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Peculiarities of the relaxation processes in $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) single crystals at room temperature in air atmosphere

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The time dependencies of the resistivity of $ReBa_2Cu_3O_{7-x}$ (Re =Y, Ho) single crystals with varying degree of deviation from oxygen stoichiometry was investigated. It was found that the accelerated transport of oxygen ions in the initial stage of the implementation process can be carried out along the one-dimensional non-stoichiometric vacancies' clusters in single file diffusion regime. The final stage of oxygen ions diffusion in $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) is described by the usual classical diffusion mechanism.

The substitution of yttrium by holmium significantly affects the charge redistribution and changes the efficient interaction of ions in CuO-planes, thereby modifying the diffusion mass transfer mechanisms in the oxygen subsystem. Thus there is a change in the duration of the time intervals, corresponding to the oxygen ions' single file and classical volume diffusion mechanisms.

Keywords: $ReBa_2Cu_3O_{7-x}$ single crystals; doping; oxygen diffusion kinetics; structural relaxation processes; single file diffusion.

Досліджено залежності від часу величини електроопору монокристалів $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) з різним ступенем відхилення від кисневої стехіометрії. Показано, що прискорений транспорт іонів кисню на початковій стадії процесу впровадження реалізується уздовж одновимірних скупчень нестехиометрических вакансій механізмом одноканальній дифузії (single file diffusion). Заключна стадія впровадження іонів кисню в $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) описується класичним механізмом об'ємної дифузії.

Заміна ітрію на гольмій істотно впливає на перерозподіл заряду і змінює ефективну взаємодію іонів в CuO-площинах, тим самим, модифікуючи дифузійне перенесення речовини в кисневій підґратці. При цьому відбувається зміна тривалості часових інтервалів, відповідних механізмів одноканальної і об'ємної дифузії іонів кисню.

Ключові слова: монокристали $ReBa_2Cu_3O_{7-x}$; допування; кінетика дифузії кисню; релаксаційні процеси; одноканальна дифузія.

Исследованы зависимости от времени величины электросопротивления монокристаллов $ReBa_2Cu_3O_{7-x}$ (Re =Y,Ho) с различной степенью отклонения от кислородной стехиометрии. Показано, что ускоренный транспорт ионов кислорода на начальной стадии процесса внедрения реализуется вдоль одномерных скоплений нестехиометрических вакансий механизмом одноканальной диффузии (single file diffusion). Заключительная стадия внедрения ионов кислорода в $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) описывается классическим механизмом объемной диффузии.

Замена иттрия на гольмий существенно влияет на перераспределение заряда и изменяет эффективное взаимодействие ионов в CuO-плоскостях, тем самым, модифицируя диффузионный перенос вещества в кислородной подрешетке. При этом происходит изменение длительности временных интервалов, соответствующих механизмам одноканальной и объемной диффузии ионов кислорода.

Ключевые слова: монокристаллы $ReBa_2Cu_3O_{7-x}$; допирование; кинетика диффузии кислорода; релаксационные процессы; одноканальная диффузия.

Introduction

Study of mass transfer processes [1,2], along with the research of charge and heat transfer processes [3-5] are important tools to understand the nature of high-temperature superconductivity (HTSC), which still remains unclear, despite the more than 30-year intensive experimental and theoretical investigations.

Notably, in HTSC compounds the diffusion processes, in addition to the classical thermally activated mechanism [1,2], can be relatively affected by the application of high pressure [6,7], and intensively occur at "aging" of the experimental samples [8-10]. Thereby, the mass transfer can be carried out by a number of specific mechanisms: single-file diffusion, upward diffusion, and others [2,11,12,13].

The $YBa_2Cu_3O_{7-x}$ crystal is a well-known and one of the most studied ionic compounds regarding the so called "high-temperature" superconductivity [14]. An important feature of the structural state of this crystal is the presence in its lattice of one-dimensional ordered clusters formed by oxygen vacancies [13]. The formation of such structural defects due to the layered nature of the crystal lattice of the compound, as well as deficiency of oxygen ions, characterized by a parameter (x). The superconducting properties of the $YBa_2Cu_3O_{7-x}$ system (for example the transition

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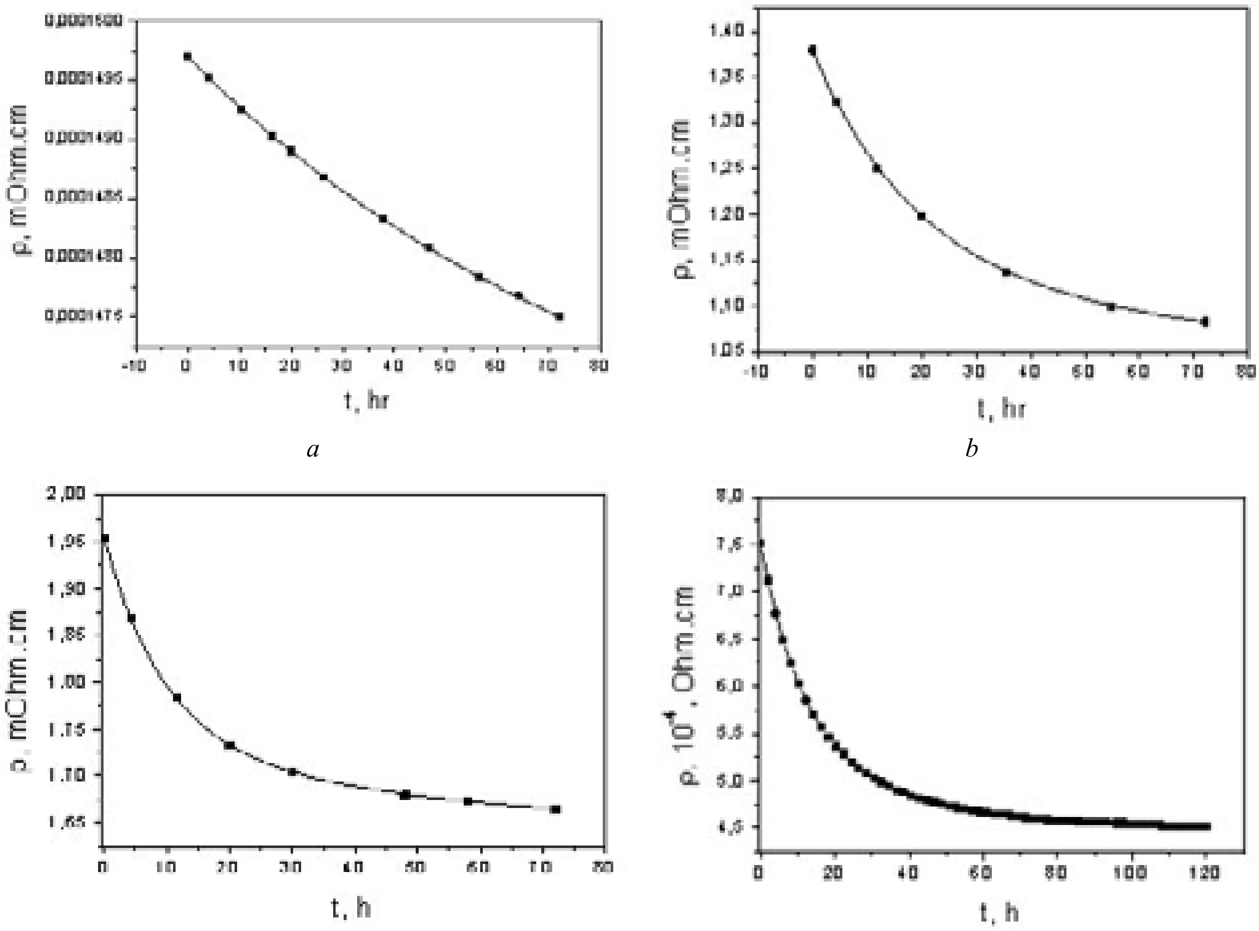

a *b*

c *d*

Fig. 1. The dependence of electrical resistivity of K1-K4 single crystals from the time of exposure in air at room temperature a – YBaCuO (T_c = 92 K); b – YBaCuO (T_c = 48 K); c – YBaCuO (T_c = 42 K); d – HoBaCuO (T_c = 73 K).

temperature to the superconducting state T_c, the electrical resistivity ρ, the critical current density J_c) are essentially depend on the degree of filling of vacancy clusters by oxygen ions, ie. on the value of the parameter (x). Thus, for example, when the value of (x) changes from ≈ 0.1 to ≈ 0.4, a decrease for the T_c is observed from $T_c \approx 92$ K to $T_c \approx 50$ K, and when the value (x) ≥ 0.5, the superconductivity in this crystal disappears [15]. Similar dependencies from the value of (x) are also observed during the investigation of other characteristics of the $YBa_2Cu_3O_{7-x}$ system. This is associated with the formation of one-dimensional chains of oxygen ions (clusters) that are formed as the clusters of vacancies are filled. Oxygen clusters together with Cu ions form the so-called U-centers that are capable to generate coupled electric charge carriers [16].

Formation of clusters occurs by the diffusion of oxygen ions during high temperature annealing of crystal in an oxygen atmosphere. As evidenced by the results of [2], the diffusion filling of the $YBa_2Cu_3O_{7-x}$ crystal by oxygen ions takes place by two different mechanisms. At the initial stage when we have a large deficit of oxygen ions ((x) ≥ 0.4) the process of filling of the crystal lattice by oxygen ions occurs in the regime of "single file" diffusion [17]. This accelerated transport of oxygen ions is replaced by the usual classical volume diffusion mechanism at the final stage of the process, when the parameter (x) → 0.1. Based on this fact, it is natural to assume that many of the relaxation processes observed in the crystal at room temperature, can also be controlled by these mechanisms of oxygen ions diffusion.

As is known [15,18], a characteristic feature of $YBa_2Cu_3O_{7-x}$ compound is the relative simplicity of the full or partial substitution of the yttrium by rare-earth ions. Thus, as in the case of other rare earth elements, when implementing the substitution of Y by the paramagnetic ions Re = Ho, Dy, the superconducting properties of the optimally oxygen doped of the $ReBa_2Cu_3O_{7-x}$ compounds with (x) ≤ 0.1, do not change significantly [15]. Apparently this is due to the localization of these ions away from the superconducting planes, which, in turn, prevents the formation of long-range magnetic order. At the same time it is known that the samples of the HTSC system 1-2-3, with non-stoichiometric composition regarding the oxygen, the rare earth ion may serve as a "sensor", sensitive to the local symmetry of its environment and to the charge density distribution, since the change in these parameters affect the

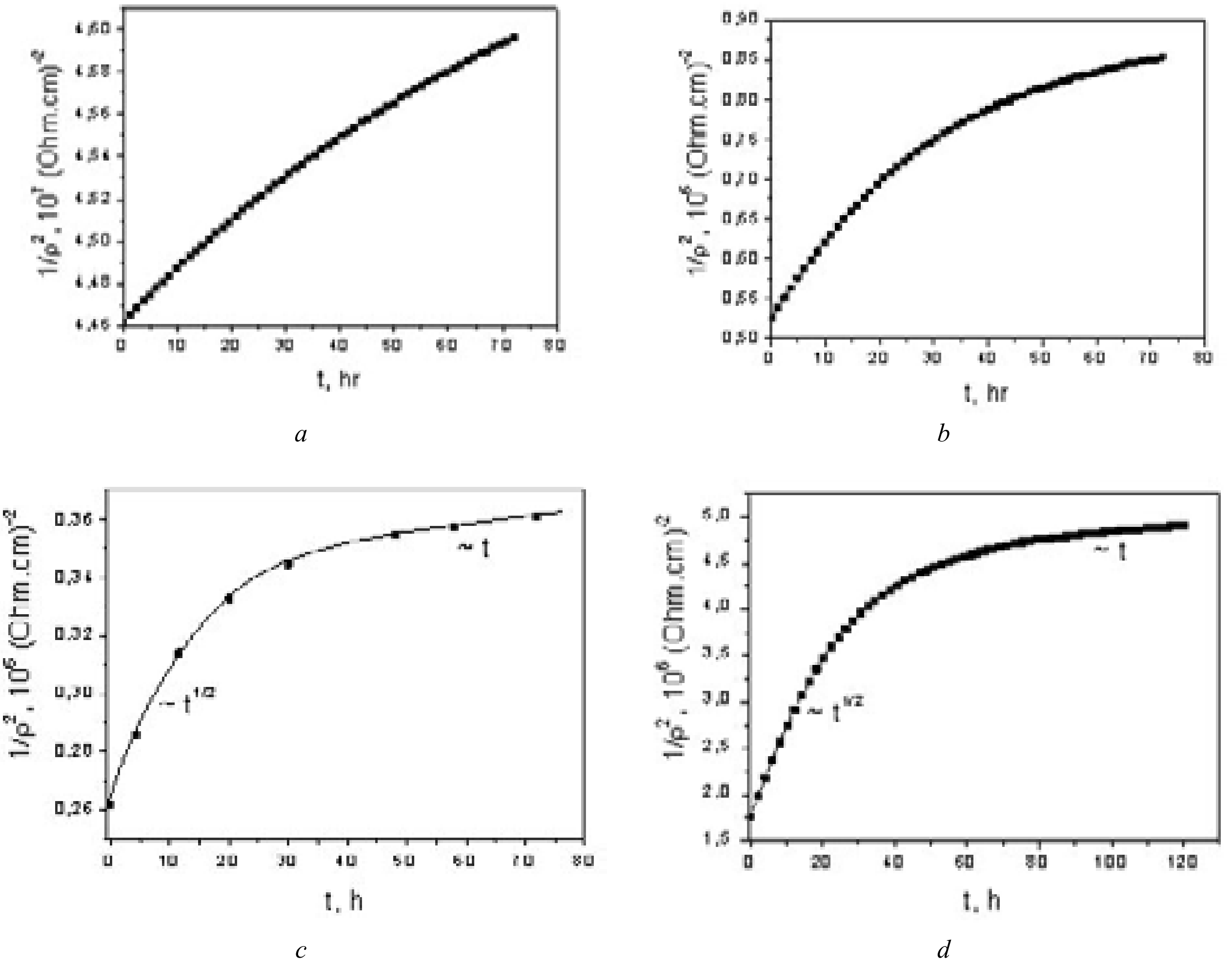

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Fig. 2. The plot of $1/\rho^2 = f(t)$ dependence for K1-K4 single crystals. The designations correspond to figure 1 a – YBaCuO ($T_c = 92$ K); b – YBaCuO ($T_c = 48$ K); c – YBaCuO ($T_c = 42$ K); d – HoBaCuO ($T_c = 73$ K).

electric field that forms the electronic structure of the ion [1,19]. Notably, in $HoBa_2Cu_3O_{7-x}$ the oxygen self-diffusion processes is affected by the larger holmium atom, leading to a change of the oxygen ions interaction in the CuO-planes [20].

Oxygen is sufficiently contained in the conventional air atmosphere in which usually-most of the crystals are stored. To verify the legitimacy of the assumptions made, we investigate the relaxation of the electrical resistance of four $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) single crystals that were kept for a long time (more than three days) at room temperature in air atmosphere. Presentation of the results of this study and their discussion is devoted to this article.

Experimental methodology

The $ReBa_2Cu_3O_{7-x}$ (Re = Y, Ho) single crystals were grown by the gold crucible solution-melt technology as described in previous work [21]. For the resistive measurements four crystals: K1, K2, K3 ($YBa_2Cu_3O_{7-x}$) and K4 ($HoBa_2Cu_3O_{7-x}$) have been used. Measurement of the electrical resistance of the samples was carried out by the standard four-point scheme using two pairs of silver contacts. The measurements were performed in the drift mode for two opposite directions of transport current to eliminate the impact of interference signal. The temperature was measured by platinum thermistor, the voltage on the sample and the control resistance by V2-38 nano-voltmeters. The critical temperature was determined at the maximum point on the dρ/dT curves in the region of the superconducting transition.

To reduce the oxygen content the samples were annealed for a day at temperature 680 ^{0}C and 690 ^{0}C ($YBa_2Cu_3O_{7-x}$ samples) and 600 ^{0}C ($HoBa_2Cu_3O_{7-x}$ sample) in vacuum. After annealing, the crystals were cooled until room temperature for 2-3 minutes. Then, they were mounted in the measuring cell and cooled until liquid nitrogen temperature for 10-15 minutes. All measurements were performed as the sample heating. To investigate the effect of annealing at room temperature, the sample after the first measurement of ρ(T), was held for several hours at room temperature and repeated measurements were performed. This procedure was repeated several times. The last series of measurements was carried out after the total exposure of the sample at room temperature for 5 days.

Results and discussion

The results of these measurements are presented in Fig. 1. As in previous work [2], we can clearly observe the two-stage process of the resistivity reducing with the exposure time. At the initial stage (approximately 20 hours), accelerated kinetics took place, which is replaced by a slower one, emerging to the saturation at up to three days exposure.

To identify the physical nature of this result, as in [2], we used the fact that at room temperature and above, the $YBa_2Cu_3O_{7-x}$, (x) = 0.6, is a common semiconductor. Accordingly, an increase in oxygen ions concentration causes an increase in the electrical conductivity and the corresponding decrease in the electrical resistivity ρ. At the same time, the change in the oxygen concentration in the crystal with time t is described by the same law as the average displacement of the diffusing oxygen ions into the crystal: $<L> = (2Dt)^{1/2}$ (where D is the diffusion coefficient) [22]. Consequently, we can determine from the time dependence ($1/\rho^2 = f(t)$ the time dependence of the mean square displacement of oxygen ions in the process of their diffusion penetration in crystal $<L^2> = f(t)$. In turn, the $<L^2> = f(t)$ dependence defines the ion diffusion mechanism: the $<L^2> \sim t^{1/2}$ dependence corresponds to a single file diffusion, and the dependence $<L^2> \sim t$ is consistent with the common classical volume diffusion [17]. Using the experimental data presented in figure 1, we processed them by using the $(1/\rho^2) = f(t)$ dependence (see. Fig. 2). From this figure it follows that the initial stage of the relaxation process $\rho = f(t)$ is controlled by a single file diffusion mechanism, and at the final stage of this process occurs in the classical diffusion regime.

At the same time it can be seen that the duration of the first stage greatly depends on the oxygen concentration in the sample, and on the type of the rare-earth ion. In the $YBa_2Cu_3O_{7-x}$ single crystals the longest stage of the $<L^2> \sim t^{1/2}$ dependence corresponding the single file diffusion is observed in the sample with the minimum $T_c \approx 42$ K (and, accordingly, with the maximum oxygen deficiency). With the increase of T_c up to 48 K (and, accordingly, as the oxygen deficiency is reduced), in crystal K2, the duration of this stage decreases and reaches to the minimum in the sample with $T_c \approx 90$ K. This result confirms the formulated our assumption that the process of filling of crystal lattice with oxygen ions in the single file diffusion regime is most easily implemented in the samples with its maximum oxygen deficiency $(x) \leq 0.4$, whereas the conventional classical mechanism dominates at $(x) \rightarrow 0.1$.

It is observed that in the case of $HoBa_2Cu_3O_{7-x}$ crystal, despite the relatively high $T_c \approx 73$ K, the single file diffusion is the dominant regime. As noted above, in the case of the Y substitution by other rare-earth elements, there is no significant change occurring regarding the electrical characteristics in the optimally doped samples $(x) < 0.15$. At the same time, as shown in [23], all the characteristic changes in the shape of the temperature dependence of the resistivity and the absolute values of the resistivity parameters that were observed during isobaric annealing of the samples at room temperature in the case of $HoBa_2Cu_3O_{7-x}$ compounds, carried a much more pronounced character in comparison with the $YBa_2Cu_3O_{7-x}$ samples. As mentioned above, in the case of $HoBa_2Cu_3O_{7-x}$ samples, a specific role in the structural ordering in the system is due to yttrium substitution by holmium, which has a much larger ionic radius, which, in turn, leads to a change in the oxygen ions' interaction in the CuO-planes. Indeed, as is known from previous studies [19], when the yttrium substituted by other rare earth elements with larger ion radius, there occurs a significant qualitative changes in $T_c(x)$ dependence. Thus, the characteristic for the $YBa_2Cu_3O_{7-x}$ dependence T_c (x) with two plateaus at 60 and 90 K degenerates into a much sharper monotonic dependence [19]. So, we can assume that in the case of deviation from oxygen stoichiometry the $HoBa_2Cu_3O_{7-x}$ compound should be characterized by a much more unstable oxygen superstructure in comparison with the $YBa_2Cu_3O_{7-x}$. This, in turn, can significantly affect to the diffusion mechanisms and the nature of the diffusion processes in the samples that we observed in the experiment. A certain role in this case may also play the specific mechanisms of quasi-particle scattering [24-29], due to the presence structural and kinematic anisotropy in the system.

It should be emphasized that and some other relaxation processes that are observed in the high-temperature oxide superconductors can also be described by similar kinetic laws. As an example, we can mention the time dependence of the temperature in which the pseudo-gap opens (T*), during exposure of the sample at room temperature in air atmosphere [23] as well as the two-stage relaxation of the electrical resistance of single crystals $YBa_2Cu_3O_{7-x}$ in the process of high hydrostatic pressure-induced redistribution of the labile oxygen [30].

Conclusions

Based on this study we can conclude that in all high-temperature oxide superconductors, characterized by oxygen ions deficiency, and in particular, in the $YBa_2Cu_3O_{7-x}$ compounds, the relaxation of the electrical resistivity at room temperature that is observed, is controlled by the single file and the classical oxygen ions volume diffusion mechanisms. The substitution of yttrium by the holmium significantly affects the charge redistribution and change the interaction of oxygen with the CuO-planes, thereby modifying the diffusive transport of matter in the oxygen sublattice. Thus, there occurs a significant shift of the time intervals corresponding to the single file and the classical oxygen ions volume diffusion mechanisms.

References

1. Marion Klaser, Joachim Kaiser, Fredy Stock, German Muller-Vogt, Andreas Erb / Physica C 306 (1998) 188-198.
2. Yu.I.Boyko, V.V.Bogdanov, G.Ya. Khadzhai, S.V.Savich, R.V.Vovk / FNT, v. 42, N10, 2016.
3. J. Ashkenazi, J. Supercond. Nov. Magn. 24, 1281 (2011).
4. R. V. Vovk, M. A. Obolenskii, A. A. Zavgorodniy, Z. F. Nazyrov, I. L. Goulatis, V.V. Kruglyak, A. Chroneos / Modern Physics Letters B (MPLB) V. 25 (27), p. 2131-2136 (2011).
5. R. V. Vovk, G.Ya. Khadzhai, I. L. Goulatis, A. Chroneos / Physica B: Condensed Matter Volume 436, 1 March 2014, Pages 88–90.
6. S. Sadewasser, J.S. Schilling, A.P. Paulicas, B.M. Veal // Phys. Rev. B. -2000. -V.61, №1. -P.741-749.
7. D.D. Balla, A.V. Bondarenko, R.V. Vovk, M.A. Obolenskii, A.A. Prodan // Low Temp. Phys. - 1997. – Vol. 23, №10. - P. 777-781.
8. Martinez, B. Sandiumenge, F. ; Pinol, S. ; Vilalta, N. ; Fontcuberta, J. ; Obradors, X. // Applied Physics Letters (1995) V. 66 , Issue: 6 P.P. 772 – 774.
9. D. A. Lotnyk, R. V. Vovk, M. A. Obolenskii, A. A. Zavgorodniy, J. Kováč, M. Kaňuchová, M. Šefciková, V. Antal, P. Diko, A. Feher, A. Chroneos // Journal of Low Temperature Physics, DOI 10.1007/s10909-010-0198-z. Journal of Low Temperature Physics V. 161, № 3-4, 387-394, (2010).
10. R.V. Vovk, N.R. Vovk, G.Ya. Khadzhai, Oleksandr V. Dobrovolskiy, Z.F. Nazyrov / J Mater Sci : Mater Electron (2014) 25: 5226-5230 DOI 10.1007/s10854-014-2292-5.
11. Solovjov, M. Tkachenko, R. Vovk, A. Chroneos / Physica C 501 (0) (2014) 24 – 31.
12. Chroneos and R. V. Vovk / Solid State Ionics 274 (2015) 1-3.
13. Esch F., Fabris S., Zhou L., Montini T., Africh C., Fomasiero P., Comelli G., Rosei R. / Science, v. 309, p. 752, 2005.
14. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu / Phys. Rev. Lett.58 (9) p.p. 908–910 (1987).
15. D. M. Ginsberg (ed), Physical properties high temperature superconductors I. – Singapore: Word Scientific, 1989.
16. K.Mitsen, O.Ivanenko, J. Exp. Theor. Phys, 100, 1082 (2005).
17. Hahn K., Karger J., Kukla V. / Physical Review, Letters, v. 76, № 15, p. 2762, 1996.
18. R.V. Vovk, N.R. Vovk, G.Ya. Khadzhai, I.L. Goulatis, A. Chroneos / Solid State Communications, V. 190, (2014), P. 18–22.
19. Lutgemeier H., Schmenn S., Meuffels P., Storz O., Schollhorn R., Niedermayer Ch., Heinmaa I., Baikov Yu. Physica C **267**, 191 (1996).
20. R.V. Vovk, G.Ya. Khadzhai, Oleksandr V. Dobrovolskiy, Z.F. Nazyrov, and A. Chroneos // Physica C 516 (2015) p.p. 58-61 doi:10.1016/j.physc.2015.06.011.
21. Obolenskii M.A., Vovk R.V., Bondarenko A.V., Chebotaev N.N.. – Low Temp. Phys., v. 32, p. 571, 2006.FNT97pinning.
22. Malkovich R.Sh., Matematika diffuzii v poluprovodnikah – Sankt–Piter–b., «Nauka»,1999, 390 pp.
23. Vovk R.V., Vovk N.R., Dobrovolskiy O.V. / J. Low Temp. Phys, v. 175, p. 614–630, 2014.
24. V.M. Apalkov and M.E. Portnoi, Phys. Rev. B **65**, 125310 (2002).
25. Ruslan V. Vovk, Georgij Ya. Khadzhai, Oleksandr V. Dobrovolskiy / *Appl. Phys. A* (2014) 117: 997-1002 DOI: 10.1007/s00339-014-8670-2.
26. N. Adamenko,K.E.Nemchenko,V. I.Tsyganok and A.I.Chervanev, Low Temp. Phys. 20 (1994) 498.
27. R.V.Vovk, C.D.H.Williams and A.F.G.Wyatt. / Phys. Rev. B **68**, 134508 (2003).
28. R.V.Vovk, C.D.H.Williams and A.F.G.Wyatt. / Phys. Rev. Lett. **91**, 235302 (2003).
29. P.G. Curran, V.V. Khotkevych, S.J. Bending, A.S. Gibbs, S.L. Lee, and A.P. Mackenzie, Phys. Rev. B 84, 104507 (2011).
30. R. V. Vovk, M. A. Obolenskii, A. V. Bondarenko / Fizika Nizkih Temperatur, v. 33, N 1, p. 126-130 (2007).