THERMODYNAMICAL AND STRUCTURAL ASPECTS OF STRUCTURAL TRANSFORMATIONS IN THE MONOCRYSTAL Cu_2Te.

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Structural transformations are investigated in the monocrystal Cu3Te by the high-temperature roentgendiffractometric method in the interval 290-1100K. Five structural transformations take place in the crystal in this temperature interval. The mechanism of given transformations is elucidated on the basis of lineary data on the heat capacity, heat of formation and entrophy, connected with structural transitions and taking into account structural parameters.

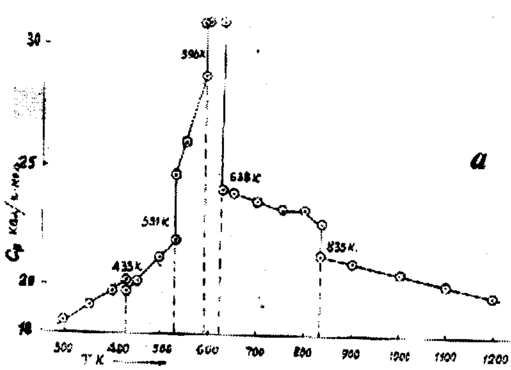
On the diagram of a condition of Cu - Te system, the compound Cu_2Te corresponds to the structure 33.33 at. % Te and fuses at the temperature 1393K [1] .It was shown in [2], that Cu_2Te crystallizes into the hexagonal structure with lattice parameters: a_0=4.237A, c_0=7.274A, sp.gr. P6mmm. elementary cell contains z=2, Density p_x=7.474g.cm^{-3}. According to [3] for Cu_2Te at the room temperature the orthorhombic structure is determined with following lattice parameters: $a=a_0$=7,319A, $b=3c_0$=22,236A, which is the over structure hexagonal phase.

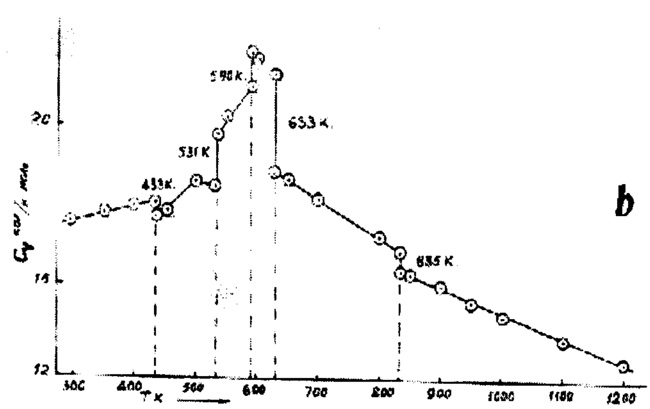
In the literature there are data on temperatures of phase transformations in Cu_2Te received by different authors and accordingly by different methods, which are shown as result in the table 1.

Table 1.

Temperatures of structural transformations in Cu_2Te.

Temperature of transformation .T,K					Methods of research	The literature
468	538	593	-	713	Roentgenography	3
463	-	583	633	823	DTA	4
433	531	590	633	835	Dilatometry	5
-	533	589	635	833	DTA	6
445	-	578-593	633	698-833	DTA	7
445	537	578	633	813	Electroconductivity	8
448	548	593	638	848	DTA	9





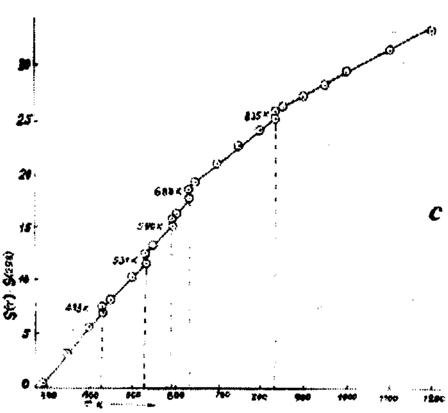


Fig. 1. Change of heat capacities C_P (a), C_v (b), and entropy S_P (c), at structural transformations in Cu $_2$Te.

In [10] the experimental data are presented on the heat capacity C_p are given, to heat of formation ΔH and entropy [$S(T)$-S(298K)] in the an interval of temperatures 290-1200K.

On the basis of these data the diagrams $C_P(T)$, $C_V(T)$ and $S(T)$ are constructed which are shown on fig. 1, a, b, c. According to these diagrams, the existence of five structural transformations in Cu_2Te confirm in the interval of temperatures 290-1200K, i.e. at 433, 531, 590, 633 and 835K. Changes of the capacity value, the heat of formation and entropy at the transformation are presented in table 2.

Table 2.

Change of thermodynamic parameters at structural transformations of Cu_2Te

Tk	ΔC_P kal mol.K.	ΔH Kkal. mol	ΔS kal/mol.
433	0.46	0.052	0.12
531	2.85	0.454	0.84
590	2.40	0.232	0.39
633	6.96	0.600	0.95
835	1.46	0.470	0.56

Thermodynamic parameters are not sufficient for the complete explanation of the mechanism of structural transformations in a solid state of substances. Therefore for the complete explanation of structural transformations, it is necessary to take into account also structural parameters of this phenomenon. These questions are successfully solved by the high-temperature roentgenography method. The research of structural transformations in the solid state of substances by this method enables also to establish the connection between general thermodynamic properties and concrete structural characteristics of separate modifications.

Temperature researches were carried out on the diffractometer "DRON-3M", with the prefix for adjustment of the temperature "URVT-2000". The experiments were carried out in vacuum 10^{-1} pa. A condition of the shooting resolution was approximately 0.°. Diffractogramm was written continuously, diffraction corners were determined by the method of measurements on the peak of intensity. The mistake of definition of reflection corners did not exceed the value $\Delta\Theta \pm 0.02°$ at experiments.

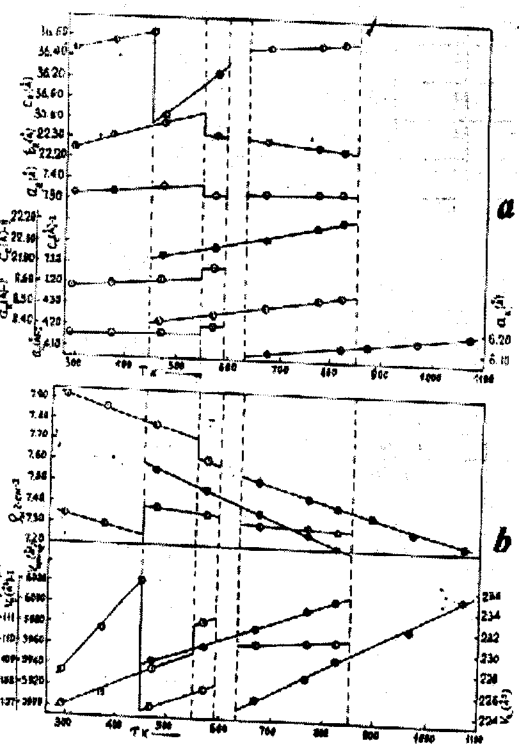


Fig. 2. Temperature dependence of parameters of a crystal lat tice on volumes and density (б) of existing modification Cu_2Te.

◒◐◑-parameters of the lattice of the orthorhombic modification

⊙ - parameters of the lattice of the hexagonal-I modification

◐● - parameters of the lattice of the hexagonal -II modification

⊗ - parameters of the lattice of the FCC modification

Records of diffraction reflections from the natural surface of the monocrystal Cu_2Te, (with sizes 4X4X2mm), split on layers of soldering, were carried out in the interval of temperatures 290-1100K, in every 100K.

On the basis of received diffraction data the parameters of the crystal lattice were calculated. Temperature areas of existing modification and results are deduced in the table 3, and are presented on fig. 2. From fig. 2 we can see: a) crystals Cu_2Te in the interval of temperatures 290-418K are biphase and consist of orthorhombic and hexagonal modification, with parameters of lattice a=7.319, b=22.236, c=36.453A and a= 4,1418, c=7.1833A accordingly. b) At 448K the second hexagonal modification from a biphase sample with parameters of the lattice a=8.4191, c=21.8733A. According to fig. 2, formed second hexagonal modification does not influence on parameters of the first hexagonal modification. However at formation of this hexagonal is allocated modification the value of the parameter with the orthorhombic modification sharply reduces Δc=0,72A. It gives us the basis to make the conclusion, that the second hexagonal modification is formed at the expense of the orthorhombic modification. c) At 540K parameters a and c of the first hexagonal modification grow by jump, and parameters a and b of the orthorhombic modification decrease by jump. In this case, probably, cations shifts occur between modification. d) At 590K the orthorhombic and first hexagonal modification turn in to second hexagonal modification and the crystal Cu_2Te becomes single-phase. So far as parameters of the second hexagonal modification don't vary in this case, then it is possible to confirm, that in this process the second hexagonal modification plays a part of the epitaxy. Thus the crystal Cu_2Te becomes single-phase in the interval of temperatures 590-638K. At 638K, with appearance of the reflection from the plane (III) of the high-temperature FCC of modification, the orthorhombic modification restored again. At 848K the orthorhombic and the second hexagonal modification turn into the FCC modification with the parameter of lattice a=6.1140 A.

All above-stated transformations are invertible, and the crystal Cu_2Te comes back to the initial condition at cooling up to the room temperature.

On fig.2 changes of the density and volume of existing modification are shown versus the temperature. As it is seen from fig. 2, at 484K with the formation of the second hexagonal modification the volume of the lattice of the orthorhombic modification reduced on the value ΔV=-72,776A^3 in comparison with the volume at 290K; at 548K as a result of reduction of parameters a and b, volume of the lattice is reduced ΔV=-25,460A^3, and at transformations at 520, 633 and 835K the volume of the lattice of the orthorhombic modification grows by jump: 3,463; 32,886 and 36,378A^3 accordingly. Volume of the elementary cell of the I-hexagonal modification grows linearly up to 548K and at this temperature the sharp growth of parameters a and c occurs with the growth of the volume of the lattice ΔV=1,4A^3, and at 590K ΔV=0,4A^3. In this case the volume of the elementary cell of II-hexagonal modification grows linearly before the transformation in FCC modification (875K).

From dependence of parameters of the lattice of all modifications, thermal expansions on the main crystal directions are calculated, which are deduced in the table 4.

Table 3

Temperature dependences of lattice parameters of modification of the monocrystal Cu_2Te.

Texp. K	Type of lattice	Parameters of lattice			Z	V(A³)	ρx gr.cm⁻³
		a (A)	b (A)	C (A)			
290	Orthorhombic	7,319	22,236	36,458	103	5933,3676	7,336
	Hexagonal-I	4,1481		7,1833			
373	Orthorhombic	7,3294	22,305	36,551	103	5975,4403	7,285
	Hexagonal-I	4,1537		7,1939		107,4861	7,863
473	Orthorhombic	7,3621	22,3663	35,8287	103	5899,659	7,378
	Hexagonal-I	4,1704		7,2225		108,783	7,77
	Hexagonal-II	8,4191		21,8733	24	1342,6522	7,554
573	Orthorhombic	7,3188	22,3099	36,2493	103	5918,8472	7,354
	Hexagonal-I	4,2008		7,276		111,1923	7,601
	Hexagonal-II	8,459		21,9564	24	1357,9858	7,469
590	Hexagonal-II	8,4602		21,9314	24	1359,3945	7,461
673	Orthorhombic	7,3912	22,2831	36,504	103	5963,3614	7,299
	Hexagonal-II	8,4912		22,0623	24	1377,5482	7,256
	FCC	6,0821			4	224,9887	7,513
773	Orthorhombic	7,3421	22,2614	36,542	103	5972,6227	7,288
	Hexagonal-II	8,5342		22,1612	24	1397,7735	7,256
	FCC	6,1021			4	227,2155	7,44
821	Orthorhombic	7,3363	22,2497	36,5636	103	5968,2938	7,293
	Hexagonal-II	8,5533		22,2216		1407,8638	7,204
	FCC	6,1138			4	228,525	7,398
873	FCC	6,1221			4	229,457	7,368
973	FCC	6,1476			4	232,3362	7,277
1073	FCC	6,1731			4	235,2393	7,186

Table 4

Thermal expansions of modification of Cu_2Te crystals.

Cu_2Te	Temperature	$\alpha_{[100]} 10^{-6}$degr⁻¹	$\alpha_{[010]} 10^{-6}$degr⁻¹	$\alpha_{[001]} 10^{-6}$ degr⁻¹	$\alpha=(2\alpha_{[100]}+\alpha_{[001]}10^{-6}$ degr⁻¹$)/3$
I-hexagonal	290-373	34,62		17,78	16,77
	290-473	3473		29,59	29,53
	290-573	50,34		45,60	45,18
II- hexagonal	473-573	37,89		37,99	37,92
	473-673	39,52		39,52	39,50
	473-773	45,571		43,874	45,005
	473-821	45,80		45,76	45,77
Orthorhombic	290-373	17,12	37,39	30,73	28,41
	290-473	32,18	32,02	-94,32	-30,12
	290-573	-0,10	11,74	-20,18	-8,54
	290-773	6,54	2,36	4,77	4,56
	290-821	4,45	1,16	5,45	3,69
FCC	673-773	32,883			
	673-821	35,216			
	673-873	32,883			
	673-973	35,898			
	673-1073	37,405			

Coefficient of thermal expansion referred to 290K I-hexagonal modification Cu_2Te, have the certain anisotropy in the interval of temperatures 290 - 590K, whereas for the II-hexagonal modification formed at temperature 448K the anisotropy of thermal expansion (a [100] =a [001]) is absent.

Orthorhombic modification has the sharply expressed anisotropy of thermal expansions.

It is necessary to note, that change of the heat capacity, heat formation, entropy (Fig. 1, a, b, c and tab. 1), results of measurements of parameters of crystal lattices, value of the atomic volume, density (table, 3; fig. 2, a and, b) and coefficients of the thermal expansion of modification of the crystal Cu_2Te at temperatures 290 - 1100K, testify that all five polymorphic transformations are the phase transition of the sort I.

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Cu_2Te MONOKRİSTALINDA QURULUŞ CEVRİLMƏLƏRİNİN TERMODİNAMİK VƏ QURULUŞ ASPEKTİ

Cu_2Te monokristalında 290-1190K temperatur intervalında yüksək temperatur rentgendifraktometrin üsulu ilə quruluş çevrilmələri öyrənilmişdir. Göstərilən temperatur intervalında Cu_2Te kristalında beş struktur çevrilməsi baş verir. Bəzi termodinamik və quruluş parametrlərindən istifadə etməklə quruluş çevrilməsinin mexanizmi aydınlaşdırılmışdır.

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ТЕРМОДИНАМИЧЕСКИЕ И СТРУКТУРНЫЕ АСПЕКТЫ СТРУКТУРНЫХ ПРЕВРАЩЕНИЙ В МОНОКРИСТАЛЛЕ Cu_2Te

Высокотемпературным рентгенодифрактометрическим методом исследовались структурные превращения в монокристалле Cu2Te в интервале 290-1100К. В этом температурном интервале в кристалле происходит пять структурных превращений. Пользуясь литературными данными о теплоемкости, теплоте образования и энтропии связанными со структурными переходами и учитывая параметры структуры, выяснен механизм этих превращений.

Received:08.05.01