

THE STRUCTURAL TRANSFORMATIONS IN $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$

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The structural phase transition in $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ were investigated by the high-temperature roentgenodiffractometric method, and it was shown, that at the room temperature $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ is two-phase and is composed of the rhombic phase with the lattice parameters $a=7.319\text{\AA}$, $b=22.236\text{\AA}$, $c=36.458\text{\AA}$ and the rhombic phase with the lattice parameters $a=3.12\text{\AA}$, $b=4.04\text{\AA}$, $c=6.87\text{\AA}$. The both rhombic phases transfer into the two primitive cubic phases with the parameters $a_1=7.0091\text{\AA}$ и $a_2=6.8787\text{\AA}$, respectively, by the temperature increase at 469K.

The Cu_2Te compound on the state diagram of the Cu-Te system corresponds to the compound 33,3 at % Te and melts at 1393 K[1]. In [2] it is shown, that Cu_2Te is crystallized in the hexagonal structure with lattice parameters: $a_0=4.237\text{\AA}$, $c_0=7.274\text{\AA}$, a space group P6mm, the elementary cell contains $Z=2$, the density $\rho_x=7.274\text{ g/cm}^3$.

According to [3] for Cu_2Te the rhombic structure with the lattice parameters $a=7.319\text{\AA}\approx\sqrt{3}a_0$, $b=22.236\text{\AA}\approx 3c_0$, $c=36.458\text{\AA}\approx 5c_0$, which is the superstructural hexagonal phase, is determined at the room temperature. In [3-9] it is shown by various authors and naturally by various methods, that in Cu_2Te five structural transformations at 448, 548, 593, 638 and 848K occur in the temperature range 290-1220K.

In [10] it is shown by the high-temperature roentgenodiffractogramic method, that:

- The second hexagonal phase with the lattice parameters $a=8.4191\text{\AA}$, $c=21.8733\text{\AA}$ is yielded at 448 K from the Cu_2Te crystal, composed of the rhombic and hexagonal phase with the lattice parameters: $a=7.319\text{\AA}$, $b=22.236\text{\AA}$, $c=36.458\text{\AA}$ and $a=4.1418\text{\AA}$, $c=7.1833\text{\AA}$. The parameter c of the rhombic phase is sharply cut $\Delta c=0.72\text{\AA}$ with the phase formation, what gives reasons to make conclusion, that the second hexagonal phase is formed at the expense of the rhombic phase.
- At 540 K the parameters a and b of the rhombic phase reduce by the jump, but the parameters a and c of the first hexagonal phase increase by the jump. The reason is the displacement of the cations and the cation vacancies.
- At 590 K the rhombic and first hexagonal phases transfer into the second hexagonal phase and crystals Cu_2Te become one-phase at the temperature range 590-638 K.
- At 638 K the diffraction reflections, belonged to the rhombic phase, are restored with the appearance of the reflection from the plane (111) of the high-temperature fcc phase.
- At 848 K the rhombic and second hexagonal phases transfer into the fcc phase with the lattice parameters $a=6.1140\text{\AA}$.

In [11] it is shown, that the crystals $\text{Cu}_{1.50}\text{Zn}_{0.50}\text{Te}$ at the room temperature, as Cu_2Te , are two-phase and composed of the hexagonal phase with the lattice parameters $a=4.2478\text{\AA}$, $c=7.2334\text{\AA}$ and the rhombic phase with the lattice parameters of the corresponded lattice parameters Cu_2Te .

At 811 ± 2 K the rhombic phase transfers into the hexagonal phase. In this process the parameters of the hexagonal phase do not suffer the jump. It testifies the fact, that at the transformation of the rhombic phase into the hexagonal, the latter is to be the primer. The hexagonal phase

itself at 970 ± 2 K transfers into the high-temperature fcc phase of the lattice parameter $a=6.1187\text{\AA}$.

It follows from the above-presented, that in crystals Cu_2Te the partial substitution of Cu atoms by the Zn atoms, having the same charge and close ion radii, cut the number of the phase transformations from five in Cu_2Te up to two in $\text{Cu}_{1.50}\text{Zn}_{0.50}\text{Te}$.

The results of the high-temperature roentgenodiffractogram researches of the influence of the partial substitution of the cooper atoms by the silver atoms on the structure, mechanism and the temperature of the structural transformations in the crystal Cu_2Te are represented in the present paper. With this purpose, the method of the direct synthesis, i.e. the chemical interaction of the initial components, is used for the receipt of the homogeneous samples of the $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ compound. The initial components, taking part in the compound, have the following purities: cooper is electrolytic, silver and tellurium are of the special pure mark (SP). The synthesis conditions and the crystals growth by the Bridgeman's method are represented in [10].

The temperature roentgenographic researches was carried out on the diffractometer DRON-3M with the temperature attachment URVT-2000.

Experiments were carried out in the vacuum (10^{-2} Pa). The condition of the survey permission was made $\sim 1^\circ$. The diffractograms are recorded persistently, the diffraction angles are determined by the method of the intensities peaks measurement. In experiments the error of the reflection angle determination did not exceed the value $\Delta\theta=\pm 0.02^\circ$.

From the crystal ingot $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ the thin plane of the size $2\times 4\times 4$ mm was cut off and at the room temperature 18 diffraction reflections (table 1) are fixed from the indicated sample in the angle interval $20^\circ\leq 2\theta\leq 80^\circ$.

For the precious indexing of the diffraction data from $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ they were compared with the calculated values of the interplane distances d_i , and corresponding indices $h_k l_i$ of the reflection planes, calculated on the base of the parameters of the elementary cell Cu_2Te , CuAgTe and Ag_2Te . As it is seen from the table 1, the experimental values are satisfactorily coincided with the calculated parameters d_i of the lattice parameters of the rhombic phase Cu_2Te . From experimental d_i , as it is seen from the table 1, some d , i.e. $d=2.4715$ (110); 2.0060 (112); 1.7177 (004); 1.5608 (200) and 1.4145 (114) are indexed on the base of the parameters of the rhombic phase CuAgTe . It follows hence, that the crystals $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ at the room temperature are two-phase, i.e. crystallized in the rhombic structure Cu_2Te and CuAgTe , besides the relative number (quantity) of Cu_2Te is more than CuAgTe .

Table 1

The diffractogram's calculation of $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$. $\text{CuK}_\alpha(\lambda_\alpha=1.5418 \text{ \AA})$, filter – Ni , Regime: 38 kV, 22 mA.

N	θ	I/I_0	$d_{\text{exp.}}(\text{Å})$	Cu_2Te		CuAgTe		Parameters of the elementary cell, Å	T_{exp} K
				$d_{\text{cal.}}(\text{Å})$	hkl	$d_{\text{cal.}}(\text{Å})$	hkl		
1	2	3	4	5	6	7	8	9	10
1	15°41'	17	2.8534	2.8534	208			Rhombic $a=7.3193$ $b=22.2435$ $c=36.3636$	293
2	16°30'	33	2.7144	2.7155	209				
3	16°52'	100	2.6574	2.6586	084				
4	17°30'	95	2.5636	2.5623	256				
5	18°11'	15	2.4715	2.4707	090	2.4716	110		
6	18°39'	42	2.4107	2.4181	302				
7	20°11'	50	2.2345	2.2340	340				
8	21°27'	40	2.1081	2.1093	099				
9	21°45'	30	2.0807	2.0807	319				
10	22°36'	42	2.0060	2.0059	348	2.0064	112		
11	22°48'	19	1.9893	1.9887	364				
12	23°29'	18	1.9352	1.9349	370				
13	24°14'	52	1.8788	1.8775	2103				
14	25°02'	11	1.8224	1.8224	411				
15	26°40'	11	1.7177	1.7185	393	1.7177	004		
16	28°44'	9	1.6040	1.6032	3105				
17	29°36'	4	1.5608	1.5614	459	1.5608	200		
18	33°02'	12	1.4145	1.4145	541	1.4111	114		
1	15°39'	10	2.8584	2.8560	208			Rhombic $a=7.3367$ $b=22.2732$ $c=36.4101$	373
2	16°29'	35	2.7173	2.7176	209				
3	16°51'	100	2.6601	2.6622	084				
4	17°28'	97	2.5688	2.5661	256				
5	18°09'	20	2.4748	2.4748	090	2.4746	110		
6	18°33'	50	2.4227	2.4239	302				
7	20°07'	48	2.2410	2.2391	340				
8	21°25'	34	2.1109	2.1110	099				
9	21°43'	30	2.0835	2.0838	319				
10	22°33'	36	2.0102	2.0089	348	2.0093	112		
11	22°46'	35	1.9920	1.9924	364				
12	23°26'	23	1.9389	1.9390	370				
13	24°12'	45	1.8807	1.8804	2103				
14	24°59'	15	1.8255	1.8259	411				
15	26°36'	13	1.7215	1.7218	393	1.7215	004		
16	28°42'	10	1.6054	1.6060	3105				
17	29°32'	10	1.5640	1.5642	459	1.5640	200		
18	33°00'	10	1.4155	1.4178	541	1.4132	114		
1	15°38'	5	2.8605	2.8595	208			Rhombic $a=7.3477$ $b=22.3092$ $c=36.4280$	423
2	16°28'	30	2.7202	2.7206	209				
3	16°49'	100	2.6647	2.6660	084				
4	17°27'	90	2.5714	2.5700	256				
5	18°07'	15	2.4788	2.4788	090	2.4784	110		
6	18°35'	50	2.4189	2.4275	302				
7	20°06'	45	2.2429	2.2428	340				
8	21°24'	32	2.1126	2.1141	099				
9	21°42'	30	2.0852	2.0865	319				
10	22°31'	35	2.0128	2.0117	348	2.0121	112		
11	22°45'	30	1.9935	1.9956	364				
12	23°24'	20	1.9413	1.9418	370				
13	24°10'	40	1.8830	1.8838	2103				
14	24°57'	14	1.8276	1.8282	411				
15	26°34'	12	1.7235	1.7247	393	1.7235	400		
16	28°40'	10	1.6070	1.6087	3105				
17	29°30'	10	1.5656	1.5663	459	1.5656	200		
18	32°54'	10	1.4192	1.499	541	1.4149	114		

After the diffraction reflection record at the room temperature, without changing the angle interval and the crystals orientation the furnace was switched on and the

record was carried out every 50 K. Before every record the corresponding temperature was kept constant during 40 min. Under this conditions, the essential changes did not occur in

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the reflection number and their intensities up to 423 K. Only at 423 K the four couple diffraction reflections (fig.1), whose calculations are represented in the table 2, are fixed in the previous angle interval. As it is seen from the table 2 and fig.1 the low-temperature two-phase crystal $\text{Cu}_{1.50}\text{Ag}_{0.5}\text{Te}$ at 469 ± 1 K transfers into the two primitive cubic phases with

the lattice parameters: $a_1=7.009\text{\AA}$ и $a_2=6.878\text{\AA}$, distinguished by the elementary cell parameters and the diffraction reflections intensities, where $I_{(220)}^1 > I_{(220)}^2$, $I_{(222)}^1 > I_{(222)}^2$, $I_{(320)}^1 < I_{(320)}^2$ and $I_{(400)}^1 < I_{(400)}^2$.

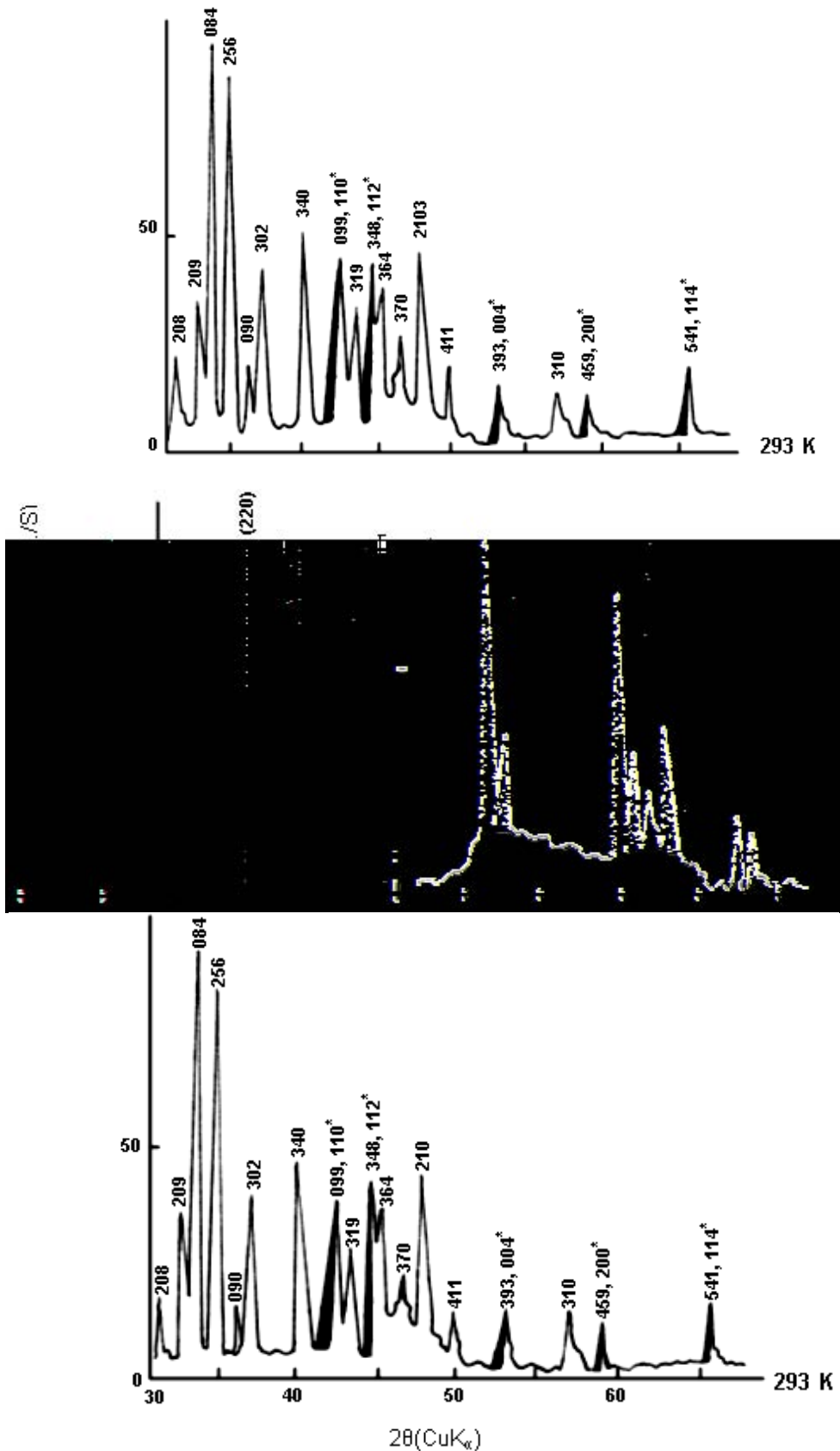


Fig.1. The crystal's diffractogram of $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$ (the rhombic phase reflex is marked by the star)

Table 2

The diffractogram's calculation of $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$.

$\frac{N}{N}$	θ	I/I_0	$d_{exp.}(\text{Å})$	$(P)_1$		$(P)_2$		Parameters of the elementary cell, Å	$T_{exp.}$ K
				$d_{cal.}(\text{Å})$	hkl	$d_{cal.}(\text{Å})$	hkl		
1	18°07'	100	2.4788	2.4781	220	-	-	$(P)_1$ $a=7.0091$	473
2	18°29'	40	2.4319	-	-	2.4320	220		
3	22°24'	80	2.0228	2.0234	222	-	-		
4	22°51'	30	1.9853	-	-	1.9857	222		
5	23°22'	40	1.9438	1.9436	320	-	-		
6	23°50'	20	1.9082	-	-	1.9078	320		
7	26°06'	10	1.7524	1.7523	400	-	-		
8	26°38'	5	1.7196	-	-	1.7197	400		
1	18°06'	100	2.4812	2.4801	220	-	-	$(P)_1$ $a_1=7.0146$	573
2	18°27'	38	2.4365	-	-	2.4362	220		
3	22°23'	83	2.0244	2.0249	222	-	-		
4	22°48'	38	1.9824	-	-	1.9891	220		
5	23°21'	22	1.9452	1.9455	320	-	-		
6	23°48'	45	1.9105	-	-	1.911	320		
7	26°05'	10	1.7536	1.7537	400	-	-		
8	26°35'	10	1.7227	-	-	1.7226	400		

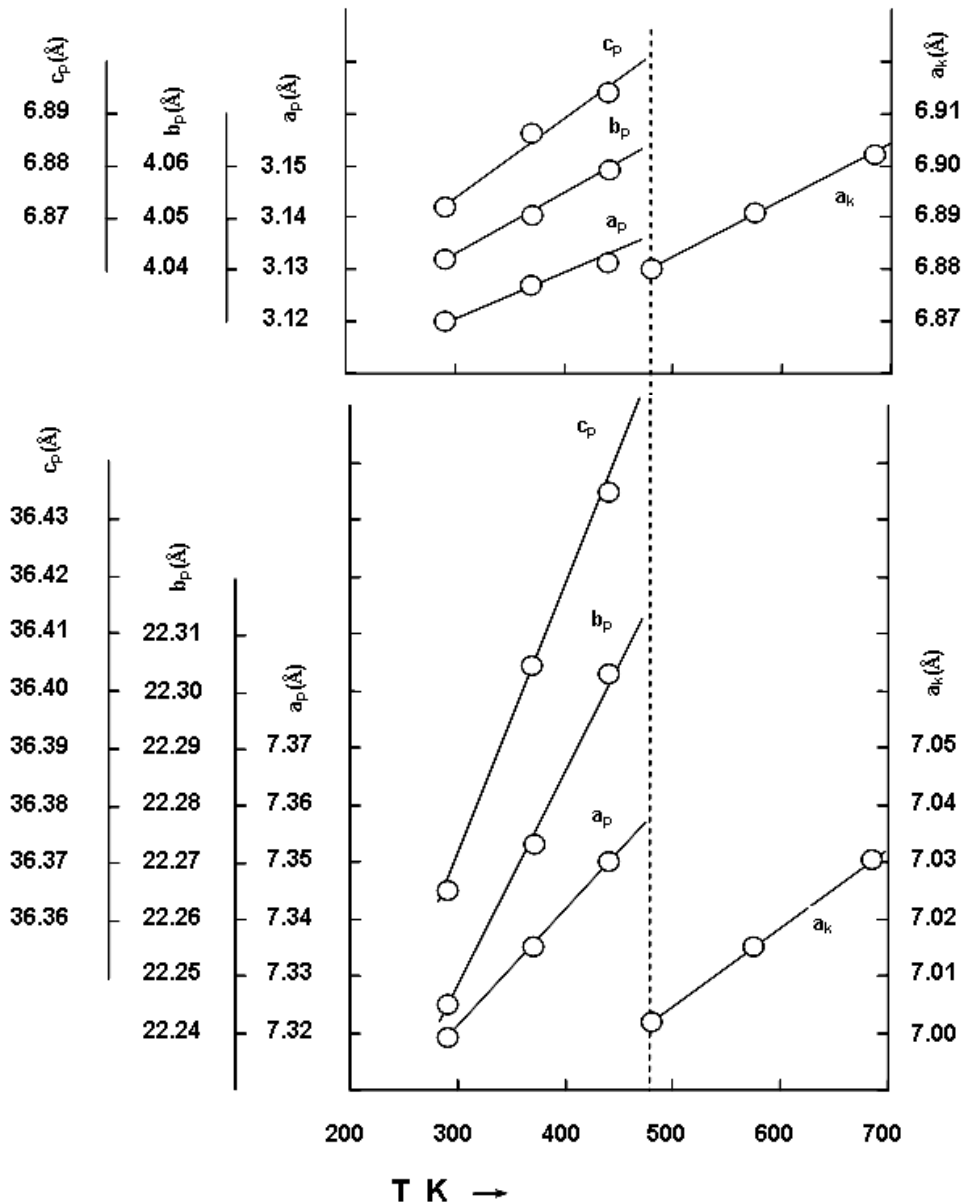


Fig.2. The temperature dependencies of the lattice parameters of both rhombic and cubic phases.

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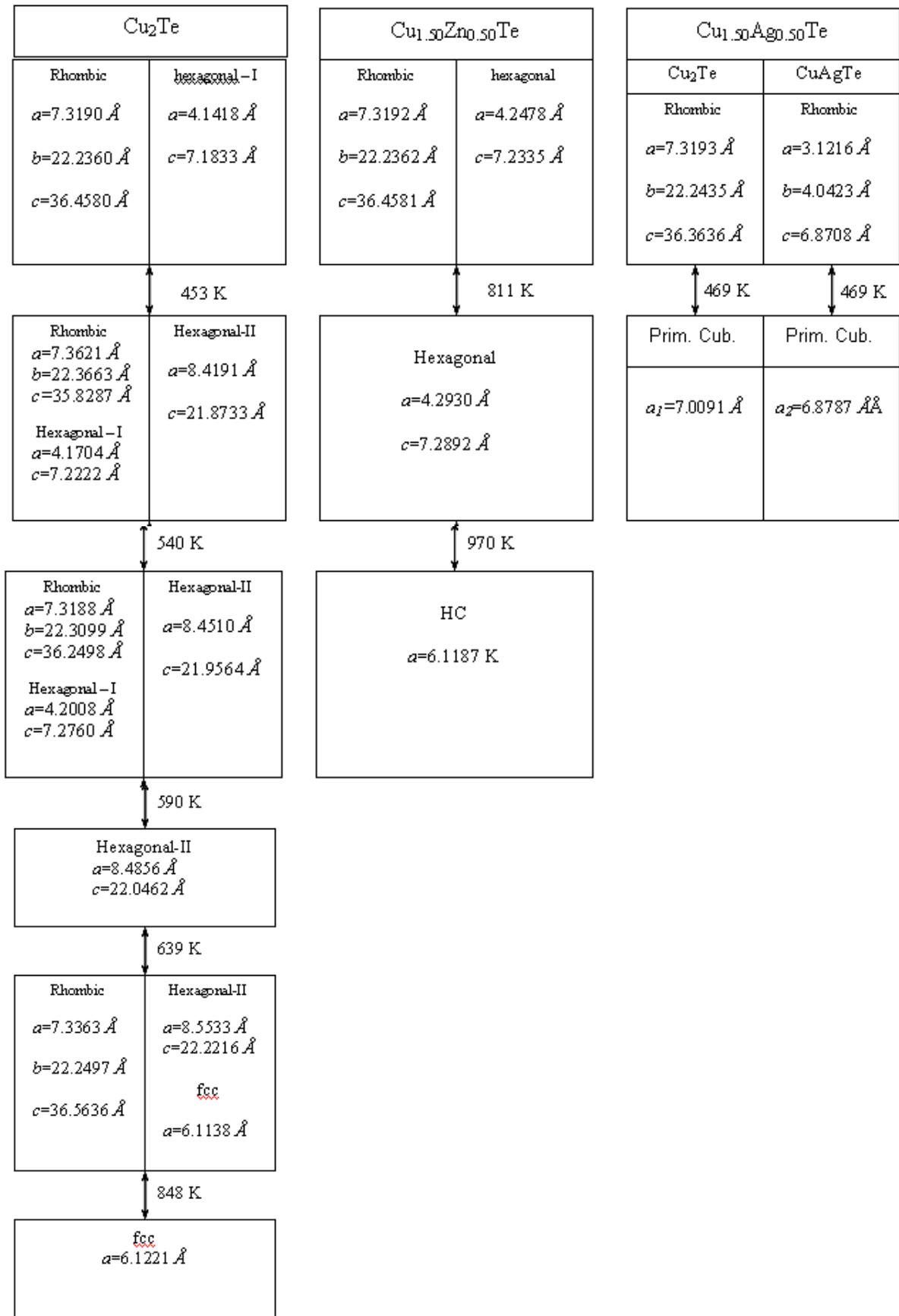


Fig.3. The scheme of the structural transformations in Cu_2Te , $\text{Cu}_{1.50}\text{Zn}_{0.50}\text{Te}$ and $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$.

At the further heating the both primitive cubic phases kept their individuality, but at the reverse cooling below 469 K they transfer into the two ordered phases, one of which is identical by the lattice parameters to the low-temperature phase Cu₂Te, and another to CuAgTe. As it was noticed, the low-temperature rhombic phase Cu₂Te after the four intermediate phase transformations at 848 K transfers into the high-temperature fcc phase with the lattice parameters $a=6.114\text{\AA}$. It is known about the second phase, i.e. CuAgTe, that at the room temperature it is crystallized in the structural type of the rhombic CuTe with the lattice parameters $a=3.12\text{\AA}$, $b=4.05\text{\AA}$, $c=6.875\text{\AA}$, $\rho=8.20\text{g/cm}^3$. However, the space groups with $Pmmm$ on $Pmm2$ (the suppression is absent) is changed with regard to the ordered substitution of the half of Cu atoms by Ag atoms.

In spite of the fact, that the compound Cu_{1.50}Ag_{0.5}Te at the room temperature is two-phase and crystallized in the structural type Cu₂Te and CuAgTe, neither the transformation temperature nor the high-temperature modifications structures do not correspond.

The schemes for the comparison of the structural transformations in Cu_{1.50}Ag_{0.5}Te, Cu₂Te and Cu_{1.50}Zn_{0.5}Te are represented on fig.2. These differences represented on the scheme are mainly connected with the spreading of two types of cations between the layers of tellurium atoms in the tetrahedral and octahedral vacuums.

The temperature dependencies of the lattice parameters Cu_{1.50}Ag_{0.5}Te are represented on fig.3. As it is seen from fig.3, the parameters $a(T)$, $b(T)$, $c(T)$, of both rhombic and $a(T)$ of both cubic phases increase in a linear fashion. The coefficient of the line expansion, calculated from the temperature dependencies of the existing phases lattice parameters.

As it is seen from the table 3, the rhombic phase, crystallized by the structural type Cu₂Te, is strongly deformed in the direction [100], i.e. $\alpha_a > \alpha_b \approx \alpha_c$ but the rhombic phase, crystallized by the structural type CuAgTe, is deformed in the direction [010], i.e. $\alpha_a < \alpha_b > \alpha_c$. It is the main reason of the instability of the both rhombic phases, which at 469 K transfer into the high-temperature primitive cubic phase.

Table 3

The heat expansion of Cu_{1.50}Ag_{0.50}Te.

$T_{str.}$ K	Modification	$T_{exp.}$ K	The line expansion coefficient 10^{-6} degree ⁻¹			
			α_a	α_b	α_c	$\bar{\alpha} = \frac{\sum \alpha_i}{3}$
469	Cu ₂ Te	293-373	29.7	16.7	16.0	20.8
		293-423	29.8	22.7	13.6	22.0
	CuAgTe	293-373	25.6	30.6	27.7	28.0
		293-423	23.7	37.9	26.0	29.2
	P ₁	473-573	0.80			
	P ₂	473-573	17.3			

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Cu_{1.50}Ag_{0.50}Te KRİSTALINDA QURULUŞ ÇEVİRİLMƏSİ

Yüksək temperatur rentgendifraktometrik metodu ilə Cu_{1.50}Ag_{0.50}Te kristalında quruluş çevrilməsi tədqiq edilmişdir və göstərilmişdir ki, otaq temperaturunda qəfəs parametrləri $a=7.319\text{\AA}$, $b=22.236\text{\AA}$, $c=36.458\text{\AA}$ və $a=3.12\text{\AA}$, $b=4.04\text{\AA}$, $c=6.87\text{\AA}$ olan iki rombik fazadan ibarət olub, 469 K-də qəfəs parametrləri $a_1=7.0091\text{\AA}$ və $a_2=6.8787\text{\AA}$ olan iki primitiv kub fazaya keçir.

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СТРУКТУРНЫЕ ПРЕВРАЩЕНИЯ В $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$

Высокотемпературным рентгенодифрактометрическим методом исследовались структурные фазовые переходы в $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$ и было показано, что при комнатной температуре $\text{Cu}_{1.50}\text{Ag}_{0.50}\text{Te}$ является двухфазным и состоит из ромбической фазы с параметрами решетки $a=7.319\text{Å}$, $b=22.236\text{Å}$, $c=36.458\text{Å}$ и ромбической фазы с параметрами решетки $a=3.12\text{Å}$, $b=4.04\text{Å}$, $c=6.87\text{Å}$. С повышением температуры при 469 К обе ромбические фазы превращаются в две примитивные кубические фазы с параметрами $a_1=7.0091\text{Å}$ и $a_2=6.8787\text{Å}$ соответственно.

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