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PECULIARITIES OF ELECTRONIC STRUCTURE
OF HYBRID ORBITALS AND INTERATOMIC INTERACTION
IN CADMIUM ANTIMONIDE CRYSTALS

This paper reports on the development of method and results of calculating parameters of electronic structure of hybrid orbitals corresponding to nonequivalent interatomic distances in cadmium antimonide crystals. On the basis of quantum-mechanical approach, calculations were made of effective charges, effective radii, as well as of the redistribution of electron density and dissociation energy of nonequivalent hybrid orbitals which can be used in the development of new CdSb-based materials with predicted properties.

Key words: nonequivalent hybrid orbitals, effective radii, effective charges, dissociation energies.

Introduction

Cadmium antimonide is a thoroughly studied semiconductor compound which is widely used in electronic equipment, and solid solutions on its basis are promising for application in thermoelectricity. The need for integrated research is due to the fact that the effect of interatomic interaction on the dynamics of chemical bond formation in low-symmetry crystals of rhombic syngony is poorly known.

In this connection, prediction of thermoelectric properties of *CdSb*-based semiconductor compounds by theoretical analysis of their electron structure is a strategic objective of materials science.

It should be noted that the attempts to create a quantitative method for calculating parameters of substance electronic structure on the basis of either strict quantum mechanical or empirical approach have not met with a success so far.

The experience of using different models taking into account concepts that are necessary for the construction of a theory shows that qualitatively new concepts should be introduced into statement of problem. To formulate them logically and mathematically, omitting generalization of experimental data does not seem possible.

Preliminary work on such generalization made within empirical approach [1 – 3] has shown that independent development of theoretical and empirical approaches must give way to a mixed method combining the advantages of quantum-mechanical method and the experience of crystal-chemical ways of studying the electronic structure of substance.

A combination of two different approaches in a single quantitative method is not a mechanical summation of any concepts or computational tricks. Theoretical comprehension of numerous empirical dependences is related to revision of established views, which is not always the result of development of the existing theories, and often denies some of them. Therefore, the way to solving the problem lies through analysis of empirical material and quantum-mechanical description of the relationship between the properties of elements and the compounds formed by them.

Quantum-chemical models of electronic structure of elements and their compounds

According to quantum mechanics [4], analysis of electron density distribution reduces to calculation of wave function ψ the square of which ψ^2 determines the possibility of electron position in the given region of the atom. A description of change in the values of ψ^2 depending on the distance r to the nucleus yields information on electron cloud distribution, summarizing qualitatively in a new fashion the data on individual characteristics of electrons. Different form of their orbitals affects electron binding forces with a nucleus, allowing the use of the Fermi statistics according to which the probability of filling any state in the atom with energy E:

$$f(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_F}{kT}\right)}, \qquad (1)$$

where E_F is the Fermi energy corresponding to $f(E_F) = 1/2$; k is the Boltzman constant; T is the absolute temperature/

Taking all this into account, in [5] it was assumed that at known dependences $\psi^2 = f(r)$ for any element with different ionization degree, as well as at certain values of ψ_F^2 and r_F (Fermi radii) the dependence of r_F on the number of electrons n in the orbitals characterizes electron configurations of interacting atoms depending on the length and number of the bonds they formed.

Attempts to connect together and generalize the analysis of versatile empirical information on the properties of atoms and their ions based on experience, as well as the existing theories and traditions of crystal-chemical approach were made in different scientific works. Thus, in $[1-3]$, a study was conducted on the relationship between electronic properties and structure of semiconductor melts with the diagrams of state, classification of melts was made according to character of chemical bond. In $[5-7]$, the empirical information on the properties of elements and the electronic structure of their compounds was analyzed from the standpoint of non-polarized ion radii R_{UH}. It was shown that both functions $r_F = f(n)$ and equations relating R_{UH} to the charge of ions allow solving the same problem, namely to determine electronic configurations of interacting atoms depending on the length and number of the bonds they formed.

Thus, the necessity of construction of semi-phenomenological equations relating the value of R_U to the number of electrons n in atomic orbitals follows from the analysis of complications of modern quantitative theories of interatomic interaction.

The specific shape of such equation systems and their solutions will depend on the half-empirical concepts which will be involved. The simplest relationships were obtained by postulating the key dependence: with a change in the number of electrons in the outer shell of atom, the logarithm of its Fermi radius changes by rectilinear law [5]. In the search for graphical solution of the problem on the relation between R_U and n, the numerical values of electronegativities turned out to be the most useful. The relationship between the slope ratio of rectilinear dependences of logarithm R_U on n $\operatorname{tg}\alpha = \dfrac{\Delta \lg R_U}{\Delta n}$ and electronegativity rules out the possibility of arbitrary variation of compared values.

A good agreement between the set of experimental data on various physical and chemical properties of atoms and their ions and the values R_U and $\operatorname{tg}\alpha$ is provided by the dependence

postulated in [6]:

$$\lg R_{UA}^{x} = \lg R_{UA}^{\text{o}} - x \, \text{tg} \, \alpha, \tag{2}$$

where R_{UA}^{o} is radius of nonexcited-state atom, and x is valence.

Coefficients R_{UA}^{o} and $\text{tg} \, \alpha$ of (2)-type equations regularly change depending on the element position in periodic table.

Thus, the utility of (2)-type equations is determined by how much their use helps to avoid difficulties in modern theories of chemical bond and to obtain rather accurate and physically meaningful description of the results of interatomic interaction.

Chemical bond formation is accompanied by reconstruction of valence electron shells of interacting atoms owing to which spherical symmetry of their electron clouds is violated. However, with any type of bond the redistribution of electrons is performed so as to assure the continuity and smoothness of wave function which mates their ion cores.

As long as equations (2) describe a change in R_U of A and B atoms with a change in the number of electrons in the orbitals of each atom, the problem reduces to formulation of the condition of equality of ψ_A^2 and ψ_B^2 at point of $\psi_{\min}^2$ with any length of A-B bond.

On the assumption of equality of the absolute values of charges of interacting atoms, dependence (2) takes on the form of the system:

$$\lg R_{UA}^{+x} = \lg R_{UA}^{\text{o}} - x \text{tg} \alpha_A \tag{3}$$

$$\lg R_{UB}^{-x} = \lg R_{UB}^{\text{o}} + x \text{tg} \alpha_B \tag{4}$$

$$d_l = R_{UA}^{+x} + R_{UB}^{-x} \tag{5}$$

From the standpoint of quantum-mechanical approach to solution of chemical bond problem the system of equations (3) – (5) formally considers geometrical conditions of contact of spherical electron clouds with different density level at their boundary, i.e. $\psi_{\min A}^2 + \psi_{\min B}^2$. In so doing, a complicated process of reconstruction of electron shells of interacting atoms reduces to transfer of electrons from the orbitals of one atom to the orbitals of the other. Therefore, additional criteria are needed which will enable crystallochemical system of equations (3) – (5) to be put in terms of quantum chemistry.

For this purpose it was necessary to analyze a dependence of interatomic distances on effective charges: $d_l = f\left(z_{eff}\right)$. It turned out that at any point of this dependence, except for $d_l = d_{\min}$, the density of states at the boundaries of ions is different. Moreover, to determine effective charges and corresponding effective atomic radii, in the bonds with $d_l < d_{\min}$ it remains to use $d_{\min}$ as parameters of the moment from which formation of (A-B) bond is accompanied by electron escape to other directions of interatomic interaction, i.e. the bond becomes donor. The values z_{eff} of atoms must be changed so as to assure the equality of density of states at the boundaries of corresponding atoms. This condition can be fulfilled in the case when removal of electrons ($+\Delta q$) or their localization ($-\Delta q$) in given bond direction equally change the values of charges that the given pair of atoms has at

$d_l = d_{\min}$, i.e. $z_{effA(B)} = z_{\min A(B)} + \left(\dfrac{\Delta q}{2}\right)$.

Conditions of preserving wave function continuity in the zone of ion core interface of interacting atoms with this approach are given by equation system [6]:

$$d_1 = R_{UA}^{ZA} + R_{UB}^{ZB} \tag{6}$$

$$\lg R_{UA}^{ZA} = \lg R_{UA}^{o} - (z_{\min_A} + \Delta q / 2) \cdot \mathrm{tg}\alpha_A \tag{7}$$

$$\lg R_{UB}^{ZB} = \lg R_{UB}^{o} - (z_{\min_B} + \Delta q / 2) \cdot \mathrm{tg}\alpha_B \tag{8}$$

In outward appearance, systems of equations (6) – (8) and (3) – (5) do not differ in principle, but in reality substitution of x value by $(z_{\min_{A(B)}} + \Delta q / 2)$ changes their physical meaning. Function $d_1 = f(z_{eff})$, calculated in conformity with traditions of crystallochemical approach $(x_A = -x_B)$, is correct from quantum-mechanical standpoint only at $d_1 = d_{\min}$, but this is enough for equation system (6) – (8) to be solved at known d_1.

This is the basis for derivation of the principles of using nonequivalent hybrid orbitals for the description of interatomic interaction and construction of rigid traceability charts of electron structure parameters and physico-chemical properties of the resulting compounds. This formulation of the problem brings to the forefront the regularities of decoding electron configurations of atoms along the length of the bond they formed. At the same time, in terms of nonequivalent hybrid orbitals, the type of structure and a set of interatomic distances must be the function of individual properties of interacting atoms. From this generalizing description follows that the difference in chemical bond nature (in terms of donor and acceptor determination in $A - B$ pair) is a consequence of the action of uniform for all compounds regularities of electrons redistribution between partners to assure the continuity of wave function ψ.

The possibility of obtaining equations (6) – (8) opens up wide prospects for solution of prediction problems.

Also, the value of this information is that to obtain equations (6) – (8), it is sufficient to study the structure of two representatives of compound-analogs group, and for the rest of its members the necessary information can be obtained by calculation. Moreover, such calculations become relevant due to the fact that the boundaries of homogeneity area of defective phases are determined by the strength of their interatomic bond, and the possibilities of solving such problems on the basis of nonequivalent hybrid orbitals theory have not yet been studied.

Effective charges and effective radii of atoms of nonequivalent chemical bonds in cadmium antimonide crystals

The specific feature of chemical bond in *CdSb* crystals is the fact that cadmium sublattice and antimony sublattice are displaced relative to each other. In so doing, each *Cd* atom in its immediate surrounding has three *Sb* atoms and one *Cd* atom, and each *Sb* atom has three nearest *Cd* atoms and one *Sb* atom. There are five nonequivalent chemical bond components altogether, which differ both in the interatomic distances and in the composition of components. Analysis of chemical bond models is given in [8].

To solve the formulated problem, it was necessary to write the system of equations (6) – (8) for each *i*- th nonequivalent hybrid orbital, and then by solving the inverse problem using known

interatomic distances d_i $(1 \leq i \leq 5)$ to find $R_{U_{Cd}}, R_{U_{Sb}}, \Delta q$.

A system of logarithmic transcendental equations was solved by variation method. An error $\varepsilon \geq d_i^{exper} - d_i^{theor}$ was specified which in our case for all $1 \leq i \leq 5$ did not exceed 0.01 %. The accuracy of calculations was restricted by the accuracy of experimental methods of finding interatomic distances.

The $\mathrm{tg}\alpha_{Cd}$ and $\mathrm{tg}\alpha_{Sb}$ necessary for generation of equation systems $(6) - (8)$ were found by the method of [5]. As a result of calculations, the numerical values were obtained:

$$\mathrm{tg}\alpha_{Cd} = 0.095; \qquad\qquad \mathrm{tg}\alpha_{Sb} = 0.076. \qquad\qquad (9)$$

For the correct use of the formalism of nonequivalent hybrid orbital method, in the numerical calculations of this work a diagram $d_i = f(z_i^{eff})$ was constructed.

The figure shows a dependence of interatomic distances d_i of c $\varphi_i(Cd_x - Sb_{-x})$ bonds (in angstroms) on the efffective charges x in the range of $-4 < x < 4$ As follows from the results, the minimum on this dependence is realized at $d_{min} = 2.9271$ Å, which exceeds real interatomic distances along the bonds $\varphi_1(Cd - Sb), \varphi_2(Cd - Sb)$ and $\varphi_3(Cd - Sb)$. A similar situation is also observed for the bonds $\varphi_4(Sb - Sb)$ and $\varphi_5(Cd - Cd)$. All this necessitated the recalculation of effective charges for each bond.
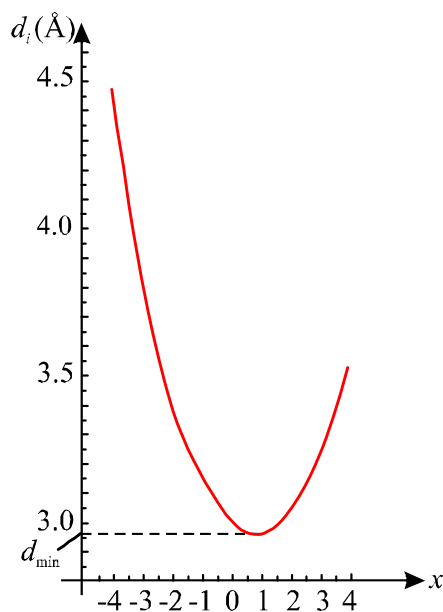

Fig. Dependence of length d_i on the effective charges x
of Cd and Sb bond $\varphi_i(Cd_x - Sb_{-x})$.

Then, with regard to the above remarks, calculations of $R_{USb}^i, R_{UCd}^i, \Delta e_i$ were performed for nonequivalent hybrid orbitals $1 \leq i \leq 5$. The advantage of this approach is that in a simple and uniform form for each compound type it generalizes information not only on the interatomic distances, but also on the parameters of electronic structure, i.e. at known $\mathrm{tg}\alpha$ and R^0 a replacement of R_{UA} and R_{UB} by expressions $(7) - (8)$ makes it possible to calculate $\Delta q, z_{eff}, R_{U_{eff}}$ and d_1. From such generalizing

description it follows that the difference in chemical bond nature (from the standpoint of determination of donor and acceptor in $(A - B)$ pair which is commonly referred to as "valence") results from the action of uniform for all compounds regularities of electrons redistribution between partners to assure the continuity of wave function. In so doing, the value of accurate quantitative picture increases due to the fact that the dependences of dissociation energy of chemical bonds $D = f(R_{UA} / R_{UB})$ have a clear physical meaning, since the ratio R_{UA} / R_{UB} determines the position and absolute value of ψ_{min} in the inter-nuclear space.

Therefore, derivation of semi-empirical dependences that can be used to calculate bond energies between inhomogeneous atoms in dimensional molecular groups can be considered as one of important problems in nonequivalent hybrid orbital theory. The possibility of uniform physical interpretation of similar equations will be largely determined by achievements in the description of interaction of individual characteristics of atoms with the types and periods of structures formed by them. The results of study on interatomic interaction in compounds differing in stoichiometry, structure, supposed type of chemical bond and physical-chemical properties, give grounds to state that the use of nonequivalent hybrid orbitals for the description of conditions for wave function continuity between bond partners allows us to proceed to solving the tasks of prediction problem in materials science.

Thus, due to account of quantum-mechanical interpretation of empirical data by combining the concepts of different approaches – logically mathematical and experimental – in a uniform quantitative method for calculation of parameters of substance electronic structure, the authors of this work were able to describe the dependence of bond energies of nonequivalent hybrid orbitals on their lengths and electronic configurations of interacting atoms in low-symmetry crystals of cadmium antimonide in one general expression:

$$D_{A-B}^{(j)} = \frac{c_1(R_{UA}^o + R_{UB}^o)}{(tg\alpha_A + tg\alpha_B)(\dfrac{1}{d_j} - \dfrac{c_2 d_j}{d_j^2 - R_{UA}R_{UB}})}, \qquad (10)$$

where R_{UA}^o and $tg\alpha_{A(B)}$ are coefficients of equations (3) – (4) for A and B atoms, and R_{UA} and R_{UB} – effective radii of their ions in $(A\text{-}B)$ bond of length d_j $(1 \le j \le 5)$.

Constants c_1 and c_2 are chosen from the following considerations: c_2 is a coefficient depending on the type of crystalline structure and reflecting quantitative relation between coefficients $tg\alpha_A$ and $tg\alpha_B$ from equations (3) – (4) and the values (R_{UA} / R_{UB}). Therefore, when solving a self-consistent variation problem, as a first approximation, c_2 is chosen equal to $c_2 \approx 0.5$ and for different compositions it can lie within $0 < c_2 < 1$. c_1 is a coefficient showing a relationship between the dimensional and energy characteristics of interatomic interaction, such as ionization potentials, screening effects, electronegativity with effective radii and interatomic distances. In case of using non-system units, when the energy is measured in electron-volts, and the distance in angstroms (Å), for all nonequivalent hybrid orbitals of *CdSb* c_1 takes on the value equal to $c_1 = 0.046$ eV $/(\text{Å})^2$.

Calculations performed according to (10) yielded numerical values of the bond energies of nonequivalent hybrid orbitals in *CdSb* crystals (which are also referred to as dissociation energies of nonequivalent hybrid orbitals). Results of calculation of effective radii of interatomic distances of electron density redistribution Δe, dissociation energy D_i are given in the table.

<u>*Table*</u>

Effective charges, effective radii and dissociation energies
of nonequivalent hybrid orbitals in CdSb crystals

φ_j / $R_{U,} \Delta l, D_j$	$\varphi_1(Cd-Sb)$	$\varphi_2(Cd-Sb)$	$\varphi_3(Cd-Sb)$	$\varphi_4(Sb-Sb)$	$\varphi_5(Cd-Cd)$
d_j^{exper} (Å)	2.84	2.91	2.81	2.81	2.99
d_j^{theor} (Å)	2.8398	2.9102	2.8104	2.81	2.9894
R_U^{Cd} (Å)	1.4408	1.4813	1.4239	–	1.4947
R_U^{Sb} (Å)	1.399	1.4289	1.3865	1.405	–
R_U^{Cd} / R_U^{Sb}	1.02988	1.03667	1.02697	1	1
Δq bond φ_j	0.21	0.086	0.263	0.185	0.05
D_j (eV)	6.78	6.95	6.71	7.598	6.414

As follows from the above results, the numerical values of dissociation energy of chemical bonds of bond energies of nonequivalent hybrid orbitals agree with the results of calculation of fine structure of chemical bond in [8 – 11] performed by methods of microscopic theory and inverse problems solutions. It is also noteworthy that the values of atomic constants, ionization potentials and affinity to electron were taken from [12].

Discussion of results

Analysis of the results obtained in the present study shows that calculations of parameters of electronic structure in low-symmetry crystals by the proposed method are different from those predicted by modern quantitative chemical bond theories. Dissociation energy of bond energies of nonequivalent hybrid orbitals in *CdSb* crystals depends on interatomic distances. With increasing interatomic distances, the interaction energy of atoms must decrease. At the same time, there is a change of electronic density on the bonds which can both amplify and weaken this effect.

What is meant here is not the refinement of quantitative estimates, but a qualitative change in the system of views on chemical bond nature which is related to rejection of one of commonly accepted concepts ($Z_A = -Z_B$) and increased attention to directional character of chemical bond.

Generalization of obtained information on the parameters of electronic structure (Z_{eff}, R_U, Δq) and its comparison to a set of physical and chemical properties (in our case to dissociation energy of bond energies of nonequivalent hybrid orbitals in *CdSb*) made it possible to identify the regularities that could be brought into a logically consistent and harmonious system only with quantum-mechanical approach.

Such a way of solving the problem holds out a hope that the imperfections of theoretical treatment of the issues raised in this paper will stimulate further study of the problems of quantitative description of interatomic interaction in low-symmetry crystals and superlattices on their basis.

Conclusions

1. On the basis of quantum-mechanical approach a method of using nonequivalent hybrid orbitals has been developed for the calculation of interatomic interaction in *CdSb* crystals.

2. Calculations were made of charge redistribution Δq on the nonequivalent hybrid orbitals characterizing formation of a bond, which is accompanied by escape of electrons to other directions of interatomic interaction, i.e. the bond becomes donor $(+\Delta q)$ or acceptor $(-\Delta q)$.

3. With regard to quantum-mechanical interpretation of empirical data, a method has been developed and calculations have been performed of dissociation energy of nonequivalent chemical bonds in *CdSb* crystals.

4. The results obtained in this paper agree with the results of chemical bond calculation by microscopic theory methods and can be used in the development of technological conditions for synthesis of new *CdSb* based materials with predicted properties.

References

1. D.P. Belotskii, O.N. Manik, On the Relationship between Thermoelectric Material Melts′ Properties and the State Diagrams 1.Regularires of Cleavage Manifestation in the State Diagrams, *J.Thermoelectricity* 1, 21 – 47 (1996).

2. D.P. Belotskii, O.N. Manik, On the Relation of Structure of Melts to the Diagrams of State in Thermoelectric Material. 2. Phase Changes and Electronic Properties of Melts, *J.Thermoelectricity* 2, 23 – 57 (1996).

3. D.P. Belotskii, O.N. Manik, On the Relationship between Electronic Properties and Structure of Thermoelectric Material Melts and the Diagrams of State. 3. Short-Range Structure and the character of Chemical Bond, *J.Thermoelectricity* 3, 3 – 24 (2001).

4. L.D. Landau, *Quantum Mechanics. Nonrelativistic Theory* (Moscow: Nauka, 1974), 752 p.

5. E.V. Prikhodko, On the Relationship between Thermodynamic Characteristics of Ions and Parameters of their Electronic Structure, *Izvestiya. Ferrous Metallurgy* 2, 1 – 4 (1991).

6. E.V. Prikhodko, On the Relationship between Thermodynamic Properties of Compounds and Parameters of their Electronic Structure, *Izvestiya. Ferrous Metallurgy* 8, 1 – 5 (1991).

7. E.V. Prikhodko, A.A. Rudenko, On the Effect of Component Effective Charges on Thermodynamic Properties of Oxide Melts, *Izvestiya. Ferrous Metallurgy* 6, 4 – 7 (1991)

8. I.V. Gutsul, O.N. Manik, T.O. Manik, Mathematical Models of Elasticity Theory and Chemical Bond in Low-Symmetry Crystals of Cadmium and Zinc Antimonides, *J.Thermoelectricity* 2, 18 –25 (2010).

9. O.M. Manik, I.V. Gutsul, T.O. Manik, A.I. Savchuk, V.R. Bilinsky-Slotylo, Structure-Energy Peculiarities of Se, Te, Sb and Fe Chemical Bond, *J. Thermoelectricity* 3, 29 – 34 (2011).

10. A.A. Ascheulov, O.N. Manik, and T.O. Manik, Volumetric Micro- and Nanostructures of Sensor Electronics Based on Low-Symmetry $A^{II}B^{V}$ Crystals, 4-th International Scientific and Technical Conference "Sensor Electronics and Microsystem Technologies", Abstracts (Ukraine, Odessa, June 28 – July 2, 2010), P.144.

11. O.M. Manik, T.O. Manik, and V.R. Bilinsky-Slotylo, Electron Structure and Dissociation Energies of Nonequivalent Chemical Bonds in *CdSb* and *ZnSb* Crystals, *Proc. of International Scientific and Technical Conference "Physico-Technological Problems of Information Transfer, Processing and Storage in Infocommunication Systems" (Ukraine, Chernivtsi, November 3-5, 2016),* P. 264.

12. *Chemical Bonds Dissociation Energy. Ionization Potentials and Affinity to Electron. Handbook.* Ed. by V.N.Kondratyev (AN SSSR Publ, 1962).

Submitted 18.11.2016