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Influence of high pressure on phase separation in underdoped $HoBa_2Cu_3O_{7-\delta}$ single crystals

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We investigate the influence of high hydrostatic pressure on the electrical resistance in the ab-plane in $HoBa_2Cu_3O_{7-\delta}$ single crystals with oxygen deficiency. It is determined that the high-pressure induced redistribution of the labile oxygen enhances the phase separation, which is accompanied by structural relaxation and ascending diffusion within the volume of the sample. It is determined that the formation of the low-temperature phase can occur at the twin boundaries.

Keywords: HoBaCuO single crystals, hydrostatic pressure, labile oxygen, metal-to-dielectric transition, pseudo-gap anomaly, twin boundaries.

В работе исследовано влияние высокого гидростатического давления на электросопротивление в ab-плоскости монокристаллов $HoBa_2Cu_3O_{7-\delta}$ с недостатком кислорода. Установлено, что индуцируемое высоким давлением перераспределение лабильного кислорода приводит к усилению фазового расслоения, которое сопровождается процессами структурной релаксации и восходящей диффузии в объеме экспериментального образца. Высказано предположение о том, что зарождение низкотемпературной фазы может происходить на границах двойников.

Ключевые слова: гидростатическое давление, границы двойникования, лабильный кислород, монокристаллы HoBaCuO, псевдощелевая аномалия, переход металл-диэлектрик.

У роботі досліджено вплив високого гідростатичного тиску на електроопір в ab-площині монокристалів $HoBa_2Cu_3O_{7-\delta}$ 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 фази може відбуватися на межах двійників.

Ключові слова: гідростатичний тиск, межі двійникування, монокристали HoBaCuO, лабільний кисень, псевдощілинна аномалія, перехід метал-діелектрик.

An important characteristic of high temperature superconducting compounds (HTSC) of the system $ReBa_2Cu_3O_{7-\delta}$ (Re = Y or rare earth ion) is the ability to realize a non-equilibrium state under a specific oxygen non-stoichiometry [1-3]. This can be initiated by external means, such as temperature [1] or high pressure [3]. The non-equilibrium state is accompanied by a redistribution process of the labile oxygen and structural relaxation, which in turn can affect substantially the electro-transport parameters of the system [1,3]. Importantly, the conductivity characteristics and the crucial parameters can be modified by substituting Y with rare-earth elements. When yttrium (Y) is substituted with holmium (Ho) that has a large magnetic momentum (more than $10\mu_B$) [4], $HoBa_2Cu_3O_{7-\delta}$ is paramagnetic in the normal state. Nevertheless, as with other rare earth elements, the substitution of Y with the paramagnetic ions Ho or dysprosium (Dy), the superconducting properties in stochiometric $ReBa_2Cu_3O_{7-\delta}$ compounds (with $\delta \leq 0.1$) do not change substantially [4]. This can be explained by the localization of Ho or Dy away from the superconducting planes, which in turn interfere with the formation of distant magnetic order. In oxygen deficient HTSC compounds of the 1-2-3 system the rare earth ion is sensitive to the local symmetry of its environment and to the charge density distribution. Their change affects the crystalline field, forming the electronic structure of this ion [5]. A characteristic peculiarity of the oxygen deficit samples (with $\delta \geq 0.3$) is the broadening of the resistivity transfers under pressure [3,6-8]. The reason of such behavior has not been completely determined. In spite of a number of studies on the relaxation processes in the 1-2-3 system under high pressure, many aspects such as the charge transfer and the nature of the redistribution of the vacancy subsystem are still undetermined. Notably, a substantial part of the experimental material was ceramic and polycrystalline samples with a high content of grain boundaries (intergrain bonds) [2,6,7]. In the case of single crystals the existence of twin boundaries (TB) [3] influences the transport properties in the normal state. This aspect is not yet sufficiently studied,

due to experimental difficulties in determining the contribution of these defects. In the present study we investigate the effect of hydrostatic pressure up to 5 kbar on the electro-transport characteristics and the structural relaxation in the *ab*-plane of oxygen deficient $HoBa_2Cu_3O_{7-\delta}$ single crystals. Two different kinds of transport current geometry were investigated: (a) parallel (**I**||TB) when the impact of the TB in the carriers scattering processes is minimized and (b) at an angle of $\alpha = 45^{\circ}$ between **I** and TB.

$HoBa_2Cu_3O_{7-\delta}$ single crystals were grown from the flux in a gold crucible using similar technology as for the growth of $YBa_2Cu_3O_{7-\delta}$ single [1,3]. To obtain samples with oxygen concentrations having $\delta \leq 0.15$, the crystals were annealed in an oxygen flow at a temperature of 370-410°C for five days. This procedure is accompanying by the formation of TB system, which effectively minimizes the elastic energy of the crystal lattice in the tetragonal-orthogonal transition [3]. For the resistance measurements the single crystals were selected from the same batch and had dimensions: 1.7 mm X 1.2 mm X 0.2 mm (sample S1) and 1.9 mm X 1.5 mm X 0.3 mm (sample S2). In these samples the ***c***-axis were oriented along the smallest dimension, which had singly-directed TB areas. The experimental geometry was selected so that the transport current vector in the *ab*-plane, was either parallel, **I**||TB, (sample S1), or at an angle of $\alpha = 45^{\circ}$ (sample S2) to the twin boundaries, as it is shown in the insets (a) of Fig.1. To reduce the oxygen concentration, the crystals were annealed in an oxygen flow at higher temperature range for three to five days. Electric contacts were formed with the standard four-contact scheme by applying silver paste onto the crystal surface and the connection of silver conductor. The resistance in the *a-b* plane was measured using the standard method for two opposite directions of a direct current up to 10 mA as it was described in detail previously [1]. The hydrostatic pressure was produced in an autonomous chamber of the piston–cylinder type [3] and was measured using a manganin manometer. The temperature measurements were performed using a copper-constantan thermocouple which was mounted at sample level on the outside surface of the chamber. To determine the influence of the structural relaxation, the measurements were made a few days after the pressure application and removal, when the relaxation processes were completed.

Fig. 1 (a) and (b) shows the temperature dependence of the resistivity in the *ab* plane, $\rho_{ab}(T)$, for the S1 and S2 single crystals measured after the high hydrostatic pressure application-removal procedure. Part of the curves in this and the following figures is not coerced for clarity. The insets (b) of Fig. 1 show the resistivity transitions to the superconducting state in $\rho_{ab}(T)$ coordinates. The analysis of the experimental curves 1, measured before the application of high pressure, show that with the reduction of the oxygen concentration the critical temperature of the sample decreases. Furthermore, this leads to the expansion of the temperature width of the resistivity transition into the superconducting state compared to the initial sample (expansion by more than 10 times from $\Delta T_c \leq 0.3$K to $\Delta T_c \approx$

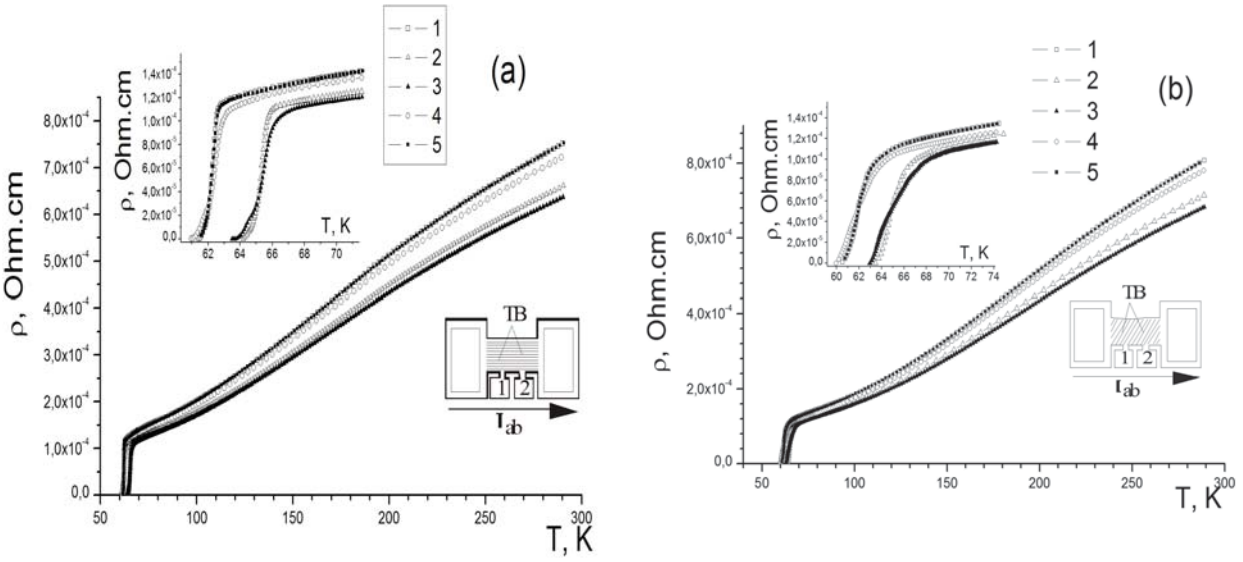

Fig. 1. (a) and (b) Temperature dependence of the resistivity $\rho_{ab}(T)$ for samples S1 and S2 at different pressures. Curve 1 was obtained prior the application of pressure; curve 2 –was obtained immediately after the application of pressure 4.8 kbar; curve 3 – was measured after keeping the samples in room temperature under pressure 4.8 kbar within a week; curve 4 – was obtained immediately after the removal of pressure and curve 5 – was measured immediately after keeping the sample for three days under zero pressure. The insets of Fig. 1 show the geometry of the experiment and the resistivity transitions to the superconducting phase.

3.5K). Additionally, the superconducting transition acquires an expressed stepwise form. This indicates that there are at least two phases, having different critical temperatures (T_{c1} and T_{c2}) to the superconducting transition [1,3]. The reduction of the oxygen concentration in both crystals leads in the transition from a quasi-metallic behaviour of $\rho_{ab}(T)$ [1,3] to the dependence with the characteristic thermally activated sagging.

The application of pressure, leads to a decrease of resistance and to an increase of T_c, with a rate $dT_c/dP \approx 0.7$ K.kbar^{-1}. This value is in consistent with previous studies [3,6-8], concerning oxygen deficient $YBa_2Cu_3O_{7-\delta}$ samples. Interestingly, the electrical resistivity is decreasing not only as a consequence of the high pressure application, but also in the isobar process of keeping the sample at room temperature just after the application of high pressure. For example, in Fig.1 (a) and (b) curves 2 and 3 show the dependence for the samples S1 and S2 respectively, measured directly after the application of pressure (4.8 kbar), as well as after the isobar process of retaining the sample at room temperature for five days following the application of high pressure. This exposure leads to an additional decrease in electrical resistance from 4-5%. Similar behaviour of $\rho_{ab}(T)$ was also observed after the removal of high pressure. Thus, in Fig. 1 curves 1 and 4 correspond to the dependence, measured before the application and immediately after the removal of pressure. Comparison of these curves indicates that the results are affected on the time that the sample is at room temperature. Immediately after the pressure removal, the value of the electrical resistance of the sample at room temperature, was approximately 4% less than the value measured prior the application of the pressure and consequently relaxed for three days to its equilibrium value. After this, the $\rho_{ab}(290K)$ value saturates and the $\rho_{ab}(T)$ dependence for both crystals almost completely coincides with the original curves, obtained before the prior the application of pressure. This confirms the reversibility of the process.

From Fig.2 (transition to the superconducting phase in $d\rho_{ab}/dT$-T coordinates), it is determined that the retention of the sample at room temperature in the application-removal of high pressure process has a significant influence on the width and shape of the superconducting transition. A characteristic feature of the influence of retaining the samples at room temperature for 3-5 days, is the significant peak displacement, up to $\Delta T_c \approx 0.5$-1.5K, in the $d\rho_{ab}(T)/dT$ dependence (according to [9] the temperature corresponding to this maximum is T_c), upwards and downwards in temperature, which indicates the change of the transport current flow paths. This in turn can occur in the case of strengthening the phase separation of the non-stoichiometric oxygen samples. The latter requires oxygen transport between phases with different T_c.

Comparing curves 2 and 3 shows, that after holding the sample under pressure for a week, the absolute value $d\rho_{ab}(T)/dT$ is reduced by about 1.5 times and the transfer itself significantly spreads. The dependence measured directly after the pressure removal (curve 4) there is change only in the absolute value of T_c, while the transfer width and value $d\rho_{ab}(T)/dT$ both remain practically unaltered. The comparison between curves 4 and 5, demonstrates that after the sample experienced atmospheric pressure for 3 days at room temperature, the width and the transfer regained their initial values. Therefore, when the pressure increases a part

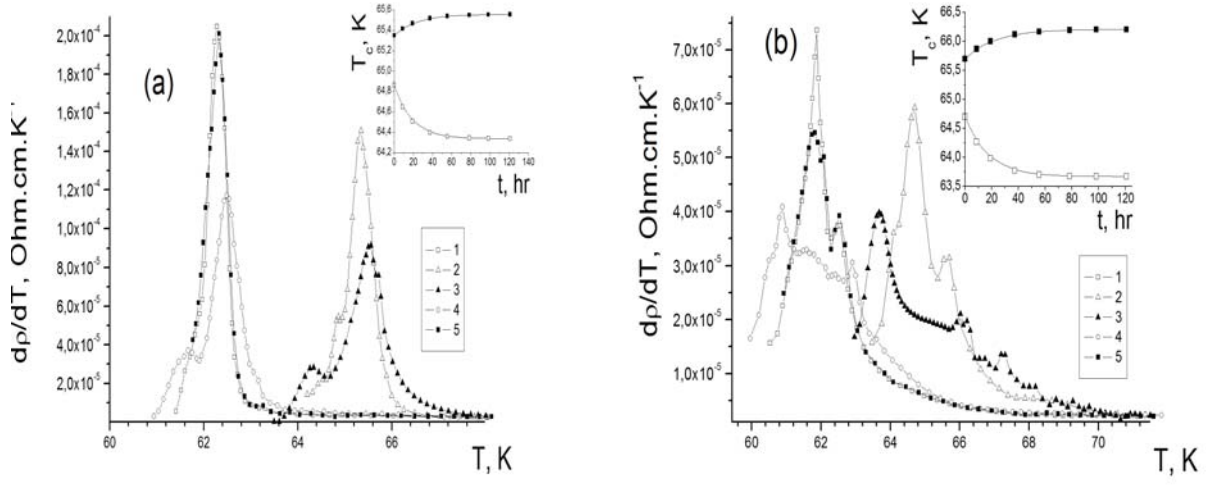

Fig. 2. The temperature dependence $d\rho_{ab}(T)/dT$ in the interval of the transition to the superconducting phase. The numbering of the curves corresponds to the numbers in Fig. 1. The insets show the temporary dependence of the isobar relaxation $T_c(t)$ of the critical temperature for high T_c and low T_c phases (dark and light symbols respectively) for both samples, obtained during the step by step annealing at room temperature after the application of pressure 4.8 kbar.

of the oxygen of the lower T_c phase, migrates to a higher critical temperature phase and when the pressure is reduced, the reverse process takes place. This effect can be possible in the case of the realisation of an ascending diffusion process [10], in which there is an inhomogeneous field of mechanical stresses (eg. due to external compression). In a compressive environment large impurity atoms (with respect to the lattice atoms) will experience larger force compared to the lattice atoms. Atoms with large ionic radius are likely to diffuse to tensile stress regions, whereas atoms with smaller volume diffuse in the region of compression. These concepts of ascending diffusion may also govern point defects [10] as in the present work oxygen vacancies. The reversibility of this effect is also an important feature. For example, when removing the external stress the reverse ordering of the concentration of the point defects in the sample will occur.

The insets to Fig. 2 (a) and (b) show the temporary dependence of the isobar relaxation $T_c(t)$ of the critical temperature for high T_c and low T_c phases (dark and light symbols respectively) for both samples, obtained during the step by step annealing at room temperature after the application of pressure of 4.8 kbar. The solid lines are presented the results by the expression proposed by Jorgencen et al. [11]:

$$T_c(t) = T_c(\infty) + [T_c(0) - T_c(\infty)]\ \exp[-(t/\tau)^{1/2}], \quad (1)$$

where $T_c(\infty)$ and $T_c(0)$ are the equilibrium and the initial value of the critical temperature, respectively, and τ is a characteristic time for the relaxation process.

Calculations with Eq. (1) show that the equilibrium value $T_c(\infty)$ in the step by step annealing is accelerated for the low temperature phases in comparison to the high temperature phases: $\tau(T_{c1})/\tau(T_{c2}) \approx 1.32$. Apparently, this phenomenon is due to a difference of the diffusion path during the high-pressure-induced redistribution of labile components. It appears that, for the same reason, the reverse process (alignment of the labile oxygen's concentrations) is occurring, after the pressure removal. In the second case, the oxygen atoms have to overcome smaller distances to leave the high-temperature (oxygen richer) phase that in the first case when the atoms of the labile oxygen have to overcome greater distances in order to find a vacancy in the low-temperature (oxygen depleted) phase.

Using the values of τ, obtained by Eq. (1) using our experimental data, we can determine the activation energy of the relaxation process in our samples [8] using the Arrhenius law:

$$\tau = \tau_0 \exp\left(\frac{E_A}{k_B T}\right), \quad (2)$$

where $\tau_0 = 1.4.10^{-12}$ s is the characteristic period [2], which, according to [8], is independent the pressure. The activation energy value obtained from our data $E_A \approx 0.94$ eV is slightly lower than the typical values for the $YBa_2Cu_3O_{7-\delta}$ compounds with reduced oxygen concentration [12]. It should also be noted that all the characteristic shape changes in the temperature dependence and absolute values of the resistivity parameters that where observed in the isobaric annealing process at room temperatures, in $HoBa_2Cu_3O_{7-\delta}$ were more pronounced compared to $YBa_2Cu_3O_{7-\delta}$. In $HoBa_2Cu_3O_{7-\delta}$ the Ho ion (which has larger ionic radius than Y) plays an important role to the structural order of the system affecting the oxygen ions interactions in the CuO planes. Previous studies confirmed that when we substitute Y to rare-earth elements with larger ions significant qualitative changes are evident regarding the $T_c(\delta)$ dependence in $ReBa_2Cu_3O_{7-\delta}$ [5]. Herewith, the characteristic for $YBa_2Cu_3O_{7-\delta}$ dependence $T_c(\delta)$ with two plateaus at 60 K and 90 K degenerates in a more sharp monotonical dependence. Additionally, the Ortho-II structure is not realized at all [5]. It can be assumed that oxygen hypostoichiometric $HoBa_2Cu_3O_{7-\delta}$ compounds have a more extended disordered oxygen hyperstructure than the $YBa_2Cu_3O_{7-\delta}$ compounds.

In previous works [13, 14], the value of critical temperature in $YBa_2Cu_3O_{7-\delta}$ was correlated with the number of holes in the CuO_2 layers via:

$$T_c = T_c^{\max}\left[1 - 82.6(n - n_{opt})^2\right], \quad (3)$$

where $T_c^{\max}$ is the maximum critical temperature and $n_{opt} = 0.25$ is the optimal number of holes in the surface (layer) for this compound. According to Eq. 3 when we increase the pressure at room temperature, the number of carriers for the low-temperature phase is reduced by about 2-3%, whereas at the same time in the high-temperature phase the reverse process is taking place as the number of holes increases. This is consistent with the concept that the application of high hydrostatic pressure leads to a diffusion redistribution of the labile components from the phase of lower critical temperature to the high-temperature superconducting phase. It is an important confirmation of the interrelation between structural and electro-transport anomalies in the system. In our case, one of the possible reasons of the phase separation could be the origination of the low Tc in the TB boundaries. Indeed, experiments on the vortex structure [15,16] have shown that the density of vortices in TB increases compared with their density in the volume of the superconductor, indicating the suppression of T_c in the TB. This can be due to the low oxygen concentration in the TB plane, which effectively implies the high concentration of oxygen vacancies [17], as a consequence of mechanical tensions. Vacancies create strong attractive fields (i.e, repulsion field for the oxygen

atoms)

This assumption can be justified by the different forms of superconducting transitions obtained with the different experimental geometries (here I ‖ TB and an angle between I and the TB of 45°). Figure 2 shows that for I ‖ TB the height of the peak of the $d\rho_{ab}(T)/dT$ dependency of the low-temperature phase is almost 3 times lower than the height of the peak corresponding to the high-temperature phase. Together with this, the more pronounced maximum, corresponding to high-temperature phase. In the second experiment geometry (angle between I and the TB of 45°) we observed an inverse $d\rho_{ab}(T)/dT$ dependence with a more pronounced maximum, corresponding to low-temperature phase. Since in the first case, the TB is parallel to the transport current there is a high probability of percolation paths mediating the current flow in the high-temperature phase. When the TB is oriented at an angle of 45° relative to the transport current vector (measurement of electrical resistance of the single crystal S2), the percolation paths of current flow in the high-temperature superconducting phase are missing. Therefore, the intensity of current carriers scattering should be minimal when the experiment geometry is I ‖ TB, which is reflected in the transformation of the shape in the corresponding dρab(T)/dT dependence. The latter preposition is indirectly confirmed by the difference of the absolute value of resistivity at room temperature, which is less than 7% in the case of the experiment geometry I ‖ TB, in comparison with the case of the experiment geometry when the angle between I and TB is 45°.

It should be noted that the final conclusion about the nature of the impact of TB on the phase separation in $HoBa_2Cu_3O_{7-\delta}$ single crystals, requires additional experimental studies. A future direction should be the investigation of superconducting transitions in untwining and twinning single crystals with a specific distribution of TB planes. In one segment of the crystal the transport current vector has to be oriented in parallel, and in another perpendicular to the TB plane. In the latter case, I⊥TB, the transport current will cross over the TB plane in one of the segments of the single crystal. As it can flow within the volume of the superconductor it passes by the TB plane in the other segment of the crystal (when I || TB). The measurements in the untwined crystals provide data regarding the existence (or lack) of the step-like form of the transition to the superconducting phase, as well as the difference (T_{c1}-T_{c2}) in the absence of plane defects in the sample.

To conclude, twin boundaries are effective scattering centres of normal carriers in $HoBa_2Cu_3O_{7-\delta}$ compounds. Reducing the oxygen stoichiometry of $HoBa_2Cu_3O_{7-\delta}$ single crystals, results to an uneven distribution of oxygen in the volume of the crystal and the formation of phases with different critical temperatures. Herewith, the substitution of yttrium with holmium significantly affects the charge distribution and the effective interaction in the CuO-planes, thereby stimulating the disordering in the oxygen subsystem. Induced by high pressure the redistribution of labile oxygen is enhances the phase separation in the volume of oxygen deficient $HoBa_2Cu_3O_{7-\delta}$ single crystals. Additionally, it stimulates ascending diffusion processes between the superconducting phases with different oxygen stoichiometry.

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