Relaxation processes in nonstoichiometric $YBa_2Cu_3O_{7-\delta}$ single crystals during annealing and at high pressure

M.A.Obolenskii, R.V.Vovk, A.V.Bondarenko

V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

The critical temperature relaxation processes and resistivity for $YBa_2Cu_3O_{7-\delta}$ single crystals with oxygen deficit $\delta \leq 0.5$ during annealing at room temperature and in case of high hydrostatic pressure up to 7 kbar have been studied. It is shown that $T_c(\delta)$ dependence evolution during annealing is in satisfactory agreement with the existing theoretic models. When the samples with oxygen deficit $\delta \approx 0.5$ are kept under pressure at room temperature, the carriers number for low-temperature phase reduces, while the opposite process of holes number increase takes place in the high-temperature phase. The authors have determined the activation energy and characteristic times for relaxation processes for isobaric and isothermal exposure of the studied samples.

Исследованы процессы релаксации критической температуры и электросопротивления монокристаллических образцов $YBa_2Cu_3O_{7-\delta}$ с дефицитом кислорода $\delta \leq 0,5$ в условиях отжига при комнатной температуре, а также в случае приложения высокого гидростатического давления до 7 кбар. Показано, что эволюция зависимости $T_c(\delta)$ в процессе отжига удовлетворительно согласуется с существующими теоретическими моделями. В случае выдержки образцов с дефицитом кислорода $\delta \approx 0.5$ под давлением при комнатной температуре число носителей для низкотемпературной фазы уменьшается, в то же время, для высокотемпературной фазы происходит обратный процесс увеличения количества дырок. Определены энергия активации и характерные времена релаксационных процессов в случае изобарической и изотермической выдержки исследуемых образцов.

A set of magnetic [1, 2], optic [3, 4], structure [5] and resistive [6] studies on different physical properties of yttrium-based high-temperature superconducting compounds of 1−2−3 system, show the presence of non-equilibrium state at a certain lack of oxygen. External factors are very important, such as temperature [6] and high pressure [7−11]: they lead to the change of lattice parameters and induce the processes of labile oxygen, which, in its turn, influences the superconductor critical parameters. So, the application of these experimental methods not only gives us progress in high-temperature superconducting

nature understanding, but also lets us determine possible empiric ways of increasing critical parameters for high-temperature superconducting compounds. One should note that for today the data on pressure influence on oxygen regulating in nonstochiometric samples of 1−2−3 system studies remain rather contradictive. One of the reasons here should be the fact that an essential part of the experimental material has been obtained on ceramic samples with a lot of intergranular connections. So, the aim of our work is to study baric, temperature and time dependencies for resisitivity and critical temperature in $YBa_2Cu_3O_{7-\delta}$ single crys-

tals with various oxygen deficit extent $0.1 < \delta < 0.5$ in wide temperature interval $4.2 < T < 300$ K and pressure $0 < P < 7$ kbar.

The methodic for single crystals growth and obtaining the samples with deviations from stochiometry has been well described in [11]. Hydrostatic pressure was created in a self-contained camera of piston-cylinder type according to the methodic, described in [12]. The pressure was measured with a manganin manometer, the temperature — with copper and constantan thermocouple, built in camera outer surface on the level of the sample location. The resisitivity in *ab*-plane was measured by standard four-contacts scheme on direct current 1–10 mA. Though the methodic used did not let us make pressure immediately at the temperatures of superconducting transition, we quickly (15–20 min) cooled the camera with the sample just after pressure application to the temperatures, at which no relaxation processes were observed, to minimize the oxygen redistribution influence. Then, at warming up, resisitivity $R(T)$ temperature dependencies were measured. Then the camera with the sample was exposed to the fixed pressure at room temperature for three days, and then $R(T)$ measurements were repeated. Value T_c was determined by the middle of resistive transition to superconducting state at $R = R_N/2$ level, where R_N is residual resistance in the normal state. The width of superconducting ΔT_c transitions was defined as the difference between T_{co} and T_{cf} temperatures (at the beginning and the end of superconducting transition), which correspond to resistance values $0.95R_N$ and $0.05R_N$.

In inset (a) to Fig. 1 one can see resistive transitions to superconducting state of single crystals K1–K7 with different oxygen content. The parameters of these 7 single crystals are given in Table. It is obvious that with the increase of oxygen deficit the
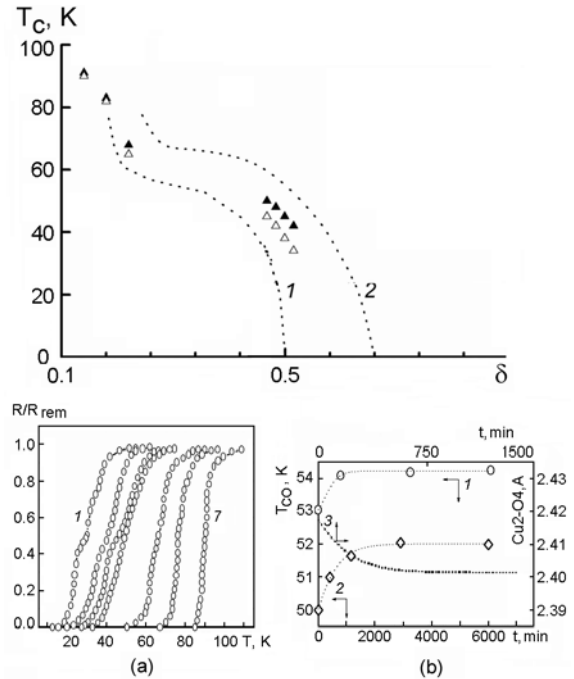

Fig. 1. Dependence $T_c(P)$ for $YBa_2Cu_3O_{7-\delta}$ compounds. Curve *1* corresponds to random vacancies distribution about chains Cu(1)–O(1), curve 2 is calculated under assumption that oxygen atoms vacancies are redistributed so that the structure with $N_{Cu(1)} = 3$ is not realized, and only structures with $N_{Cu(1)} = 4$, $N_{Cu(1)} = 2$, corresponding to ortho- and tetra-phases are possible [14]. Points "Δ" are obtained immediately after sample cooling from temperatures ~ 650°C, points ♦ — after crystals annealing at T_{300} for 3 days. Inset (a): Resistive transitions to the superconducting state of K1–K7 single crystals with different oxygen content. Inset (b): $T_{co}(t)$ dependence (superconducting transition start temperature) for sample K2 (curve *1*), obtained at $P = 6.3$ kbar, $T_{co}(t)$ for crystal K3 (curve *2*), obtained during annealing at room temperature and distance $d_{Cu2-O4}(t)$ — the data of [5] (curve *3*). Point lines are calculations by formula (2).

Table. The parameters of single crystals with different superconducting transition temperature

Crystal designation	T_c, K	ΔT_c, K	ρ_{300}, $\mu\Omega \cdot cm$	δ
K1	42	14	8200	0.52
K2	45	10	7500	0.5
K3	48	8	5200	0.48
K4	50	2.4	750	0.46
K5	68	10	620	0.15
K6	82	5	450	0.1
K7	90	0.3	200	<0.1

critical temperature decreases, and the majority of samples begin to show the stepwise form of superconducting transition, which may be caused by system breakdown into several phases with different oxygen content and different T_c. Really, according to the existing theoretic models [13], high-temperature superconducting cuprates doping by other-valence substitution or oxygen content change, leads to system breakdown into two types of electroneutral regions — metal ones, with high carriers concentration, and dielectric. Ordering dopants can impose the type of domains. The absence of steps in the resistive transitions for crystals K4 and K7 doesn't exclude the co-existence of two or more phases with different T_c. In fact, in the presence of percolation ways of current passing through the phase with high T_c, on the resistive transition there will occur the transition into the superconducting state of exactly this phase. The details will be discussed below.

The literature data show that the decrease of oxygen content in $YBa_2Cu_3O_{7-\delta}$ compounds caused the increase of specific resistance and the decrease of critical temperature T_c. The value of T_c for the compounds with nonstoichiometric composition here depends on the oxygen order strength (see, for example, [6]). The dependence $T_c(\delta)$ is characterized by two plateaus at $T_{c1} = 90$ K and at $T_{c2} = 60$ K. According to the theoretic model [14], the two plateaus in the dependence $T_c(\delta)$ can be formed due to the two possible states realization for bistable oxygen sublattice of apical atoms O(4). When oxygen atoms leave the position O(1), they cause the change of copper atoms Cu(1) number ($N_{Cu(1)} = 4$ for $\delta = 0$) and imply the surface change of two-pit potential, in which the apical atoms O(4) move. The critical temperature T_c can be calculated [14] as the average of distribution for critical temperature realized in the crystal with the sublattice of O(4) atoms with the potential ($q°_1$, $q°_1$, $u°_1$), at $\delta = 0$, or (q^t_1, q^t_2, u^t_1) — at $\delta > 0$:

$$T_c = \{T_c[1 - P^{(b)}(x)] + T^t{}_c P^{(b)}(x)\} P^{(b)}(x_4), \quad (1)$$

where x is relative concentration of copper atoms Cu(1) with the coordination number $N_{Cu(1)} < 4$, $T_c^{°,t}$ being the critical temperature of superconducting transition in the crystal with bistable sublattice O(4) and ($q^{0,t}_1$, $q^{0,t}_2$, $u^{0,t}_1$) potential, $P^{(b)}(x_4)$ defines the probability continuous sublattice exist-

ence in the crystal. The sublattice consists of O(4) atoms, connected with copper Cu(1) atoms by coordinative number $N_{Cu(1)} = 4$.

Fig. 1 shows that the dependence $T_c(\delta)$, obtained for the samples, quickly cooled from high temperatures, is displaced to the theoretic curve *1*, describing vacancies random distribution, at the same time, the dependence $T_c(\delta)$, obtained for single crystals, annealed at room temperatures, moves to theoretic curve *2*, calculated in the absence of structure with $N_{Cu(1)} = 3$, which testifies the regulation in the oxygen-vacancy system. In the region of oxygen concentration $\delta < 0.15$, annealing at room temperatures almost does not change the value T_c. But, as it is shown in [15], low-temperature hardening at temperatures from 100 to 270 K can lead to T_c increase for 5 K, which the authors explained by the transition from one prior type of vacancy superstructure to another one, the average vacancies concentration being unchanged. This again testifies the conclusion that value T_c is determined not only by the absolute value of oxygen content, but also by the state of the oxygen subsystem and its transition (at certain thermodynamic conditions) from the unordered state to the ordered one.

An important aspect of T_c increase is the change of crystal lattice parameters and, in particular, the change of Cu–O and Cu–Cu distances in *ab*-plane [5]. Really, as one can see from inset (b) to Fig. 1, an obvious correlation of T_c change is observed during the annealing (curve *1*) and distance $d_{Cu(2)-O(4)}$ (curve *3* [5]). So, the smaller values of lattice parameters correspond to the higher rate of oxygen ordering. The reverse also seems logical — the higher ordering in oxygen-vacancy system should correspond to the smaller value of lattice parameters. One of the most important methods in clearing up the question is the use of high hydrostatic pressures. As it has been noted above, in papers [7–11] it was shown that defining dT_c/dP, one should distinguish two effects, connected with the reducing of unit cell volume and oxygen redistribution. As one can see from inset (a) to Fig. 2, the critical temperature, evaluated by the middle of superconducting transition, virtually does not depend upon the time of sample exposure to room temperature, and is determined only by the value of applied pressure. At the same time, the width of superconducting transition increases under these conditions and almost does not change at the measurements taken immediately after pressure ap-

plication and removal, which must be caused by oxygen redistribution.

This assumption is confirmed by the results given in Fig. 2, in which the dependencies of baric derivatives of the "real" critical temperature change on the oxygen index $dT_{ci}/dP(\delta)$ for the compounds with various strontium content taken from [10] (curves *2, 3*) and our results (curve *1*) are shown. The graph makes it obvious that in this case the behavior of the dependences $dT_c/dP(\delta)$ is qualitatively similar for all the compounds, in spite of serious difference in the character of $T_c(\delta)$ dependences. At the same time, $T_c(\delta)$ with two plateaus at 60 and 90 K for $YBa_2Cu_3O_{7-\delta}$, partial barium substitution by strontium up to 0.5 concentrations makes the plateau at 90 K disappear and another plateau to appear at 45 K, and further increase of strontium content up to 1 causes monotonous dependence $T_c(\delta)$ [10].

On the other hand hydrostatic pressure application leads to the change of width and form (steps height) of oxygen deficit samples YBaCuO superconducting transition at fixed T_c, which can be caused by oxygen redistribution between the phases, which are characterized by different oxygen content and its ordering type [11]. For example, at pressure increase a part of the oxygen from the phase with a smaller T_c migrates to the phase with a higher critical temperature, and pressure decrease is accompanied by the inverse redistribution. Here the clusters size evaluation $L_o = (Dt)^{1/2}$ produces the value 30–300 Å, which is comparable with distance 50–400 Å, obtained from the neutronographic [16] and optic [4] studies, at which the oxygen ordering in single crystals with $\delta \approx 0.5$ at room temperature is realized.

So, to divide the contributions of real and relaxation effect of the pressure, it seems important to distinguish labile oxygen redistribution processes for phases with different critical temperatures within one sample. In the inset (a) to Fig. 2 the dependencies of baric derivatives for the relaxation part of superconductiong transition start (high-temperature phase) $dT_{cor}/dP(\delta)$ (curve *1*) and superconductiong transition end (low-temperature phase) — $dT_{cfr}/dP(\delta)$ (curve *2*) are shown. The holes number change under pressure $\Delta n(P)$ was calculated according to the ratios obtained in [17] for critical temperature (T_c) dependence on pressure $T_c(P)$ and with account to the data shown in Fig. 2. The results of the
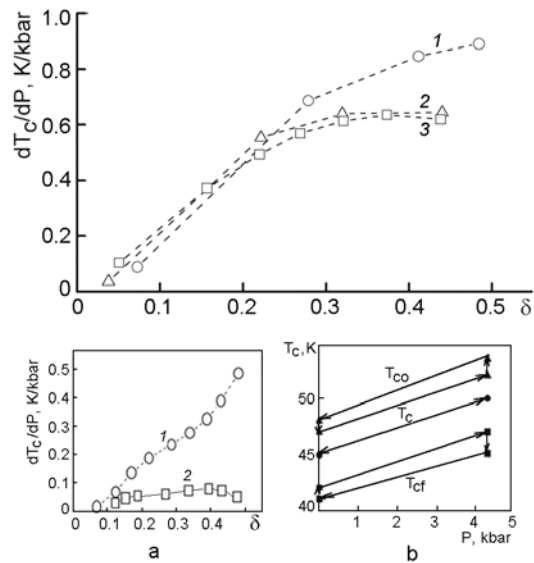

Fig. 2. $dT_c/dP(\delta)$ dependence, determined by the middle of superconducting transition (curve *1*) and data for the "real" pressure effect (curves *2* и *3*) [10]. Inset (a): Critical temperature "relaxation" change baric derivatives dependence on oxygen index $dT_c^r/dP(\delta)$ for the start (curve *1*) and the end (curve *2*) of superconducting transition. Inset (b): The evolution of the start (T_{co}), end (T_{cf}) and the middle (T_c) of sample K2 superconducting transition during application and removal of 4.3 kbar pressure.

calculation testify that with pressure increase, during the exposure to room temperature, the carriers number for low-temperature phase reduces, while with the high-temperature one the opposite process of holes number increase is observed. This confirms the above-mentioned assumption that the high hydrostatic pressure application causes diffusion displacement of the labile component from the phase with lower T_c to the high-temperature phase.

The results of time dependencies $T_{co}(t)$ (superconducting transition start temperature) for samples K2 (curve *1*) measurements, obtained at $P = 6.3$ kbar and $T_{co}(t)$ of K3 crystal (curve *2*), taken during the annealing at room temperature after quick cooling from temperatures ~650 C, are shown in the inset (b) to Fig. 1. The point lines in the dependencies 1 and 2 are the results of evaluation made according to the method suggested in [5, 10]. It is supposed that the oxygen redistribution process can be conventionally divided in to the main galloping process with time constant τ_1, responsible for oxygen ordering within frag-

ments Cu–O of the chains, and a slower process, with characteristic time τ_2, defining the two-dimension ordered structure forming. Then the dependence $T_c(P = const, t)$ can be described by the following two-exponential law:

$$T_c(t,a,\tau_1,\tau_2) = T_c(\infty) - [T_c(\infty) - T_c(0)] \times \quad (2)$$
$$\times \{a\exp(-t/\tau_1)^{0.5} + (1 - a)\exp(-t/\tau_2)^{0.5}\},$$

where a is weighting coefficient for two relaxation processes; $T_c(0)$ and $T_c(\infty)$ are the superconducting transition temperatures before and after the relaxation respectively.

The values $\tau_1 \approx 50-90$ min and $\tau_2 \approx (2-4)\cdot10^3$ min, obtained by the given formula, are in satisfactory agreement with the dependencies 1 and 2, as well as with the data [5, 10]. This confirms that superconducting transitions evolution both under pressure and during annealing at room temperature is defined by labile oxygen redistribution within Cu–O planes. This assumption is also confirmed by the results of resisitivity isothermic relaxation under hydrostatic pressure measurements shown in Fig. 3. As one can see from the figure, the time of resisitivity relaxation to the equilibrium value is about 50 hours at temperature 293 K, while the baric dependence $R_{300}(P)$, measured just after hydrostatic pressure application, has a pronounced linear character (see the inset to Fig. 3). It is necessary to note that resisitivity relaxation after pressure application (removal) was observed at low temperatures too. But the relaxation rate sharply reduced with temperature decrease, and at liquid nitrogen temperature we observed no changes for seven days, which testifies for the thermoactivation mechanism of resisitivity relaxation.

Taking this fact into account and comparing the resisitivity relaxation time dependencies during the annealing at room temperatures and hydrostatic pressure application, we found out that the pressure change for 1 kbar is equivalent to temperature change for 17 K. Using the curves tilt angle change method and cuttings method [18], we determined the process activation energy in both cases. The activation energy $3\cdot10^3$ K was obtained from the measurements. We should note that after samples exposure to room temperature for 20 h, the activation energy value in the first case increased to $12\cdot10^3$ K. Such activation energy dependence on sample exposure time at
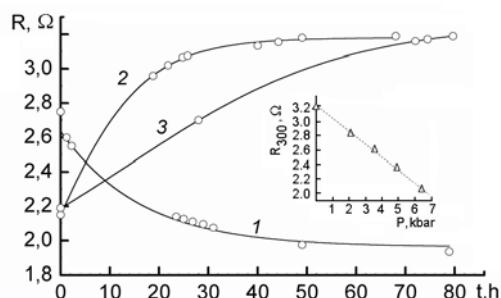

Fig. 3. Time dependencies of $YBa_2Cu_3O_{7-\delta}$ $\delta \approx 0.5$ single crystal resisitivity at 6.4 kbar pressure application (curve *1*) and pressure decrease to the atmospheric one from 6.4 and 4.3 kbar (curves *2* and *3*). The inset shows the baric derivative of the given sample at room temperature $R_{300}(P)$.

fixed temperature shows that activation energy is a function of oxygen distribution.

In the conclusion, we should again emphasize the importance of dividing the effect of immediate unit cell reducing and oxygen redistribution due to pressure application to YBaCuO samples of nonstochiometric content. At the same time, several times increase of activation energy value for resisitivity relaxation process in case of annealing at room temperatures and exposure to hydrostatic pressure can confirm the transition to another labile component ordering mechanism. For instance, the dominating galloping process of oxygen ordering within Cu–O chains [5] can be replaced by a slower process of fragments and chains uniting into two-dimension structure [10, 19]. This assumption is also confirmed by 2 orders change of the characteristic time constants of relaxation processes during isothermic and isobaric samples exposure, obtained from our experimental data. Besides, it seems important to distinguish the processes of labile oxygen redistribution for the phase with different critical temperatures within one sample, dividing the contributions of real and relaxation pressure effects. The calculations of carriers number change under pressure $\Delta n(P)$ we made taking into consideration the dependencies shown in Fig. 2 testify that with pressure increase, during the exposure at room temperature, the carriers number for low-temperature phase reduces, while the inverse process of hole number increase takes place for high-temperature one.

Thus, dependence $T_c(\delta)$ evolution during annealing at room temperature is in satisfactory agreement with Saiko-Gusakov theo-

retical model. During the exposure of samples with oxygen deficit $\delta \approx 0.5$ under pressure at room temperature, the carriers number for low-temperature phase reduces, while the inverse process of hole number increase takes place for high-temperature one. This can be caused by oxygen redistribution between the phases, characterized by different oxygen content and its ordering type. In case of annealing at room temperatures and exposure to hydrostatic pressure the characteristic relaxation processes time constants change for two orders, and the activation energy of resistivity relaxation process increases four times, which can be caused by labile oxygen ordering mechanism change.

References

1. B.W.Veal, H.You, A.P.Paulicas et al., *Phys. Rev. B*, **42**, 4770 (1990).

2. H.Claus, S.Yang, A.P.Paulicas et al., *Physica C*, **171**, 205 (1990).

3. J.Kircher, M.Cardona, A.Zibold et al., *Phys. Rev. B*, **48**, 9684 (1993).

4. K.Widder, A.Zibold, M.Merz et al., *Physica C*, **232**, 82 (1994).

5. J.D.Jorgencen, P.Shiyou, P.Lightfoot et al., *Physica C*, **167**, 571 (1990).

6. M.A.Obolenskii, A.V.Bondarenko, R.V.Vovk, A.A.Prodan, *Low Temp. Phys.*, **23**, 882 (1997).

7. J.Metzler, T.Weber, W.H.Fietz et al., *Physica C*, **214**, 371 (1993).

8. W.H.Fietz, R.Quenzel, K.Grube et al., *Physica C*, **235**, 1786 (1994).

9. M.Baran, V.P.Dyakonov, L.Gladczuk et al., *Physica C*, **241**, 383 (1995).

10. V.P.Dyakonov, L.Gladczuk, G.G.Levchenko, G.Shimchak, *Fiz. Tverd. Tela*, **38**, 3283 (1996); M.Baran, L.Gladczuk, V.P.Dyakonov et al., *Fiz. Nizk. Temp.*, **22**, 1360 (1996).

11. D.D.Balla, A.V.Bondarenko, R.V.Vovk et al., *Low Temp. Phys.*, **23**, 777 (1997).

12. Ye.S.Itzkevich, *Pribory i Techn. Eksper.*, **4**, 148 (1963).

13. M.A.Ivanov, V.M.Loktev, *Fiz. Nizk. Temp.*, **25**, 1325 (1999).

14. A.P.Saiko, V.Ye.Gusakov, *Fiz. Nizk. Temp.*, **21**, 821 (1995).

15. A.A.Mamaluy, L.S.Palatnik, K.V.Bednov et al., *Fiz. Nizk. Temp.*, **19**, 1180 (1993).

16. F.Heinmaa, H.Lutgenemejer, *Appl. Magn. Reson.*, **3**, 689 (1992).

17. R.P.Gupta, M.Gupta, *Phys. Rev. B*, **51**, 11760 (1995).

18. A.C.Damask, G.J.Dienes, Point Defects in Metals, Gordon and Breach Science Publishers, New-York-London (1963).

19. G.Ceder, R.McCormack, D.de Fotaine, *Phys. Rev.*, **B44**, 2377 (1991).

Релаксаційні процеси у нестехіометричних монокристалах YBa$_2$Cu$_3$O$_{7-\delta}$ внаслідок відпалювання і високого тиску

М.О.Оболенський, Р.В.Вовк, О.В.Бондаренко

Досліджено процеси релаксації критичної температури та електроопору монокристалічних зразків YBa$_2$Cu$_3$O$_{7-\delta}$ з дефіцитом кисню $\delta \le 0{,}5$ в умовах відпалювання при кімнатної температури, а також у разі докладання високого гідростатичного тиску до 7 кбар. Показано, що еволюція залежності $T_c(\delta)$ у процесі відпалювання задовільно узгоджується з існуючими теоретичними моделями. У разі витримування зразків з дефіцитом кисню $\delta \approx 0{,}5$ під тиском при кімнатній температурі кількість носіїв для низькотемпературної фази зменшується, водночас для високотемпературної фази відбувається зворотний процес збільшення кількості дірок. Визначено енергію активації та характерні терміни процесів релаксації за умов ізобаричного та ізотермічного витримування зразків, що досліджувалися.