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Theoretical models of chemical bonding in melts of Bi-Sb-Se-Te based thermoelectric materials

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A comprehensive approach has been developed for building theoretical models of ordered alloys of quaternary systems of thermoelectric materials. Calculations of effective charges, effective radii, redistribution of electron density, dissociation energy of nonequivalent hybrid orbitals (NHO) in the Bi-Sb-Se-Te system were carried out depending on the interatomic distances, type of crystal structure, and chemical bond. The results obtained can be used in the development of technology for obtaining new Bi-Sb-Se-Te based thermoelectric materials.

Keywords: theoretical models, state diagrams, phase transitions, chemical bond, nonequivalent hybrid orbitals, effective radii, dissociation energy.

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Introduction

The problem of the liquid state is one of the key issues in materials science [1-2]. It is associated with such technological processes as melting and crystallization. The theoretical explanations used in the analysis of these processes are semi-phenomenological and based on the method of analogies. Various theories were built in order to match the observed phenomena with a certain interpretative model. Such approach resulted in the absence of a complete microscopic theory of disordered systems by now. The formation of such a theory revealed the need to expand the empirical base of existing theoretical developments.

However, it should be noted that the generalization of experimental data alone does not provide the values of the parameters of phase transitions of multicomponent systems. Non-traditional methods and approaches are needed that would give versatile characteristics of the thermodynamic, statistical, and quantum laws of the processes of melting and crystallization of such systems taken as a single entity.

The topicality of such research is also due to the fact that multicomponent systems are complex, nonlinear, and the known theoretical approaches developed for simple (one- and two-component) systems no longer reveal the conditions for the appearance of the necessary properties and their change in the desired direction. Here the question of the relationship between physics and chemistry in technological research has already been raised. The emergence of quantum chemistry has changed traditional ideas about the relationship between these two scientific disciplines. Such a union became possible due to interdisciplinary synthesis. The basis of such a synthesis is the union of the electronic, vibrational and configurational components of the energy of a molecule as a single whole, as a general measure of various types of interaction [3]. This enabled calculating the processes of ordering in alloys of multicomponent systems by statistical methods; the regularities of the formation of short-range order of chemical bonding in melts by quantum chemical methods; redistribution of electron density and dissociation energy of nonequivalent chemical bonds in ternary systems by methods of microscopic theory using solutions of inverse problems and molecular models [4-5].

Here, the original model of quantum mechanics changed (the model of the hydrogen atom to the model of the hydrogen molecule) and the basis of the theory is no longer a one-center, but a two-center problem. In this regard, quantum chemistry is often called the theory of chemical bonding. Now quantum chemistry explains and implies various properties of crystals based on the electronic structure of molecules.

This work is devoted to the complex calculation of the parameters of the chemical bond of four Bi-Sb-Se-Te melts using solutions of inverse problems and molecular models.

I. Theoretical models of chemical bonding in ordered Bi-Sb-Se-Te alloys.

While constructing theoretical models of quaternary systems, it was primarily necessary to generalize the results of theoretical studies of both individual initial components Bi; Sb; Se; Te; and binary and ternary alloys based on them. For this purpose, it was essential to obtain the dependences of the number of electrons *n* on the outer shell of an atom on the Fermi radius r_F by statistical methods and to combine empirical information about the properties of atoms and ionic radii based on the crystal chemical approach [4-5].

Analysis of such consideration showed that the functions that include the Fermi radii $r_F = f(n)$ and the equations that include the ionic radii R_{un} determine the electronic configurations of interacting atoms depending on the interatomic distances and the number of bonds formed by them. This gave grounds for considering r_F and R_{un} identical and denoting electronic ionic radii.by the symbol R_u.

The next stage of searching for the dependence of R_u on n is associated with the use of empirical criteria of electronegativity and polarizability, which made it possible to identify the relationship $\mathrm{tg}\,\alpha = \frac{\Delta \log R_u}{\Delta n}$, where α is the angle of inclination of the straight lines in the coordinates $\log R_u = f(n)$.

Good agreement of experimental data on the physicochemical properties of atoms and their ions with the values of R_u and $\mathrm{tg}\,\alpha$ gives the dependence [5-6]:

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

Where $R_{UA}^{(0)}$ are radii of atoms A in the unexcited state, and x is valence.

Despite the imperfection of empirical criteria from a theoretical point of view, their positive role is beyond doubt. Generalization of experimental data through their quantum interpretation can provide important information concerning the nature of interatomic interactions. The availability of such information allows the formation of rheological models at the junctions of different sections of physics, chemistry, mathematics and other sciences. Such models reflect irreversible processes; viscosity anomaly; residual deformations during extrusion; formation of a chemical bond in solid solutions during peritectic reactions. Furthermore, the relationship between stresses and deformations and their changes in time are also considered indirectly, through other parameters of complex systems.

The above-mentioned advantages of such multifactor models can be successfully applied while solving technological problems. For example, the use of ionic radii to describe the processes of chemical bond formation by valence shell rearrangements enabled writing equation (1) in the form [4-5]:

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

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

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

Where d_l is internuclear distance A-B, equal to the sum of the ionic radii.

System (2)-(4) considers the geometric conditions of contact of spherical electron clouds with different density levels at the boundary. From the position of the crystal-chemical approach, the presence of d_{min} and the values of effective charges for $d_l > d_{min}$ is justified by the increase in the internuclear distance when the ionicity and covalence are changed between the same parameters.

The main disadvantage of this approach is that in many cases the internuclear distances (A-B) are less than the values of d_{min} which makes it impossible to calculate the ion charge according to such a scheme. Additional conditions are required to translate system (2)-(4) written from the position of the crystal-chemical approach into the language of quantum chemistry. To do this, it is necessary to take into account that during the formation of a chemical bond, the spherical symmetry of the electron density of the initial components is broken by the transition of electrons to other directions of interatomic interaction and this bond becomes donor. This is done under the condition that the removal (+Δe) or localization (-Δe) of electrons in a given direction of the chemical bond equally changes the value of the charges that this pair has at $d_l = d_{min}$, i.e.

$Z_{e\varphi}A(B) = Z_{min}A(B) + (\frac{\Delta e}{2})$. Thus, we obtain a new system of equations.

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

$$log\, R_{UA}^{ZA} = log\, R_{UA}^{(0)} - (Z_{min}A + \frac{\Delta e}{2})\, tg\, \alpha_A, \tag{6}$$

$$log\, R_{UB}^{ZB} = log\, R_{UB}^{(0)} - (Z_{min}B + \frac{\Delta e}{2}) x\, tg\, \alpha_B, \tag{7}$$

Replacing x in equations (2), (3) with $(Z_{min} + \frac{\Delta e}{2})$ changes the physical meaning of system (2)-(4): if the function $d_l = f(Z_{e\varphi})$ according to (2)-(4) is calculated in the approximation ($Z_A = -Z_B$) and is correct from a quantum point of view at $d_l = d_{min}$, which is enough for system (5)-(7) to be solved at a known d1. Thus, it was possible to find the dependence of the chemical bond parameters on the interatomic distances, to find the conditions for the formation of donor and acceptor effects by redistributing the electron density for each group of chemical bonds. In addition, taking into account the quantum interpretation allowed us to obtain an analytical expression for the dissociation energy of the chemical bond in the form:

$$D_{A-B}^{(i)} = \left(\frac{c_1 (R_{UA}^{(0)} + R_{UB}^{(0)})}{\mathrm{tg}\,\alpha_A + \mathrm{tg}\,\alpha_B}\right)\left(\frac{c_2 d_i}{d_i^2 - R_{UA} R_{UB}} - \frac{1}{d_i}\right), \tag{8}$$

Table 2.

Effective radii R_i, effective charges Δq_i, and dissociation energies at interatomic distances d_i Bi-Bi.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$d_i(A^0)$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$R_{UBi}(A^0)$	1.35	1.4	1.45	1.5	1.55	1.6	1.65	1.7	1.75
Δq	1.2037	0.9715	0.7473	0.531	0.321	0.12	-0.078	-0.0269	-0.442
$D(\varphi_i)(ev)$	2.96	2.854	2.755	2.663	2.578	2.497	2.421	2.35	2.283

Table 3.

Effective radii R_i, effective charges Δq_i, and dissociation energies at interatomic distances d_i Se-Se.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$d_i(A^0)$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$R_{USe}(A^0)$	1.35	1.4	1.45	1.5	1.55	1.6	1.65	1.7	1.75
Δq	0	-0.1795	-0.353	-0.52	-0.68	-0.84	-0.99	-1.14	-1.28
$D(\varphi_i)(ev)$	1.894	1.827	1.763	1.705	1.65	1.598	1.55	1.504	1.461

Table 4.

Effective radii R_i, effective charges Δq_i, and dissociation energies at interatomic distances d_i Sb-Sb.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$d_i(A^0)$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$R_{USb}(A^0)$	1.35	1.4	1.45	1.5	1.55	1.6	1.65	1.7	1.75
Δq	0.42	0.206	0	-0.2	-0.391	-0.578	-0.758	-0.934	-1.1
$D(\varphi_i)(ev)$	2.42	2.333	2.252	2.177	2.107	2.041	1.98	1.921	1.87

Table 5.

Effective radii R_i, effective charges Δq_i, and dissociation energies at interatomic distances d_i Te-Te.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$d_i(A^0)$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$R_{UTe}(A^0)$	1.35	1.4	1.45	1.5	1.55	1.6	1.65	1.7	1.75
Δq	0.863	0.655	0.454	0.261	0.073	-0.108	-0.284	-0.455	-0.62
$D(\varphi_i)(ev)$	2.551	2.46	2.374	2.295	2.221	2.152	2.087	2.025	1.968

Where $R^{(0)}_{UA(B)}$, $tg\,\alpha_{A(B)}$ are coefficients of equation (2)-(4) for atoms A and B; R_{UA} and R_{UB} are effective radii of ions in bonds (A-B) of length d_i; I is the number of non-equivalent hybrid orbitals φ_i of each group of chemical bonds (A-B): C_1 is a coefficient reflecting the relationship of the dimensional parameters of the interatomic interaction (measured in electron volts); C_2 is a coefficient dependent on the crystal structure and chemical bond and is chosen to be dimensionless

It should also be noted that the value of the coefficient C_1 in all processes is constant. As for the coefficient C_2, it can be specified as additional factors that form the structure of the material are further taken into account. In this work, the coefficients C_1 and C_2, in the first approximation, were chosen equal to unity. The results of the calculations of the chemical bond parameters carried out in this work are presented in tables 1-11.

The effective charges (Δq_i), effective radii Rui and dissociation energies for the nearest neighbors at different interatomic distances d_i ($1 \le i \le 9$) of the structural modifications of bismuth, selenium, antimony and tellurium are given in Tables 2–5.

As follows from the results given in tables (2)-(5), with increasing interatomic distances, the dissociation energy of the corresponding chemical bonds decreases, and the redistribution of the electron density Δq_i changes sign differently, so for Bi-Bi bonds the sign changes in the interval $3.2 \le d_i \le 3.3$; for Te-Te bonds it is in the interval $3.1 \le d_i \le 3.2$; for Sb-Sb bonds the interval is $2.9 \le d_i \le 3$; for Se-Se bonds within the interval $2.7 \le d_i \le 2.8$;

Table 1.

Coefficients of equations (1-4) of the initial components

Z	**Elements**	$R^{(0)}_U(A^0)$	$tg\,\alpha$
83	Bi	1.63	0.068
52	Te	1.57	0.076
51	Sb	1.45	0.074
34	Se	1.35	0.088

This means that under certain conditions these bonds can be both donor and acceptor, which in turn confirms the experimentally established fact that these elements can have different oxidation states and can exhibit electronic properties in melts[1-2].

As for the above parameters for the compounds Bi-Sb; Bi-Se; Te-Se; Sb-Se; Sb-Te; Bi-Te; they are given in tables 6-11.

As for the compounds Bi-Te: Bi-Se; Bi-Sb; Sb-Te; Sb-Se; Te-Se; with the increase in interatomic distances, the redistribution of electron density also occurs in them and electronic properties can manifest themselves in melts as metallizing liquids and semiconductors with one- and two-sided delamination [1-2].

The obtained results of calculations of effective charges, effective radii, and dissociation energies are in good agreement with the results of thermal rearrangement

Table 6.

Effective radii R_i, charges Δq_i, and dissociation energies at interatomic distances d_i Bi-Sb.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$\mathbf{d_i}(\mathbf{A^0})$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\mathbf{R_U^{Bi}}(\mathbf{A^0})$	1.435	1.485	1.54	1.59	1.64	1.69	1.74	1.79	1.84
$\mathbf{R_U^{Sb}}(\mathbf{A^0})$	1.265	1.315	1.36	1.41	1.46	1.51	1.56	1.61	1.66
$\mathbf{\Delta q}(\varphi_i)$	0.8	0.58	0.37	0.15	-0.05	-0.25	-0.4	-0.6	-0.8
$\mathbf{D}(\varphi_i)(\mathbf{ev})$	2.664	2.569	2.48	2.4	2.322	2.25	2.182	2.119	2.06

Table 7.

Effective radii R_i, charges Δq_i, and dissociation energies at interatomic distances d_i Bi-Se.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$\mathbf{d_i}(\mathbf{A^0})$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\mathbf{R_U^{Bi}}(\mathbf{A^0})$	1.495	1.545	1.59	1.65	1.69	1.74	1.78	1.83	1.88
$\mathbf{R_U^{Se}}(\mathbf{A^0})$	1.205	1.255	1.31	1.35	1.41	1.46	1.52	1.57	1.62
$\mathbf{\Delta q}(\varphi_i)$	0.55	0.35	0.15	-0.08	-0.22	-0.4	-0.57	-0.75	-0.9
$\mathbf{D}(\varphi_i)(\mathbf{ev})$	2.322	2.242	2.168	2.094	2.031	1.97	1.914	1.858	1.806

Table 8.

Effective radii R_i, charges Δq_i, and dissociation energies at interatomic distances d_i Te-Se.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$\mathbf{d_i}(\mathbf{A^0})$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\mathbf{R_U^{Te}}(\mathbf{A^0})$	1.46	1.51	1.56	1.61	1.66	1.71	1.76	1.8	1.85
$\mathbf{R_U^{Se}}(\mathbf{A^0})$	1.24	1.29	1.34	1.39	1.44	1.49	1.54	1.6	1.65
$\mathbf{\Delta q}(\varphi_i)$	0.4	0.2	0.05	-0.15	-0.32	-0.5	-0.67	-0.84	-0.98
$\mathbf{D}(\varphi_i)(\mathbf{ev})$	2.179	2.102	2.03	1.964	1.902	1.843	1.788	1.738	1.687

Table 9.

Effective radii R_i, charges Δq_i, and dissociation energies at interatomic distances d_i Sb-Se.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$\mathbf{d_i}(\mathbf{A^0})$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\mathbf{R_U^{Sb}}(\mathbf{A^0})$	1.404	1.45	1.5	1.545	1.591	1.638	1.684	1.732	1.779
$\mathbf{R_U^{Se}}(\mathbf{A^0})$	1.296	1.35	1.4	1.455	1.509	1.562	1.616	1.668	1.721
$\mathbf{\Delta q}(\varphi_i)$	0.2	0	-0.2	-0.37	-0.55	-0.72	-0.89	-1.04	-1.2
$\mathbf{D}(\varphi_i)(\mathbf{ev})$	2.13	2.054	1.983	1.918	1.852	1.8	1.745	1.694	1.646

Table 10.

Effective radii R_i, charges Δq_i, and dissociation energies at interatomic distances d_i Sb-Te.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$\mathbf{d_i}(\mathbf{A^0})$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\mathbf{R_U^{Sb}}(\mathbf{A^0})$	1.3	1.345	1.392	1.44	1.49	1.535	1.58	1.63	1.68
$\mathbf{R_U^{Te}}(\mathbf{A^0})$	1.4	1.455	1.508	1.56	1.61	1.665	1.72	1.77	1.82
$\mathbf{\Delta q}(\varphi_i)$	0.63	0.435	0.23	0.0045	-0.16	-0.35	-0.52	-0.69	-0.86
$\mathbf{D}(\varphi_i)(\mathbf{ev})$	2.481	2.392	2.308	2.232	2.161	2.093	2.029	1.97	1.913

Table 11.

Effective radii R_i, charges Δq_i, and dissociation energies at interatomic distances d_i Bi-Te.

Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9
$\mathbf{d_i}(\mathbf{A^0})$	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\mathbf{R_U^{Bi}}(\mathbf{A^0})$	1.39	1.438	1.48	1.535	1.58	1.63	1.68	1.728	1.77
$\mathbf{R_U^{Te}}(\mathbf{A^0})$	1.31	1.362	1.42	1.465	1.52	1.57	1.62	1.672	1.73
$\mathbf{\Delta q}(\varphi_i)$	1	0.8	0.6	0.4	0.2	0	-0.2	-0.36	-0.54
$\mathbf{D}(\varphi_i)(\mathbf{ev})$	2.74	2.643	2.552	2.467	2.388	2.314	2.262	2.178	2.116

of atoms during the formation of short-range chemical bond order in the systems Bi-Te: Bi-Se; Bi-Sb; Sb-Te; Sb-Se; Te-Se;[3]

Conclusions

The comprehensive approach to technological problems ensured developing theoretical models that combine generalized experimental information and theoretical approaches and describe the processes of interatomic interaction formation from the standpoint of chemical bonding.

The novelty ofthe work is that quaternary systems in the context of existing experimental and theoretical studies of the initial components, binary compounds and alloys based on them using triangulation methods, molecular models and inverse problems were considered for the first time.

The results presented can be used in the development of technological modes for obtaining new thermoelectric materials based on the quaternary systems Bi-Sb-Se-Te; expand technological capabilities when considering phase transformations influenced by factors such as the destruction of existing chemical bonds and the formation of new ones; enable the calculation of the influence of the composition of the initial components on the formation of nuclei of a new phase; the effect of the distribution of phase components on the physical properties of the resulting materials.

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Теоретичні моделі хімічного зв’язку в розплавах термоелектричних матеріалів на основі Bi-Sb-Se-Te

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Розроблено комплексний підхід для побудови теоретичних моделей упорядкованих сплавів четвірних систем термоелектричних матеріалів. Проведено розрахунки ефективних зарядів, ефективних радіусів, перерозподілу електронної густини, енергії дисоціації нееквівалентних гібридних орбіталей (НГО) в системі Bi-Sb-Se-Te в залежності від міжатомних віддалей, типу кристалічної структури та хімічного зв’язку. Отримані результати можуть бути використані при розробці технології одержання нових термоелектричних матеріалів на основі Bi-Sb-Se-Te.

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