DOI: 10.63527/1607-8829-2023-3-5-18

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THEORETICAL MODELS OF ORDERED ALLOYS OF TERNARY SYSTEMS OF THERMOELECTRIC MATERIALS. 5. CHEMICAL BOND AND STATE DIAGRAMS OF *Cd-Sb-Te*

Theoretical models of ordered alloys of promising thermoelectric materials of ternary systems based on Cd-Sb-Te have been developed. Using inverse triangulation methods, isothermal cross-sections and diagrams of the distribution of phase regions in ternary systems were constructed using binary state diagrams of the initial components (Cd-Sb; Cd-Te; Sb-Te). Calculations of the effective radii of interatomic interaction, electron density redistribution, and dissociation energy of the corresponding chemical bonds forming the Cd-Sb-Te crystal structure depending on the interatomic distances are presented.

Key words: theoretical models, chemical bond, effective radii, dissociation energy, state diagrams, non-equivalent hybrid orbitals (NHO).

Introduction

Ternary systems of tellurides and antimonides are increasingly attracting the attention of specialists in thermoelectricity [1]. This is due to the presence of a number of concentration and structural features in such systems. With a change in the concentration of the initial elements, solid phases of variable composition with a crystalline structure from a densely packed crystal lattice to layered structures are formed. The chemical bond in such systems varies from metallic (in the original components) to covalent (in compounds) and intermediate (in solid solutions). This leads to phase transformations, ordering processes in melts and alloys that shape the physical and chemical properties of the obtained materials [2], [3]. At the same time, all technological issues of the synthesis of new materials based on ternary systems have to be solved experimentally. The reason is that ternary systems are complex, nonlinear, and the well-known developed theoretical approaches for problems of phase transformations of simple systems no longer reveal the conditions for the appearance of ternary properties with the prospect of their change in the desired direction. There is still no consistent theory of phase transformations from the standpoint of chemical bond.

This is why new approaches to solving complex, multifactorial problems are needed to solve technological issues in ternary systems. Their solution is beyond the power of individual disciplines.

Multidimensional understanding of this circumstance requires an unconventional understanding of the theory and the methods of its application in this analysis.

The question of how general principles can be fruitfully used to analyze real systems and to solve specific, multifactorial problems is becoming especially relevant [4], [5].

In this regard, the task set in this work was to develop theoretical models of ordered alloys that would allow generalizing the capabilities of existing models by combining thermodynamic, statistical, and quantum-mechanical approaches, taking into account chemical bond.

The peculiarity of this approach is that a number of considered factors are interconnected and their influence on the properties of the studied materials is revealed indirectly through the parameters of theoretical models. In this case, the considered approach allows solving the inverse problem both at each stage in particular and as a whole. In this case, the initial conditions are chosen as the values of the parameters of physical quantities that the materials should receive, and the result of the research should be the technological parameters of the modes of obtaining these materials. The availability of such information allows us to theoretically describe the processes of melting and crystallization in ternary systems *Cd-Sb-Te* and optimize the synthesis of new materials based on them.

Theoretical models of state diagrams

In constructing the theoretical model of *Cd-Sb-Te*, it was necessary to generalize the results of studies of the physicochemical properties and quantum regularities of the initial components [6 – 8]. The next stage of research is devoted to establishing the dynamics of the formation of a chemical bond by analyzing the interatomic interaction in the initial components, binary systems of the initial components (*Cd-Sb*; *Cd-Te*; *Sb-Te*) and isothermal sections of ternary systems *Cd-Sb-Te* at different temperatures.

The results of theoretical studies of the features of the chemical bond of cadmium are presented in [6]. Analysis of diverse information on the crystal structure, thermodynamic and quantum laws of cadmium made it possible to establish a theoretical model of the chemical bond, determine the force constants of the microscopic theory, characteristic temperatures that must be taken into account when choosing technological solutions for obtaining new thermoelectric materials based on cadmium.

The next constituent element of the *Cd-Sb-Te* ternary system is antimony. This element can be both a constituent component of many binary semiconductor compounds and widely used as an alloying additive. The increased interest in this element is due to the presence of polymorphic transformations in it – its ability to coexist in several structural forms with the same chemical composition. Solving the problem of polymorphic transformations from the standpoint of chemical bond leads to the emergence of new technological approaches to obtaining high-quality materials. In this regard, in [7], research was carried out on the features of the chemical bond and the possibilities of using antimony in the further technological development of new thermoelectric materials. The analysis of the crystal structure given in [7] showed that in antimony compounds the degree of oxidation is – 3, + 3, + 5. Antimony is also known in four metallic allotropic (existing at different pressures) and three amorphous modifications. Under normal conditions, only the crystalline rhombohedral structure is stable. There is also a hexagonal modification of antimony. The physical nature of their occurrence has not yet been determined.

Highly pure single crystals of antimony are plastic at 293 K and brittle at 233 K. Depending on the manufacturing technology, these materials are characterized by different values of physicochemical parameters. Studies of the features of the chemical bond and polymorphic modifications of antimony [7] showed that in the range of 200 – 1000 K, the considered modifications are characterized by the presence of a fine chemical bond structure with non-equivalent interatomic distances. In this case, the temperature of formation of the first component of the chemical bond of the hexagonal modification $T^{(1)}_{\text{hex}}$ and the melting temperature T_{m} coincide ($T_{\text{m}} = T^{(1)}_{\text{hex}} = 903$ K). In the case of the rhombohedral modification, the temperature $T^{(1)}_{\text{rhomb}}$ exceeds T_{m} and the first component of the chemical bond is formed in the liquid phase with overheating. This means that the synthesis of new materials based on antimony must be carried out with regard to the fine structure of the chemical bond.

The examination of the initial components of the studied ternary system is completed by tellurium. Comprehensive studies of tellurium are carried out in [8], where a review of experimental and theoretical works is given, the crystal structure, force and energy parameters of tellurium are considered from the standpoint of chemical bond. It is noted that tellurium is a typical scattered element. It has eight stable and about twenty unstable artificially obtained isotopes. Tellurium is in group VI and period V between selenium and polonium, with which it is similar, although selenium is a metalloid and polonium is a metal. According to the period, tellurium is placed between antimony and iodine, of which antimony is a metal, and iodine is a metalloid.

Tellurium belongs to semiconductor substances and crystallizes in the hexagonal system, forming spiral chains. The tellurium atoms in the chains have a covalent bond, and the chains are bound together by metallic forces. Such a qualitative description of the chemical bond makes it possible to explain some of the physical properties of tellurium. However, in order to obtain materials with the given properties, it is necessary to calculate the technological parameters in terms of chemical bond. Therefore, complex studies of the dynamics of chemical bond formation using the methods of vibration theory, elasticity theory, and molecular models were carried out in [8].

Thus, the studies conducted in [8] showed that tellurium has a complex hexagonal crystal structure, characterized by five different interatomic distances and a consistent structure of melting and crystallization. It was established that the increase in the ratio of the parameters of the hexagonal structure c/a causes a redistribution of the electron density in such a way that d-shells begin to take part in the formation of chemical bonds in the processes of crystallization and melting through the formation of "new" and destruction of "old" chemical bonds of tellurium. In addition, it was established that the selection of specific values of the characteristic frequencies and their corresponding temperatures make it possible not only to control the dynamics of the formation of the tellurium chemical bond, but also the quality of the obtained materials based on tellurium, due to the selection of the composition and structure of the initial components.

The next stage of research is devoted to establishing the dynamics of the formation of chemical bonds of the initial components in going to the structures of binary alloys [9] and heterogeneous equilibria [10] of ternary systems.

To describe the dependence of primary crystallization temperatures on the composition of binary systems, the state diagrams of *Cd-Sb*, *Cd-Te, Sb-Te* [9] shown in Fig. 1 were used.

When constructing the distribution diagram of the *Cd-Sb-Te* phase regions, triangulation methods [10] and calculation of chemical bond parameters by quantum-chemical methods [4, 5] were used.

From the analysis of the phase diagrams shown in Fig. 1 it follows that antimony in compounds with cadmium and tellurium behaves similarly, has a double eutectic, and the *Cd-Te* compound melts congruently at 1098 °C and forms degenerate eutectics with its components.

The dependence of the melting temperature on pressure shows that with increasing pressure the melting temperature decreases to 996 °C, and at the triple point the sphalerite structure goes over to the *NaCl* type structure. Subsequently, with increasing pressure, the melting temperature begins to increase [2, 3]. The reason for such behaviour in the *Cd-Te* system has not been established.

Analyzing the phase diagram of *Sb-Te*, it should be noted that there are continuous solid solutions between antimony and Sb_2Te_3 during slow cooling. During rapid cooling of the melt, peritectic reactions with the formation of solid solutions do not have time to occur, and a nonequilibrium eutectic crystallizes from the melt – continuous solid solutions of Sb-Sb_2Te_3 are absent.

Of all the components, cadmium antimonide is considered the most studied. The works [2, 3] systematize and summarize publications on the properties of *Cd-Sb*, provide state diagrams, information on phase transformations; physical and chemical interaction of components in liquid and solid states. When studying the properties of *Cd-Sb* near the melting point, in addition to the thermal effect at 456 °C, which corresponds to the melting of *Cd-Sb*, another one was found on the thermograms at 464 °C, accompanied by a sharp increase in electrical conductivity and caused by changes in the short-range order and its transition from a semiconductor to a metallic state. The reason for the appearance of such effects may be the features of the crystalline structure of *Cd-Sb* and the supersaturation of the phase with antimony, which leads to a decrease in the melting temperature. Based on the data on the formation of polymorphic compounds in the *Cd-Sb* system, it was concluded that in the *Cd-Sb* system there is only one stable *Cd-Sb* and two unstable – Cd_4Sb_3 Cd_3Sb_2 compounds, which correspond to one stable and two metastable state diagrams. The short-range order corresponding to *CdSb* molecules exists only up to 500 °C. In liquid alloys of the Cd-Sb system, an irreversible process of rearrangement of the short-range order structure occurs in the sequence $CdSb \rightarrow Cd_4Sb_3 \rightarrow Cd_3Sb_2$, which depends on heat treatment. This information, as well as the data presented above, were obtained experimentally. At the same time, how the initial components in the ternary systems *Cd-Sb-Te* will interact, what will be the regions of extreme points of the dependence of the primary crystallization temperature on the composition, what will be the coordinates of the ternary eutectics of the concentration triangle - there is no answer from the standpoint of chemical bond yet. This work is a continuation of complex studies [3-8] and is devoted to the construction of theoretical models of ordered alloys of ternary systems *Cd-Sb-Te*. A new feature in the study of antimonides and tellurides was the use of a method based on the geometric properties of a triangle [10]. This mathematical approach, the triangulation method, is used in chemistry when studying the state diagrams of ternary systems and allows their distribution into simpler binary systems, taking into account chemical interaction.

In this paper, the inverse problem of triangulation is solved: based on the experimentally established and presented in [9] phase diagrams of binary alloys, taking into account the chemical interaction (solubility; substitution; exchange; formation of compounds; formation of solid solutions and mechanical mixtures) between the elements *Cd*, *Sb*, *Te*, located at the vertices of the triangle, a diagram of the distribution of phase regions for various isothermal sections in the *Cd-Sb-Te* system is constructed, and the parameters of phase transformations are calculated theoretically using quantum chemistry methods [4, 5]. Next, the quantitative ratios of coexisting phases were determined and the limits of phase equilibrium in the liquid-crystal regions were established. The obtained results are shown in Fig. 1 – 4, where the following designations are entered:

α – solid phase based on *Cd*;
β – solid phase based on *Te*;
γ – solid phase based on *Sb*;
ε – solid phase based on *Cd-Te*;
ρ_1 – solid phase based on $Sb_{0.7}Te_{0.3}$;
ρ_2 – solid phase based on $Sb_{0.4}Te_{0.6}$;
ρ_3 – solid phase based on $Sb_{0.1}Te_{0.9}$;
δ – solid phase based on *Cd-Sb*;

δ_1 – solid phase based on $Cd_{0.9}Sb_{0.1}$;

δ_2 – solid phase based on $Cd_{0.42}Sb_{0.58}$;

σ – solid phase based on intermediate ternary compound *Cd-Sb-Te*;

L – liquid.

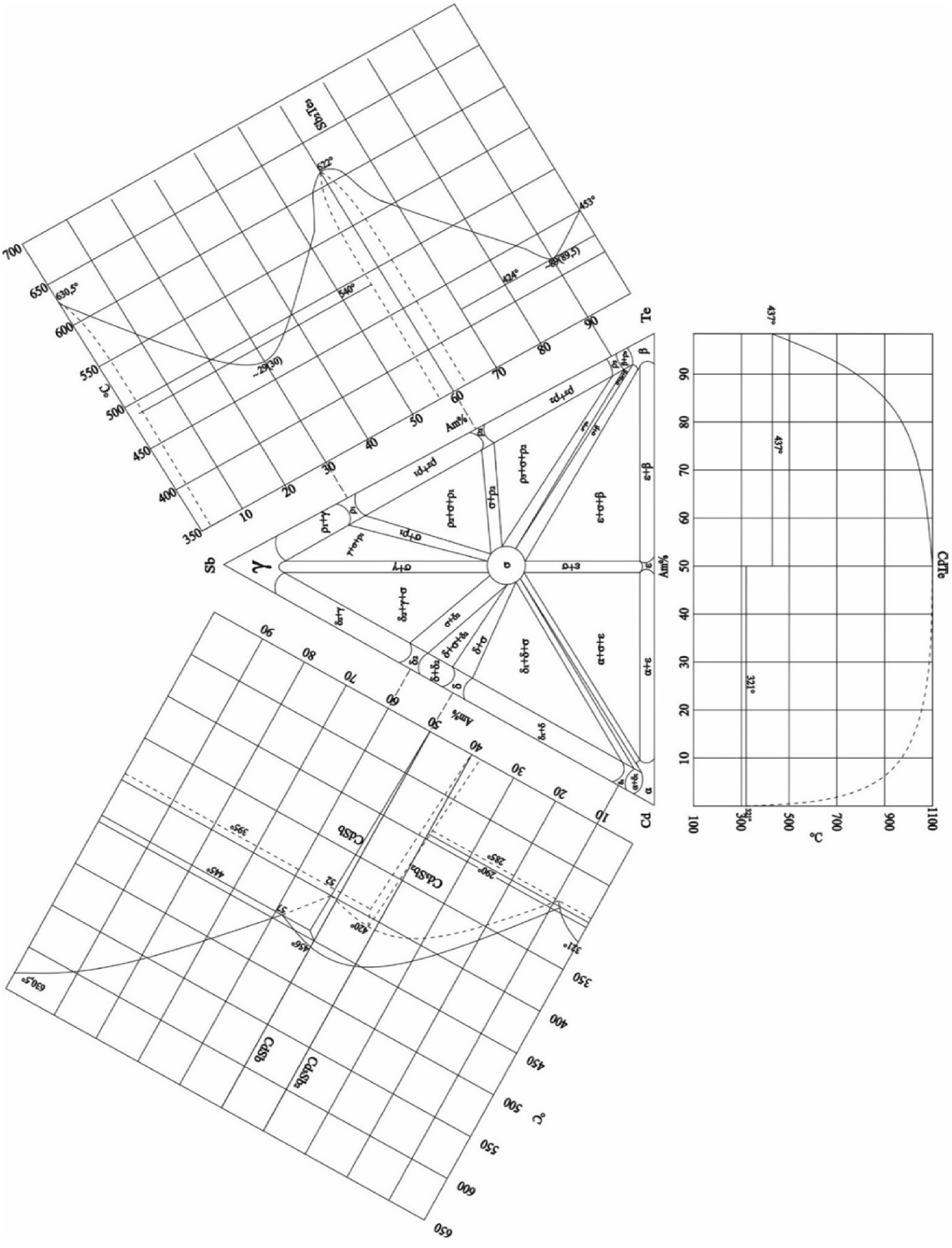

Fig. 1. Diagram of distribution of Cd-Sb-Te phase regions for equilibrium in the solid state.

Fig. 1 shows a diagram of the distribution of *Cd-Sb-Te* phase regions in the solid state. The division of the *Cd-Sb-Te* ternary system into ten ordered ternary subsystems is traced. This makes it possible to consider the issue of interatomic interaction both from the standpoint of stable and metastable phases of state diagrams, as well as chemical bond and temperature.

Fig. 2 shows an isothermal section at a temperature of t = 300 °C, which is lower than the melting point of the components *Cd*, *Sb, Te*, and at the same time higher than the temperature of the first eutectic of the *Cd-Sb* system. Unlike the previous case, the section contains conoid triangles with equilibrium phases ($L + \alpha + \sigma$) and ($L + \delta1 + \sigma$), which are realized by primary crystals α, as well as σ and δ1 crystals and liquid.

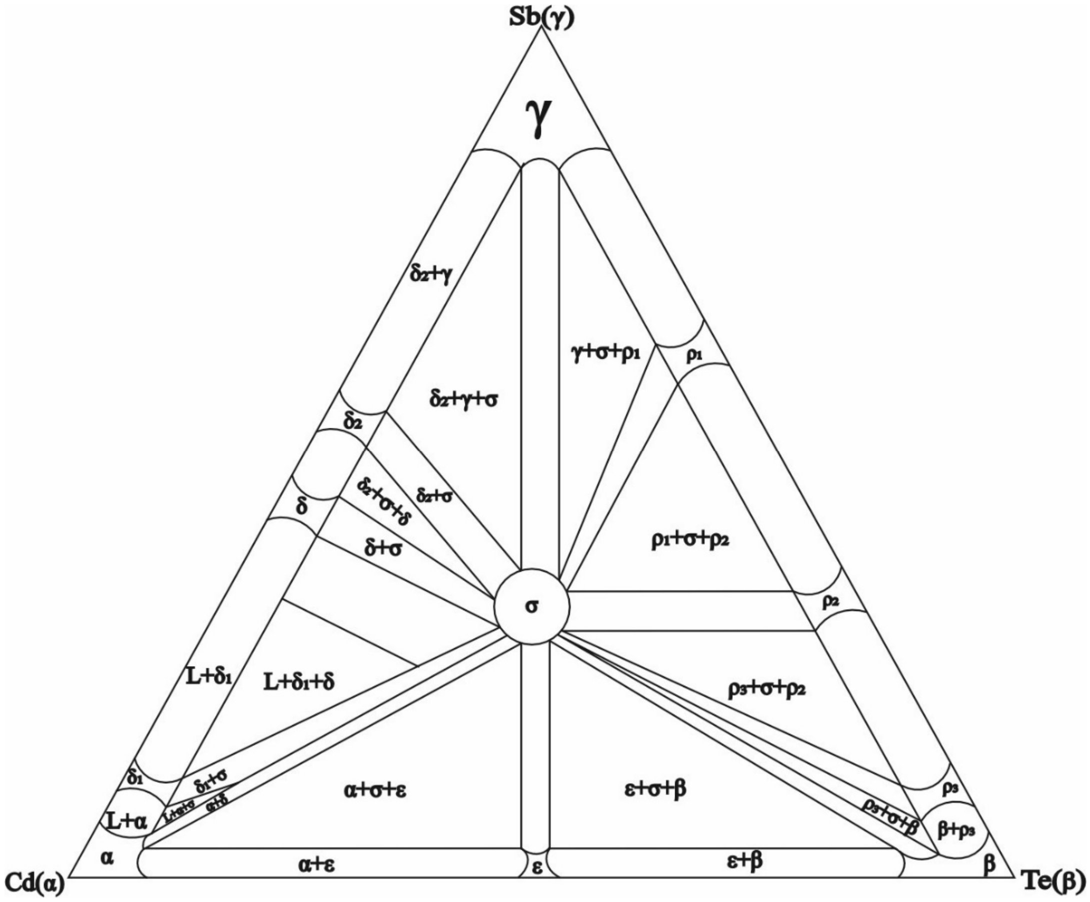

Fig. 2. Cd-Sb-Te isothermal section at t = 300 °C.

This division of ternary systems into separate sectors of binary phase diagrams allows studying the fine structure of cooling and heating of individual elements depending on their environment and the processes of formation of short-range order of chemical bonds.

Fig. 3 shows an isothermal section at a temperature of t = 400 °C, which is higher than the melting point of cadmium, but lower than the melting point of tellurium and antimony. In the *Cd-Sb* diagrams, three-phase equilibria are represented by conoid triangles with phases ($L + \alpha + \sigma$), ($L + \delta1 + \sigma$), and ($L + \delta + \sigma$). Alloys of the triangle (ε, γ, β) are in the solid state at this temperature.

Fig. 4 shows the isothermal section at t = 600 °C, which is higher than the melting temperature of cadmium and tellurium, but lower than the melting temperature of antimony. Most of the *Cd-Sb* cross-section is occupied by liquid, and on the *Cd-Te, Sb-Te* diagrams, three-phase equilibria are represented by conoid triangles with phases (*L* + ρ2 + γ), (*L* + ρ2 + σ) and (*L* + σ + ρ3), (*L* + β + σ), (*L* + β + ε), (*L* + α + β), (*L* + α + ε).

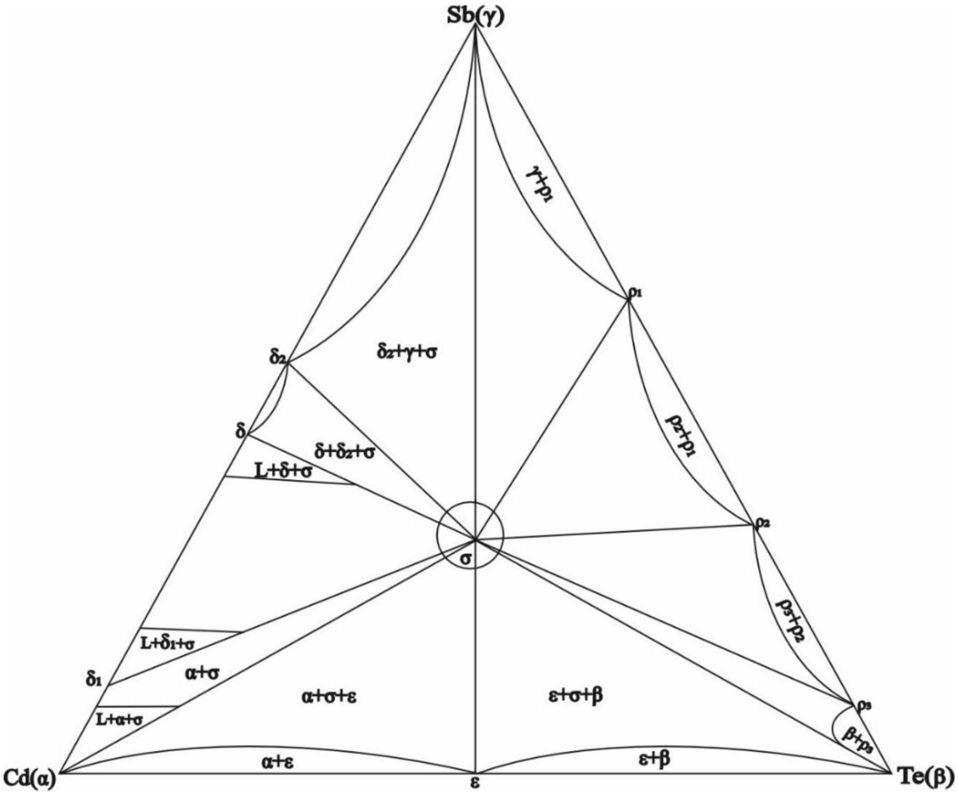

Fig. 3. Cd-Sb-Te isothermal section at t = 400 °C.

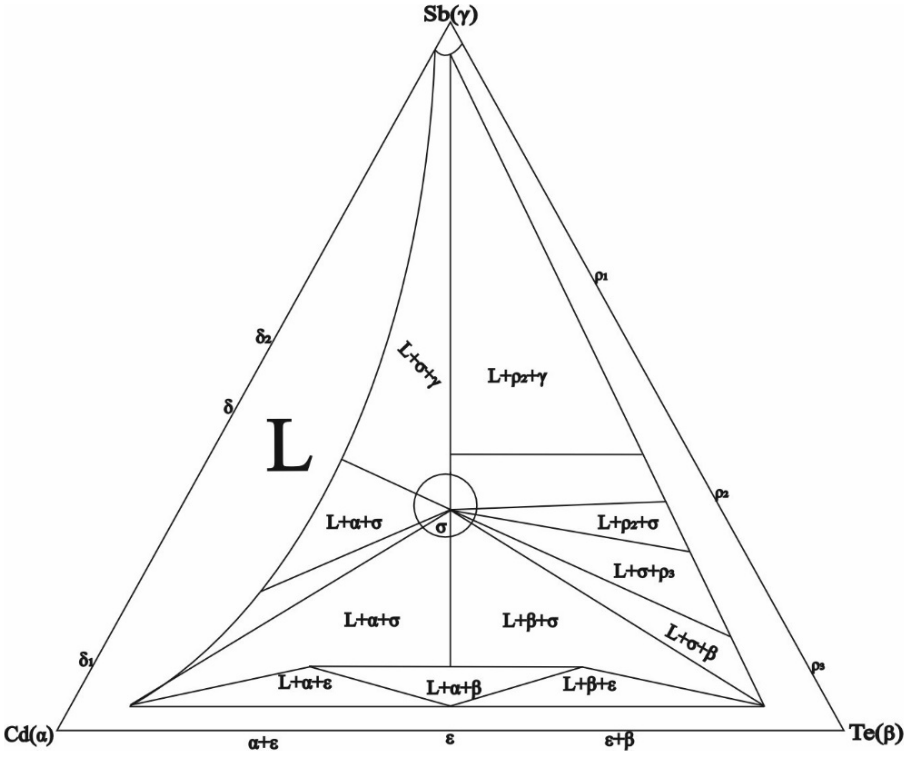

Fig. 4. Cd-Sb-Te isothermal section at t = 600 °C.

Thus, the presented isothermal sections make it possible to separate the limits of phase equilibrium for eutectic and peritectic type diagrams and to optimize the technological modes of obtaining new materials based on *Cd-Sb-Te*.

However, isothermal sections alone do not yet indicate the temperatures of phase transitions of multicomponent systems. Theoretical models are needed that combine generalized experimental data with calculations of the interatomic interaction of components in both phases depending on interatomic distances and increase the role of theoretical calculations in constructing phase diagrams of multicomponent systems.

Theoretical models of chemical bonding of ordered alloys *Cd-Sb-Te*

Theoretical analysis of crystallization processes of thermoelectric materials requires a revision of the fundamentals of the theory of interatomic interaction. The reason for this is that theoretical approaches reflecting the regularities of ordering processes in crystals contradict the formation of a chemical bond, accompanied by the rearrangement of the valence electron shells of interacting atoms and the redistribution of electron density along chemical bonds [5].

On the other hand, taking into account statistical regularities made it possible to obtain the dependence of n electrons on the outer shell of an atom on the Fermi radius r_F, which can be considered the beginning of the quantitative chemical bond theory [11].

Analysis of empirical information about the properties of atoms based on a crystal-chemical approach made it possible to generalize the concept of the Fermi radius to the case of electronic configurations of interacting atoms depending on the length and number of bonds formed by them and to introduce effective ionic radii R_U. The most useful relationship in searching for the connection of R_U with n proved to be the relationship $tg\alpha = \frac{\Delta log R_U}{\Delta n}$ with the properties of atoms in the coordinates $log R_U = f(n)$. Good agreement between the experimental data on the properties of atoms and their ions and the values of R_U and $tg\alpha$ is given by the postulated dependence:

$$log R_{UA}^{x} = log R_{UA}^{0} - x tg\alpha, \tag{1}$$

where R_U^0 is radius of atoms in the unexcited state; x is valence.

The use of the system of ionic radii to describe the chemical bond follows from the principles of quantum mechanics. Since the equation of the system of ionic radii describes the change in R_U of atoms *A* and *B* with a change in the number of electrons in the orbitals of each, then dependence (1) takes the form of a system of equations [11]:

$$log R_{UA}^{+x} = log R_{UA}^{0} - x tg\alpha_A, \tag{2}$$

$$log R_{UB}^{-x} = log R_{UB}^{0} + x tg\alpha_B, \tag{3}$$

$$d_1 = R_{UA}^{+x} + R_{UB}^{-x}, \tag{4}$$

The presence of a minimum interatomic distance d_{min} from the standpoint of the crystal chemical approach is justified by the increase in the internuclear distance with a change in ionicity between the same partners. The disadvantage of this approach is that in many cases the internuclear distances *A*-*B* in compounds and alloys are less than $d_{min}$and it is impossible to calculate the ion charge using the $Z_{ef} = f(d)$ diagrams. Difficulties can be overcome only by abandoning the attempt to interpret the solution of system (2) – (4) from the standpoint of a crystal-chemical approach. Additional conditions are necessary to translate the crystal chemical system (2) – (4) into the language of quantum chemistry.

It should be taken into account that during the formation of A-B bonds, the spherical symmetry of the electron density of atoms A and B is broken and is accompanied by the transition of electrons to other directions of interatomic interaction.

The thus calculated effective charges and effective radii characterize for an arbitrary d_1 the conditions for preservation of continuity of wave function in the zone of interacting atoms. This condition is fulfilled if the extraction ($+\Delta e$) of electrons or their localization ($-\Delta e$) change the values of charges that this pair has at $d_1 = d_{min}$, i.e. $Z_{ef}A(B) = Z_{min}A(B) + \left(\frac{\Delta e}{2}\right)$ and are described by the system of equations:

$$d_1 = R_{UA}^{ZA} + R_{UB}^{ZB}, \tag{5}$$

$$logR_{UA}^{ZA} = logR_{UA}^{0} - (Z_{minA} + \left(\frac{\Delta e}{2}\right))tg\alpha_A, \tag{6}$$

$$logR_{UB}^{ZB} = logR_{UB}^{0} - (Z_{minB} + \left(\frac{\Delta e}{2}\right))tg\alpha_B, \tag{7}$$

Replacing x in the system of equations (2) – (4) with $(Z_{min} + \left(\frac{\Delta e}{2}\right))$ in (5) – (7) changes the physical content of these equations. The function $d_1 = f(Z_{ef})$ is calculated from the standpoint of the crystal-chemical approach, $(Z_A = -Z_B)$ is correct from the quantum-molecular point of view only when $d_1 = d_{min}$, but this is sufficient for the system (5) – (7) to be solved for a known d_1 and for the effective radii and redistribution of the electron density to be found. With this approach, system (5) – (7) allows us to agree the theoretical part with the experimental part for all possible values of d_1 in the compounds under consideration. Thus, taking into consideration the quantum interpretation of the empirical material made it possible to obtain

$$D_{A-B}^{(i)} = \left(\frac{C_1(R_{UA}^0 + R_{UB}^0)}{(\text{tg}\,\alpha_A + \text{tg}\,\alpha_B)}\right)\left(\frac{C_2 d_i}{d_i^2 - R_{UA}R_{UB}} - \frac{1}{d_i}\right), \tag{8}$$

where $R_{UA(B)}^0$, $tg\alpha_{A(B)}$ are the coefficients of equations (2) – (4) for atoms A and B, and R_{UA}, R_{UB} are the effective radii of their ions in $A - B$ bonds of length d_i, i is the number of non-equivalent interatomic distances in the considered compounds; C_1 is the coefficient reflecting the relationship between dimensional and energy characteristics of interatomic interaction (measured in electron volts); C_2 is a coefficient that depends on the type of crystal structure and chemical bond and is chosen dimensionless.

The above equations were used in the calculations of effective charges, effective radii and dissociation energies of non-equivalent chemical bonds of *Cd-Sb-Te* ternary systems.

The results of calculations of the coefficients of equations (2) – (4) R_U^0 and $tg\alpha$ of the initial components are given in Table 1.

Table 1

Coefficients of equations of the initial components

Z		Element	R_U^0(Å)	$tg\alpha$
48		*Cd*	1.51 Å	0.097
51		*Sb*	1.45 Å	0.074
52		*Te*	1.57 Å	0.076

Effective charges Δq_{i}, effective radii $R_{U\mathrm{i}}$ and dissociation energies for the nearest neighbours at different interatomic distances $d_{\mathrm{i}} (1 \leq i \leq 6)$ of the structural modifications of cadmium are given in Table 2. The results of calculations for antimony and tellurium are given in Tables 3 and 4.

Table 2

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies D_i of chemical bonds φ_i for the nearest neighbours at different interatomic distances d_i of structural modifications of cadmium

φ_i / Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_{UCd}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q(\varphi_i)$	+ 0.33	+ 0.18	+ 0.025	– 0.05	– 0.27	– 0.4
$D_i(eV)$	1.853	1.789	1.730	1.674	1.622	1.572

Table 3

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies D_i of chemical bonds φ_i for the nearest neighbours at different interatomic distances d_i of structural modifications of antimony

φ_i / Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_{USb}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q(\varphi_i)$	0.2	0	– 0.2	– 0.39	– 0.6	– 0.75
$D_i(eV)$	2.332	2.252	2.177	2.107	2.041	1.98

Table 4

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies D_i of chemical bonds φ_i for the nearest neighbours at different interatomic distances d_i of structural modifications of cadmium

φ_i / Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_{UTe}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q(\varphi_i)$	0.653	0.454	0.26	– 0.0073	– 0.108	– 0.284
$D_i(eV)$	2.46	2.374	2.295	2.221	2.147	2.087

As regards the above parameters for *Cd-Te*, *Sb-Te* and *Cd-Sb* compounds, they are given in Tables 5, 6, 7.

Table 5

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies D_i of chemical bonds φ_i for the nearest neighbours at different interatomic distances d_i of structural modifications of Cd-Te

Parameters \ φ_i	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_{UCd}(Å)	1.355	1.41	1.465	1.515	1.576	1.63
R_{UTe}(Å)	1.445	1.49	1.535	1.585	1.624	1.67
$\Delta q(\varphi_i)$	0.497	0.318	0.134	– 0.022	– 0.195	– 0.34
$D_i(eV)$	2.116	2.044	1.977	1.913	1.855	1.798

Table 6

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies D_i of chemical bonds φ_i for the nearest neighbours at different interatomic distances d_i of structural modifications of Sb-Te

Parameters \ φ_i	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_{USb}(Å)	1.345	1.444	1.46	1.48	1.53	1.58
R_{UTe}(Å)	1.455	1.456	1.54	1.62	1.67	1.72
$\Delta q(\varphi_i)$	0.43	0.227	0.03	– 0.159	– 0.324	– 0.521
$D_i(eV)$	2.392	2.314	2.235	2.159	2.092	2.029

Table 7

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies D_i of chemical bonds φ_i for the nearest neighbours at different interatomic distances d_i of structural modifications of Cd-Sb

Parameters \ φ_i	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_{UCd}(Å)	1.43	1.48	1.53	1.58	1.63	1.68
R_{USb}(Å)	1.37	1.42	1.47	1.52	1.57	1.62
$\Delta q(\varphi_i)$	0.287	0.106	– 0.069	– 0.239	– 0.403	– 0.562
$D_i(eV)$	2.059	1.989	1.922	1.860	1.802	1.748

In the tables, the values of coefficients C_1 and C_2 in the calculations in the first approximation are chosen to be equal to unity.

Discussion of the results and conclusions

As follows from the results obtained in the work, given in Tables 1 – 7 and in Figs. 1 – 4, the application of a complex approach to technological problems made it possible to build theoretical models for the description of ordering processes in alloys of ternary systems based on *Cd-Sb-Te*.

This approach allowed us to describe the processes of formation of interatomic interaction at different technological levels from the standpoint of chemical bond. This is, first of all, the formation of a crystal structure based on the initial elements (*Cd, Sb, Te*), where information on the physicochemical properties and chemical bond of the initial elements (Tables 1 – 4) was taken into account, binary compounds based on the initial elements (*Cd-Te, Sb-Te, Cd-Sb*) (Tables 5 – 7). What was new was that the paper calculated the dependence of chemical bond parameters on the interatomic distances (effective radii, redistribution of electron density on the corresponding chemical bonds, and dissociation energy of bonds forming the crystal structure).

What was new in the study of ternary *Cd-Sb-Te* systems was that, when constructing the distribution diagram of phase equilibrium regions, the method of inverse triangulation was used using information on the binary compounds of the initial components and their state diagrams. This made it possible to determine quantitative phase ratios and establish the limits of phase equilibrium in the liquid-crystal regions; to separate the boundaries of diagrams of eutectic and peritectic type for solving technological problems of stable and metastable phases, predict cases of congruent and incongruent melting. The obtained results can be used in the development of technological modes of obtaining new materials based on *Cd-Sb-Te*.

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Submitted: 21.06.2023.

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ТЕОРЕТИЧНІ МОДЕЛІ ВПОРЯДКОВУВАНИХ СПЛАВІВ ПОТРІЙНИХ СИСТЕМ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ.
5. ХІМІЧНИЙ ЗВ'ЯЗОК ТА ДІАГРАМИ СТАНУ *Cd-Sb-Te*

Розроблено теоретичні моделі впорядковуваних сплавів перспективних термоелектричних матеріалів потрійних систем на основі Cd-Sb-Te. Методами оберненої триангуляції побудовано ізотермічні перерізи та схеми розподілу фазових областей в потрійних системах з використанням бінарних діаграм стану вихідних компонентів (Cd-Sb; Cd-Te; Sb-Te). Представлено розрахунки ефективних радіусів міжатомної взаємодії, перерозподілу електронної густини та енергії дисоціації відповідних хімічних зв'язків, що формують кристалічну структуру Cd-Sb-Te в залежності від міжатомних віддалей.

Ключові слова: теоретичні моделі, хімічний зв'язок, ефективні радіуси, енергія дисоціації, діаграми стану, нееквівалентні гібридні орбіталі (НГО).

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Надійшла до редакції: 21.06.2023.