DOI: 10.63527/1607-8829-2021-2-31-40

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THEORETICAL MODELS OF ORDERED ALLOYS OF THERMOELECTRIC MATERIAL TERNARY SYSTEMS.
1. CHEMICAL BOND AND STATE DIAGRAMS OF *In-Cd-Sb*

Using the developed comprehensive approach for building theoretical models of ordered alloys of ternary systems of thermoelectric materials, a diagram of the distribution of phase regions for equilibrium in the solid state and isothermal sections based on intermediate binary compounds In-Sb, Cd-Sb, In-Cd are constructed. Calculations of effective charges, effective radii, electron density redistribution, and dissociation energy of nonequivalent hybrid orbitals (NHOs) in the In-Cd-Sb system depending on interatomic distances are presented. The results of theoretical calculations can be used in the development of technology for new thermoelectric materials based on ternary In-Cd-Sb systems. Bibl. 13, Fig. 4, Tabl. 3.

Key words: state diagrams, phase transitions, chemical bond, nonequivalent hybrid orbitals, dissociation energy.

Introduction

The search for new promising thermoelectric materials is increasingly reduced to the need to study multicomponent systems. Several main features of such systems should be noted. First and foremost, it is the formation of solid phases of variable composition within which there is a continuous transition in chemical composition and a gradual transition from densely packed crystal lattices to layered structures with corresponding changes in physical properties.

The nature of the chemical bond in such compounds varies from metallic to ionic non-polar in layered sublattices. In turn, a change in the chemical bond of the aforementioned compounds is reflected in a change in the structure of the short-range order of the interatomic interaction, which, in turn, is associated with the peculiarities of the phase diagrams and phase transformations, both in the solid state and in melts.

However, it should be noted that there is no consistent theory of phase transformations from the standpoint of chemical bonding. In this regard, the task was to obtain theoretical schemes of state diagrams of ternary systems (for example, *In-Cd-Sb*) using state diagrams of double alloys and to calculate the necessary parameters using molecular models of microscopic theory. This approach allows us to generalize the experimentally obtained results for binary and intermediate quasi-binary state diagrams [1-4] in the case of ternary systems. In turn, this would make it possible to additionally use the capabilities of these state diagrams: information on the nature of the phases and phase composition of a substance depending on temperature, pressure and concentration, volume, strength of electric and magnetic fields in the development of technologies for obtaining thermoelectric materials based on ternary compounds. The availability of such information makes it possible to approach the solution of the problem of a theoretical description of the processes of melting and crystallization of such systems.

State diagrams

To solve this problem, it is necessary to generalize the results of experimental studies of binary state diagrams [3-7], physicochemical properties and theoretical studies of quantum regularities of the initial components [8, 9] when constructing state diagrams of ternary compounds. The developed theoretical approaches were tested on *In-Cd-Sb* ternary compounds. The choice was not accidental, because these compounds analyzed the effect of low-temperature element *In* on the formation of stable and metastable phases in ternary systems. The action of In was carried out by constructing intermediate quasi-binary isothermal sections *In-Cd-Sb* (*In-Cd, In-Sb, Cd-Sb*) and solving the inverse problem. Its essence is that when the analysis of a complex multicomponent system with intermediate compounds is impossible, the study of such systems should be carried out by dividing them into simpler, according to established rules and patterns [10]. The elements *In, Cd, Sb* and state diagrams of binary compounds *In-Cd, In-Sb, Cd-Sb* were selected as initial data. A triple state diagram of *In-Cd-Sb* should be constructed on the basis of the analyzed theoretical and experimental rules and regularities.

The presented work begins with the assumption that intermediate ternary compounds with the desired properties based on the elements *In, Cd, and Sb* exist and it is necessary to find the conditions for their production. Fig. 1 shows a diagram of the distribution of phase regions for equilibrium in the solid state of *Cd-In-Sb*. Fig. 2-4 show isothermal cross sections at temperatures: t_2 = 200 °C, t_3 = 300 °C, t_4 = 400 °C.

In Figs. 1-4 the following designations are introduced:

δ – solid phase based on intermediate ternary compound *In-Cd-Sb*;
α – solid solution based on *Cd*;
β – solid solution based on *In;*
γ – solid solution based on *Sb*;
L – liquid (liquid phase);
ε – solid solution based on intermediate binary compounds *Cd-In*;
ρ – solid solution based on *In-Sb*;
σ – solid solution based on *Cd-Sb.*

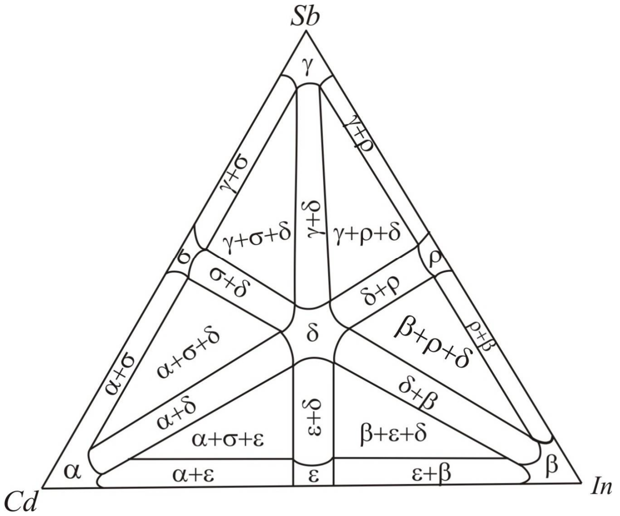

Fig. 1. Distribution diagram of phase regions for equilibrium in the solid state of Cd-In-Sb

According to Fig. 1, each quasi-double cross-section based on the ternary compound corresponds to a closed set of points and lines of compatible crystallizations of the two phases. These quasi-double cross-sections divide the total three-component *In-Cd-Sb* system into six secondary ternary systems. It should be noted that in the presence of additional experimental data on intermediate quasi-double sections in the ternary system, the number of secondary ternary systems may be greater.

Fig. 2 shows the isothermal section at a temperature t = 200 °C, which is lower than the melting point of *Cd* and *Sb*, but higher than the melting point of In. From Fig. 2, it can be concluded that a significant part of the section is occupied by liquid *L*. Present in Fig. 2 is a condom triangle with equilibrium phases $L + \alpha + \varepsilon$; $L + \beta + \varepsilon$. Two-phase equilibrium is realized by primary precipitates of $\sigma + \gamma$ crystals; $\rho + \gamma$, as well as ε – crystals (based on the *In-Cd* compound) and liquid.

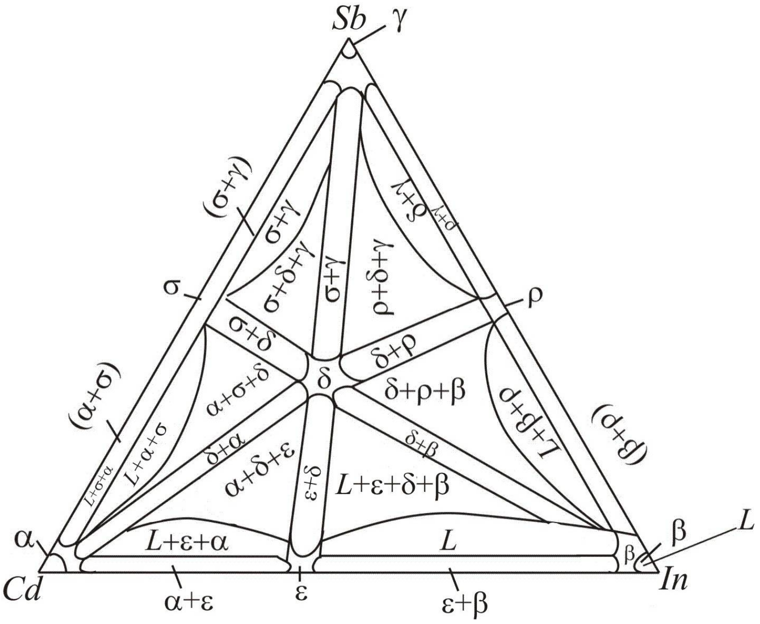

Fig. 2. Isothermal section of Cd-In-Sb at t= 200°C

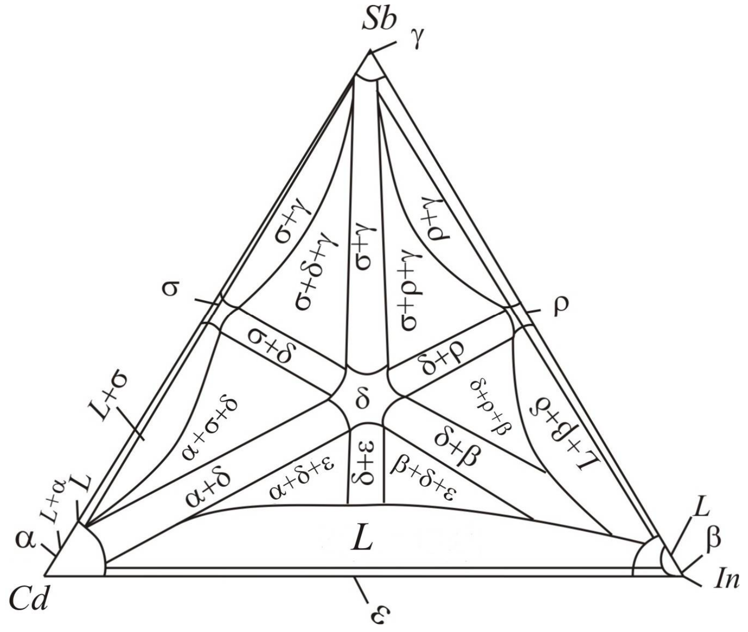

Fig. 3.Isothermal section of Cd-In-Sb at t= 300°C

Fig. 3 shows an isothermal section at t = 300 °C, which is below the melting point of *Sb*, close to the melting point of *Cd* and above the melting point of *In*. There are conode triangles with equilibrium phases $L + \alpha + \varepsilon$; $L + \beta + \varepsilon$; $\sigma + \delta + \gamma$; $\rho + \delta + \gamma$. The primary precipitates of *Cd* and *In* crystals and the intermediate binary compound *Cd-In* are in equilibrium with the liquid.

The third isothermal section corresponds to $t = 400$ °C (see Fig. 4), which is higher than the melting point of *Cd* and *In* and below the melting point of *Sb*. Three-phase equilibria are represented by conode triangles $\alpha + \sigma + \delta$; $\gamma + \sigma + \delta$; $\gamma + \rho + \delta$; $\beta + \rho + \delta$, two-phase equilibria – by linear surfaces $\alpha + \sigma$; $\sigma + \gamma$; $\rho + \gamma$; $\rho + \beta$; $\delta + \rho$; $\delta + \gamma$; $\delta + \sigma$.

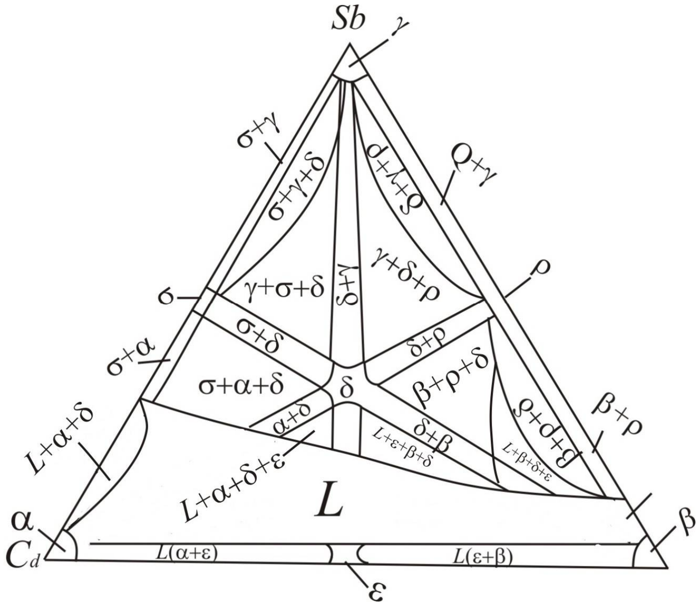

Fig. 4.Isothermal section of Cd-In-Sb at t= 400 °C

Thus, these isothermal sections make it possible to:

1. determine the quantitative ratios of coexisting phases and their concentrations;
2. establish the limits of phase equilibrium in the liquid-crystal regions (melting diagram), as well as the equilibrium of the phases associated with polymorphic transformations in the solid state;
3. distinguish state diagrams corresponding to a continuous series of solid solutions with points of equal concentrations where liquidus and solidus touch (the composition of both phases at these points is the same);
4. separate the boundaries of eutectic-type state diagrams, when the components are mixed in all ratios in the liquid state, from diagrams with limited solubility in the solid phase of the peritectic type;
5. predict cases of incongruent melting, when the chemical compound during melting decomposes into solid and liquid phases, the composition of which differs from the composition of the original compound.

However, isothermal sections do not indicate the temperature points of the phase transitions. In such cases, for multicomponent systems, methods are used that combine analytical and topological approaches with calculations of the energy of interaction of components in both phases, which increases the role of theoretical calculations in constructing state diagrams of ternary systems.

It should also be borne in mind that the theoretical analysis of numerous empirical dependencies is associated with a revision of views on the problem of interatomic interaction, as well as with the emergence of qualitatively new concepts, which are not always the result of the development of existing theories, but generally deny some of them.

Theoretical models of ordered alloys and chemical bond

The simplest relations reflecting the quantum regularities of the structure and interatomic interaction of binary compounds were given in [8, 9]. They were obtained by postulating the linear dependence of the number of electrons on the outer shell of the atom on the logarithm of its Fermi radius R_u. The relationship between the tangent of the angle of inclination $tg\alpha = \dfrac{\Delta \lg R_u}{\Delta n}$ and the electronegativities does not allow changing compared values arbitrarily.

A good agreement of the experimental data gives the following dependence:

$$\lg R_u^x = \lg R_{uA}^{(o)} - x tg\alpha_A, \tag{1}$$

where $R_{uA}^{(o)}$ is the radius of the atom in the unexcited state and x is valence.

Since equation (1) describes the change in R_u of A i B atoms with a change in the number of electrons in the orbits of each, then, assuming the equality of the absolute values of the charges of interacting atoms, dependence (1) takes the form of a system of equations:

$$\lg R_{uA}^{+x} = \lg R_{uA}^{(o)} - x tg\alpha_A, \tag{2}$$

$$\lg R_{uB}^{-x} = \lg R_{uB}^{(o)} + x tg\alpha_B, \tag{3}$$

$$d_1 = R_{uA}^{+x} + R_{uB}^{-x}, \tag{4}$$

d is the sum of ionic radii equal to the interatomic distance.

The system of equations (2) - (4) considers the geometric conditions of contact of spherical electron densities with different levels of density at the boundary. Therefore, additional criteria are needed to translate system (2) - (4) into the formalism of quantum chemistry, taking into account the fine structure of the chemical bond. For this, it is necessary to analyze the dependence of interatomic distances on effective charges. The analysis results showed that at an arbitrary point, apart from $d_1 = d_{min}$, the charge density at the ion boundary is different. The formation of the AB bond is accompanied by the transition of electrons to other directions of interatomic interaction, that is, the bond becomes donor. In this case, the escape of electrons ($+\Delta q$) or their localization ($-\Delta q$) in the given direction of the bond equally changes the values of the charges that this pair has at $d_1 = d_{min}$. With this approach, the system of equations (2) - (4) turns into a system that allows the theoretical part to be matched with the experimental one and was solved with a known d_1. Thus, as a result of taking into account the quantum interpretation of the empirical material, the expression for the energy of chemical bonds takes the form:

$$D_{A-B}^{(i)} = \frac{c_1\left(R_{uA}^{o} + R_{uB}^{o}\right)}{\left(tg\alpha_A + tg\alpha_B\right)}\left(\frac{c_2 d_i}{d_1^2 - R_{uA}R_{uB}} - \frac{1}{d_i}\right), \tag{5}$$

where $R_{uA(B)}^{o}$ and $tg\alpha_{A(B)}$ are coefficients of equations (2) - (4) for atoms A and B, and R_{uA} and R_{uB} are effective radii of their ions, in A-B bonds of length d_i; i is the number of nonequivalent interatomic distances in compound; c_1 and c_2 are constants, c_1 is coefficient reflecting the relationship between the dimensional and energy characteristics of the interatomic interaction (in the case of using non-systemic units, when the distance is measured in angstroms, c_1 is measured in electron volts) and c_2 is a coefficient depending on the type of crystal structure and chemical bond and is chosen dimensionless.

The equations presented were used to calculate the effective charges, effective radii, and dissociation energies of nonequivalent chemical bonds described by nonequivalent hybrid orbitals in melts of cadmium and indium antimonides. The peculiarity of the chemical bond in crystals is that each *Cd* atom in its immediate environment has three *Sb* atoms and one *Cd*, and each *Sb* atom has three nearest *Cd* atoms and one *Sb* atom. Altogether five NHO families, differing both in the interatomic distances and the composition of components (φ_1, φ_2, φ_3 correspond to *Cd-Sb* bonds of different length, as well as φ_4 (*Sb-Sb*) i φ_5 (*Cd-Cd*). The structure of In-Sb was similarly evaluated. The results of calculations of the coefficients of equations (2) - (4) of the initial components are given in Table. 1. Effective charges, effective radii and dissociation energies of NGOs in *CdSb* and *InSb* crystals are given in Tables 2 and 3. In this case, the values of the coefficients c_1 and c_2 in the first approximation are chosen equal to one.

Table 1

Coefficients of equations (2) - (4) of the initial components

Z	Element	R_u^0 (Å)	tgα
48	*Cd*	1.51	0.097
49	*In*	1.66	0.106
51	*Sb*	1.45	0.074

Table 2

Effective charges, effective radii and dissociation energies of CdSb NHOs

Parameters	*Cd-Sb*			*Sb-Sb*	*Cd-Cd*
	φ_1	φ_2	φ_3	φ_4	φ_5
$d_j^{експ}$ (Å)	2.8400	2.9100	2.8100	2.8100	2.9900
$d_j^{теор}$ (Å)	2.8390	2.9102	2.8102	2.810	2.9846
R_u^{Cd} (Å)	1.4406	1.4813	1.4239	-	1.4947
R_u^{Sb} (Å)	1.3990	1.4290	1.3860	1.405	-
Δq (φ_j)	0.2100	0.0860	0.2630	0.185	0.0500
D^i (eB)	2.0300	1.9800	2.0500	2.3180	1.734

<u>*Таблиця 3*</u>

Effective charges, effective radii and dissociation energies of InSb NHOs

Parameters	*InSb*
	φ_1
$d_j^{експ}$ (Å)	2.7973
$d_j^{теор}$ (Å)	2.797
R_u^{In} (Å)	1.1839
R_u^{Sb} (Å)	1.6137
Δq (φ_j)	0.385
D^i (eB)	1.9893

Discussion of results

Analysis of the results obtained has shown that the algorithm of distribution of phase regions of equilibrium of ternary systems in solid state and the refinements introduced by constructing isothermal cross-sections and calculating the energy of interatomic interaction of the initial components depending on the interatomic distances are in good agreement with the results of studies of thermal rearrangements of atoms when forming the short-range order of chemical bond which is responsible for the appearance of stable and metastable phases in the melts of ternary systems presented in [11 – 13].

The results presented in the article expand the technological possibilities of obtaining new materials by taking into account the peculiarities of the fine structure of the chemical bond, triple phase diagrams, eutectic-peritectic and exothermic and endothermic reactions during the formation of short-range order in melts of *In-Cd-Sb* ternary systems.

A diagram of the distribution of phase regions in the solid state and isothermal sections have been constructed, which refine the dynamics of the formation of short-range order of chemical bonds in ternary systems of *In-Cd-Sb* melts.

Conclusions

1. A diagram of the distribution of phase regions in the solid state and isothermal sections have been constructed, which refine the dynamics of the formation of short-range order of chemical bonds in ternary systems of *In-Cd-Sb* melts.
2. A method for calculating chemical bonding parameters in ternary *In-Cd-Sb* systems is proposed.
3. Calculations of effective radii and dissociation energies in ternary *In-Cd-Sb* systems are performed.
4. The obtained theoretical results are consistent with the results of calculations of the parameters of chemical bond, using the methods of microscopic theory and the results of studies of thermal rearrangement of atoms in melts, and can also be used in the development of technological modes for obtaining new materials based on *In-Cd-Sb* for use in thermoelectricity.

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Submitted 14.04.2021

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ТЕОРЕТИЧНІ МОДЕЛІ УПОРЯДКОВУВАНИХ СПЛАВІВ ПОТРІЙНИХ СИСТЕМ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ. 1. ХІМІЧНИЙ ЗВ’ЗОК ТА ДІАГРАМИ СТАНУ *In-Cd-Sb*

Використовуючи розроблений комплексний підхід для побудови теоретичних моделей упорядковуваних сплавів потрійних систем термоелектричних матеріалів побудовано схему розподілу фазових областей для рівноваги у твердому стані та ізотермічні перерізи на основі проміжних бінарних сполук In-Sb, Cd-Sb, In-Cd. Представлено розрахунки ефективних зарядів, ефективних радіусів, перерозподілу електронної густини та енергії дисоціації нееквівалентних гібридних орбіталей (НГО) в системі In-Cd-Sb в залежності від міжатомних віддалей. Результати теоретичних розрахунків можуть бути використані при розробці технології одержання нових термоелектричних матеріалів на основі потрійних систем In-Cd-Sb. Бібл. 13, рис. 4, табл. 3.

Ключові слова: діаграми станів, фазові переходи, хімічний зв’язок, нееквівалентні гібридні орбіталі, енергія дисоціації.

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ТЕОРЕТИЧЕСКИЕ МОДЕЛИ УПРАВЛЯЕМЫХ СПЛАВОВТРОЙНЫХ СИСТЕМ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ. 1. ХИМИЧЕСКАЯ СВЯЗЬ И ДИАГРАММЫ СОСТОЯНИЯ *In-Cd-Sb*

Используя разработанный комплексный подход для построения теоретических моделей упорядочиваемых сплавов тройных систем термоэлектрических материалов построена схема распределения фазовых областей для равновесия в твердом состоянии и изотермические сечения на основе промежуточных бинарных соединений In-Sb, Cd-Sb, In-Cd. Представлены расчеты эффективных зарядов, эффективных радиусов, перераспределения электронной плотности и энергии диссоциации неэквивалентных гибридных орбиталей (НГО) в системе In-Cd-Sb в зависимости от межатомных расстояний. Результаты теоретических расчетов могут использоваться при разработке технологии получения новых термоэлектрических материалов на основе тройных систем In-Cd-Sb. Библ. 13, рис. 4, табл. 3.

Ключевые слова: диаграммы состояний, фазовые переходы, химическая связь, неэквивалентные гибридные орбитали, энергия диссоциации.

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Submitted 14.04.2021