

## Structural relaxation of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single-crystals with a reduced oxygen content in the process of application and removal of hydrostatic pressure

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The influence of hydrostatic pressure ( $P = 0, 4.8$  kbar) on the electron conduction characteristics and structural relaxation of the  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystal with a reduced oxygen content ( $\delta \approx 0.35$ ) is investigated. The formation of two superconducting phases with  $T_{c1}$  and  $T_{c2}$  is associated with the redistribution of labile oxygen in the volume of the sample under pressure by the mechanism of a diffuse coalescence of vacancies. Temperature dependences of the resistance in the  $T_c$ -300K range are analyzed by the Bloch-Gruneisen model, while  $T_c$  ( $T > T_c$ ) interval is analyzed by the Aslamazov-Larkin 3D model for the fluctuation conductivity.

**Keywords:** single-crystal HTSS; structural relaxation; diffuse coalescence; vacancies; oxygen clusters; single-file diffusion; fluctuation conductivity.

Досліджено вплив гідростатичного тиску ( $P = 0, 4,8$  кбар) на характеристики електронної провідності та структурну релаксацію монокристалів  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  з нестачею кисню ( $\delta \approx 0,35$ ). Формування двох надпровідних фаз з  $T_{c1}$  і  $T_{c2}$  пов'язується з перерозподілом лабільного кисню у об'ємі зразка під тиском шляхом механізму дифузійної коалесценції вакансій. Температурні залежності опору в діапазоні  $T_c$ -300К аналізуються за моделлю Блоха-Грюнайзена, а в інтервалі поблизу  $T_c$  ( $T > T_c$ ) - за моделлю Асламазова-Ларкіна для флуктуаційної провідності.

**Ключові слова:** монокристали ВТСП; структурна релаксація; дифузна коалесценція; вакансії; кисневі кластери; одноканальна дифузія; флуктуаційна провідність.

Исследовано влияние гидростатического давления ( $P = 0, 4,8$  кбар) на характеристики электронной проводимости и структурную релаксацию монокристаллов  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  с недостатком кислорода ( $\delta \approx 0,35$ ). Формирование двух сверхпроводящих фаз с  $T_{c1}$  и  $T_{c2}$  связывается с перераспределением лабильного кислорода в объеме образца под давлением путем механизма диффузионной коалесценции вакансий. Температурные зависимости сопротивления в диапазоне  $T_c$ -300 К анализируются согласно модели Блоха-Грюнайзена, а в интервале вблизи  $T_c$  ( $T > T_c$ ) – согласно модели Асламазова-Ларкина для флуктуационной проводимости.

**Ключевые слова:** монокристаллы ВТСП; структурная релаксация; диффузионная коалесценция; вакансии; кислородные кластеры; одноканальная диффузия; флуктуационная проводимость.

### Introduction

An important feature of the high-temperature superconducting system (HTSS) compounds in the 1-2-3  $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system ( $\text{Re} = \text{Y}, \text{Ho}$  or other rare-earth ion) is the possibility of realization of a non-equilibrium state at a certain degree of oxygen deficit [1-3], which can be induced by external factors of high temperature [4] or pressure [2,5]. This state is accompanied by the redistribution of labile oxygen and structural relaxation, which has a significant effect on the electron conduction parameters of the system [1-5]. An important role is devoted to the replacement of yttrium by its isoelectronic rare-earth analogs. A yttrium

replacement by holmium, which has a sufficiently large (more than  $10 \mu_B$ ) magnetic moment [6], ensures the paramagnetism of the compound in the normal state. Nevertheless, Y replacement with paramagnetic ions  $\text{Re} = \text{Ho}, \text{Dy}$ , do not change significantly the superconducting properties of the optimally oxygen-doped  $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds for  $\delta \leq 0.1$  [6]. Apparently, remote localization of such ions from the superconducting planes prevents the formation of long-range magnetic order. At the same time, rare earth ion can serve as an indicator which is sensitive to the local symmetry of its environment and distribution of the charge density in samples of the high-temperature

superconducting system 1-2-3 (non-stoichiometric in oxygen composition), since their change affects the crystal field, which forms an electronic structure of the ion [7].

An outstanding feature of samples with oxygen deficiency  $\delta \geq 0.3$  is the broadening of their resistive transitions to the superconducting state under pressure [2, 8, 9]. The reason of this behavior is not completely defined. It should be also noted, that many aspects of relaxation processes in the 1-2-3 system under high-pressure conditions (e.g. charge transfer and the nature of the redistribution of the vacancy subsystem [10]) remain unclear. Obviously, a decent fact is that an essential part of the experimental material was obtained from ceramic and polycrystalline samples with a high level of intergranular connections [8, 9]. The presence of twinning boundaries in single-crystal samples is an additional complication [11-13], which is associated with experimental difficulties of determining the contribution of these defects [14].

The effect of pressure changes in the 0-5 kbar interval on the resistivity in the ab-plane of the  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystal was investigated [15], where Bloch-Gruneisen formula acts as an approximated function to the temperature dependence of the resistance in the normal state [16]. We have also investigated the effect of hydrostatic pressure up to 5 kbar on the electron conduction characteristics and structural relaxation in the ab-plane of single-crystal  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples with a reduced oxygen content, when the transport flows are parallel to the twin boundaries (TB) and the influence of twins on carrier scattering processes is minimized [12]. In contrast to [15], we described the temperature dependence of the resistance in the entire interval of  $T_c$ -300 K, using the Bloch-Gruneisen formula for the normal state [16] and Aslamazov-Larkin 3D model for the fluctuation area [17-20].

#### The object and procedure of the experiment

$\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystal was grown in a gold crucible by the standard solution-melt technology for yttrium single-crystals [21], with the replacement of yttrium compounds in the initial mixture with similar ones containing the content of holmium. For conducting resistive measurements, a single-crystal measuring 1.7x1.2x0.2 mm was chosen (the smallest dimension corresponded to the direction along the c axis). To reduce the oxygen content, the sample was annealed for three days in a stream of oxygen at a temperature of 600 K. The temperature  $T_c$  for samples with oxygen deficiency decreased to a value of  $\approx 63$  K. According to the published data, this transition temperature corresponds to the parameter  $\delta \approx 0.35$  [6]

The electrical contacts were made of silver conductors, which were connected to the crystals using a silver paste. The electrical resistance in the ab-plane was measured at a constant current of up to 10 mA with two opposite directions of current in a standard four-contact technique. Hydrostatic

pressure was created in an autonomous chamber of the piston-cylinder type [22]. The pressure was measured with a manganin manometer, the temperature with a copper-constantan thermocouple mounted in the outer surface of the chamber at the sample position. To determine the degree of influence of structural relaxation, measurements were made after several days after application of pressure, as the relaxation processes were completed.

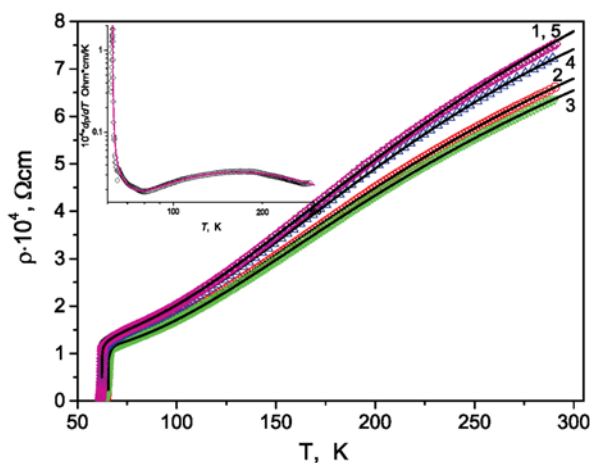
The temperature dependences of  $R(T)$  were first measured during heating of the multiplier at atmospheric pressure. The pressure was then gradually increased at room temperature. Having reached the desired value of pressure, the multiplier was cooled to a temperature  $T < T_c$  and after that  $R(T)$  measurements were made. After measurement at the maximum pressure, it was reduced to atmospheric pressure and the  $R(T)$  dependences were again measured.

In addition to the  $R(T)$  dependence, isothermal measurements of the change in the electrical resistance R at a temperature of 300 K as a function of time t under the action of a pressure of 4.8 kbar were carried out, and also after its removal. In this experiment the time of maximum exposure reached  $\approx 120$  hours.

### Results and discussion

#### Effect of pressure on the temperature dependence of the resistance of samples and their phase composition.

In Fig. 1 shows the temperature dependences of the electrical resistance in the basal ab-plane parallel to the TB,  $\rho_{ab}(T)$ , measured during the application-removal of



*Fig.1.* The temperature dependences of the electrical resistivity in the ab plane are parallel to the TB for  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystals. Curve 1 - initial state ( $P = 0$ ); 2 - after application of pressure  $P = 4.8$  kbar; 3 - after holding at  $P = 4.8$  kbar for a week; 4 - after depressurization ( $P = 0$ ); 5 - after exposure at  $P = 0$  for three days. On the inset is the derivative,  $dp/dT$ , for curve No. 5 (for the remaining curves, the derivatives look similar). The points are the experiment, the lines are the approximations according to expressions (5) – (7).

high hydrostatic pressure. The application of pressure leads to a general decrease in the electrical resistivity, probably as a result of an increase in the density of matter and, correspondingly, of the density of charge carriers (see, for example, [23]). One can clearly see the "metal-like" nature of the  $\rho_{ab}(T)$  dependences. Curves 1 and 5 practically coincide, which indicates an almost complete reversibility of the charge transfer processes with changes in hydrostatic pressure within the limits studied.

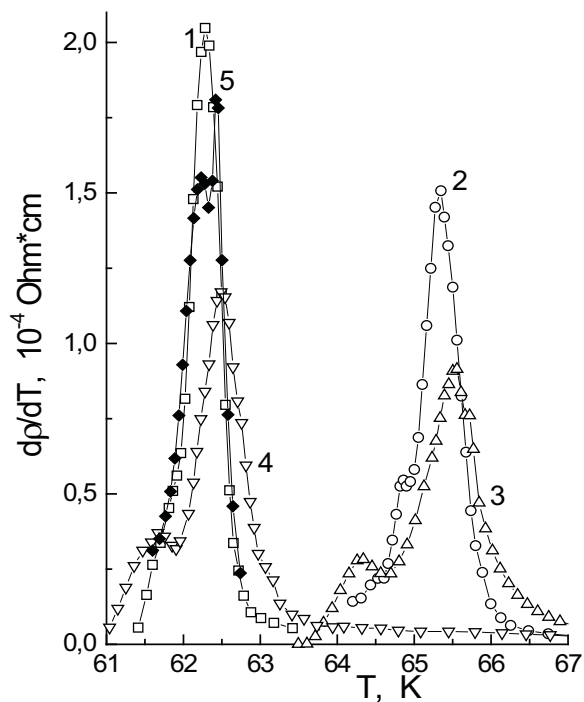
In the inset to Fig. 1 that the derivative,  $d\rho(T)/dT$ , as a function of temperature, has two maxima in the  $T_c$ -300K interval the low-temperature one, due to the transition of the sample to the superconducting state, and the high-temperature charge carrier associated with scattering features in the normal state (for the sample No. 5  $T_{max} \approx 177$  K).

Derivatives,  $d\rho/dT$ , in the region of the superconducting transition are shown in Fig. 2(a).

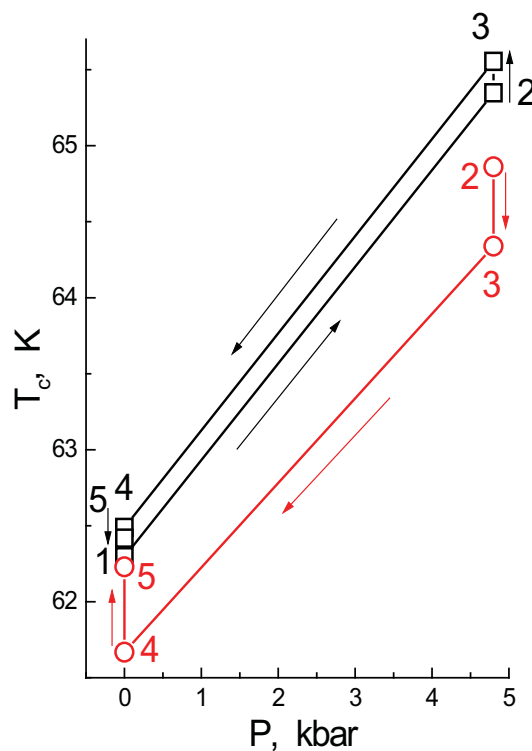
It can be seen that the application of hydrostatic pressure leads to the splitting of the low-temperature SC-maximum  $d\rho/dT$  into two (curves 2-5), which means the formation of at least two superconducting phases in the sample [24-26]. The low-temperature SC phase (forming an infinite cluster) is generated immediately after application of the pressure and manifests itself as a "shoulder" on the left slope of the maximum at about 65 K (curve 2). A low-temperature SC-maximum  $d\rho/dT$  is formed only after holding under pressure for a week (curve 3). Return to zero pressure (curve 4) and holding at  $P = 0$  and room temperature for 3 days (curve 5) are insufficient to completely restore the homogeneity of the sample - the SC-maximum  $d\rho/dT$  remains split and its height is less than in the initial state.

In Fig. 2b shows the changes in  $T_c$  during the application of the pressure-relief for both phases. It is seen that for both phases the application of pressure leads to an increase in  $T_c$  (Fig. 2b) with a velocity  $dT_c/dP \approx 0.6$  K / kbar (state 1→2). This qualitatively agrees with the literature data [8, 9, 24] obtained for samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with a reduced oxygen content. The increase in  $T_c$  as a result of the increase in pressure is probably due to a change in the lattice parameters, electron-phonon interaction, bonds between layers, etc. – the so-called "true" pressure effect [27].

In Fig. 2b it is also seen that holding at constant pressures (4.8 kbar and 0, states 2→3 and 4→5) leads to opposite changes in  $T_c$ : for the high-temperature SC phase, holding at  $P = 4.8$  kbar causes an increase in  $T_c$ , and holding at  $P = 0$  leads to a decrease in  $T_c$ ; for a low-temperature  $T_c$  phase,  $T_c$  decreases at  $P = 4.8$  kbar and increases at  $P = 0$ . These "relaxation" effects are apparently due to a change in the number of holes under pressure, which in turn is caused by the redistribution of labile oxygen [27, 28]. For underdoped samples (as in our case), the increase in the



a



b

Fig.2. The effect of pressure on the phase composition of  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystals. (a) is the temperature dependence of the derivatives  $d\rho/dT$  in the region of the superconducting transition, (b) is the change in  $T_c$  under pressure changes:  $\square$  – is the high-temperature superconducting phase;  $\circ$  – is the low-temperature SC phase. The numbering of curves (a) and states (b) is the same as in Fig. 1.

oxygen content leads to an increase in  $T_c$ , so it is natural to assume that the low-temperature SC phase differs from the high-temperature lower oxygen content, and holding at constant pressures causes a redistribution of oxygen between these phases. At 4.8 kbar, oxygen migrates into a phase with a larger  $T_c$ , where oxygen is already greater, that is, ascending diffusion takes place. At  $P = 0$  oxygen migrates into a phase with a smaller  $T_c$ , that is, the oxygen content in the sample is equalized due to ordinary diffusion and, ultimately, one SC phase remains in the sample. Thus, relaxation under pressure leads to the formation of two SC phases in the sample as a result of the ascending diffusion, and relaxation at zero pressure leads to the disappearance of the phase separation and to the preservation of one phase phase due to ordinary diffusion. We note that the value of the "true" pressure effect does not depend on whether the pressure increases or decreases, and the magnitude of the "relaxation" effect does not depend on the pressure at which relaxation occurs (0 or 4.8 kbar). Therefore, the changes in  $T_c$  in the investigated pressure interval are reversible.

**Redistribution of oxygen ions in  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single-crystals ( $\delta = 0.35$ ) and intensification of this process by external hydrostatic pressure.** Let us consider in more detail the possible mechanism for the redistribution of labile oxygen, the essence of which is that the pressure intensifies the process of diffusion coalescence of microscopic clusters of oxygen vacancies of different sizes formed in the crystal under investigation in connection with oxygen deficiency. As a result of coalescence, the oxygen ions in the crystal are redistributed, which leads to an increase in the number of ordered one-dimensional clusters of oxygen ions (clusters) that are sufficiently large in size. Since in our experiments we studied crystals characterized by the value of the parameter  $\delta \approx 0.35$  and the transition temperature  $T_c \approx 63$  K, in the structure of the crystal under study, in connection with the deficit of oxygen ions, there was a certain number of clusters not completely completed to the optimum stoichiometric composition. In fact, the crystal under investigation is a thermodynamically nonequilibrium system, which in its structure has defects in the form of microscopic clusters of oxygen vacancies of various sizes. The behavior of such a system on the way to the establishment of an equilibrium state can be described within the framework of the theory of diffusion coalescence of the separation of an extraneous phase from a supersaturated solution [29]. In our case, the extraneous phase is the emptiness associated with the presence of clusters formed by oxygen vacancies. In this case, a situation is observed that corresponds to the final stage of the evolution of the two-phase system, when the separation of the extraneous phase (accumulation of vacancies) has already been formed and only the change in their sizes occurs.

According to [30], the diffuse flux of a substance in the saturated phase (in our case, the flux of vacancies) per unit cluster surface is described by the expression:

$$J_v = -D_v (dc/dr)_{r=L} \approx -(D_v/L) (C - C_L), \quad (1)$$

where  $D_v$  – is the vacancy diffusion coefficient,  $L$  – is the effective size of the accumulation of vacancies:  $L \approx (3V / 4\pi)^{1/3} \approx (3N\Omega / 4\pi)^{1/3}$ , where  $V$  is the volume of the cluster formed by  $N$  vacancies,  $\Omega$  is the volume per vacancy.

$C$  – is the concentration of vacancies in the crystal,  $C_L$  – is the concentration of vacancies in the immediate vicinity of the cluster,  $r$  – is the coordinate.

The value of  $C_L$  is determined by the well-known formula:  $C_L \approx C_0 (1 + \alpha/L)$ , where  $C_0$  is the equilibrium concentration of vacancies,  $\alpha = 2\gamma\Omega / k_B T$  ( $\gamma$  is the specific surface energy,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature). Taking into account the relation (1), and also the fact that in our case "satiation" of vacancies in a crystal is characterized by the parameter  $\delta = (C - C_0) / C_0$ , the reduced concentration of vacancies, the change in cluster size with time  $t$  can be described as follows:

$$dL/dt \approx -(DL) (\delta - \alpha/L), \quad (2)$$

where  $D = D_v C_0$  – is the diffusion coefficient of oxygen ions.

It follows from relation (2) that for each saturation value of the crystal nonequilibrium (nonstoichiometric) vacancies, that is, for each value of the parameter  $\delta > 0$ , there are clusters of vacancies that are in an equilibrium state. For them the following condition is satisfied:  $(dL / dt) = 0$ . These vacancy clusters are characterized by some critical size  $L^*$ :

$$L^* = \alpha/\delta. \quad (3)$$

The existence of a critical size  $L^*$  means that for  $L > L^*$ , in connection with the system's desire to establish an equilibrium state, the accumulation of vacancies increases its size, and when  $L < L^*$  decreases it, that is, it dissolves. Note that the "satiation" value, characterized by the parameter  $\delta$ , and, respectively, the  $L^*$  value vary with time and as we approach the equilibrium, when  $\delta \rightarrow 0$ ,  $L^* \rightarrow \infty$ . Thus, in an equilibrium state, all the clusters of nonstoichiometric vacancies in oxygen that are present in the crystal must disappear in a diffuse way, combining with the largest "accumulation of emptiness" - the surface of the crystal.

If a hydrostatic pressure  $P$  is applied to the crystal, then, in connection with the decrease in the vacancy concentration near the  $C_L$  cluster, the "saturation" of the crystal with vacancies decreases. Accordingly, the critical cluster size  $L^*$  increases. It is easy to show that there is a connection between the critical cluster size in the absence of pressure ( $L^*$ ) and its presence ( $L_p^*$ ):



$$L_p^* = L^*/(1-\beta_p), \tag{4}$$

where  $\beta = L^*/2\gamma$ .

It follows that under the influence of pressure, the accumulation of vacancies of "supercritical" size ( $L > L_p^*$ ) goes to the category of "subcritical" ( $L < L_p^*$ ), that is, dissolving. Thus, the pressure intensifies the process of dissolution of clusters of vacancies in a crystal.

Now we take into account the fact that the flow of vacancies in any direction causes the flow of oxygen ions in the opposite direction:  $J_v = -J_o$ . Consequently, the process of coalescing of vacancy clusters (the process of their dissolution to complete extinction) simultaneously means the coalescence of oxygen clusters, that is, as the crystal approaches the equilibrium state, oxygen clusters must increase in size (grow). Thus, reaching the equilibrium stoichiometric state, that is, having reached the value of the parameter  $\delta \approx 0$ , the deficit of oxygen ions disappears and simultaneously all the ordered chains of oxygen ions (clusters) become fully equipped. Thus, in accordance with the above considerations, external hydrostatic pressure contributes to the coalescence of oxygen clusters and should, accordingly, intensify the process of phase formation, which has a higher transition temperature  $T_c$ . This is what we observed in our experiments (see Fig. 2b).

We note that in the process of establishing the equilibrium state, the parameter  $x$  characterizing the degree of "saturation" of the crystal with oxygen vacancies, as well as the average cluster size  $L_{mean}$ , depend not only on the temperature, but also on the time  $\delta \approx \lambda t^{1/3}$ , where  $\lambda \approx (\alpha^{2/3} D^{-1/3})$ ;  $L_{mean} \approx (D\alpha)^{1/3} t^{1/3}$  [29]. In addition, the diffusion of oxygen ions in the crystal under study at various stages of the establishment of the equilibrium state can be realized both by the conventional classical mechanism and by the more accelerated mechanism of single-file diffusion [31]. This circumstance complicates the character of the kinetic dependences  $\delta(t)$  and  $L_{mean}(t)$ , which ultimately determine the nature of the relaxation curves  $\rho(t)$  (see Fig.3)

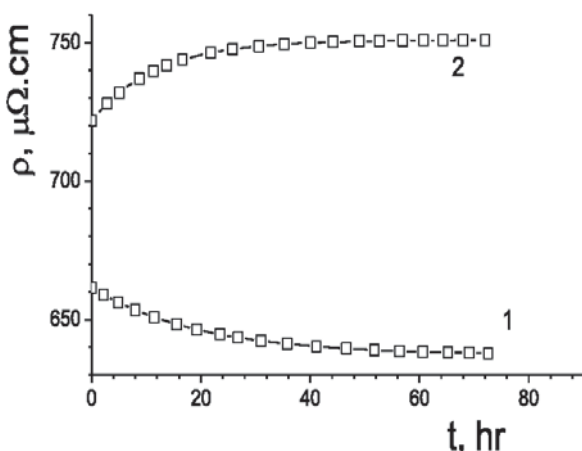


Fig. 3. Relaxation dependences of electrical resistance  $\rho(t)$  at  $T = 300K$ , measured after application of pressure 4.8 kbar (1) and after its removal (2).

Curve 1 of the present figure corresponds to the dependence of  $R(t)$ , measured after application of pressure 4.8 kbar, and curve 2 - after its removal. It is seen that the establishment of the equilibrium value of the resistance  $R(t \rightarrow \infty)$  after the pressure is released is almost two times faster than under pressure conditions. This experimental fact is also explained in the framework of the proposed mechanism for the coalescence of oxygen clusters. Indeed, under conditions of pressure, the process of filling clusters with oxygen ions by the accelerated mechanism of "single-file" diffusion is realized only at the initial stage, and in the future this process and, accordingly, the decrease in resistance are limited more slowly by the mechanism of classical diffusion. After the removal of the pressure, the process of intensive increase in the size of the oxygen clusters ceases. In this case, the number of incompletely completed clusters increases with time, and accordingly the resistance  $R$  is relaxed. Under these conditions, oxygen ions are displaced much less distances and can be realized in the single-file diffusion regime until the equilibrium value  $R(t \rightarrow \infty)$ .

In conclusion, we present some quantitative estimates confirming the effectiveness of the coalescence mechanism (increase in dimensions) of the oxygen clusters in the crystal under investigation, as well as the role of pressure in this process.

According to formula (3), the value of the critical size of the vacancy accumulation can be estimated using the relation:  $L^* \approx 2\gamma\Omega / k_B T \delta$ . Substituting in this relationship the values of the constants  $\gamma \approx 10^{-1} J/m^2$ ,  $\Omega \approx 3 \cdot 10^{-29} m^3$ ,  $k_B T \approx 3 \cdot 10^{-21} J$  ( $T \approx 300K$ ), and also  $\delta \approx 0.4$ , we obtain:  $L^* \approx 5 \cdot 10^{-9} m$ . In addition, it follows from relation (4) that at a pressure  $P^* \approx 2\gamma/L^*$  the quantity  $L^*$  becomes infinite, that is, all the nonstoichiometric vacancies in the crystal must be dissolved by a diffuse mechanism, turning into oxygen clusters. Assuming  $L_p^* \approx L^*$  (the initial stage of the coalescence process), and substituting this value in the formula for  $P^*$ , we have:  $P^* \approx 10^8 N/m^2 \sim 1$  kbar. This rough estimate means that a pressure of several kbar can affect the coalescence of oxygen clusters in the crystal under study. It is this effect that we observed in our experiments.

**Approximation of the temperature dependence of the resistance in the range of  $T_c$ -300 K.** The temperature dependence of the resistance of the metallic type is described by the standard Bloch-Gruneisen formula, taking into account scattering of charge carriers by phonons, i.e. effects of electron-phonon interaction (EPI) [15], and defects. In our case, one should also take into account the appearance of a fluctuation conductivity near  $T_c$ . For the latter, the use of the Aslamazov-Larkin 3D model [17,20] gives the smallest error. Therefore, the general expression for the conductivity has the form:

$$\sigma = \rho_{met}^{-1} + \Delta\sigma_{AL} \tag{5}$$

$$\rho_{met}(T) = \frac{(\rho_0 + \rho_{ph})}{1 + C_0 \exp\left(-\frac{T_1}{T}\right)}; \quad (6)$$

$$\rho_{ph} = C_n \left(\frac{T}{\theta}\right)^n \int_0^{\theta/T} \frac{x^n e^{-x}}{(e^x - 1)^2} dx$$

$$\Delta\sigma_{AL} = \frac{e^2}{16\hbar\xi_c(0) \sqrt{2\varepsilon_0 \sinh\left(\frac{2\varepsilon}{\varepsilon_0}\right)}} \quad (7)$$

In (6),  $\rho_0$  is the residual resistance;  $\rho_{ph}$  is the resistance due to scattering of electrons by phonons [15], in our case  $n = 3$ , which corresponds to interband (s-d) scattering;  $\theta$  is the Debye temperature; the factor  $[1 + C_0 \exp(-T/T_1)]^{-1}$  describes the deviation of the dependence of  $\rho_{met}(T)$  on the linear motion at high temperatures. In our case, there is a deviation downward, that is, the tendency of the dependence of  $\rho(T)$  to saturation. This factor is used to describe the dependences of  $\rho(T)$  alloys of transition metals at high temperatures and can be related, for example, to the influence of one of the electronic bands whose bottom energy is above the Fermi energy by the value of  $k_B T_1$  [23, 32]. The saturation of the  $\rho(T)$  alloys is considered in more detail in [27, 28, 32-34].

The expression for the fluctuation conductivity in the plane of the layers (3) is chosen to limit the region of its influence [35],  $\varepsilon = \ln(T/T_c)$  is the reduced temperature,  $T_c$  is the critical temperature in the mean-field approximation,  $T > T_c$ ,  $\xi_c$  is the transverse length coherence,  $\varepsilon_0$  determines the temperature range of superconducting fluctuations –  $\varepsilon_0 = \ln(T_{fluct}/T_c)$ ,  $T_{fluct}$  is the characteristic temperature above which there are no superconducting fluctuations.

We note that, according to [20], the appearance of fluctuation Cooper pairs above  $T_c$  causes a decrease in the density of one-electron states at the Fermi level, that is, leads to the appearance of a pseudogap at  $T \approx T_{fluct}$ . However, it is difficult to take into account the corresponding change in the normal resistance, since a much more singular fluctuation conductivity acts in parallel, which determines  $\rho(T)$  near  $T_c$ .

By varying the parameters of expressions (5) - (7), it is possible to minimize the average error of approximation to a level close to the experimental error –  $\sim 0.5 \div 0.9\%$ . Thus, for each experimental  $\rho(T)$  dependence, a set of approximation parameters was obtained by (5). The solid lines in Fig. 1 are carried out in accordance with (5) - (7). The optimal set of approximation parameters is given in the table.

Note that the derivatives,  $d\rho/dT$ , calculated from (5)-(7) adequately approximate the behavior of  $d\rho/dT$ , calculated from the experimental data in the entire fitting interval (see the inset in Fig. 1).

We also note that the formation of the second phase does not in any way affect the approximation error. This is possible if one phase shunts the other ( $R_{f1} \gg R_{f2}$ ) or if the phases are practically indistinguishable from each other (at least according to the temperature dependence of the resistance).

The analysis of the changes in the obtained approximation parameters as a function of pressure changes allows one to estimate the effect of "true" and "relaxation" pressure effects on the processes of charge transfer and scattering of its carriers.

**Effect of pressure on the parameters of the temperature dependence of the resistance in the normal state.** In Fig. 4 shows the relative changes in the parameters of approximation of the temperature dependence of the normal resistance - formula (6) - with a change in pressure.

*Table 1.*

The parameters of approximation of the temperature dependence of the resistance in the interval  $T_c$ -300 K according to (5)-(7).

	1 - P=0	2 - P=4. kbar	3 - P=4.8 kbar, t=7 days	4 - P=0	5 - P=0, t=3 days
$T_c$ , K	62.280	65.337	65.498	62.483	62.288
$\rho_0 \cdot 10^4$ , Ohm·cm	1.091	0.9245	0.8935	1.076	1.094
$C_3 \cdot 10^3$ , Ohm·cm	4.23	3.81	3.68	4.05	4.235
$\theta$ , K	670	667.5	667	675	670
$T_p$ , K	785	730	722	990	795
$C_0$	1.9	1.97	1.965	3.8	2.0
$\xi_c(0)$ , Å	5.5	4.4	4.1	3.8	4.5
$\Delta T_{fluct}$	5.2	0.3	1.2	5.0	4.5

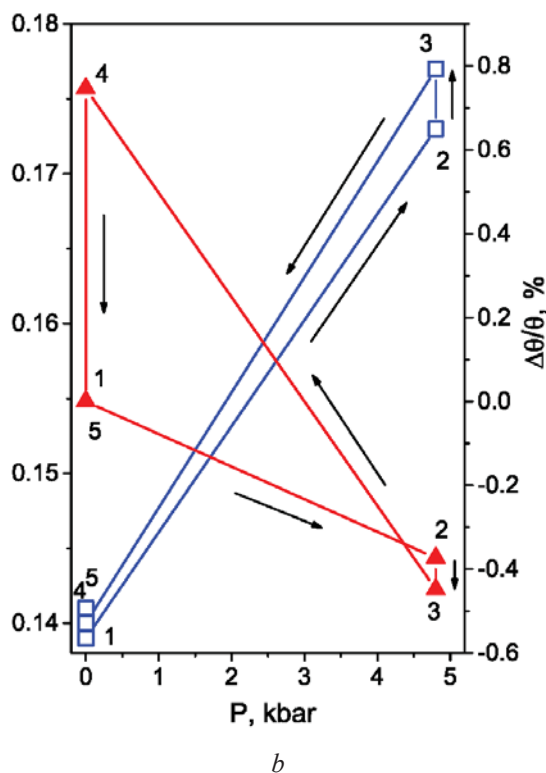
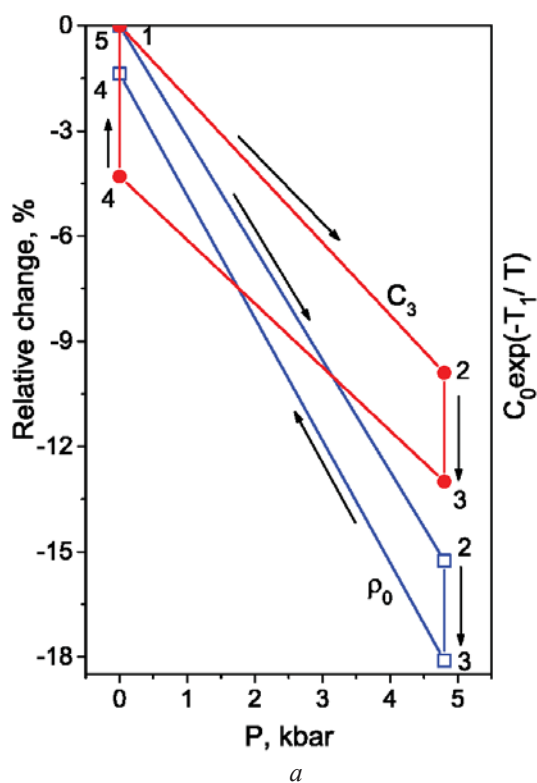


Fig. 4. Effect of pressure on the parameters of the temperature dependence of the resistance in the normal state. (a). - relative changes: the residual resistance  $\rho_0$  –  $\square$  and the interband (s-d) scattering parameter,  $C_3$  –  $\circ$ ; (b). - deviation of the dependence of  $\rho_{met}(T)$  on linear motion at high temperatures,  $C_0 \cdot \exp(-T_1/T)$  –  $\square$ , (left scale); relative changes: Debye temperatures  $\theta$  –  $\blacktriangle$  (right scale).

It is seen that the residual resistance,  $\rho_0$ , and the parameter  $C_3$  (Figure 4a) decrease with compression, and the "true" pressure effect (sections 1-2 and 3-4) is much larger than the "relaxation" (sections 2-3 and 4-5). It is also seen that the values of these parameters at the pressure drop return to their initial values after holding at  $P = 0$  – points 1 and 5 practically coincide. Thus, the parameters describing the actual scattering of charge carriers by phonons and defects vary with the pressure reversibly. Analogous to the behavior of  $T_c$  (Fig. 2b), the magnitude of the "true" pressure effect does not depend on whether the pressure increases or decreases (sections 1-2 and 3-4), and the magnitude of the "relaxation" effect does not depend on the pressure at which there is a relaxation (0 or 4.8 kbar).

Since the factor  $[1 + C_0 \exp(-T_1/T)]^{-1}$ , which describes the tendency of the dependence of  $\rho(T)$  to saturation, has several explanations - see, for example, [27, 28, 32-34], it makes sense to consider its changes depending on changes in pressure entirely, and not on individual parameters. This dependence is shown in Fig. 4b (left scale). It can be seen that, as in the previous cases, the value of the "true" effect is much larger than the "relaxation" effect and does not depend on whether the pressure increases or decreases and the magnitude of the "relaxation" effect does not depend on the pressure at which relaxation occurs (0 or 4.8 kbar).

For the Debye temperature  $\theta$ , which characterizes the phonon spectrum of the sample, the situation is somewhat different - Fig. 4b (right scale). The magnitude of the "true" effect with increasing pressure (section 1-2) is less than with decreasing pressure (section 3-4). The magnitude of the "relaxation" effect at 4.8 kbar (section 2-3) is very small, but holding at 0 kbar (section 4-5) leads to a significant decrease in  $\theta$  practically to the initial value.

Such a behavior of  $\theta$  under pressure changes may be due to the fact that the time of pressure increase is much longer than the pressure release time. With a relatively slow increase in pressure, the structure improves (for example, the concentration of vacancies decreases), and the pressure drop leads to order disruption with the formation of excess (nonequilibrium) defects, whose concentration at  $P = 0$  relaxes to the initial equilibrium value [22].

**Influence of pressure on parameters of fluctuation conductivity.** The magnitude of the transverse coherence length,  $\zeta_c(0)$ , is about  $5\text{\AA}$  (see table), which corresponds to the literature data (see, for example, [36]). The changes in  $\zeta_c(0)$  and the temperature interval for the existence of superconducting fluctuations,  $\Delta T_{fluct} = T_{fluct} - T_c$ , with the pressure changes are shown in Fig.5

It can be seen that for all pressure changes,  $\zeta_c(0)$  decreases (sections 1-2, 2-3 and 3-4), and only holding at  $P = 0$  causes an increase in  $\zeta_c(0)$  (section 4-5), however the time of such exposure - 3 days - was insufficient for complete relaxation of  $\zeta_c(0)$  to the initial state - the difference between the states 5 and 1 is about 20% (see

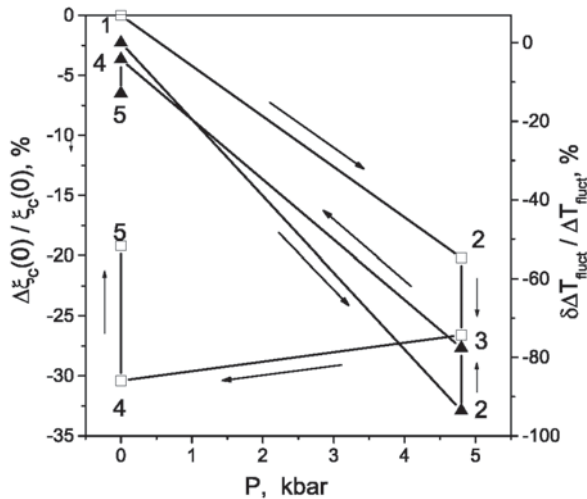


Fig. 5. Effect of pressure on the parameters of fluctuation conductivity. The transverse coherence length is  $\xi_c(0)$  – □ (left scale); temperature range of existence of superconducting fluctuations,  $\Delta T_{fluct} = T_{fluct} - T_c$  – ▲ (right scale).

Table and Figure 5). It can be assumed that this behavior of  $\xi_c(0)$  is due to the fact that at all stages of the pressure change the phase composition of the sample was not in equilibrium. In particular, the exposure at  $P = 0$  and room temperature for 3 days is insufficient and to completely restore the homogeneity of the sample (Fig. 2a, curve 5). Thus, the characteristic times of the processes leading to the formation of superconducting phases are much shorter than the time of our experiment, which in turn is shorter than the time for restoring the homogeneity of the sample.

As for the temperature interval for the existence of superconducting fluctuations, in [35] this parameter was introduced rather formally. Therefore, we note here only the fact that for  $\Delta T_{fluct} = T_{fluct} - T_c$  "the true" effect is much greater than the "relaxation" effect, that is, the times of the processes causing the appearance of the pseudogap are sufficiently small.

### Conclusion

We have observed a significant change in the character of the  $\rho(T)$  dependence and the appearance of two SC phases with different values of  $T_c$  in samples after 7 days under 4.8 kbar pressure. Moreover, the difference is increasing with the holding time. This fact is explained by the redistribution of the labile component of the oxygen subsystem by the mechanism of ascending diffusion. After the removal of pressure and relaxation, the electron conduction characteristics of a single-crystal tend to be restored due to the usual diffusion of oxygen ions. Redistribution of labile oxygen can be described by the mechanism of diffuse coalescence. A single-channel diffusion regime appears at the initial stages of relaxation and is followed by the classical diffusion mechanism.

The temperature dependences of the resistance over the entire  $T_c$ -300 K interval and for all pressures are satisfactorily described by the Bloch-Gruneisen formula in the normal state, and by the Aslamazov-Larkin 3D model for the fluctuation conductivity in  $T_c$  state:

$$\sigma = \rho_{met}^{-1} + \Delta\sigma_{AL}$$

Analysis of the dependences of the fitting parameters and the residual resistance (i.e. parameters describing the actual scattering of charge by phonons and defects)  $T_c$  on the pressure and holding time indicates the reversibility of the processes. The magnitude of the "true effect" is substantially greater than the value of the "relaxation effect" and does not depend on whether the pressure increases or decreases. The magnitude of the "relaxation effect" does not depend on the pressure at which relaxation occurs. Regarding the temperature interval of superconductive fluctuations, the "true effect" is much greater than the "relaxation", i.e. the duration processes causing the pseudogap is quite small.

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