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Superconductivity suppression at twin boundaries and longitudinal and transversal transport anisotropy in oxygen deficient $YBa_2Cu_3O_{7-x}$ single crystals

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The temperature dependences of the conductivity along and across the basis plane have been measured in $YBa_2Cu_3O_{7-x}$ single crystals with different oxygen non-stoichiometry. In the oxygen-deficit samples, an inhomogeneous oxygen distribution within the crystal bulk is found, that results in the formation of phases with different critical of superconducting transition temperatures. The accordance of the experimental results with the predictions of different theoretical models has been considered. It has been revealed that the anisotropy of the normal resistivity $\rho_c/\rho_{ab}(T)$ is described well using the universal "law of 1/2", for thermal activation of the hopping conductivity.

Измерены температурные зависимости проводимости вдоль и поперек базисной *ab*-плоскости в монокристаллах $YBa_2Cu_3O_{7-x}$ с различной степенью кислородной нестехиометрии. Показано, что в образцах с дефицитом кислорода реализуется неравномерное распределение кислорода по объему кристалла, которое приводит к образованию фаз с различными критическими температурами. Проанализировано соответствие полученных экспериментальных результатов с предсказаниями различных теоретических моделей. Обнаружено, что анизотропия нормального электросопротивления $\rho_c/\rho_{ab}(T)$ хорошо описывается посредством универсального "закона 1/2" для термоактивационной прыжковой проводимости.

The layered structure is a characteristic feature of high-temperature superconducting compounds (HTSC) [1–3] that defines a substantial anisotropy of their properties both in the normal and in the superconducting state. An important HTSC is $YBa_2Cu_3O_{7-x}$ (YBCO) for which an important peculiarity is the strong dependence of its physical properties, in particular, its electrical conductivity, on the oxygen concentration [1–4]. In spite of numerous works dedicated to the study of the longitudinal and transversal transport in the 1-2-3 system, many aspects of this dependence are still uncertain. For example, in the theoretical work [5], the resonance tunneling mechanism of charge carriers has been proposed between the conducting CuO_2 planes through the localized states in the CuO chains. According to [5], the temperature dependence of the resistivity anisotropy $\rho_c/\rho_{ab}(T)$ should be described by the following relation:

$$\rho_c/\rho_{ab} \sim T\cosh^2(T_0/T), \qquad (1)$$

where T_0 is the process activation energy. The experimental verification for this model was performed in [2] for $YBa_2Cu_3O_{7-x}$ single crystal samples. It was demonstrated, however, that although the theoretical pre-

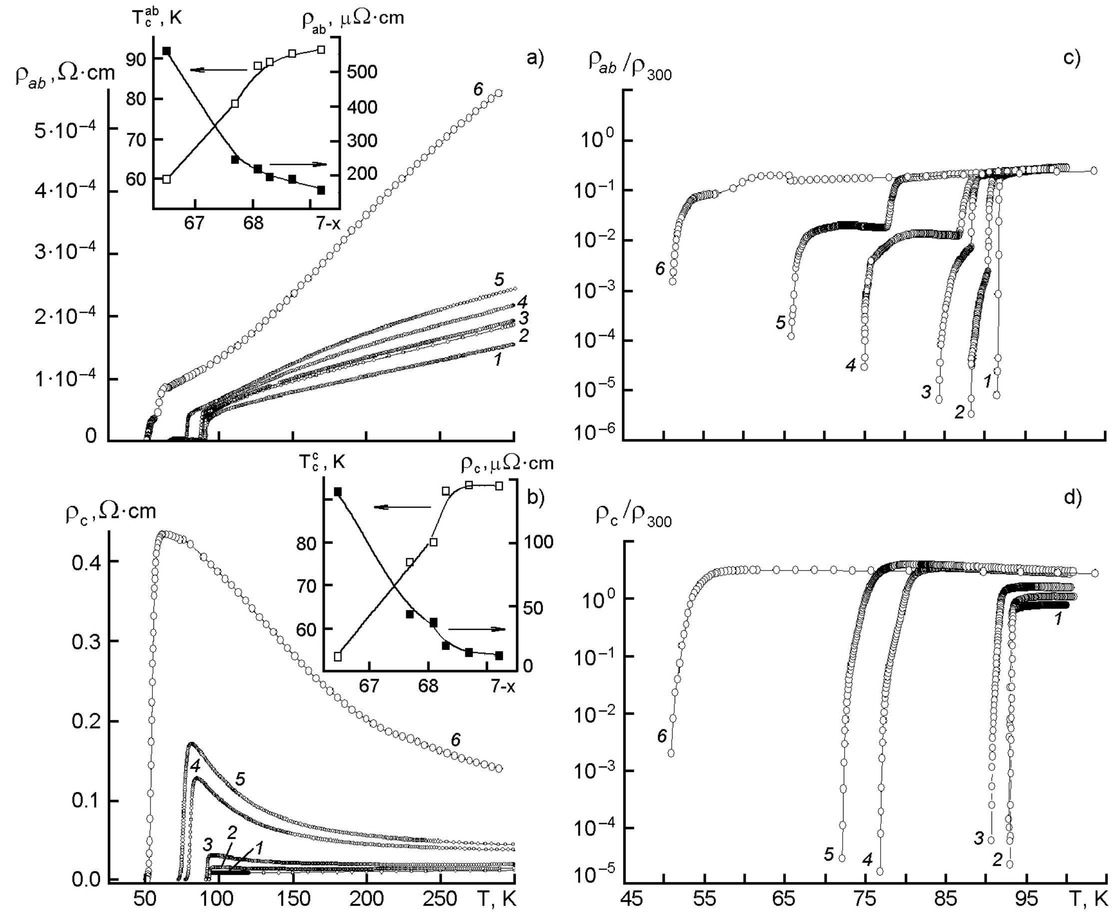

Fig. 1. Temperature dependences of resistivity: (a), in the *ab*-plane, $\rho_{ab}(T)$; (b), along *c* axis, $\rho_c(T)$. In the corresponding insets, the concentration dependences are shown: $T_c(7-x)$ (light symbols) and $(\rho_{300}(7-x)$ (dark symbols). The superconducting transitions are represented in $\lg(\rho/\rho_{300})$ $-T$ coordinates in Fig. 1 (c) for *ab* plane and in Fig. 1 (d), along the *c* axis. The curves *1–6* are measured after annealing at 670; 720; 760; 790; 810 and 890 K, respectively.

dictions [5] are in qualitative agreement with the experiment, the data is better described by the relation:

$$\rho_c/\rho_{ab} \sim \exp(\Delta/T). \qquad (2)$$

It is to note that in [2], all the measurements were carried out using samples with a significant oxygen deficit ($x > 0.3$). It is more interesting to study single crystals with a small deviation from the stoichiometry where the peculiarities of the so-called "pseudo-gap state" are clearly demonstrated. This has been discussed in detail by us in a recent work [4]. It should be noted that an additional source of anisotropy in the YBCO single crystals is the existence of twin boundaries (TB) [6], the influence of which on the transport properties in the normal state is inadequately studied, due to the experimental difficulties in determining the contribution of these defects. Taking the above under consideration, we have studied in this work the longitudinal and the transversal conductivity in single crystals of $YBa_2Cu_3O_{7-x}$ ($0.1 \le x \le 0.35$) differing in the transport current geometry. The transport current geometry was either parallel (**I**||TB) when the TB effect on the carrier scattering processes is minimized, or at an angle of $\alpha = 45°$ between **I** and TB.

The $YBa_2Cu_3O_{7-x}$ single crystals were grown in a gold crucible by the self-flux method (temperature range 850–970°C) using the techniques described in detail in [1, 4]. For the resistivity measurements in the *ab* plane and along the **c** axis, two single crystals (grown simultaneously) were selected. These have dimensions 2×0.3×0.02 mm³ (K1 sample) and 0.3×0.5×0.1 mm³ (K2 sample), with the *c* axis oriented along the smallest di-

Table. Experimental sample parameters

T_a, K	$7-x$	ρ_{ab}, μΩ·cm	ρ_c, μΩ·cm	T_c^{ab}, K	T_c^c, K	$(T_c^{ab} - T_c^c)$, K	Δ, K
670	6.92	155	11.625	91.74	93.08	−1.34	128
720	6.87	186	14.205	90.85	93.28	−2.43	172
760	6.83	192	19.266	88.71	91.87	−3.16	216
790	6.81	216	37.487	87.89	80.04	7.85	318
810	6.77	243	44.247	78.52	75.26	3.26	349
890	6.65	558	139.5	59.81	53.2	6.61	502

mension. To obtain samples with optimal oxygen content, the crystals were annealed in oxygen flow at 400°C for five days. To reduce the oxygen concentration, the crystals were annealed in oxygen flow at higher temperatures for three to five days (see Fig. 1 and Table). The oxygen concentration "x" was determined in accordance to the oxygen flow annealing duration and temperature, as in calibration tables [7]. The electric contacts were formed according to the standard four-contact scheme by applying silver paste onto the crystal surface and the connection of silver conductors. The resistance in the *ab*-plane and along the *c* axis was measured using the standard method for two opposite directions of dc current up to 10 mA as described in detail in [1]. The temperature was measured with a copper-constantan thermocouple; the voltage was measured across the sample and the reference resistor with V2-38 nano-voltmeters. The voltmeter signals were transferred to a PC through an interface. As the critical temperature (T_c), the temperature value was accepted corresponding to the main maximum in the $d\rho(T)/dT$ dependences in the superconductive transition, according to [8]. The measurements where carried out in the temperature drift mode at about 0.1 K/min near T_c and at about 5 K/min when $T > T_c$.

Figs. 1 (a) and (b) present the temperature dependences of the electrical resistance in the *ab*-plane and along the *c* axis, after the samples were annealed in oxygen flow at different temperatures. The corresponding resistivity transitions into superconducting condition are shown in Figs. 1 (c) and (d). The resistivity parameters of the samples are presented in Table.

It is seen in Fig. 1(a) that the conductivity nature in *ab*-plane in all cases is quasi-metallic, as it will be described in detail below. As the annealing temperature increases and, accordingly, the oxygen concentration drops, the absolute resistance value increases and the critical temperature (T_c) lowers (see inset in Fig. 1 (a)). The rather small superconducting transition width of the initial sample ($\Delta T_c \approx 0.3$ K) rises significantly with the increasing annealing temperature, and the transition takes a step-like form (Fig. 1 (c)). The height and width of the lower step increase with the annealing temperature. This behavior indicates that T_c is inhomogeneous over the single crystal volume and that there exist two phases, one with a higher T_c and another with a lower one. The presence of the step evidences the absence of percolation passing paths for the transport current in the high-temperature phase. The increase of the step width with the increasing annealing temperature indicates that the distinction in the critical temperatures of the low- and high-temperature superconducting phases increases as the oxygen concentration drops. In particular, the increase of the low step height indicates that the low-temperature phase volume increases with the decreasing oxygen concentration.

It is seen from Fig. 1 (b) that the quasi-metallic nature of the conductivity temperature dependence measured along the *c* axis, changes to a semi-conducting character as the annealing temperature increases. Similarly to the resistance measurements along the *ab*-plane, the absolute resistance value increases, the critical temperature drops (see Table and inset to Fig. 1 (b)) and the width of the superconducting transition increases with the decreasing oxygen concentration (Fig. 1 (d)); however, the step-like nature of the transition becomes substantially smoothed. This evidences that even though there is an inhomogeneity of the oxygen concentration in the crystal and, respectively, the phases with different critical temperatures are present, percolation paths seem to exist for the transport current in the high-temperature phase (at the resistance measurements carried out along the *c* axis).

One of the possible reasons for the difference in the superconducting transition forms at the longitudinal and transversal resistance measurements is the generation of a low-temperature phase at twin boundaries. As it was noted above, the TB planes are oriented along *c* axis of the single crystal and at an angle of $\alpha = 45°$ to **a** and **b** axes, that is, at an angle to the transport current vector, when measuring the electric resistance along the *ab*-plane of the K1 single crystal. Assuming that the low-temperature superconducting phase is generated at the TB, then, at the resistance measurements along the *ab*-plane, the percolation paths for the transport current in the high-temperature phase are absent. In the resistance measurements carried out along the *c* axis, probably percolation passing paths exist for the transport current in the high-temperature phase, as the TB planes are oriented along the *c* axis.

The supposition that the TBs are the low-temperature phase generation centers seems to be quite probable. In fact, the experiments on decorating the vortex structure [9, 10] have shown that the vortex density in the TB is raised in comparison to their density in the superconductor bulk, that means suppression of the order parameter at TB. This, in turn, may be due to the reduced oxygen concentration in the TB planes that may act as effective channeling centers of oxygen vacancies [11]. The supposition on the order parameter suppression at the TB in $YBa_2Cu_3O_{7-x}$ single crystals is confirmed also by the micro contact spectroscopy results [12].

A second important resistance peculiarity regarding the samples with lowered T_c consists in a significant (of about 8 K) difference between the critical temperatures measured along and across the basic plane (see Table). A similar effect was observed in $Bi_2Sr_3Ca_xCu_2O_{8+x}$ [13] and in $YBa_2Cu_3O_{7-x}$ [14] single crystals with a large deviation from stoichiometry in oxygen. In [14], the effect is explained by a possible Fridel transition [15], which consists in the suppression of the transversal superconductivity within a temperature range $T_f < T < T_c$ under the critical one (T_f is the Fridel temperature), through a specific growth mechanism of Josephson vortices in layered superconductors. In the theoretical work [16], such a mechanism could be realized in a real crystal in the case of some disruption of the periodical distribution of conductivity layers. According to [14], such a situation arises when the layers with different T_c separating each other are present within the sample. This is confirmed by the results from [17] which show that the oxygen concentration reduction in $YBa_2Cu_3O_{7-x}$ single crystals causes the conducting sub-system disintegration into several phases with different T_c. As it was mentioned in [14], a second possible reason for the observed effect is the presence of plane defects within the samples (in our case, twin boundaries). Twin boundaries act as weak connections between layers where the superconducting current arises at temperatures lower than the layers' T_c. A similar situation is realized, in particular, in granular superconductors [18], to be explained in more detail in what follows. As is shown in Table, the maximum difference ($T_c^{ab} - T_c^{c}$) is observed in the region of oxygen concentrations of $x = 0.2-0.25$, which could be connected with an Ortho I-Ortho II transition and, accordingly, with the type change of the oxygen hyper-structure.

It is necessary to point out that the final conclusion about the distribution nature of the high and low temperature phases, as well as the influence on the TB effect on the superconducting properties anisotropy in $YBa_2Cu_3O_{7-x}$ single crystals, needs to be studied additionally. It is logical to carry out additional measurements of the superconducting transitions in non-twinned and twinned single crystals with a specific TB plane distribution. In one segment of the crystal, the transport current vector has to be oriented in parallel, while in another one, perpendicular to the TB plane. In the latter case, the transport current inevitably crosses the TB plane in one of the single crystal segments (when $\mathbf{I}\perp$TB) and can flow within the superconductor volume of the, omitting the TB plane in another crystal segment (when $\mathbf{I}\|$TB). The measurements in the non-twinned crystals should provide data concerning the existence (or lack) of the step-like superconducting transition form, as well the difference $[T_c^{ab} - T_c^{c}]$ in the absence of plane defects in the sample.

As it was mentioned above, in the basis plane, in $\rho_{ab}(T)$ dependences in relatively high temperature region, the wide enough linear section is kept even under a significant oxygen deficit ($x \geq 0.35$). To explain this kind of dependence, various theoretical models were proposed, among them, the well-known RVB-theory [19] and the NAFL model [20]. According to the first one, the scattering process in HTSC compounds is

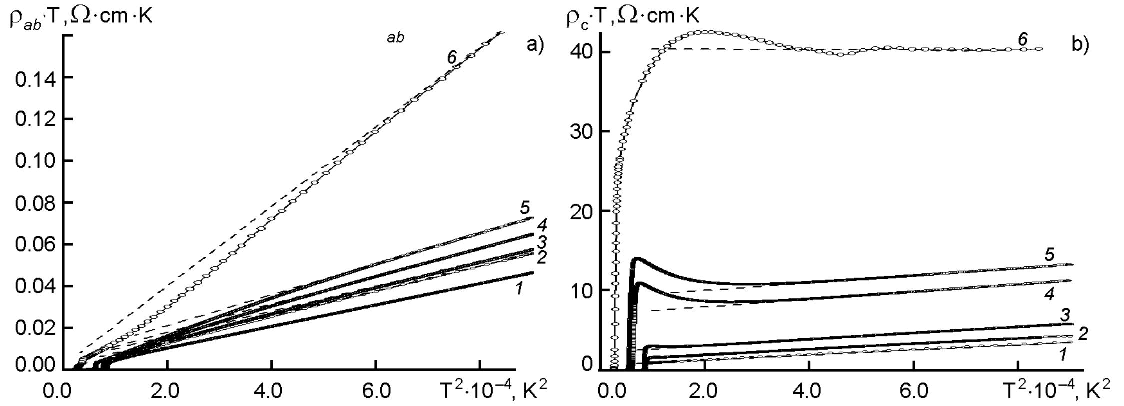

Fig. 2. Temperature dependences of resistance in $\rho{\cdot}T - T^2$ coordinates: (a), in the *ab*-plane; (b), along the *c* axis. The curves are numbered as in Fig. 1. The dashed lines illustrate the approximation of the linear sections of the experimental curves.

realized by means of the interaction between the carriers and the two types of the quasi-particular excitations — spinons and holons [19]. Herewith, the temperature dependence of resistance assumes, in addition to the item linear with respect to temperature, an additive proportional to $1/T$ [17], in both the longitudinal as well as the transversal resistance:

$$\rho(T) = AT^{-1} + BT. \tag{3}$$

Indeed, as it is seen in Fig. 2, the $\rho_{ab}(T)$ and $\rho_c(T)$ resistivity dependences under an oxygen doping close to the optimal level become straightened in the $\rho{\cdot}T - T^2$ coordinates. However, in the medium-doped and underdoped samples, the experimental curves cannot be described by the equation (3). According to the NAFL model [20], the carrier scattering in HTSC systems is defined by antiferromagnetic interaction. For this, the existence of a linear section in the $\rho(T)$ dependences evidences reliably the normal state of the system. Even so, none of the theoretical models, explaining this behavior of $\rho(T)$ curves in the relatively high temperature region, could describe satisfactory the deviation from the linearity taking place at temperatures lower than a characteristic value T^* corresponding to the pseudo-gap opening [3, 4].

The temperature dependences of the $\rho_c/\rho_{ab}(T)$ anisotropy are shown in Fig. 3 in $\rho_c/\rho_{ab} - T$ and $\ln[(\rho_c/\rho_{ab})/T] - 1/T^{-1/2}$ coordinates. Those are in agreement with the description of the function $\rho_c/\rho_{ab}(T)$ in the second case by means of the following analytical expression:

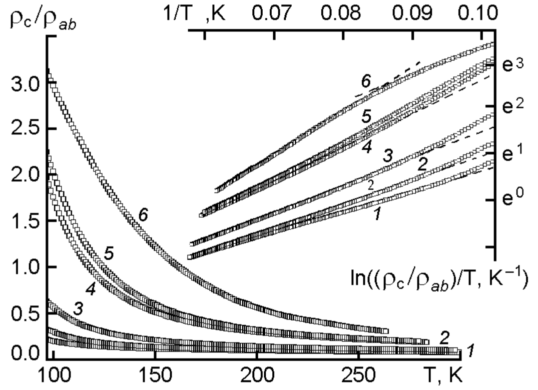

Fig. 3. Temperature dependences of the resistivity anisotropy $\rho_c/\rho_{ab}(T)$ in $\rho_c/\rho_{ab} - T$ and $\ln[(\rho_c/\rho_{ab})/T] - 1/T^{1/2}$ coordinates. The curves are numbered as in Fig. 1. The dashed lines illustrate the approximation of the experimental curves by equation (4).

$$\rho_c/\rho_{ab} \sim T\exp(T_0/T)^{1/2}, \tag{4}$$

where T_0 — constant. It is known that the equation (4) is typical for the hopping conductance with a variable hopping length – "law of 1/2" [21].

Reduction of the oxygen concentration is seen to result in a significant increase of the absolute anisotropy value ρ_c/ρ_{ab}. From the experimental data analysis, it can be concluded that, although equation (2) provides a qualitative description of the experimental dependence $\rho_c/\rho_{ab}(T)$ in the region of relatively high temperatures, it is not as an efficient description as equation (4) of the hopping conductivity. It is known from the theory that the "law of 1/2", is usually treated as a Coulomb gap in the energy spectrum of the carriers, more typical of semiconductors [22]. On the contrary, as it was shown in [21], the equation (4) is more general and can be applied for a broader class of conducting compounds with a significant structural disorder. In particular, it can be used for a dispersion of small metal granules within a dielectric matrix [21]. It is known that doping HTSC cuprates either by substituting with isovalent analogues, or by changing the oxygen concentration, causes the system disintegration into electron-neutral regions of two types — metallic, with a high carrier concentration, and dielectric [23]. The kind of domains can be"imposed" also by ordering dopants. It is obvious that under adequately small dimension inclusions with metallic conductance, the system may take features typical of the granular metals.

It is evident from Fig. 3 that the slope of the curves increases in parallel with the oxygen deficiency. This implies that the activation energy also increases. It should be also noted that for the curve 6, with the lowest T_c, at temperatures around 135 K, the slope changes more than twice. This, in turn, evidences a reduction of the activation energy, and reflects the presence of phase transitions observed in [1] for the YBCO single crystals. According to [1], the phase transitions of this type influence the charge transport kinetics. A certain deviation from the linear dependence for the curves 1–5 occurring in the relatively low temperature region could be due to the increasing contribution from the fluctuation component to the longitudinal conductivity that becomes essential near the superconducting transition temperature [4].

Thus, the analysis of the obtained experimental data gives rise to supposition that the decrease of the oxygen content in $YBa_2Cu_3O_{7-x}$ single crystals results in localization of the carriers along the direction of c axis and in a modification of the layer interaction. The temperature dependence of the resistivity anisotropy $\rho_c/\rho_{ab}(T)$ is described well within a wide temperature range by the universal "law of 1/2" for the thermal activated hopping conductivity.

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Пригнічення надпровідності на двійникових межах і анізотропія поздовжнього і поперечного транспорту у монокристалах $YBa_2Cu_3O_{7-x}$ з дефіцитом кисню

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Виміряно температурні залежності провідності вздовж і поперек базисної *ab*-площини у монокристалах $YBa_2Cu_3O_{7-x}$ з різним ступенем кисневої нестехіометрії. Показано, що у зразках з дефіцитом кисню реалізується нерівномірний розподіл кисню в об'ємі кристала, який викликає утворення фаз з різними критичними температурами. Проаналізовано відповідність одержаних експериментальних результатів з передбаченнями різних теоретичних моделей. Виявлено, що анізотропія нормального електроопору $\rho_c/\rho_{ab}(T)$ добре описується за допомогою універсального "закону 1/2" для термоактиваційної стрибкової провідності.