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Evolution of normal electrical resistance in oxygen underdoped $Ho_1Ba_2Cu_3O_{7-\delta}$ single crystals in the process of application-removal of high hydrostatic pressure

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The influence of high hydrostatic pressure on electrical resistance in *ab*-plane of oxygen underdoped $Ho_1Ba_2Cu_3O_{7-\delta}$ has been studied. It was found that high-pressure-induced redistribution of labile oxygen leaded to increasing phase separation, which was accompanied by a process of structural relaxation and uphill diffusion in the bulk of the pilot sample. It has been suggested that the generation of low-temperature (oxygen-depleted) phase can occur at twin boundaries. The temperature dependence of the resistivity above T_c can be accurately approximated by the model s–d-electron scattering by phonons. Application of high pressure leads to a decrease of the resistance, which at high temperatures is much larger than at low temperatures. This may be due to the weakening the electron-phonon interaction with increasing pressure.

Исследовано влияние высокого гидростатического давления на электросопротивление в *ab*-плоскости монокристаллов $Ho_1Ba_2Cu_3O_{7-\delta}$ с недостатком кислорода. Установлено, что индуцируемое высоким давлением перераспределение лабильного кислорода приводит к усилению фазового расслоения, что сопровождается процессами структурной релаксации и восходящей диффузии в объеме экспериментального образца. Высказано предположение о том, что зарождение низкотемпературной (обедненной кислородом) фазы может происходить на границах двойников. Температурные зависимости электросопротивления выше T_c могут быть с высокой точность. аппроксимированы в рамках модели s–d-рассеяния электронов на фононах. Приложение высокого давления приводит к уменьшению сопротивления, которое при высоких температурах существенно больше, чем при низких. Это может быть связано с ослаблением электрон-фононного взаимодействия при увеличении давления.

1. Introduction

Despite the fact that since the time of high conductivity (HTSC) discovery [1] more than two decades passed, the microscopic nature of this unique phenomenon is still not fully understood. According to modern concepts [2], it is believed that the keys to understanding the nature of high-temperature superconductors can be considered the physical phenomena, which were observed in the normal state at temperatures near and above the critical temperature (T_c). Such phenomena, in particular, include the appearance of a wide temperature HTS excess paraconductivity area in the basal *ab*-plane [3], incoherent electrotransport [2], metal-insulator type transition [4], the pseudogap anomalies (PG), and so etc. All of the above phenomena are extremely important to address one of the main basic and applied problems in solid state physics — creation of the new functional materials with high current-carrying capacity. Great importance in the study of these phenomena is to understand the mechanisms of charge transfer and carrier scattering. Invaluable role is played by the use of high pressure as an instrument which allows not only to test the adequacy of various theoretical models, but also to identify empirical ways of improving the critical parameters of superconducting compounds, that is important for practical applications.

An important feature of high-T_c compounds 1-2-3 system $ReBa_2Cu_3O_{7-\delta}$ (Re=Y, Ho or other rare-earth ion) is the ability to implement them in a nonequilibrium state with a certain degree of oxygen deficiency [3–5], which can be induced by external influences such as temperature [4] and high pressure [3, 5]. This condition is accompanied by a redistribution of labile oxygen and structural relaxation, which in turn have a significant impact on the electrotransport system parameters [3–5]. An important role is played by the replacement of its isoelectronic rare earth yttrium analogs. Particular interest in this respect is the replacing yttrium by holmium with sufficiently large (more than 10 mV) the magnetic moment [6], which provides connections paramagnetism in the normal state. However, as well as in the case of other rare earth elements in the implementation of replacing Y by paramagnetic ions Re = Ho, Dy superconducting properties of optimally doped with oxygen compounds $ReBa_2Cu_3O_{7-\delta}$ with $\delta \le 0.1$ do not vary significantly [6]. Apparently this is due to the localization of the ions far from superconducting planes, which, in turn, prevents the formation of long-range magnetic order. At the same time, we know that in the samples of high-T_c 1-2-3 system with non-stoichiometric oxygen composition, rare earth ion can act as a sensor that is sensitive to the local symmetry of the environment and the distribution of charge density, since their change affects the crystal field forming the electronic structure of the ion [7]. A characteristic feature of samples with oxygen deficiency $\delta \ge 0.3$ is the broadening of the resistive transition to the superconducting state under pressure [3, 5, 8, 9]. The reason for this behavior to date has not been established. It should also be noted that, despite the large number of studies on the relaxation processes in 1-2-3 system under high pressure, many aspects of this phenomenon, such as the nature of the charge transfer and redistribution vacancy subsystem, are still completely not understood. Obviously, a role is played here by the fact that significant part of the experimental data was obtained from ceramic and polycrystalline samples with a high content of intergranular bonds [8, 9]. In the case of single-crystal an additional complexity is created by the presence of twin boundaries (TB) [10], whose influence on the transport properties in the normal state are poorly understood, due to the experimental difficulties in determining the contribution of these defects. Taking into account the above mentioned information, in the present work it was investigated the effect of hydrostatic pressure up to 5 kbar at electrotransport characteristics and structural relaxation in the *ab*-plane of single-crystal $Ho_1Ba_2Cu_3O_{7-\delta}$ with low oxygen content, the different geometry of the transport current flowing: $I \| TB$, when the influence of twins on the processes of carrier scattering is minimized, as well as the angle between I and TB was 45°.

2. Experimental

$Ho_1Ba_2Cu_3O_{7-\delta}$ single crystals were grown by solution-melt method in gold crucible using technology similar to the technology of synthesis of $YBa_2Cu_3O_{7-\delta}$ single crystals [2–5]. For crystals with oxygen saturation to the optimum concentration $\delta \le 0.15$ their annealing was performed in a stream of oxygen at 370÷410°C for five days. It is known [5], that such a procedure is accompanied by the formation of a developed system of twin boundaries that minimize the elastic energy of the crystal lattice at the tetra-ortho transition. To conduct resistivity measurements from one growth batch size single crystals were selected: K1 — $1.7\times1.2\times0.2$ mm^3 and K2 — $1.9\times1.5\times0.3$ mm^3 (smallest point in the direction along c axis), in which there were areas with a one-way system of twin boundaries. Made from selected single crystals the experimental samples distinguished in orientation of twinning planes relative to the direction of the transport current in the *ab*-plane ($I \| TB$ for K1 (Fig. 1a) and 45° for the crystal K2 (Fig. 1b). For reducing oxygen content the samples were annealed for three — five days in a stream of oxygen at higher temperatures. Electrical contacts were made of silver wire, which was connected to the crystals with silver paste. Resistivity in the *ab*-plane was measured at constant current up to 10 mA in two opposite directions of the current using standard four-contact method. Hydrostatic pressure was created in the autonomous cell type pis-

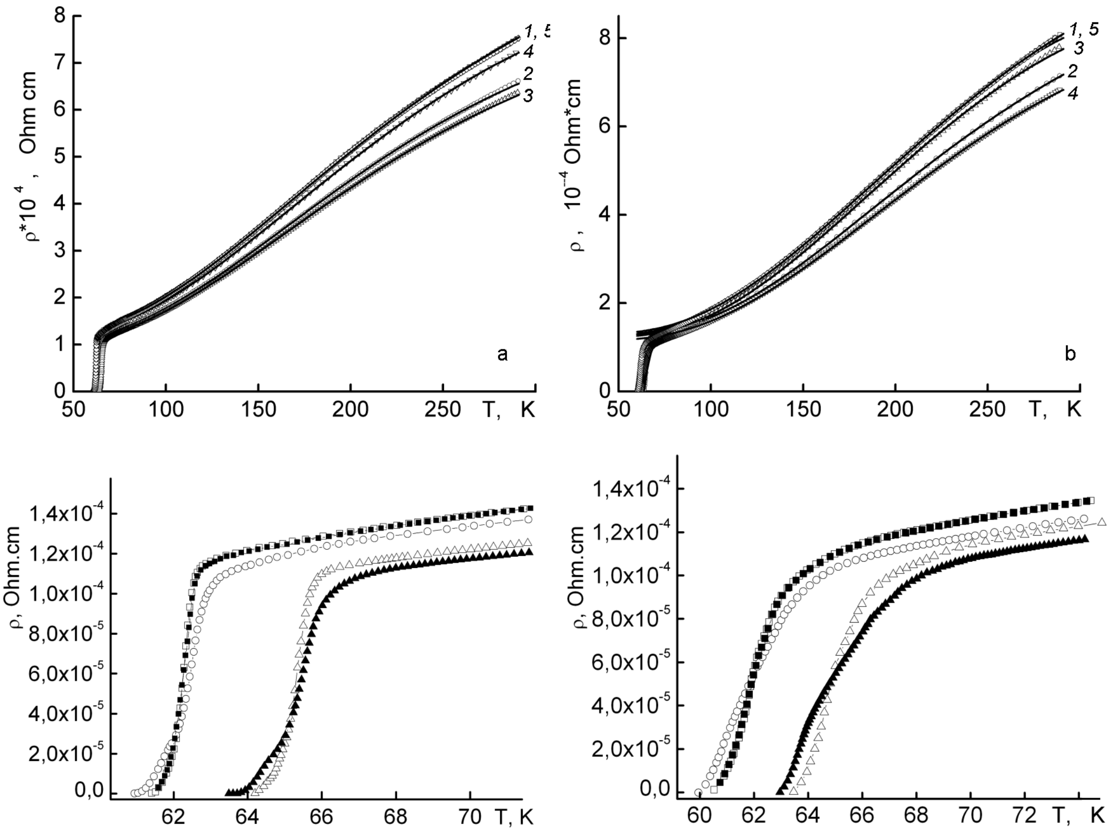

Fig. 1. Dependences $\rho_{ab}(T)$ at different pressures and directions of the current relative to the twin boundaries. a — the "parallel" to the b — "45°" orientation. Curve *1* was measured before application of pressure, curve *2* was measured immediately after application of pressure of 4.8 kbar, curve 3 — after keeping the sample at room temperature under pressure of 4.8 kbar in the week, and curve *4* — immediately after removal of pressure and curve *5* was measured after exposure sample at zero pressure for three days. Solid lines through an approximation of (1). In the insert — the superconducting transition.

ton-cylinder [3, 5]. Value of pressure was measured by manganin gauge, temperature — by copper-constantan thermocouple mounted to the outer surface of the chamber at the level of the sample. To determine the impact of structural relaxation measurements were carried out after a few days after pressure application/removal, upon completion of the relaxation processes.

3. Results and discussion

Fig. 1a,b shows the temperature dependences of the resistivity in the basal *ab*-plane $\rho_{ab}(T)$ for samples K1 and K2, which were measured after the application-removal of high hydrostatic pressure. Part of the curves in this and the following figures is not shown to simplify the picture. Resistive transition to superconducting state is shown in the corresponding insets in Fig. 1a and b. Analysis of the curves *1*, measured before the application of high pressure, shows that decrease in oxygen content in addition to lowering the critical temperature leads to an increase of the width of the resistive transition to superconducting state in more than 10 times as compared with the initial sample (from $\Delta T_c \leq 0.3$ K to $\Delta T_c \approx 3.5$ K), and the superconducting transition acquires a stepped form. This apparently indicates an appearance in the sample at least two phases, which have, respectively, the different critical temperatures (T_{c1} and T_{c2}) of the transition to superconducting state [3, 5]. Reduction of oxygen content in the both crystals also resulted in transfer of the curves of quasimetallic $\rho_{ab}(T)$ [2, 3] to appearance of the dependences with a characteristic thermally activated basin, as more fully described below.

Application of pressure leads to a decrease in the electrical resistance and an increase in T_c (see Table) at $dT_c/dP \approx 0.7$ K/kbar, which is qualitatively consistent with the

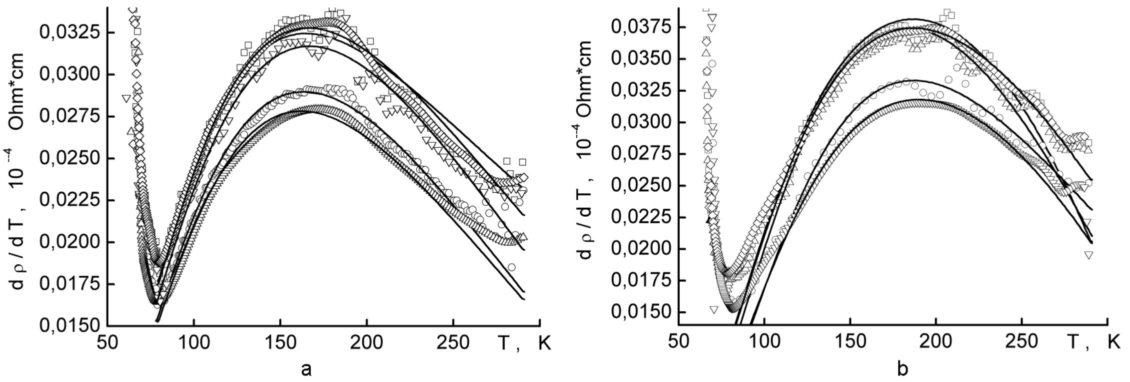

Fig. 2. Temperature dependences of the derivative $d\rho/dT$ calculated at different pressures above the superconducting transition. The curves correspond to Fig. 1.

literature data [3, 8, 9], obtained for samples of $YBa_2Cu_3O_{7-\delta}$ with low oxygen content. It is important to note that decrease in the electrical resistance is not only a result of the influence of hydrostatic pressure, but also result of the process of isobaric keeping the sample at room temperature immediately after the high pressure application. For example, in Fig. 1a and b the curves 2 and 3 correspond to dependences, measured for samples K1 and K2 immediately after the application of pressure of 4.8 kbar and after isobaric keeping of the sample at the same pressure at room temperature for five days, respectively. It is evident that such exposure leads to an additional decrease in the resistivity on 4÷5 %.

Qualitatively similar behavior of the curves $\rho_{ab}(T)$ was observed after removal of the high pressure. Thus, in the same figure curves *1* and *4* correspond to the dependences measured before application and immediately after removal of the pressure. A comparison of these curves shows that the measurement results depend strongly on the exposure time of the sample at room temperature. Thus, immediately after removal of the pressure, the value of resistivity of the sample at room temperature was on approximately 4 % lower than the value measured before application of pressure. The value continued to relax for about three days till the equilibrium value. Then the value of ρ_{ab}(290 K) reached the saturation, and dependences $\rho_{ab}(T)$ for both crystals were in agreement with the original curves, measured prior to the application of high pressure. This demonstrates the reversibility of the process.

As was noted above, the decrease in oxygen content leads to the reducing T_c (from 92 to 63 K) and to the transformation of the form of dependency $\rho_{ab}(T)$, which is expressed in the transition from quasimetallic

Table. Change the of the approximation parameters (1) in the cycle of application-removal of the pressure

	$I \| TB$	45° between I and DG
	Minimum error is reached, assuming *s–d* scattering	Minimum error is reached, assuming *s–s* scattering
ρ_0	maximum change of 16 %, a return to the original value, up 1.5 %	maximum change of –8 %, a return to the original value, up 3.5 %
	C_3 — the maximum change of 17 %, a return to the original value, up 0.2 %	C_5 — maximum change –12.5 %, a return to the original value with an accuracy of 0.5 %
θ	maximum change of 1 %, a return to the original value, up 0.4 %	maximum change of 10 %, a return to the original value with an accuracy of 0.3 %
C_4	maximum change of 110 %, the initial value is not returned, remaining bigger than the original 54 %	maximum change of 84 %, the initial value is not returned, remaining less than the original 60 %
T_1	maximum change of 33 %, the initial value is not returned, remaining bigger than the original 20 %	maximum change of –43 %, the initial value is not returned, remaining less than the original 20 %

behavior of the curves characteristic for the optimally doped samples [3, 10], to dependences with a characteristic deflection. In [11, 12], the temperature dependence of resistance for high-temperature superconductor ReBaCuO (Re = Pr, Nd) was associated with the presence of metallic and semiconducting phases, and the resistance of the metallic phase was described as $r_0 + aT$, which is typical for the scattering of electrons by phonons at high temperatures ($T > \theta$). In [13] the temperature dependence of the resistivity for the layered compound $Nb_{1-x}Sn_xSe_2$ was qualitatively similar to our results (Fig. 1), and it has been described in terms of the assumption of the scattering of electrons by phonons with the additional contribution to the conductivity of the electronic states of the band, the energy of the bottom is higher than the energy Fermi [14]. Following this work, we have tried to describe the experimental curves (solid lines in Fig. 1) above the superconducting transition using the same method.

If one of the phases is almost completely bypasses another one ($R_{phase1} > R_{phase2}$) or if the phases are virtually indistinguishable from each other (at least, from the temperature dependence of the resistance), then the temperature dependence of the resistivity can be approximated as a single-phase model [15]:

$$\rho(T) = (\rho + \rho_{ph}) \cdot [1 - C_4 \cdot \exp(-\frac{T_1}{T})]; \qquad (1)$$

$$\rho_{ph} = C_n \cdot (\frac{T}{\theta})^n \cdot \int_0^{\theta/T} \frac{X^n e^X}{(e^X - 1)^2} dX.$$

Here ρ_0 — residual resistance; ρ_{ph} — resistance due to the scattering of electrons by phonons [15], θ — Debye temperature, thermal activation factor $1 - C_4 \cdot \exp(-T_1/T)$ is associated with the possible influence of the semiconducting phase [11, 12]. By varying the parameters of (1), you can minimize the average error of approximation to a level close to the experimental error — ~0.5 %. Thus for each of the experimental dependences $\rho(T)$ it was obtained a set of parameters for the approximation (1). The solid lines in Fig. 1 and Fig. 2 held in accordance with (1).

If the current is parallel to the twin boundaries, the smallest approximation error is achieved when $n = 3$, which corresponds to s–d scattering (in particular, for the initial curve ($P = 0$) $\rho_0 = 1.090$ Ohm·cm and $\theta = 679$ K). If the current is directed at angle of 45° to the twin boundaries, the smallest approximation error is achieved when $n = 5$, which corresponds to s–s scattering, and for the initial curve ($P = 0$) $\rho_0 = 1.240$ Ohm·cm and $\theta = 669$ K. Analysis of changes in the parameters of the approximation due to cycles of $P = 0 \rightarrow$ application pressure $P = 4.8$ kbar $\rightarrow$ exposure at $P = 4.8$ kbar for a week $\rightarrow$ pressure relief $P = 0$ for three days" is shown in the Table.

The Table shows that:

1) Under $I \| TB$, s–d scattering dominate, and if the angle between I and TB is 45° — s–s scattering is predominant. It means that s–d scattering of electrons by phonons occurs in the sample, and s–s scattering related to the twin boundaries, thermally activated factor is also influenced by twin boundaries. Indeed, experiments on decoration of the vortex structure [16, 17] showed that the density of vortexes at the TB is increased compared with their density in the bulk superconductor. It indicates the suppression of the order parameter on the TB. This, in turn, may be due to low oxygen content in the plane of the domain wall, which can serve as effective centers of the flow of oxygen vacancies [18], as a consequence of stress, creating a potent attraction for the lattice vacancy (i.e. field of repulsion for oxygen atoms). The latter assumption can be supported by the existence of different forms of superconducting transitions obtained in parallel and 45° th geometries [5]. At 45° the second geometry SP transition is almost 2 times wider and more diffuse than in parallel (see the inset in Fig. 1). Obviously, in the second case it is probable the presence of percolation paths of current flow on the high temperature phase [19]. At the same time, in the second 45° geometry (measuring electrical resistance of a single crystal K2) percolation current path for the high-temperature superconducting phase seems to be lacking [20]. Thus the intensity of the scattering of charge carriers should be minimal at the geometry of the experiment $I \| TB$, which is reflected in the transformation of the form of the underlying relationships $d\rho_{ab}(T)/dT$ and $\rho_{ab}(T)$. The last assumption is indirectly confirmed by the difference in the absolute value of the resistivity at room temperature, which is about 7 % less than in the case of parallel geometry in comparison with the case of the second 45° geometry. A certain role can be

played by the specific mechanisms of quasiparticle interaction due to the presence in the system of structural and kinematic anisotropy [21–23].

2) The parameters ρ_0, C_3, C_5 and θ vary slightly and after discharge they returned to baseline (or close) values, i.e. electron scattering by defects and phonons is reversible with respect to the removal of pressure.

3) Thermal activation factor varies strongly and it does not return to the initial value during 3 days, i.e. its changes may be irreversible.

4) In the parallel and 45° th geometries the parameters of thermally activated factor (C_4 and T_1) are changed in the opposite ways, in particular at 45° geometry the role of this factor decreases, i.e. under the influence of twin boundaries temperature dependence of the resistance becomes more "metal."

It should be noted that the final conclusion about the nature of the influence of TB on the phase separation in $Ho_1Ba_2Cu_3O_{7-\delta}$ single crystals requires additional experimental studies. It seems logical to perform the measurements of superconducting transitions in untwinned and twinned single crystals with a specific distribution of the TB-planes: in one of the parts of the crystal the current transport vector should be oriented parallel to and in the other part — perpendicular to the plane of the domain wall. In the latter case, the transport current is inevitably crosses the plane of the wall in one part of the single crystal (when $I \perp TB$) and can flow in the bulk of the superconductor, bypassing the plane walls in another part of the single crystal (when $I \| TB$). Measurements on the same untwinned crystals give information about the existence (or absence) of a step-like form of the superconducting transition and the difference ($T_{c1}-T_{c2}$) in the absence of planar defects in the sample. It should be also noted that all characteristic changes in the shape of the temperature dependences of the electrical resistance and in the absolute values of resestivity parameters (observed during isobaric annealing at room temperature for $HoBa_2Cu_3O_{7-\delta}$ compounds) were much more pronounced in comparison with the samples $YBa_2Cu_3O_{7-\delta}$ [3]. Apparently, in the case of the samples $HoBa_2Cu_3O_{7-\delta}$ a certain role in the structural order in the system has been played by replacement yttrium by holmium, which has a much larger ionic radius that in turn leads to a change in the interaction of oxygen ions in CuO-planes. Indeed, as it is known from the literature [7], the replacement of yttrium by other rare earth elements with large ionic radius results in significant qualitative change in the $T_c(\delta)$. The characteristic for $YBa_2Cu_3O_{7-\delta}$ dependence $T_c(\delta)$ with two plateaus at 60 and 90 K degenerates into much sharper monotonic dependence, and ortho-II structure is not implemented at all [7]. Thus, we can assume that in the case of deviation from stoichiometry on oxygen the compound $HoBa_2Cu_3O_{7-\delta}$ should be characterized by a much more disordered oxygen superstructure in comparison with $YBa_2Cu_3O_{7-\delta}$.

4. Conclusions

To conclude let us briefly summarize the main results obtained in this study. Lowering the degree of doping by oxygen of single crystals $HoBa_2Cu_3O_{7-\delta}$ leads to an uneven distribution of oxygen in the crystal volume and the formation of phases with different critical temperatures. Thus replacing yttrium by holmium affects the charge distribution and effective interaction in CuO-planes, thereby encouraging disorder in oxygen subsystem. Redistribution of labile oxygen induced by the high pressure leads to an increase in the amount of phase separation in $HoBa_2Cu_3O_{7-\delta}$ single crystals with an oxygen deficiency. It also leads to the stimulation of uphill diffusion processes between the superconducting phases with different degrees of deviation from the oxygen stoichiometry in the crystals. The temperature dependence of the electrical resistance of $HoBa_2Cu_3O_{7-\delta}$ (above T_C) in the plane of the layers at different hydrostatic pressures can be accurately approximated by the model of the scattering of electrons by phonons. The parameters characterizing the electron scattering by defects and phonons change in a reversible manner under the pressure change. Twin boundaries are effective scattering centers of normal carriers in compounds $HoBa_2Cu_3O_{7-\delta}$. In the volume of the sample the interband (s—d) scattering of electrons by phonons dominates, but near the twin boundaries the intraband (s–s) scattering dominates and the temperature dependence of the resistance becomes more "metal." Thermally activated factor changes irreversibly under the pressure change.

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Еволюція нормального електроопору в недодопованих киснем монокристалах $Ho_1Ba_2Cu_3O_{7-\delta}$ у процесі прикладання-знімання високого гідростатичного тиску

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Досліджено вплив високого гідростатичного тиску на електроопір в *ab*-площині монокристалів $Ho_1Ba_2Cu_3O_{7-\delta}$ з нестачею кисню. Встановлено, що індукований високим тиском перерозподіл лабільного кисню приводить до посилення фазового розшарування, що супроводжується процесами структурної релаксації і висхідної дифузії в об'ємі експериментального зразка. Висловлено припущення про те, що зародження низькотемпературної (збідненої киснем) фази може відбуватися на межах двійників. Температурні залежності електроопору вище T_c можуть бути з високою точністю апроксимовані у рамках моделі $s-d$-розсіювання електронів на фононах. Прикладання високого тиску приводить до зменшення опору, яке при високих температурах істотно більше, ніж при низьких. Це може бути пов'язано з послабленням електрон-фононної взаємодії при збільшенні тиску.