THE MEASUREMENTS OF THERMAL-EXPANSION COEFFICIENT IN $Cu_{2-x}Te$ CRYSTALS (x=0; 0,10; 0,15; 0,20; 0,25) BY X-RAY METHOD

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The measurements of thermal-expansion coefficient in crystals by the method of high-temperature roentgenography are described in detail. The thermal-expansion coefficients are calculated from temperature dependence of crystal lattice parameters of existing modifications in $Cu_{2-x}Te$ (x-0; 0,10; 0,15; 0,20; 0,25) and surfaces of thermal-expansion coefficients are shown in each case.

The study of thermal-expansion coefficient (TEC) of crystals by the method of high-temperature roentgenography is seemed enough trivial task as the same questions with less experimental difficulties and with bigger accuracy are solved with application of dilatometric method [1-3]. However, the possibility of investigation carrying out on micro-samples is the advantage of the method of high-temperature roentgenography. The study of TEC anisotropy (tensor of thermal expansion in common case) on one-phase crystals and also TEC measurement in phase mixture can be carried out with the help of method of high-temperature roentgenography. TEC definition is led to equation differentiation for temperature dependence of crystal lattice parameters.

As the interplanar spacing d of system of reflecting crystalline planes is connected with glancing angle θ and wave length λ of X rays by the equation $d=\frac{\lambda}{2}\frac{1}{\sin\theta}$ so increase of distance d is fixed on variation of value θ with temperature increase.

Differentiating the given equation over θ we obtain:

$$\frac{\partial d}{d\theta}=-\frac{\lambda}{2}\sin\theta\, ctg\theta=-d\, ctg\theta \quad \text{or} \quad \frac{\partial d}{d}=ctg\theta\,\partial\theta .$$

From this equation it is seen that $\partial\theta$ value for the given change of ∂d increases from the finite value up to infinitely bigger one on θ approximation to 90^0. Therefore, θ and $\theta-\Delta\theta$ will be at reflection of monochromatic beam of X rays falling on crystal at two different temperatures.

If d_1 and d_2 are interplanar spacings of the given system of crystal planes at T_1 and T_2 temperatures so

$$d_1=\frac{\lambda}{2\sin\theta_1} \quad \text{and} \quad d_2=\frac{\lambda}{2\sin\theta_2} .$$

Let's obtain TEC from the equation

$$d_2=d_1\left[1+\alpha\left(T_2-T_1\right)\right]$$

or

$$\alpha=\frac{d_2-d_1}{d_1\left(T_2-T_1\right)}.$$

Substituting d_1 and d_2 value, we obtain:

$$\alpha=\frac{\frac{\lambda}{2}\left(\frac{1}{\sin\theta_2}-\frac{1}{\sin\theta_1}\right)}{\frac{\lambda}{2\sin\theta_1}(T_2-T_1)}=\frac{\sin\theta_1-\sin\theta_2}{\sin\theta_2\left(T_2-T_1\right)} .$$

This exact expression is necessary to use if the change of θ angle at crystal expansion is comparable with (π-2θ) on the value. The formula for α obtained by differentiation of $d=\frac{\lambda}{2}\frac{1}{\sin\theta}$ equation is correct only at the condition that change of θ angle is less in comparison with (π-2θ).

The number of independent linear expansion coefficients is different for crystals of different crystal systems. The linear expansion tensor for cubic crystals "degenerates" in scalar; the two independent coefficients are for tetragonal, hexagonal and trigonal crystals; the three independent coefficients are for orthorhombic ones; the four independent coefficients are for monoclinic ones and six independent coefficients are for triclinic ones.

The homogeneous deformation at the change of crystal temperature is described by symmetric second-rank tensor

$$\alpha_{ik}=\begin{vmatrix}\alpha_{11}\,\alpha_{12}\,\alpha_{13}\\ \alpha_{12}\,\alpha_{22}\,\alpha_{23}\\ \alpha_{13}\,\alpha_{23}\,\alpha_{33}\end{vmatrix} . \qquad (1)$$

i is defined by the following formula on arbitrary direction:

$$\begin{aligned}\Delta_i &= c_{1i}^2\alpha_{11}+c_{2i}^2\alpha_{22}+c_{3i}^2\alpha_{33}+2c_{1i}c_{2i}\alpha_{12}+\\ &+2c_{1i}c_{3i}\alpha_{13}+2c_{3i}c_{2i}\alpha_{33}\end{aligned} . \qquad (2)$$

Here, c_1, c_2, c_{3i} are direction cosines of i direction with X, Y, Z axes. One can find such coordinate system X', Y', Z' in which equation (2) has the form:

$$\Delta_i=\alpha_{11}c_{1i}^2+\alpha_{22}c_{2i}^2+\alpha_{33}c_{3i}^2 \qquad (3)$$

and (α_{ik}) tensor transform into diagonal tensor (α_{ii}). The axes of X', Y', Z' coordinate system are the main directions of thermal-expansion tensor.

$$\alpha_{ii}=\begin{vmatrix}\alpha_{11}\;0\;0\\ 0\;\alpha_{22}\;0\\ 0\;0\;\alpha_{33}\end{vmatrix} .$$

The position of the main axes of thermal-expansion tensor in crystals of higher crystal systems is described by crystal symmetry uniquely. The tensor definition in these cases is lead to measurement of TEC value along the one (cubic crystal system), two (hexagonal and trigonal ones) or three (orthorhombic one) crystallographic axes.

In crystals of low crystal systems the task of thermal-expansion tensor finding is difficult by the fact that position of their main axes isn't defined by crystallographic coordinate system uniquely. Only one of main tensor axes (α_{ik}) in monoclinic crystals coincides with axis [010]. The tensor can have the different orientation with respect of this axis and therefore, this tensor has the four independent components. For their definition it is necessary to measure any four interplanar spacing d_{hkl} as temperature functions. For calculations it is comfortable to measure d_{010} and three values d_{h0k}. In triclinic crystals the tensor (α_{ik}) can has any orientation with respect of crystallographic axes and has six components. For their definition it is necessary to measure any six d_{hkl}. For calculation it is comfortable to measure six following values: d_{100}, d_{010}, d_{001}, d_{110}, d_{101}, d_{011}.

The orientation finding of main directions of thermal-expansion tensor and the definition of TEC main values is mathematically are reduced to definition of quadratic form (2) and to sum of squares (3).

The thermal expansion of $Cu_{2-x}Te$ (x=0; 0,10; 0,15; 0,20; 0,25) crystals in the given work is calculated from temperature dependence of elementary cell parameters in temperature interval involving all possible structural changes. The parameters of crystal elementary cell change at decrease of its temperature on ΔT. Let's designate the parameter values of crystal elementary cell by primed letters at the change of its temperature on ΔT, then:

$$a' = a(1+\alpha_1 \Delta \mathrm{T})$$
$$b' = b(1+\alpha_1 \Delta \mathrm{T})$$
$$c' = a(1+\alpha_1 \Delta \mathrm{T})$$

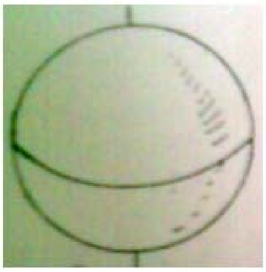
From these equations TEC on main crystallographic equations will be:

$$\alpha_{[100]} = \frac{a'-a}{a(T_2-T_1)},\quad \alpha_{[010]} = \frac{b'-b}{b(T_2-T_1)},$$
$$\alpha_{[001]} = \frac{c'-c}{c(T_2-T_1)},\quad \text{where } T_2>T_1.$$

The technique of roentgenographic thermal-expansion tensor definition in low-symmetrical crystals is described in detail in [4-8]. In the cases of higher and average crystal systems the thermal-expansion tensor can be led to main axes coinciding with main crystallographic directions:

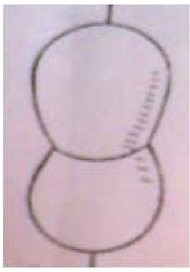
$$\varepsilon_{[100]} = \alpha_{[100]}\Delta T;\ \varepsilon_{[010]} = \alpha_{[010]}\Delta T;$$
$$\varepsilon_{[001]} = \alpha_{[001]}\Delta T$$

As it is mentioned above the topology of CTR surfaces is investigated in [5] and it is shown that surface of thermal-expansion coefficients in the case of cubic crystals (isotropic distribution) has the form of sphere (fig.1, a) having the higher symmetry $\frac{\infty}{\infty m}$.



a) CTR surfaces

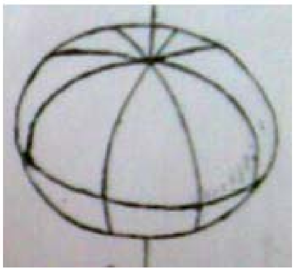
$\alpha' = \alpha_{[100]} = \alpha_{[010]} = \alpha_{[001]} > 0$



b) CTR surfaces

$\alpha' = \alpha_{[100]}(c_1^2 + c_2^2) + \alpha_{[001]}c_3^2$

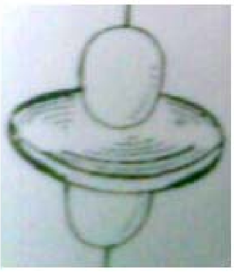
$\alpha_{[100]}, \alpha_{[001]} > 0;\ \alpha_{[001]} > \alpha_{[100]}$



c) CTR surfaces

$\alpha' = \alpha_{[100]}(c_1^2 + c_2^2) + \alpha_{[001]}c_3^2$

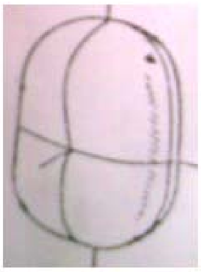
$\alpha_{[100]}, \alpha_{[001]} > 0;\ \alpha_{[100]} > \alpha_{[001]}$



d) CTR surfaces

$\alpha' = \alpha_{[100]}(c_1^2 + c_2^2) + \alpha_{[001]}c_3^2$

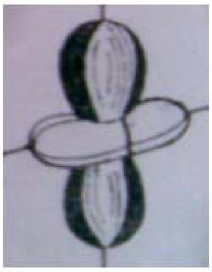
$\alpha_{[001]} > 0;\ \alpha_{[100]} < 0\ \alpha_{[001]} > 0$



e) CTR surfaces

$\alpha' = \alpha_{[100]}c_1^2 + \alpha_{[010]}c_2^2 + \alpha_{[001]}c_3^2$

$\alpha_{[100]}, \alpha_{[010]}, \alpha_{[001]} > 0$



f) CTR surfaces

$\alpha' = \alpha_{[100]}c_1^2 + \alpha_{[010]}c_2^2 + \alpha_{[001]}c_3^2$

$\alpha_{[100]}, \alpha_{[010]} > 0;\ \alpha_{[001]} < 0$

The two independent coefficients are for tetragonal, hexagonal and trigonal crystals. The surface of thermal=expansion coefficients for these crystals which have $\alpha_{[100]}=\alpha_{[010]}\neq\alpha_{[001]}$ becomes the oval-like and oblong at $\alpha_{[001]}>\alpha_{[100]}$ (fig.1, b) or flattened at $\alpha_{[100]}>\alpha_{[001}$ along [001] axis (fig.1, c), surface symmetry is $\frac{\infty}{\infty m}$. If $\alpha_{[001]}>0$, $\alpha_{[100]}<0$ for the same crystal systems, so CTR surfaces consists of two positive (white) egg-shaped regions and one toroidal negative region (black region (fig.1,d).

The coefficient surfaces have the form of ellipsoid (fig.1,e) for orthorhombic crystals which have $\alpha_{[100]}\neq\alpha_{[010]}\neq\alpha_{[001]}$, the one prolonged positive region and two negative egg-shaped regions (fig.1,f) exist at the one negative coefficient (for example $\alpha_{[001]}$).

The listed six types of TEC surfaces describe all possible cases of crystal thermal expansion.

The coefficient (α_v) of volumetric expansion is equal to the sum of three main linear expansion coefficients, i.e. $\alpha_v=\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}$.

TEC is the one of few thermodynamical values which are accessible to direct measurement (including roentgenographic one). Being the second derivative over thermodynamical potentials, TEC characterizes the system behavior especially in points of polymorphous transforms.

1. Crystal thermal-expansion coefficients of existing Cu_2Te phases

In work [12] it is shown that Cu_2Te crystals at room temperature are two-phased ones and consist of hexagonal and its superstructural orthorhombic modification independently on growth conditions. At 453K the second hexagonal modification forms. At 450K a and c parameters of hexagonal modification increase by jump and a and b parameters of orthorhombic modifications decrease by jump. At 590K first hexagonal and orthorhombic modifications transform into second hexagonal modification and the crystal becomes one-phased one in temperature interval 590-660K. At 660K the reflections relating to orthorhombic modification recondition with appearance of (111) reflection of high-temperature HCC modification. The orthorhombic and second hexagonal modifications at 821K transform into high-temperature HCC modification. TEC are calculated on main crystallographic directions from temperature dependence of lattice parameters of existing modification which are given in table 1.

Table 1.

Thermal-expansion of existing modifications of Cu_2Te ($\cdot 10^{-6}K^{-1}$)

Modification	Temperature, K	$\alpha_{[100]}$	$\alpha_{[010]}$	$\alpha_{[001]}$	$\overline{\alpha}=\frac{\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}}{3}$
Hexagonal-I	290-373	16,27		17,78	16,77
	290-473	29,38		29,82	29,53
	290-573	44,89		45,13	44,97
Hexagonal-II	473-573	37,89		37,99	37,92
	473-673	39,49		39,52	39,50
	473-821	45,80		45,76	45,79
Orthorhombic	290-373	17,12	37,39	30,73	28,41
	290-473	32,13	32,02	-94,32	-10,04
	290-573	-09,66	11,14	-20,18	-6,03
	290-821	4,45	1,16	5,45	3,69
HCC	821-873	26,11			26,11
	821-973	36,37			36,37
	821-1073	38,49			38,49

As it is seen from the table 1 the anisotropy of thermal-expansion coefficient is almost absent in both hexagonal modifications, i.e. $\alpha_{[100]}\leq\alpha_{[001]}>0$. TEC surface for these modifications becomes the oval-like one as it is shown on the fig.1,b. TEC surfaces have symmetry $\frac{m\cdot 2}{m}$ for orthorhombic modification which has $\alpha_{[100]}\neq\alpha_{[010]}\neq\alpha_{[001]}$. The one elongated positive region and two negative egg-shaped regions (fig.1,f) are at the one negative coefficient.

In the case of cubic modification TEC surface has the form of sphere (fig.1,a) having the highest symmetry $\frac{\infty}{\infty m}$.

II. Thermal-expansion coefficients of $Cu_{1,90}Te$ crystal

Single crystals $Cu_{1,90}Te$ at room temperature as Cu_2Te ones are two-phased ones and consist of hexagonal and orthorhombic modifications [12]. At 673K orthorhombic modification transforms into hexagonal one and the crystal becomes the one-phased one in temperature interval 673-773K and c parameter of hexagonal modification decreased by the jump and a parameter increases by the jump with appearance of reflections from high-temperature HCC modifications. At 873K the hexagonal modification transforms into HCC modification. These anomalous changes of hexagonal modification parameters also influence on thermal expansions which are given in table 2.

As it is seen from table 2 the surface of thermal-expansion coefficients becomes the oval-like one, oblate one at $\alpha_{[100]}>\alpha_{[001]}$ along [001] axis (fig.1,c) surface symmetry is $\frac{\infty}{\infty m}$.

TEC surfaces have symmetry $\frac{m\cdot 2}{m}$ for orthorhombic modifications which have $\alpha_{[100]}\neq\alpha_{[010]}\neq\alpha_{[001]}$. The surface has the ellipsoid form (fig.1,e) at all positive coefficients.

TEC surface has the sphere form (fig.1,a) at cubic modifications and has the highest symmetry $\frac{\infty}{\infty m}$.

Table 2.

Thermal-expansion coefficients of existing modifications of $Cu_{1,90}Te$ ($\cdot 10^{-6}K^{-1}$)

Modification	Temperature, K	$\alpha_{[100]}$	$\alpha_{[010]}$	$\alpha_{[001]}$	$\overline{\alpha}=\frac{\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}}{3}$
Hexagonal	293-373	27,48		29,51	28,16
	293-473	77,92		28,70	61,51
	293-573	65,07		33,72	54,62
	293-673	59,07		31,14	49,76
	293-773	103,81		-19,49	62,71
	293-873	117,39		52,27	95,68
Orthorhombic	293-373	21,34	95,69	197,17	104,73
	293-473	36,42	57,17	114,35	69,31
	293-573	25,66	47,93	93,89	55,83
	293-673	40,22	44,23	72,84	52,43
HCC	773-873	41,83			41,83
	773-973	41,83			41,83
	773-1073	41,83			41,83

III. Thermal-expansion coefficient $Cu_{1,85}Te$ crystal

Single crystals $Cu_{1,85}Te$ [11] crystallize at room temperature in hexagonal crystal system and at 707K hexagonal modification transforms into high-temperature HCC modification. TEC are calculated from temperature dependence of crystal lattice parameters which are given in the table 3.

Table 3.

Thermal-expansion coefficients of existing modifications of $Cu_{1,85}Te$ ($\cdot 10^{-6}K^{-1}$)

Modification	Temperature, K	$\alpha_{[100]}$	$\alpha_{[001]}$	$\overline{\alpha}=\frac{2\alpha_{[100]}+\alpha_{[001]}}{3}$
Hexagonal	293-373	13,15	37,93	21,41
	293-473	27,95	40,45	32,12
	293-573	35,43	39,58	36,81
	293-673	32,30	29,21	31,27
HCC	673-726	37,10		37,10
	673-773	34,90		34,90
	673-873	36,29		36,29

The surface of linear-expansion coefficients of hexagonal modification satisfies to condition $\alpha_{[100]}$, $\alpha_{[001]}>0$; $\alpha_{[001]}>\alpha_{[100]}$ and that's why has the form shown on fig.1,b and TEC surface of HCC crystals (isotropic expansion) has the sphere form (fig.1,a).

IV. TEC of crystal modifications $Cu_{1,80}Te$

Single crystals $Cu_{1,80}Te$ as $Cu_{1,85}Te$ ones crystallize in hexagonal crystal system at room temperature and at 730K the hexagonal modification transforms into HCC modification [9]. TEC for hexagonal and HCC modifications which are given in table 4, are calculated from temperature dependence of crystal lattice parameters.

TEC surface of hexagonal modification satisfies to condition $\alpha_{[100]}$, $\alpha_{[001]}>0$; $\alpha_{[001]}>\alpha_{[100]}$ and that's why has the form shown on fig.1,b and TEC surface of HCC crystals (isotropic expansion) has the sphere form (fig.1,a).

Table 4.

Thermal-expansion coefficients of existing modifications $Cu_{1,90}Te$ ($\cdot 10^{-6}K^{-1}$)

Modification	Temperature, K	$\alpha_{[100]}$	$\alpha_{[001]}$	$\overline{\alpha}=\frac{2\alpha_{[100]}+\alpha_{[001]}}{3}$
Hexagonal	290-373	22,48	69,72	38,23
	290-473	19,73	44,52	27,99
	290-573	37,02	36,81	36,95
	290-673	32,66	35,29	33,54
HCC	773-873	19,89		19,89
	773-973	19,89		19,89
	773-1073	19,89		19,89

V. TEC of $Cu_{1,75}Te$ crystal modifications.

Single crystals $Cu_{1,75}Te$ [10] has the hexagonal structure at room temperature. This modification at 698K transforms into HCC modification. TEC is calculated from temperature dependence of lattice parameters of both modifications the results of which are given in table 5.

As it is seen from table 5 the condition $\alpha_{[100]}$, $\alpha_{[001]}>0$; $\alpha_{[001]}>\alpha_{[100]}$ are fulfilled and that's why TEC surface shown on the fig.1,b. TEC surface has the sphere form (fig.1,a) in HCC modification.

The cations in $Cu_{2-x}Te$ (x-0; 0,10; 0,15; 0,20; 0,25) gradually decrease from stoichiometric composition (Cu_2Te) up to non-stoichiometric one ($Cu_{1,75}Te$) and the influence of cation lack on crystalline structure, mechanism of structural transformations, phase formation, temperature and also number of phase transformations has revealed. It is established that perfection and fact that phases one-phase grown crystals mainly depend on cation lack, i.e. the crystals become one-phase ones with lack increase of cuprum cations.

The strong anisotropy of thermal expansion on the main crystallographic directions in all considered crystals leads to weakening of chemical bond in the structure and by this reason all low-temperature structures transform in HCC modification in which the atom thermal oscillations in crystalline lattice at definite temperature.

Table 5.

Thermal-expansion coefficients of existing modifications of $Cu_{1,90}Te$ ($\cdot 10^{-6}K^{-1}$)

Modification	Temperature, K	$\alpha_{[100]}$	$\alpha_{[001]}$	$\bar{\alpha} = \frac{2\alpha_{[100]} + \alpha_{[001]}}{3}$
Hexagonal	290-373	22,48	69,72	38,23
	290-473	19,73	44,52	27,99
	290-573	37,02	36,81	36,95
	290-673	32,66	35,29	33,54
HCC	773-873	19,89		19,89
	773-973	19,89		19,89
	773-1073	19,89		19,89

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$Cu_{2-x}Te$ (x=0; 0,10; 0,15; 0,20; 0,25) KRİSTALLARINDA İSTİDƏN GENİŞLƏNMƏ ƏMSALLARININ RENTGEN METODU İLƏ TƏYİNİ

Tədqiq olunan kristallarda yüksəktemperatur rentgen metodu ilə istidən genişlənmə əmsallarının təyini verilmişdir. $Cu_{2-x}Te$ (x=0; 0,10; 0,15; 0,20; 0,25) kristallarındakı modifikasiyaların qəfəs parametrlərinin temperaturdan asılılığından istidən genişlənmə əmsalları təyin edilmiş və hər hal üçün istidən genişlənmə əmasallarının səthi göstərilmişdir.

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ИЗМЕРЕНИЯ КОЭФФИЦИЕНТОВ ТЕПЛОВОГО РАСШИРЕНИЯ В КРИСТАЛЛАХ $Cu_{2-x}Te$ (x=0; 0,10; 0,15; 0,20; 0,25) РЕНТГЕНОВСКИМ МЕТОДОМ

Подробно изложено измерения коэффициента теплового расширения в кристаллах методом высокотемпературной рентгенографии. Из температурной зависимости параметров кристаллической решетки существующих модификаций в $Cu_{2-x}Te$ (x=0; 0,10; 0,15; 0,20; 0,25) рассчитаны коэффициенты теплового расширения и в каждом случае показаны поверхности коэффициентов теплового расширения.

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