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Studies of the correlation between superconducting transition temperature and anion defectivity in thallium-based ceramics

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The paper presents the results of studies of the influence of the anion defectiveness on the transition temperature to the superconducting state of thallium-containing superconductors. It is shown that the anion defectiveness is associated with a change in the oxygen O3 *content in the thallium plane and oxygen* O1 *in the copper plane. It was found that the transition temperature depends on the bond lengths* Tl-O3, Cu-O2 *and* Cu-O1.

Anion defectivity in superconducting ceramics is one of the sources generating charge carriers (holes) in them.

The aim of this work is to study the effect of anion defectivity on the transition temperature to the superconducting state in two-layer thallium-based superconductors.

The studies were performed on ceramic superconductors of the compositions $Tl_2Ba_2CuO_x$ (Tl-2201) and $Tl_2Ba_2CaCu_2O_x$(Tl-2212), containing two layers of thallium. The two-layer samples of the phases under study were obtained by solid-phase synthesis according to the two-stage technology [1]. The composition of the samples was controlled by X-ray diffraction analysis. The crystal structure parameters were specified by the Rietveld method using the "GSAS" program.

Anion defectiveness was created in samples as a result of vacuum annealing carried out with use of the thermal analyzer TGA 92-16.18. Ceramics were heated at a rate of 5 ^{o}C/min to temperatures of 400−500 ^{o}C at which samples were kept for 4−6 h. The transition temperatures of the ceramics to the superconducting state were determined by means of resistivity measurements.

The initial ceramics $Tl_2Ba_2CuO_x$ and $Tl_2Ba_2CaCu_2O_x$ before annealing had transition temperatures T_c to the superconducting state of 47 K and 86 K, respectively. After annealing in vacuum at 450 ^{o}C, the transition temperatures of the superconductors were 72 K for Tl-2201 and 82 K for Tl-2212.

According to the data obtained by specifying the parameters of the crystal structure of the samples (Table 1), the oxygen losses in the superconducting samples of both phases are related mainly to the escape of oxygen O3 from the thallium plane (the initial sample Tl-2201 n = 0,83, annealed n = 0,32; initial sample Tl-2212 n = 0,94, annealed n = 0,56) and to a lesser extent with O1 oxygen escape from the copper plane (Tl-2201 n = 1,0, annealed n = 0,99; Tl-2212 n = 1,0, annealed n = 0,94).

Table 1

Crystal structure parameters of samples Tl-2201 and Tl-2212 with different degree of anion defectivity

Tl-2201	Parameters	Source T_c = 47 K	Samples, after annealing T_c = 72 K	Tl-2212	Parameters	Source T_c = 86 K	Samples, after annealing T_c = 82 K
Tl^{+3}/Cu^{+1} (0,5, 0,5, z)	z n U-Tl^{+3} U-Cu^{+1}	0,2021 0,963/0,037 0,019 0,041	0,2024 0,839/0,141 0,017 0,010	Tl^{+3}/Ca^{+2} (0,0,z)	z n U	0,2138 0,77/0,23 0,0128	0,2137 0,73/0,27 0,0128
Ba^{+2} (0,0,z)	z n U	0,0841 1,0 0,005	0,0835 1,0 0,006	Ba (0,5,0,5,z)	z n U	0,1216 1,0 0,0135	0,1213 1,0 0,0138
Cu^{+2}/Tl	z	0,0076	0,0242	Cu	z	0,0565	0,0544

$^{+1}$ (0,5,0,5, z)	*n* U	0,964/0,036 0,005	0,859/0,141 0,010	(0,0,z)	*n* U	1,0 0,0277	1,0 0,0093
-	-	-	-	Ca^{+2}/Tl^{+3} (0,5,0,5,0)	*n* U	0,92/0,08 0,0036	0,88/0,12 0,0086
O(1) (0,0,5,0)	*z* *n* U	0,0 1 0,102	0,006 0,987 0,059	O(1) (0,0,5,z)	*z* *n* U	0,0526 1,0 0,0148	0,0455 0,94 0,00925
O(2) (0,5,0,5,z)	*z* *n* U	0,1098 1,0 0,004	0,1019 1,0 0,001	O(2) (0,0,z)	*z* *n* U	0,13124 1,0 0,047661	0,1374 1,0 0,0361
O(3) (x,0,5,*z*)	*x* *z* *n* U	0,5 0,3087 0,834 0,087	0,502 0,3114 0,324 0,103	O(3) (0,0,z)	*z* *n* U	0,27896 0,94 0,2336	0,2802 0,56 0,1988
	R_{wp}	0, 08	0,08			0,07	0,08

The increase in the number of charge carriers for the Tl-2201 phase is determined by both oxygen non-stoichiometry and cationic non-stoichiometry associated with isomorphic substitution of some proportion of Tl^{+3} atoms in their main positions by Cu^{+1} atoms. For Tl-2201 samples after vacuum annealing the fraction of substituted thallium atoms increases (for the initial sample Tl^{+3}/Cu^{+1} n = 0,96/0,037, for annealed n = 0,85/0,15) (Table 1), which in turn also leads to an increase in hole conductivity.

In Tl-2212 superconductors, the fraction of thallium atoms occupying their main positions decreases by 7 % after annealing (Table 1), while the fraction of Tl^{+3} ions replacing Ca^{+2} ions increases by 5 %, which also leads to a change in the number of charge carriers in superconductors. The observed loss of oxygen in the thallium and copper planes in the Tl-2212 samples leads to an increase in the number of holes, while the total change in the number of charge carriers in the ceramics is such that the transition temperature to the superconducting state in Tl-2212 superconductors decreases. Consequently, we can say that the dependence of the superconducting transition temperature on the number of carriers for the two-layer thallium-containing phases is not linear.

The geometry of the structures of ceramic samples of high-temperature Tl-2201 and Tl-2212 phases can be clearly compared on the basis of the data obtained for the interatomic distances (Table 2).

In superconducting ceramic samples of Tl-2212 phase the Cu-O1 distance value, according to Table 2, has values lying in the range (1,936 – 1,947) Å. The apical oxygen O2 in the ceramics of Tl-2212 phase is not closer than 2.43 Å to copper, whereas the lowest Cu-O2 distance in the samples of Tl-2201 phase is 1.81 Å. The character of changes in the distances from copper ions to apical oxygen ions with increasing transition temperature to the superconducting state for the Tl-2201 and Tl-2212 phases is the same (the distances decrease).

Table 2

Main interatomic distances of superconducting samples of phases Tl-2201 and Tl-2212 with different degrees of anion defects

Interatomic distances, Å	Tl-2212 $T_c = 86$ K	Tl-2212, $T_c = 82$ K after vacuum annealing at 450 ^{o}C	Tl-2201 $T_c = 47$ K	Tl-2201 $T_c = 72$ K after vacuum annealing at 450 ^{0}C
Tl - O3	2,558	1,956	2,467	2,532
Ba - O2	2,763	2,808	2,796	2,765
Ba - Cu	3,333	3,359	3,353	3,719
Cu -O1	1,936	1,947	1,939	1,970
Cu - O2	2,491	2,431	2,368	1,806
Tl - O2	2,422	2,226	2,135	2,339
Cu-O1-Cu angle (in degrees)	180,0	180,0	180,0	179,1

The results obtained for the Tl-2201 phase containing no calcium planes (Table 2) show that the Cu-O bond length in CuO2 layers increases from 1,94 to 1,97 Å for samples with higher Tc, and the copper-versus-oxygen distance along the c axis decreases from 2,37 Å to 1,81 Å. The increase of cationic and anionic defectiveness of $Tl_2Ba_2CuO_x$ ceramic samples leads to the decrease of Cu-O_1-Cu angle, which causes "corrugation" of Cu-O planes [2], while for Tl-2212 phase "corrugation" is not characteristic.

The dependence of the superconducting transition temperature on the distances between Cu and O1 ions (Fig. 1) has been obtained from the studies of the Tl- 2212 phase ceramics. It follows that superconductors of the $Tl_2Ba_2CaCu_2O_x$ composition will have a superconducting transition temperature of about 100 K and higher provided that the Cu-O1 distance is (1,92 – 1,925) Å.

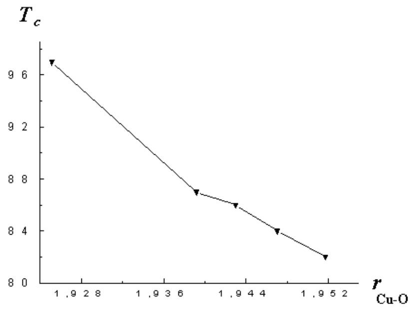

Fig. 1. Dependence of T_c (K) on $r_{\text{Cu-O}}$ distances (Å)

Thus, the study of the influence of anion defectivity on the phase transition temperature has shown that the superconducting transition temperature in the ceramic two-layer samples $Tl_2Ba_2CuO_x$ and $Tl_2Ba_2CaCu_2O_x$, regardless of the presence of a calcium layer, is determined by the value of Cu-O1 interatomic distances. The dependence obtained for the $Tl_2Ba_2CaCu_2O_x$ phase should be taken into account when choosing methods to increase the T_c of thallium-based superconductors.

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Studying the magnetic field of a multilayer solenoid in the laboratory physics workshop

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This paper presents the theory of the magnetic field of a multilayered solenoid of finite length with an arbitrary number of coils. It describes the methods of experimental and theoretical investigation of solenoid magnetic field distribution in laboratory practice for students of physics and engineering specialties.

In the conditions of implementation of the international students' training program within the framework of the joint department of BNTU and TSTU (Tashkent) on training engineers-technicians it is necessary to develop and implement into the educational process methodical and laboratory support, which would allow to combine not only educational, but also scientific and research technologies to the fullest extent. This is especially relevant when teaching students according to the modular-block system, when the course of physics is studied in a certain period of time determined by the curriculum. This development