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Normal and longitudinal electronic transport of HTS compounds $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = Y or lanthanides) under extreme exposure

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Large part of the theoretical and experimental papers, reflecting the current state of research on normal electric HTSC-compounds $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = Y or lanthanides) in extreme impacts are reviewed. We discuss the crystal structure and defects of these compounds, as well as their impact on the various modes of the electrical conductivity of these compounds at low temperatures and high magnetic fields and high pressures. It is shown that the use of such effects can not only verify the adequacy many theoretical models but outline empirical ways to improve the critical parameters of high-temperature superconductors - compounds.

Keywords: YBaCuO single crystals, hydrostatic pressure, excess conductivity, crossover, coherence length, fluctuation conductivity, pseudogap state, high-temperature superconductivity, critical temperature

Наведено огляд значної частини теоретичних і експериментальних робіт, що відображають сучасний стан досліджень нормального електротранспорту ВТНП-сполук $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = Y або лантаноїди) в умовах екстремальних зовнішніх дій. Детально розглянуто кристалічну структуру і структурні дефекти цих сполук, а також їх вплив на різні режими електропровідності при низьких температурах, високих магнітних полях і високому тиску. Показано, що застосування таких впливів дозволяє не тільки перевірити адекватність численних теоретичних моделей, але і окреслити емпіричні шляхи підвищення критичних параметрів ВТНП - сполук.

Ключові слова: монокристали YBaCuO, допущання, гідростатичний тиск, надлишкова провідність, кросовер, флуктуаційна провідність, псевдощільний стан, високотемпературна надпровідність, критична температура

Приведен обзор значительной части теоретических и экспериментальных работ, отражающих современное состояние исследований нормального электротранспорта ВТСП-соединений $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = Y или лантаноиды) в условиях экстремальных воздействий. Детально рассмотрена кристаллическая структура и структурные дефекты этих соединений, а также их влияние на различные режимы электропроводности при низких температурах, высоких магнитных полях и высоких давлениях. Показано, что применение таких воздействий позволяет не только проверить адекватность многочисленных теоретических моделей, но и очертить эмпирические пути повышения критических параметров ВТСП - соединений.

Ключевые слова: монокристаллы YBaCuO, допирование, гидростатическое давление, избыточная проводимость, кроссовер, флуктуационная проводимость, псевдощелевое состояние, ввысокотемпературная сверхпроводимость, критическая температура

2016 marked 30 years since the discovery of the high-temperature superconductivity phenomenon (HTS). During this period there have been published thousands of articles and tens of reviews (see, for example, [2-4]). However, there is no unambiguous explanation of the HTS phenomenon for now. There also no explanations of the pseudogapped state phenomenon, Fermi surface structure, linear dependence phenomenon of electrical resistance et cetera [4]. The roles of spin fluctuations in Cooper pairing, electron-phonon coupling in the HTS emergence remain open problems [5-11]. The shortcomings of experimental research consist in uncertified test samples (high defect films or polyphase objects) [3-10]. The problems in the development of an appropriate theoretical model are connected with a proper account for the multiparticle interaction in systems with strong correlations. It was only

made clear that the symmetry of d-type superconductivity, gap, is aeolotropic and it has zero values in nodal directions of Brillouin zone, and the superconductive gap is preceded by the pseudogap [2,3]. But its role in the superconductivity state formation has not been clearly determined yet.

1.1 Crystal structure, defects and electronic transport in 1-2-3 HTS system on the basis of yttrium.

1.1.1. Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound.

The structure and properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are directly related to δ index which characterizes the oxygen vacancy content. The compounds are superconductive and have orthorhombic symmetry when $\delta < 0.4$ with $\text{YBa}_2\text{Cu}_3\text{O}_7$ interphase. For $\delta > 0.4$ they become semiconductors with $\text{YBa}_2\text{Cu}_3\text{O}_6$ interphase. Their structure can be regarded

as the perovskite structure with the lack of oxygen [12]. In general case perovskite represents a pack of BO_6 octahedrons where B - small metal cation (for example, copper) surrounded by 6 oxygen ions. Atom positions between 8 octahedrons centered in cube corners are occupied by large cations of A metal (yttrium). Removing oxygen atoms from the ideal lattice of perovskite we obtain the most oxygen-rich $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound (fig.1).

Its unit cell can be presented in the form of layered sequence perpendicular to c axis: a) Cu - O in which there are two oxygen vacancies in comparison with the initial perovskite; copper ion Cu (1) situated in this layer has coordination number 4 and it is surrounded by four oxygen ions; b) Ba - O; c) Cu - O where copper ion Cu (2) situated in this layer has coordination number 5 and it is surrounded by five oxygen ions forming a polyhedron; d) yttrium layer in which there are four oxygen vacancies in comparison with the initial perovskite. The cell extension is symmetrical relatively to this yttrium ion layer and the Ba-O and Cu-O layers described earlier are repeated again there.

However, copper ions are situated in atom positions of two types: Cu (1) in the plane of CuO_4 , and Cu (2) - in the pyramid with the square base of CuO_5 . It is the polyhedron layers separated by yttrium ion layers that define the two-

dimensional nature of the structure. The presence of cuprate planes, as well as two-dimensional structure and quasi-two-dimensional structure is a common feature of all high temperature superconductive compounds. The bonding force between cuprate layers are usually quantitatively expressed in terms of the anisotropy parameter Γ :

$$\Gamma = (\xi_{ab}/\xi_c)^2 = (\lambda_c/\lambda_{ab})^2, \quad (1)$$

where ξ_{ab} , ξ_c и λ_c , λ_{ab} - coherence length and penetration depth through the length and breadth of layers, respectively. In this case the anisotropy value varies from $\Gamma > 29$ for yttrium HTS, to $\Gamma > 3 \cdot 10^3$ for bismuth and $\Gamma > 10^5$ for thallium compounds.

Neutron diffraction and electron microscopy methods [13] show with a high resolution that oxygen vacancies are situated in the plane of square CuO_4 but not in the pyramids of CuO_5 . With increase of vacancy concentration the Cu - O chains along b axis become completed, and Cu atoms (1) change their coordination number from 4 to 2 for the most oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound.

While comparing cubic and rhombohedral structure of perovskite (LaCuO_3) with the structures of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ compounds it turns out that the chains develop in three dimensional directions in perovskite, only in b direction in $\text{YBa}_2\text{Cu}_3\text{O}_7$, and they do not exist in $\text{YBa}_2\text{Cu}_3\text{O}_6$.

1.1.2. Structural defects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound.

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ pure crystals depending on the oxygen deficit and synthesis technology we observe the following structural defects: point defects as oxygen vacancy defects which are formed in CuO planes, planar defects of (001) type, twin boundaries, dislocations and so called $2\sqrt{2} \times 2\sqrt{2}$ structures [14] observed under oxygen deficit $\delta = 6.8 - 6.9$.

Planar defects are twin formation planes which are formed under "tetra-ortho" transition and minimize elastic crystal energy. The boundaries of twins represent planes with tetragonal structure as a result of presence of the layers containing oxygen vacancies situated along the twin boundary [14, 15]. Electronic and microscopic researches showed [15] that in the initial stage of tetra-ortho transition there emerge domain nuclei in which two families of coherent separation surfaces (110) and (110) are formed. This can cause formation of a structure such as "tweed" under overlapping of close micro twins. The period of such structure depends on the oxygen content and can be stimulated by doping with a three-valence metal and, specifically, with aluminium [15,16]. In the initial stage of microdomain formation the formation of separation interface takes place by means of diffusion of structural vacancies in CuO layers. The propagation of interface separation occurs by means of voltage controlled movement of twin dislocations.

Linear defects (dislocations) are rather characteristic

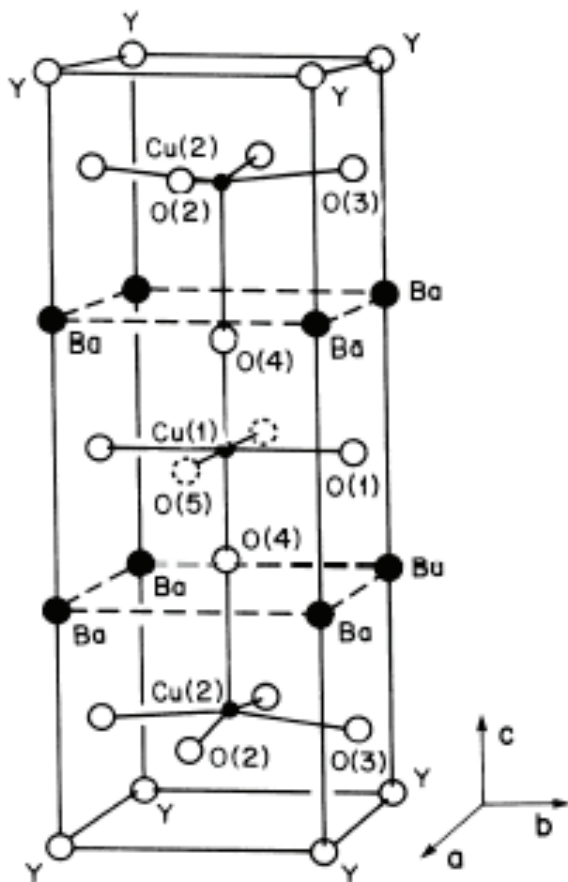


Fig.1 Crystal lattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound according to [12].

for epitaxially grown films and texture samples. Defects of this type can be caused by imperfect dislocations produced by the support film interface in film samples, and imperfect dislocations produced at the interface of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_5$ phases in textured melted samples. The dislocation density in films can reach about $1.4 \cdot 10^8 / \text{cm}^2$ [17].

High dislocation density in single crystals $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can be obtained in a crystal growth during the peritectic reaction [18], which is probably due to small inclusions of $\text{YBa}_2\text{Cu}_3\text{O}_5$ phase. But the dislocation density equals to about $5 \cdot 10^3 / \text{cm}^2$ [19] in the crystals grown with the solution-melt method. It should be noted that the dislocation density can be increased under the thermomechanical treatment of materials [20].

Point defects (oxygen vacancies) are present at all $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples, which is due to the nonstoichiometric oxygen content. Besides, the filling factor is close to one for all oxygen positions, except CuO (1). Depending on oxygen content the superstructure formation is possible under the periodic distribution of oxygen vacancies. The density of oxygen vacancies is relatively large and at $\delta = 0.03$ it equals to about $10^{26} / \text{m}^3$.

In the literature there is also some evidence about copper deficit in CuO planes that can reach the value of 0.09 in compounds [21]. Point defects can also be obtained under doping. As a rule, doping elements (except rare-earth elements and Sr) embed in Cu positions (1) [6]. But the ions of rare-earth metals and K replace yttrium atoms, and Sr embed in the positions of Ba atoms.

Additional defects can be created under bombardment [22,23]. Depending on the type of particles and their energy there can be obtained both point and linear defects (tracks of high energy heavy particles) [24].

1.1.3. Influence of defects on transport properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor in the normal state.

Transport properties of HTS materials depend very heavily on the structure imperfection and, specifically, on the oxygen content [25] and impurities [26, 27]. The specific electrical resistivity at room temperature of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with the oxygen content close to stoichiometric equals to $\rho_{ab} = 200 \text{ m}\Omega \text{ cm}$ in ab – plane, and $\rho_c = 10 \text{ m}\Omega \text{ cm}$ along c axis [2]. In perfect single crystals the electrical conduction is quasi-metal in all crystallographic directions [1-3, 28]. However, even a small stoichiometric deviation $\delta \leq 0.1$ leads to quasi-semiconductor dependence $\rho_c(T)$ under preservation of the quasi-metal type of the dependence $\rho_{ab}(T)$. Further reduction of the oxygen content leads to the density reduction of current, heat and conductivity carriers of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor, and under oxygen deficiency $\delta \geq 0.6$ the metal-insulator transition is observed [28]. Doping of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with metal elements, with the exception of

cases described above, leads to the replacement of copper atoms in CuO planes. In this case the data regarding the level of influence of such replacement are substantially contradictory. For example, in the work [29] it is reported that according to the data from different authors the growth of ρ_{ab} value in $\text{YBa}_2\text{Cu}_{3-z}\text{Al}_z\text{O}_7$ crystals at $z = 0.1$ can be less than 10%, or it will increase twofold at the same Al concentration. The reason for such divergence is likely to be the inhomogeneous Al distribution throughout the volume of crystals because under single-crystal growth in corundum crucibles the Al implantation occurs in an uncontrolled way. In particular, wide transitions in superconductive state $T_c \approx 2 \text{ K}$ are representative of inhomogeneous Al distribution. There is also a significant spread in superconductive state parameters. Doping of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under replacement of yttrium by rare-earth metal ions practically does not change transport characteristics of the normal and superconductive state [3, 24]. The replacement of yttrium atoms by praseodymium atoms is an exception. In the area of $y \leq 0.05$ concentrations the current carrier concentration and ρ_{ab} in $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor weakly depend on Pr concentration [30]. At $y \approx 0.5$ we observe a sharp fall of the current carrier concentration and at $y > 0.5$ we observe $\rho(T)$ dependence typical for superconductors [30,31].

As mentioned above, there are flat defects, twin boundaries, in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. The work [32] deals with the influence of these defects on transport properties in the normal state. It shows that the twins are effective scattering centres of current carriers. According to [32] the free path of electrons in single crystals is measured equal to $0.1 \mu\text{m}$, which is one order less than the intertwine distance. Therefore, the maximum increase of electrical resistance due to scattering can make up 10%. It was observed approximately the same resistance increase under current flow across twins in comparison with the resistance under current flow along twins [33].

1.1.4. Fluctuation conductivity and 2D-3D crossover in HTS.

As it is generally known, small coherence length value and quasi-laminated structure of HTS leads to emergence of a wide fluctuation area on temperature dependences of conductivity near the superconducting transition temperature [3, 8, 9, 33, 34, 36-39]. Besides, the change of oxygen content and impurities has a significant impact on the formation processes of fluctuation Cooper pairs and, respectively, on the realization of different modes for existence of fluctuation conductivity (FC) at temperatures higher than the critical temperature (T_c) [3,5,8,9,33,34]. It is widely agreed now that the FC existence domain can be conditionally divided into three characteristic temperature intervals defined by the correlation between the coherence length perpendicularly to ab-plane $\xi_c(T)$ and the interlayer distance d :

1) $\xi_c(T) \ll d$ – 2D-area (the most distant from T_c);

2) $\xi_c(T) \approx d - 3D$ -area (the closest to T_c);

3) narrow section in the immediate vicinity to T_c – so called «beyond - 3D» mode [5,34].

The last mode mechanism emergence is still not clear enough. It is assumed that the mode fits so called “first level pairing” [5, 34]. The 3D-area fits the mode where Josephson interaction between pairs is realized throughout the body of superconductor. It is thought that in this area the capital contribution to FC is due to Cooper pairs emerging spontaneously at $T > T_c$ as a result of the classical mechanism that was first described in the well-known paper of Aslamazov-Larkin [35]. According to [35] this contribution to HTS can be written as:

$$\Delta\sigma_{AL}(T) = [e^2 / 32\hbar\xi_c(0)]\varepsilon^{1/2}, \quad (2)$$

where $\varepsilon = (T - T_c)/T_c$ – reduced temperature (T_c – critical temperature in mean field approximation). Here $\Delta\sigma_{AL}$ practically does not depend on the sample structure imperfection.

In 2D-area the two-particle tunneling between layers is ruled out. As a result superconductive and normal carriers are situated directly in the planes of conductive layers. In this case taking into account the irregularity level of the sample structure is of prime importance. The influence of the structure imperfection on FC mode in film samples of $YBa_2Cu_3O_{7-\delta}$ compound was researched in the works [8, 9]. Here it was shown that for pure samples the dominating contribution in FC in 2D-area is due to the additional contribution substantiated by Maki-Thompson [36] and defined as a result of interaction for fluctuation pairs with normal charge carriers. Such contribution depends on the lifetime of fluctuation pairs and it is defined by unpairing processes in a specific sample. According to [36]:

$$\Delta\sigma_{MT}(T, H) = \frac{e^2}{8\hbar d(1 - \alpha/\delta)\varepsilon} \times \ln \left\{ \frac{\delta}{\alpha} \cdot \frac{1 + \alpha + \sqrt{1 + 2\alpha}}{1 + \delta + \sqrt{1 + 2\delta}} \right\} \quad (3)$$

If there are structural irregularities in the sample, $\Delta\sigma(T)$ dependence is defined with Lawrence-Doniach [37]:

$$\Delta\sigma_{LD} = [e^2 / (16\hbar d)](1 + 2\alpha)^{1/2} \varepsilon^{-1} \quad (4)$$

Here $\alpha = 2\xi_c^2(T)/d^2 = 2[\xi_c(0)/d]^2 \varepsilon^{-1}$ – coupling parameter, and $\delta = 1.203(1/\xi_{ab}(0))(16/\pi\hbar)[\xi_c(0)/d^2]k_B T \tau_\phi$ – unpairing parameter. Here l – free path length, ξ_{ab} – coherence length in ab-plane and τ_ϕ – lifetime of fluctuation pairs. It should be noted that we have a crucial issue regarding the temperature range where the $\Delta\sigma(T)$ dependence can be described within the fluctuation theory because, according to current concepts, the excess conductivity at temperatures rather distant from the critical $T \gg T_c$ is an effect of the

so-called “pseudogap anomaly”. It was experimentally discovered earlier [3] that at a rather large temperature increase above T_c the fluctuation conductivity decreases more quickly than the theory predicts. It was supposed that the reason for this process is in underestimation of short-wave order-parameter fluctuations while it increases with the temperature growth. In the works of Varlamov with co-authors [38, 39] the microscopic estimation of $\Delta\sigma(T)$ was made taking into account all order parameter components. The comparison of experimental data with the theory [38, 39] was made, in particular, in [40]. In this case there was an agreement with the theory for the temperatures up to near $T \approx 1.35 T_c$. Under further temperature increase the $\Delta\sigma(T)$ decreases more quickly than the theory predicts [38, 39]. Apparently, it is this temperature area where the transition to the pseudogap mode occurs [40]. The pseudogap mode will be considered more thoroughly in the next chapter.

1.2. Pseudogap state in HTS- compounds

In high-temperature superconductors, as it follows from the phase diagram (see fig. 2.2), under change of the oxygen index the dielectric antiferromagnetic phase will be replaced by metal one and then by superconducting phase which does not have an ordered magnetic structure [41]. There was discovered the emergence of the pseudogap phase (considerable density decrease of electronic states) above the superconducting transition point under the oxygen content less than optimal. The pseudogap phase is observed in numerous magnetic [42, 43], neutron diffraction [44], optical [45,46] and nuclear magnetic resonance researches [47], and in experiments of the angle-resolved photoelectron spectroscopy (ARPES) as well. In resistive measurements the pseudogap anomaly is displayed in the departure $\xi_{ab}(T)$ from linearity under the temperature decrease below some representative value T^* [2,8,9,40,50], which is an evidence of the emergence of some excess conductivity. There are two dividing lines: “upper” pseudogap (there begin resistance deviations from the linear law) and “lower” pseudogap (pseudogap proper) in many phase diagrams.

At present the literature intensively discusses two main scenarios of the pseudogap anomaly emergence in HTS-systems. According to the first one the pseudogap emergence is linked to “dielectric” short-range order fluctuations, for example antiferromagnetic fluctuations, spin and charge density waves et cetera (see, for example, review [41]). The second scenario supposes the formation of Cooper pairs even at temperatures considerably higher than the critical $T^* \gg T_c$ with the subsequent establishment of their phase coherence at $T < T_c$ [40,51].

In recent years the model of fluctuating antiferromagnetic clusters has been intensively researched in theoretical works of Sadovsky with co-authors [41,

[52]. Thus, for example, in [52] the authors generalized dynamic medium field theory by including the terms that depend on the correlation length of pseudogap fluctuations in the corresponding equations. These summands are expressed by means of some additional self-energy which in its turn depends on the impulse and describes nonlocal dynamic correlations induced by short-range collective fluctuations such as antiferromagnetic spin-density or antiferromagnetic charge-density waves. It should be noted that the conclusions of the above-mentioned paper are based on the results of ARPES researches which are often used for explanation of other different pseudogap models as well. [48, 49].

There was applied an approach based on the approximation within the framework of the effective field theory in the recent large theoretical paper [53]. It should be noted that the phase diagram substantiated in the paper [53] does not have a transition curve into the “weak” pseudogap phase. Besides, it is assumed that the spin-spin fluctuations leading to pseudogap effects are formed not in localized moments but in the conduction band.

As mentioned previously, the concept of uncorrelated electron pairs or so called paired clusters [54] in the explanation of the pseudogap anomaly in HTS is also a subject of a rather wide discussion in scientific works. Among the works upholding this point of view the crossover theory from Bardeen–Cooper–Schrieffer mechanism to the mechanism of Bose–Einstein condensation should be noted. Within this crossover theory there were obtained pseudogap temperature dependences for weak and strong pairing cases [55, 56]:

$$\Delta(T) = \Delta(0) - \frac{\Delta(0)}{2} \times \frac{T}{\sqrt{\mu^2 + \Delta^2(0)}} \exp\left(-\frac{\sqrt{\mu^2 + \Delta(0)^2}}{T}\right) \quad (5)$$

where Δ – pseudogap value, and μ – chemical potential.

The authors of this work specify their point of view on the nature of the cuprate pseudogap based on the concept of uncorrelated pairs. However, in the article they write that their research does not include the influence of antiferromagnetic spin fluctuations.

The attempt to unite concepts was made in the work [57]. It is the upper border of “weak” pseudogap that was given special attention in this work. The analytical treatment made in [57] is based on the concept of the resonant valence band which was first proposed in the well-known Anderson RVB model [58, 59]. Here, however, the authors suppose that there are areas of both Bose (b-RVB) and Fermi (f-RVB) types. Whereas Bose area is responsible for the “strong” pseudogap, Fermi area – for the “weak” area respectively. According to these

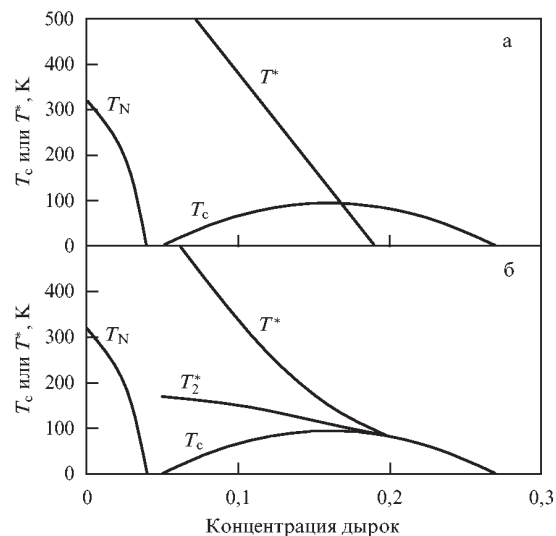


Fig. 2 Phase diagram variants for HTS-cuprates according to [41].

views in the area of the “strong” pseudogap, which is situated just behind the superconducting transition curve, the reduced density of states is caused by the existence of uncorrelated Cooper pairs. But in the “weak” pseudogap area situated above in the phase diagram (fig. 2 (b)), there is an orbital magnetic-ordered state which is destroyed at higher temperatures. However, as it was shown in the works of Boyarsky (see [60] and references to it), the whole set of considerations and facts contains multiple internal contradictions. Besides, up to now there are no substantial experimental proofs of its validity.

In recent years one of dominating concepts for pseudogap anomaly emergence in HTC has been so called cluster model [61–63]. Thus, for example, in the recent theoretical work [61] it was found that the critical temperature T_c and the temperature of pseudogap opening T^* in the compound $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ are uniquely related to the dimensions of superconducting clusters. The superconducting clusters are generated by oxygen ions forming the negative U centres (NUC) responsible for the carrier generation in the compound. Besides, it is affirmed that the pseudogap observed in different experiments is nothing less than the same superconductive gap but emerging at $T > T_c$ as a result of large fluctuations of the particle number between the NUC pair level and the oxygen area [61]. Here it is supposed that under reduction of the doping level by oxygen the average dimension of clusters decreases, and the relative fluctuations of NUC occupation density increase, which, in its turn, must create rise of T^* and drop of T_c [61]. In the work [62] within the framework of the impurity mechanism for the high-temperature superconductivity, on the hypothesis that finite superconducting clusters exist in the area adjoining to the superconductive phase from the doping less than optimal (pseudogap area) and the boundary of the superconductive

phase corresponds to the threshold of existence for an infinite superconductive cluster, there was obtained an upper boundary of the pseudogap state. There was made an attempt to explain the pseudogap state on the basis of the percolation theory on the hypothesis that the coherence length is proportional to $T^* - T$ in the work of Abrikosov [63]. Among experimental works dealing with this matter one should note the experiments where the clusters in HTS were observed by means of the scanning tunnelling spectroscopy [64, 65] and the works [66-69] dealing with the optical studies of oxygen ordering processes as well. However, despite the considerable stored scientific material it is not completely clear both the nature of structural cluster anomalies and the mechanisms of their formation in HTS.

1.3. Redistribution of labile oxygen and evolution of resistive characteristics of

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals under heat treatment at low temperatures.

The researches of superconductive [25,61-67] and optical [68, 69] properties of the single crystals $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ hardened from high temperatures with the oxygen deficiency $\delta \approx 0.5-0.6$ showed that these properties depend not only on the oxygen index value but also on the anneal time at room temperature. Thus, for example, the anneal at room temperature leads to increase of the critical temperature T_c , which can reach $\Delta T_c \approx 15$ K depending on the oxygen index value [25, 66, 67]. The optical researches show [68, 69] that under anneal at room temperature one can observe the increase of the single crystal reflectivity which is explained by the authors as a result of an increase of the current carrier concentration.

Neutron diffraction researches [13] of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic samples hardened from 500°C temperature are evidence of the lattice parameter change under anneal of sample at room temperature: all lattice parameters decrease (Fig. 3), and the degree (a-b) increases (Fig. 4). However, we do not observe a considerable change in the filling factor of oxygen positions in Cu-O plane along a and b axes. The main changes of the critical temperature, (Fig. 4), the lattice parameters (Fig. 3) and the reflectivity under anneal are observed in the early stage of anneal: approximately 85% of general variation value of these characteristics is realized during the first 24 hours.

The influence of anneal at room temperatures on the critical temperature, current carrier concentration and on the lattice parameters change of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxygen-deficit samples is explained as a result of oxygen atoms ordering in Cu-O plane without change of the oxygen content in the sample. The three issues that arise then are: (1) what is the cause of the critical temperature increase (oxygen ordering or lattice parameters change)?, (2) what range of δ values does the ordering occur in? and (3) What

nature and typical scale does this ordering have?

It is known that it is anomalously large increase of the critical temperature of LaBaCuO superconductor under the hydrostatic pressure P , $dT_c/dP=0.64$ K/kbar [70] that stimulated search of new superconductors which have Cu-O layers drawn together due to “internal pressure” caused by the small ionic radius separating these layers. But in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor the baric derivative of the critical temperature is not constant and depends on δ index.

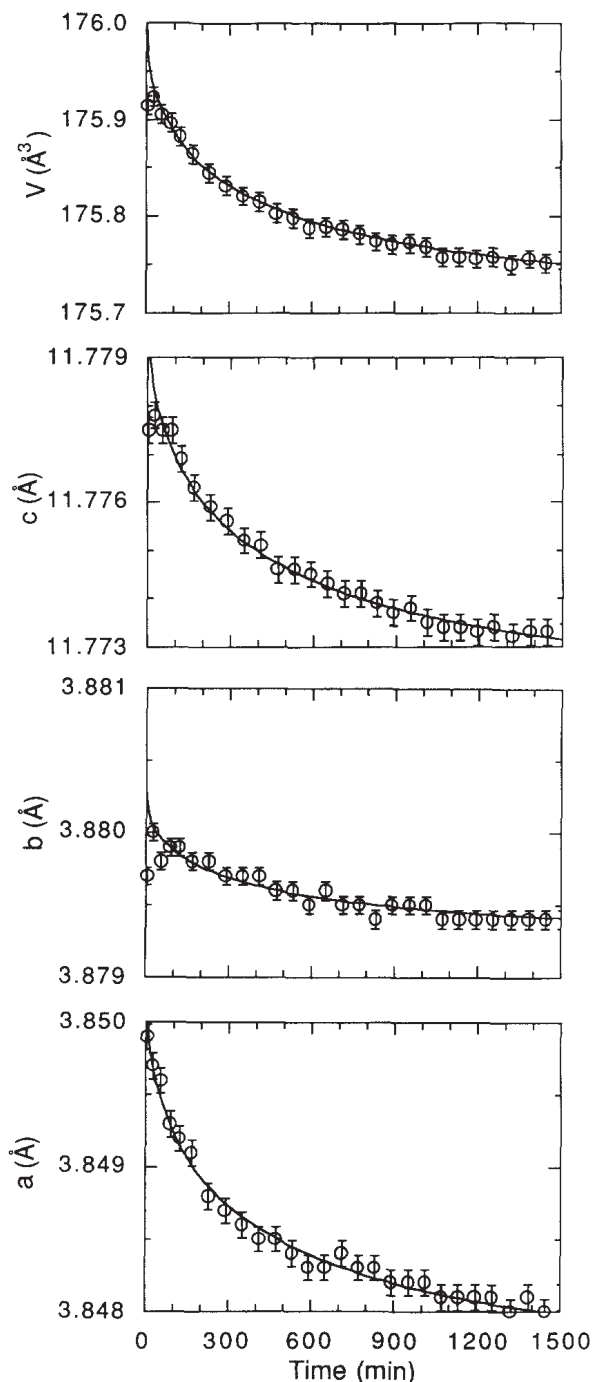


Fig. 3. Dependence of volume and unit cell parameters on anneal time at room temperature for hardened sample $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ [13].

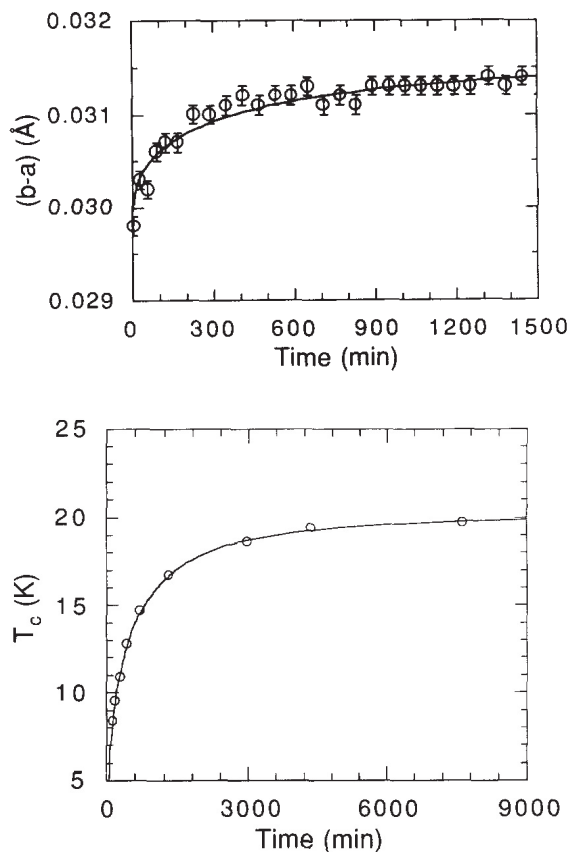


Fig. 4. Dependence of (b-a) difference and critical temperature T_c on anneal time at room temperature for hardened sample $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ [13]. Critical temperature was defined from the beginning of diamagnetic response appearance.

Besides, the derivative value has its maximum at $\delta \approx 0.4$ – 0.5 and equals to $(0.1 \div 1)$ K/kbar [71–74]. Therefore, the slight decrease of lattice parameters under low-temperature anneal can lead to the considerable critical temperature increase. On the other hand, the authors of the work [66] believe that the T_c increase is due primarily to the change of the local environment of copper atoms in Cu-O planes that leads to the charge distribution in these planes.

The research of oxygen index influence on the critical temperature increase under low-temperature anneal [67] showed that ΔT_c value decreases at δ reduction, and at $\delta \approx 0.2$ there were not observed any changes of T_c value under anneal. However, it should be noted that T_c value is not sensitive to the oxygen index change at $\delta \leq 0.2$ [66], and, therefore, the issue regarding possibilities of the oxygen redistribution in the specified range of δ variation should be investigated further.

The structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at $\delta \approx 0$ is defined by Cu-O chains presence, that is, the oxygen positions of O(1) are fully occupied and the positions of O(5) are vacant. Under oxygen deficit $\delta \approx 0.5$ the structure is defined by interchange of chains where the oxygen positions of O(1) are fully occupied, and of chains where the positions of

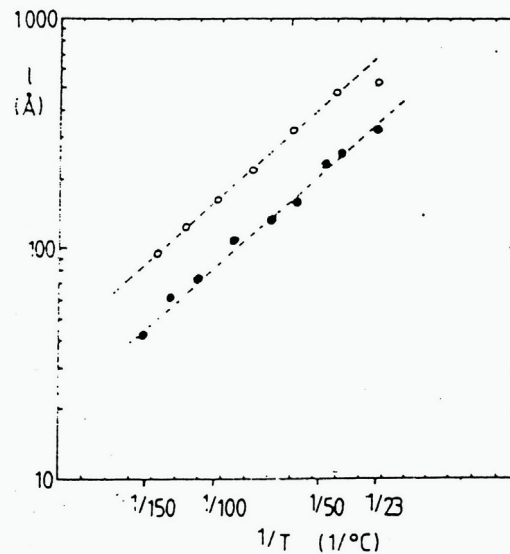


Fig. 5. The average length of chains in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (shaded circles) and $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ (hollow circles) as reciprocal temperature function [69].

O(1) are vacant. The realization of such ordered structures is possible at a stoichiometric ratio between the oxygen concentration and the vacancies, which is equal to 1:0 и 1:1 in these examples. The experimental research of different physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample with the oxygen deficit $\delta \approx 0.4$ made it possible for the authors of the work [77] to substantiate the concept of superconductive cluster with the structure close to ordered one under the concentration ratio between oxygen concentrations and vacancies equal to 5:1, 4:1, 3:1 и 2:1. For instance, it is thought that under 5:1 ratio in every sixth chain the oxygen positions of O(1) are vacant and in other chains they are occupied. Under stoichiometric ratio between oxygen concentrations and vacancies it is possible either disordering in the oxygen-vacancies system or the formation of ordered phase-clusters mixture. The issue remains open. The results of the works [13, 68] point to the existence of the ordered state at room temperature. However, the ordering scale obtained from the neutron diffraction [13] researches (≈ 30 Å) is less by an order of magnitude than the value 300 Å obtained from the optical [69] researches (see fig. 5). It should also be noted a possibility of change for the oxygen subsystem state under low-temperature hardening starting from the temperatures $T_a = 100 \div 300$ K. The research of hardening influence on the electrical resistance and the critical temperature of the sample from c $T_c \approx 91$ K [78] show that there is increase of T_c and decrease of the specific electrical resistance ρ in the plane (a,b). The variation value of T_c and ρ depended both on the value T_a and on the holding time at T_a . The authors interpreted the obtained results by means of microdiffusion mechanism for the formation of the lattice state with the increased value of T_c . The behaviour of ρ depending on value T_a showed that there was disordering of the initial

state of the oxygen vacancies and their further ordering.

It should also be noted that under resistive measurements the transition to the pseudogap mode is displayed in faster than linear fall of the electrical resistance value in the basis plane $\rho_{ab}(T)$ (emergence of the so called excess conductivity) when the temperature decreases less than some representative value T^* which is observed in HTS samples [2, 8, 9, 40]. Since the electrical resistance of such compounds is rather sensitive to the state of the oxygen subsystem, the redistribution of the labile component must have an effect on the temperature dependences $\rho_{ab}(T)$. As far as we know there have not been published any experimental researches regarding the influence of labile oxygen redistribution in the nonequilibrium state (at fixed oxygen concentration in the sample) on the pseudogap anomaly in 1-2-3 system.

Conclusions

In conclusion it should be mentioned that there was considered only a rather small part of scientific publications dealing with different aspects of normal electron transport in HTS in this very brief scientific literature review. The more detailed consideration of the above-mentioned phenomena can be found in the reviews [4, 41]. Nevertheless, following on from the results of the analysis performed we can set up some problems that do not have the ultimate experimental and theoretical solution up to now, such as: (i) what is the nature of the high pressure influence on formation of the pseudogap anomaly in low praseodymium-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals and what is the role of singularities in the electronic spectrum of these compounds under compressional change of the critical temperature and the lateral coherence length? (ii) What is the role of the structural relaxation induced by the temperature step change in realization of different modes of the longitudinal electron transport? And, in this aspect, what is the influence of isovalent and nonisovalent substitution on the processes of labile component redistribution in the oxygen subsystem? (iii) What is the role of structural defects of different morphology on the realization of specific dynamic transitions in the magnetic subsystem of single-domain single-crystal samples $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with a small deviation from the oxygen stoichiometry? What way does the layer structure have an influence on order-disorder transitions?

The performed analysis of the scientific literature dealing with different aspects of unusual properties display of the normal electron transport in HTS in this review made it possible to define some problems that have not been fully-investigated up to now. Despite a considerable body of existing experimental and theoretical works dealing with research of the effects observed in the normal (nonsuperconducting) state we do not have comprehensive understanding of the mechanisms causing these effects.

In particular, the examples may include the anomalously wide temperature area of fluctuation paraconductivity phenomenon, so called "pseudogap anomaly", incoherent electron transport, metal - insulator transitions and a number of other issues.

From this perspective it is very important today to conduct researches concerning determination of the influence level of different morphology defects on single crystal samples with a given defect structure topology. It should also be noted that despite the absence of the microscopic theory there is a special demand for experimental procedures using the extreme exposure of different types (low temperatures, high magnetic fields and high pressures). These procedures makes it possible not only to test the validity of multiple theoretical models but also outline the empiricism for critical parameters increase of HTS compounds.

Consequently, the above-mentioned issues are the base for the solution of the problem involving determination of the influence physics of point and flat defects on magnetoresistive properties of $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds ($\text{Re} = \text{Y}$ and other rare-earth elements), and establishment of laws concerning the conduction state formation such as insulator-metal transition, superconductor - Fermi - liquid metal - nonsuperconductor under carrier concentration variation, under change of the labile component concentration in a wide range and replacement of constituent elements of these compounds as well.

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