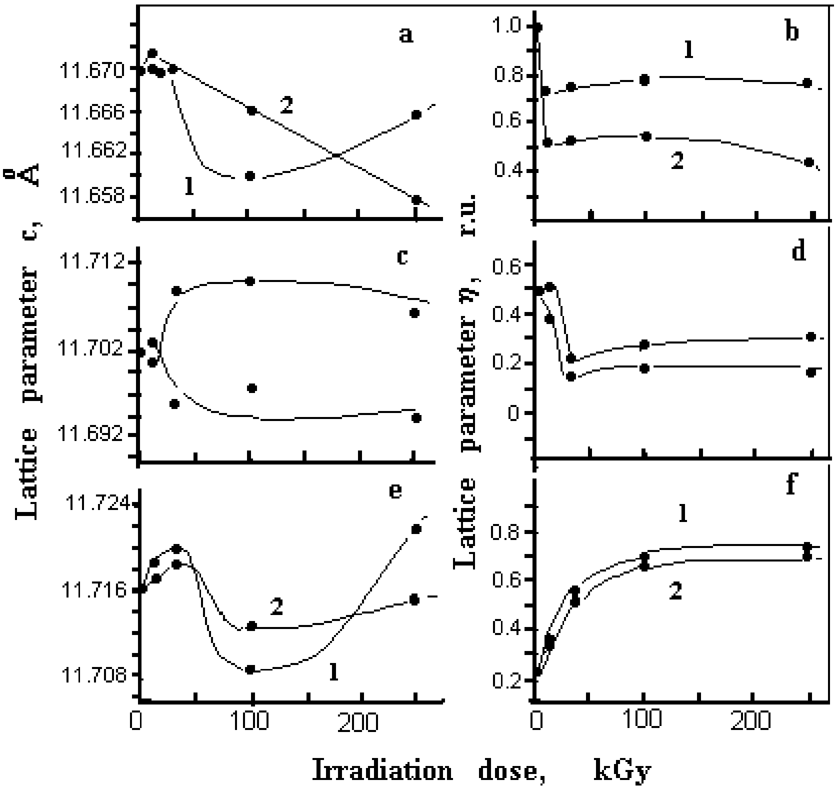

Fig. 4. The lattice parameters **c** and η in $YBa_2Cu_3O_{7-\delta}$ superconductors with δ=0 (*a*, *b*), δ=0.3 (*c*, *d*) and δ=0.55 (*e*, *f*) at irradiation temperatures 300 (*1*) and 77 K (*2*).

Note that γ-irradiation does not change an oxygen content in the nonstoichiometric compounds, since upon heating the curves of mass variation due to oxygen desorption and adsorption are identical in the irradiated and unirradiated samples.

Thus, in $YBa_2Cu_3O_{7-\delta}$ compounds the effect of γ-irradiation with low doses on the parameters of positron annihilation and the crystal lattice depends on the oxygen content. In $YBa_2Cu_3O_7$ high temperature superconductors the irradiation stimulates the non-monotone reduction in λ_f, growth of υ and O1→O5 transitions, which are enhanced with decreasing temperature, do not correlate with the number of radiation defects and apparently caused by the common mechanism of defect formation in the intermediate layers. In $YBa_2Cu_3O_{6.45}$ superconductors the changes in λ_f, υ and **c** have the random character and weaken as temperature lowers. Their behavior does not correlate with increasing order of the Cu-O chains as D rises, which does not depend on temperature that can be related to a predominant role of defect formation in the cuprate layers. In $YBa_2Cu_3O_{6.7}$ compound the irradiation effect has the intermediate character and is manifested in the slight random variations of λ_f and υ which do not practically depend on temperature and behavior of the **c** parameter, though a similarity of the η(D) and λ_f(D) dependencies at T_r=77 K may be caused by the common mechanism of defect formation and transitions of O1 atoms in the intermediate layers.

In the case of oxygen thermodesorption the reduction in λ_f is caused by the drop in electron density and the non-involvement of the core electrons of O1 atoms in annihilation. Under irradiation the drop in λ_f may be explained by a predominant creation of the Ba and Cu1 defects. The annihilation rate is related to the charge density of electrons $n^-(\mathbf{r})$ and positron $n^+(\mathbf{r})$ by [13]:

$$\lambda_f = \frac{\pi r r_o^2 c}{e^2}\int d^3\mathbf{r} n^+(\mathbf{r}) n^-(\mathbf{r})\varepsilon[n^-(\mathbf{r})], \qquad (4),$$

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, $\mathbf{k}\le\mathbf{k}_F$, $\mathbf{k}_F$ is the Fermi quasi-momentum of electrons, *l* is the band number, *n* is the positron number, c, r_o are the light speed and classical radius of electron, $\varepsilon[n^-(\mathbf{r})]$ is the enhancement factor. The electron density in intermediate layers includes the density of core electrons ρ_{core} of Cu1, Ba, O1, O5, O4 atoms, the electron density in the *B2* band ρ_{B2} formed by *pd*-orbitals of the Cu1, O1, O4, Cu2 atoms, in which carriers enter as the number of O1 atoms arises, and the vacant band *B3* ρ_{B3} built by *dp*-orbitals of the Cu1, O4, O1 atoms [14-16]. Hence, one can write [3]:

$$\lambda_f = \pi r_o^2 c\varepsilon\rho \approx \pi r r_o^2 c\varepsilon(\rho_{core} + \mu_{B2} + \rho_{B3}) \qquad (5),$$

where the enhancement factor is given by [17]:

$$\varepsilon(r_s) = 1 + 0.1512 r_s + 2.414 r_s^{3/2} - 2.01 r_s^2 + 0.4466 r_s^{5/2} + 0.1667 r_s^3 \qquad (6)$$

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

After desorption of O1 atoms to a value δ=0.55 the reduction in λ_f corresponds to a density change $\Delta\rho \approx 4\times10^{22}$ cm^{-3}, which exceeds the density of free carriers $\rho_{B1} + \rho_{B2} + \rho_{B3} \approx 5\times10^{21}$ [1] (ρ_{B1} is the density of carriers in the *B1* band formed by *dp*-orbitals of Cu2, O2, O3 atoms in the cuprate layers, which do not participate in annihilation), 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

$$\Delta\lambda_f = \pi r_o^2 c\varepsilon\Delta\rho \approx \pi r_o^2 c\varepsilon\Delta\rho_{core}, \qquad (7),$$

hence the reduction in λ_f is caused by the exit of core electrons of O1 atoms from the annihilation process.

In $YBa_2Cu_3O_7$ under irradiation at T_r=300 and 77 K the changes in λ_f correspond to the density drop $\Delta\rho \approx 1.2\cdot10^{22}$ and $2.5\cdot10^{22}$ cm^{-3} that is also caused by the reduction in ρ_{core}. Since the oxygen content in the intermediate layers is constant, the defects whose electrons do not participate in annihilation are the vacancies and interstitial atoms of Ba and Cu1. Occupying interstices, the positive charge of cations repels positrons, decreases the overlap of $\Psi_{\mathbf{k},l}(\mathbf{r})$, $\Psi_n^{\ +}(\mathbf{r})$ and prevents to the annihilation of core electrons with positrons that reduces ρ. Besides, the Ba, Cu1 atoms may be repelled in interstices of the Cu2-O and Y layers where positrons do not penetrate. In this case, the ρ is reduced due to the formation of vacancies in the intermediate layers.

The creation of Cu1 and Ba vacancies is in agreement with a decrease of the **c** parameter and an absence of the reduction in T_c, whose behavior is sensitive to an amount of oxygen defects or oxygen. An appearance of the cation defects essentially lowers the electron density in the intermediate layers, however the hole concentration in the cuprate layers responsible for the high temperature superconductivity and behavior of T_c may be unchanged.

The exit of O4 and O1 atoms in interstices of the intermediate layers 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 core electrons in annihilation is improbable. The oxygen transitions from O1 in O5 sites does not apparently affect on λ_f, since oxygen atoms remain in the annihilation volume. The exit of a high amount of oxygen atoms in interstices of cuprate layers is improbable because the Tc is unchanged.

The number of defects in the intermediate layers $n_d \approx \Delta\rho/n_e$ can be estimated assuming that the average number of core electrons of Ba and Cu1 atoms, which does not participate in the annihilation, is $n_e \approx 45$. Then n_d equals $2.7 \cdot 10^{20}$ and $5.6 \cdot 10^{20}$ cm^{-3} after irradiation at 300 and 77 K. The obtained values of n_d are probably understated, since the deep core electrons of defects are not involved in the annihilation.

It should be noted that the reduction in λ_f may be related to the accumulation of a high number of defects in the thin surface layer of $YBa_2Cu_3O_7$ crystals which is manifested in the blocking of diffusive transitions of the metal atoms after γ-irradiation [18] and may lower the atomic concentration and electron density in the annihilation volume. If the diffusion length $L \approx \sqrt{D_+\tau_b} \approx 1.4 \cdot 10^4$ Å ($\tau_b = (I_1/\tau_1 + I_2/r_2)^{-1} \approx$ 180-200 ps is the bulk lifetime of positrons) essentially exceeds a thickness of the surface layer, the major part of positrons annihilate in the crystal bulk, where the number of Ba, Cu atoms and ρ are lower than in the initial samples.

The non-monotone change of the amount of Cu1 and Ba defects as D arises and the enhancement of defect formation with lowering T_r indicates the non-impact mechanism of defect formation. Thus, if the number of radiation defects is proportional to D [19] and in the interval 8- 250 kGy N_d rises in about 31 times, the n_d non-monotonously arises at T_r=300 K or when T_r=77 K that is constant in the range D≤100 kGy and slightly lowers as D increases. Besides, the non-impact mechanism of defect creation is manifested in O1→O5 transitions, since their quantity does not depend on D and sharply rises with lowering temperature.

The number of defects n_d formed by doses D≤250 kGy is less or exceeds the minimum content of radiation defects N_d^m which give rise to the reduction in T_c. The magnitude of N_d^m can be estimated assuming that the concentrations of radiation defects formed under γ-irradiation with dose D_m=4 kGy [10] and fast neutrons with fluency $\phi_m = (5-7) \cdot 10^{18}$ cm^{-2} [20] are equal. The number of defects formed under irradiation by fast neutrons is

$N_d = \upsilon(E) N_a \phi \sigma_d$ (8),

where $\upsilon(E) = 2M_n M_a E_n / [(M_n + M_a)^2 E_d]$, M_n, M_a are the masses of neutron and atom, E_n is the neutron energy, N_a is the number of atoms in 1 cm^{-3}, σ_d is the collision cross-section. If the mean energy of neutrons E_n=2 MeV, $E_d = 24$ and 20 eV for Cu1 and Ba atoms [21, 22], $\sigma_d = 2 \cdot 10^{-24}$ cm^2 [23], the minimum content of Cu1, Ba defects is $N_d^m = (3.4\text{-}4.7) \cdot 10^{20}$ cm^{-3}. Then in the interval 8-250 kGy the doses are differed in D_m/D=500-16 times, while the concentrations of defects in N_d^m / n_d=1.2-1.7 and 0.6-0.8 times at T_r=300 and 77 K. Hence, at T_r=77 K the number of defects n_d created under γ-irradiation with doses D«D_m exceeds the amount of defects N_d^m formed under irradiation with D_m=4 MGy owing to the impact displacement of atoms. The formation of a high number of defects $n_d > N_d$ under irradiation with low doses shows that the low-energy subthreshold mechanism of defect formation occurs in the intermediate layers. Besides, when the defect content in the intermediate layers is $n_d > N_d^m$, an absence of the reduction in T_c may indicate the dominant role of cuprate layers in the mechanism of high temperature superconductivity.

The single defects of Ba, Cu, O1 created under irradiation do not apparently capture the positrons, since the dependencies of υ(D) and λ_f(D) do not correlate. When $271 \leq \tau_2 \leq 492$ ps the vacancy clusters are by positron traps [24]. The capture rate is related to the concentration N_+ and radius of vacancy clusters r_+ by relation [25]

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

where $N_+ = \int_r^\infty P_+(R) dR$, $P_+(R)$ is the distribution function of defects 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 [26]

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

here m is the electron mass, $\hbar$ is Planck's constant, U is the depth of the potential well of defects, $x=1/y\{\lambda_f\tau_2/[(1+y^2)-1]\}$ and $x= \pi-$ arctan1/y. Assuming that $U=2$ eV [27], D_+=0.1 cm^2/s [28] in the initial samples we can get $N_+ = 13 \cdot 10^{15}$ cm^{-3}, r_+=2.8 Å (see the Table), i.e. the traps are vacancy clusters consisting of about 7 point vacancies. Note, in spite of estimated values of the cluster parameters their variations register the transport and transformation of defects enhanced by irradiation in the crystal bulk. From the Table it is seen, when D≤30 kGy the behavior of υ(D) is caused by growth of N_+ and weak reduction in r_+ that can be ascribed to association of Ba, Cu1, O5, O1 single vacancies in the clusters. In the range D>30 kGy the behavior of υ(D) is caused by lowering N_+ when r_+ is constant or rises. This may be evidence that the transformations of clusters, such as the partial dissociation, recombination on the surface or association with single defects take place. Besides, the changes in r_+ and N_+ indicate the enhanced defect transport under irradiation.

Thus, in the intermediate layer of $YBa_2Cu_3O_7$ under γ-irradiation the subthreshold formation of Ba, Cu1, O1 defects dominates. The defect formation is accompanied by the transformation of vacancy clusters. Both processes occur in the normal and superconducting states and are enhanced as T lowers.

The subthreshold ejection of atoms from lattice sites in the Cu1-O, Ba-O layers and the defect transport are possible in the modulated field of weakly damped collective excitations. The Ba and Cu cations are pushed out into interstices in the field of charge antinodes of moving holes (heavy h-holes) in the *B2* band, which are predominantly localized at oxygen atoms, whose *p*-orbitals yield the major contribution to the hybrid *pd*-orbitals of the band. The O1→O5 transitions are probably caused by the mutual repulsion of charge antinodes on the adjacent O1 atoms that leads to the similarity of λ_f(D) and η(D) dependencies. The number of defects does not depend on the dose, since the total subsystem of h-holes is excited under irradiation with any dose and takes part in the defect formation.

In the *B2* band the weakly damped plasmons may propagate along the **c** axis. Since in $YBa_2Cu_3O_{7-\delta}$ the energy of plasma vibrations along the **c** axis is 10-40 meV [29], the condition of the subthreshold defect formation $\hbar\Omega_{\mathbf{q}} \leq \omega_D$ ($\hbar\omega_D \approx 0.05$ eV [30]) is correct. Besides, when the plasmons are propagated along the **c** axis the screening of the subthreshold ejection of atoms by the carriers (light l-holes) in the *B1* band may be weakened. Note that the energy of plasma vibrations in the plane of cuprate layers is $\hbar\Omega_l \approx 1.3\text{-}2.8$ eV [31], therefore the plasma frequency is $\Omega_l \gg \omega_D$ and the subthreshold defect formation is improbable with participation of the l-carriers.

The enhancement of subthreshold defect formation and transformation of vacancy clusters with lowering temperature may be ascribed to a rise of the number of weakly damped plasmons and a weakening of the plasmon damping. The increase of N(ω,T) is improbably, since the spectral density of plasmon states [9]

$$S(\omega,T) \approx \frac{\pi}{2} - \arctan\left[\frac{\varpi_{pl}}{2Tsh(\varpi/2T)}\right] \quad (11),$$

where $\varpi_{pl} \approx W_h(1+\frac{m_l^* T}{\pi n_h})$, W_h, n_h are the band width and concentration of h-carriers, m_l^* is the effective mass of l-carriers, reduces with lowering T. Note that at superconducting transition the spectrum of the weakly damped plasmons may broaden due to particles with energy $\hbar\Omega < 2\Delta$ (Δ is the superconducting gap). Besides, as T lowers the Landau damping of excitations is weakened due to a decrease of the thermal diffusion of Fermi distribution of l and h-carriers, which may promote the transport of defects and suppression of recombination, the defect formation and transformation of vacancy clusters.

In $YBa_2Cu_3O_{6.7}$ superconductors under irradiation the changes in λ_f correspond to the reduction in the electron density, which do not exceed the density of free carriers and are accompanied by transitions of $7\cdot10^{20}$ cm^{-3} oxygen atoms from O1 in O5 sites that indicates an essential weakening of the defect formation in the intermediate layers in contrast to $YBa_2Cu_3O_7$ system. In addition, the parameters of vacancy clusters are slightly varied. In initial samples $N_+ \approx 8.6\cdot10^{15}$ cm^{-3} and $r_+ \approx 3.5$ Å, after irradiation the N_+ and r_+ are changed in 1.4-1.6 and 1.1 times (see the Table), which shows the weakening of defect transport. The random character of the changes in λ_f indicates an absence of the dominant subthreshold defect formation in the intermediate layers, though the run of η(D) and the correlation with λ_f(D) at T_r=77 K may be ascribed to the exhibition of the subthreshold ejection of atoms at low temperatures and in the O1→O5 transitions. Therefore the behavior of λ_f(D) and υ(D) is caused by the impact and subthreshold defect formations, the radiation-stimulated redistribution of defects among the cuprate and intermediate layers.

In $YBa_2Cu_3O_{6.45}$ superconductors the random character of the changes in λ_f(D), υ(D) and **c**(D) indicates an absence of the subthreshold defect formation in the intermediate layers caused by the weakly damped excitations. The dependence of O5→O1 transitions from D shows the impact mechanism of defect formation in the intermediate layers, which does not depend on temperature. In addition, with lowering temperature the transformations of vacancy clusters are weakened. In initial samples $N_+ \approx 1.2\cdot10^{16}$ cm^{-3}, $r_+ \approx 3.1$ Å, after irradiation at T=300 K the maximum changes in N_+ and r_+ are 3.5 and 1.2 times, respectively, while when T_r=77 K the N_+ and r_+ are varied in 2.4 and 1.1 times. The behavior of N_+ and r_+ indicates that the diffusion of defects weakens as T lowers. The random character of defect distribution among the cuprate and intermediate layers under irradiation apparently gives rise to the random variations in λ_f(D), υ(D) and **c**(D), whose reduction with temperature may be caused by weakening of the defect diffusion. The changes in λ_f correspond to variations of the electron density caused by a decrease or increase of the **c** parameter, which show that the formed defects are the metal and oxygen atoms. Note that in $YBa_2Cu_3O_{6.45}$ at T_r=300 K an enhancement of defect formation may be caused by relaxation of the localized electron states which are created in the *B2* band in the cuprate layers when δ arises and the band is destroyed. In contrast of *B2* the *B1* band and Fermi distribution of l-carriers are slightly changed when

$\delta \leq 0.6$ [15], therefore the subthreshold defect formation with participation of the l-carriers is improbable.

Conclusions

Thus, in $YBa_2Cu_3O_{7-\delta}$ superconductors the enhancement of defect formation is observed in the intermediate layers when oxygen content arises in the interval $0 \leq \delta < 0.3$ caused by the additional subthreshold formation of defects. The subthreshold defect formation may be realized in the field of collective excitations which are propagated along the **c** axis and testify to the appearance of low-frequency collective excitations in $YBa_2Cu_3O_{7-\delta}$ high temperature superconductors when $\delta < 0.3$. In $YBa_2Cu_3O_{7-\delta}$ with $\delta \geq 0.3$ the impact mechanism of defect formation is dominated.

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