DETERMINATION OF THE BASE PARAMETERS OF SEMICONDUCTOR CUBIC CRYSTALS VIA THE LATTICE CONSTANT

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UDC 532
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Similarly to the Periodic Table of Elements (PTE), a method for the characterization of the principal parameters of diamond-like crystals, which is based on the single-valued function of the lattice constant L, is proposed. Using this approach, the dependences of basic crystal parameters, such as the forbidden gap energy E_g, coefficients of covalency, metallicity, and ionicity, melting temperature, T_m, microhardness, H, and electron affinity, X_{opt}, on the lattice constant has been proposed in the form of a monotonous exponential function, $F_n(L)$. The value of L can be calculated using the well-known values of the valence radii of elements, r_A, r_B (or the distances between the neighboring atoms, A and B, in a crystal) according to the formulas: $L = \frac{2}{\sqrt{3}} r_{AB}$, $r_{AB} = (r_A + r_B)$. The obtained dependences of the crystal parameters on L open the way to predict the crystal parameters of a number of new materials such as superhard nitrogen-borocarbon (BN_2C), nitrocarbon (C_3N_4), diamond-like nanohydrocarbon ($CH_x(sp^3/sp^2)$), etc., as well as narrow-gap multicomponent semiconductors such as SiGePb(Sn) and new nanosized materials.

1. Introduction

As is known, PTE was proposed by D.I. Mendeleev more than a century ago and has the exclusive influence on the development of the basic knowledge in physics, chemistry, and other fields of science, being based on the periodic structure of the electron orbits of atoms. At present, it would be desirable to possess a similar system (from the viewpoint of the systematization) for crystals. Such a system can be naturally based on the fundamental parameters of crystals which are the interatomic distances, $r_A + r_B$ or, in our particular case, the lattice constants, L.

However, the previous attempts to construct such a table were not successful. Even for the groups of crystals with coordinated valences ($N_{\rm don}(A) = N_{\rm acc}(B)$, where the atoms of types A and B form the crystal, any systematic dependence of crystal parameters (such as the energy gap E_g, etc.) on L was not observed [1,2].

Let us consider separately the groups of crystals with similar types of the lattice structure and their characteristics which are determined by the parameters of electron bands.

Below, we carry out the analysis for the crystals with diamond-like configurations, namely, with the fcc symmetry of a tetrahedral elementary cell. The monotonic dependence of some basic parameters such as the energy gap E_g, optical and electrical characteristics, melting temperature T_m, and microhardness H on the lattice constant L, which is a well-determined crystal parameter, can be established in this case for single-component semiconductors. The value of the lattice constant L can be estimated with a reasonable accuracy from the reference values of the atomic valence radii of cubic crystals, r_v, according to the following formulas: for single-component crystals: $L = \frac{4}{\sqrt{3}} r_v$, for two-component crystals (of type AB): $L_{AB} = \frac{2}{\sqrt{3}} (r_{vA} + r_{vB})$, for three-component crystals (of type ABC): $L_{ABC} = \frac{4}{3\sqrt{3}} (r_A + r_B + r_C)$.

The latter case is represented by such new compounds as $Si_xC_{1-x}Ge_y$, $Si_xC_{1-x}Sn_y$, etc.

2. Analyses of the Basic Formulas of the Electron Theory of Crystals

The initial analysis of the energy band parameters of crystals of IV group of PTE (C, Si, Ge, and Sn) was carried out in a series of publications [3—12]. The electronic properties of fcc crystals with dominating valence and metallic bonds were analyzed in several approximations (LCAO, tight-binding pseudopotential, *ab initio* in the Carparinello approach) by many authors. An important general conclusion was drawn that the valence bond energy E_v and some other parameters have a similar monotonic dependence on the lattice constant L for all the crystals of elements of group IV of PTE (β-C, Si, Ge, Sn, SiC, SiGe) (Fig. 1). This dependence is also observed for a number of crystals of groups III—V with a relatively small part of ionic bonds (Fig. 2, curves *1, 2*). The physical reason for such a conclusion was that the energies of valence bonds are mainly determined by matrix elements of the interaction between the nearest atoms through the overlap of sp^3 hybrid orbitals. The

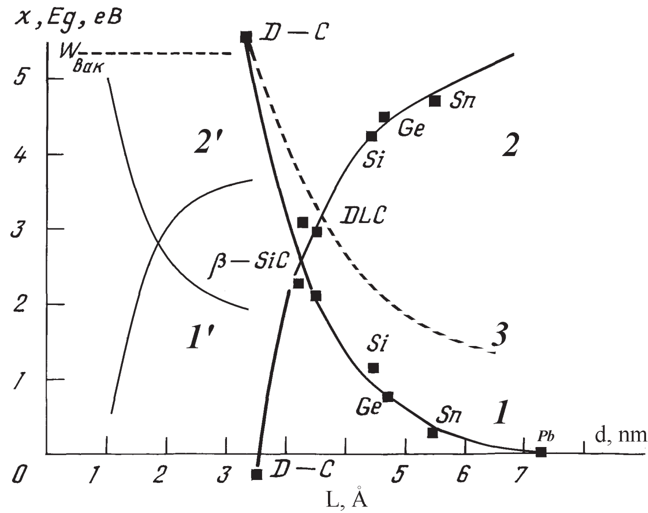

Fig. 1. Theoretical dependences of the energy gap, E_g (1), and the electron affinity, X (2), on the lattice constant, L, as well as the respective experimental data for different IV-group cubic crystals (points). Curves in the left part of the figure represent E_g and X versus the diameter for Si quantum dots

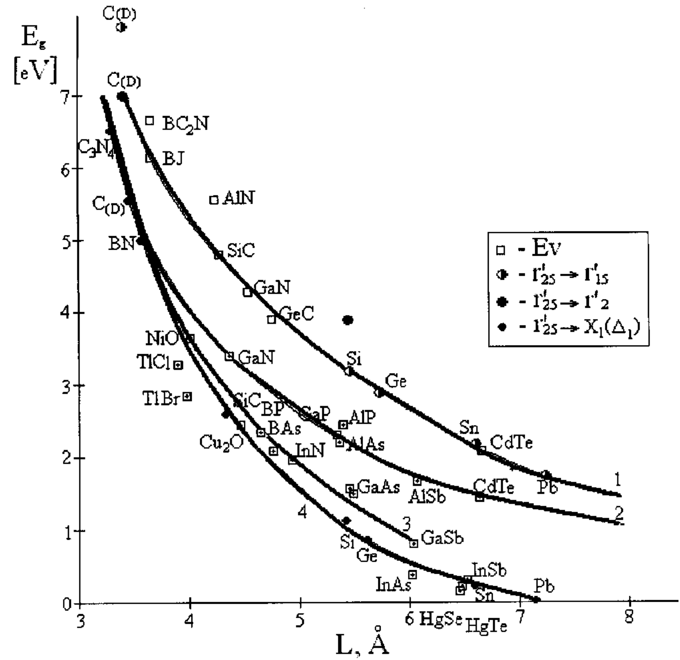

Fig. 2. Dependences of the valence matrix element energy, $V_v \sim 1/L^2$, and the energy gap, E_g, (differences between C and V bonds for direct interband transitions: $\Gamma_{25'} \rightarrow \Gamma_{15}$, $\Gamma_{25'} - \Gamma_{2'}$, and indirect transitions $\Gamma_{25'} - X(L)$), as functions of L. Open square dots — theoretical data from [10], black circles — for IV group of elements, and squares with points — experimental data on E_g for direct-gap crystals. Curve *1* — V_ν (L) $\sim 1/L^2$, $E_g(L) \sim 1/L^2$ (direct interband transition) — theoretical line for large polar crystals ($\alpha_i > 0.7$). Curve *2* — theory for $E_g = E_{gD}/L^2$, when the polarity growth is completely compensated by metallicity (i.e. for the middle polarity $\alpha_i < 0.5$, when $(1+\alpha_i^2)^{1/2}(1-\alpha_m) \cong 1$) (index D denotes the parameters for diamond). Curve *3* — general mechanism including valence, metallic, and small polar components $\alpha_i \leq 0.5$, which is typical of classical semiconductors. Curve *4* — combined energy gap $E_g = E_{gv}(1-\alpha_m) = E_{gv}^c \left(\frac{L_D}{L}\right)^2 \cdot \left(1-\left(\frac{L}{2L_0}\right)^2\right)$ calculated taking into account only valence and metallic bonds (nonpolar crystals)

Hamiltonian of this overlap, $H_{12} = \langle h^1|H|h^2\rangle$, determines the energy of valence bonds, V_v. Harrison and Pantelides were the first who proved a simple relation for valence bond matrix elements in the form $V_v \sim d^2$ [9, 10].

The minimization of the intrinsic energy can be realized through the secular matrix equation, in which different terms are related to different (by their origin) binding energies. If each atomic bond includes two electrons, then this state become rather stable.

The solution of the secular equation presents also the energy bands of an electron in the k-space. Under the relative weak hybridization of the s- and p-orbitals, they have the form [10]

$$E_v^P = \varepsilon_p + \sum_{x,y,z}^{3} V_v^* \cos(k_{x,y,z}a) \approx \varepsilon_p + 6V_{vi} = \varepsilon_p + V_v, \quad (1)$$

$$E_c^S = \varepsilon_s - V_v \sum_{i=1}^{6} e^{ik} r(i) = \varepsilon_s - V_v \quad (2)$$

for the center of bands, where $k = 0$. Here, the valence term arises due to the overlapping of the neighbor electron orbitals. For a hybrid state, it is necessary to change the separate orbital energies ε_s and ε_p by the energies of hybrid bonds $\varepsilon_h = \frac{1}{4}(\varepsilon_s + 3\varepsilon_p)$ (for elements ot group IV). Hence, the lower bonding states correspond to the valence band, and the upper antibonding ones do to the conduction band. Below, we limit ourselves by ground states with small k-vectors ($k \approx 0$, i.e. point $\Gamma(000)$ of the Brillouin zone), because this simple case includes the basic energy properties of cubic crystals. Then, the forbidden band is determined by two components of different origin [the valence bond V_v and metallic bond $V_m \sim (\varepsilon_s - \varepsilon_p]$:

$$E_g = E_c - E_v = (\varepsilon_p - \varepsilon_s) + V_v = V_v - 4V_m. \quad (3)$$

Below, we consider a general tendency in the changes of electron energy bonds for the diamond-like structures in the framework of tight-binding theory, using the concepts of the degrees of metallicity and ionicity (in addition to valence energy bonds).

The factor of metallicity always appears for hybrid bonds. From the physical viewpoint, it is determined by the splitting of the s- and p-terms of atomic orbits, ε_s and ε_p, during the formation of crystal solids. Here,

$$\varepsilon_s = \langle h_s|H|h_s^*\rangle, \quad \varepsilon_p = \langle h_p|H|h_p^*\rangle,$$

and the hybrid term

$$\varepsilon_h = (\overline{\varepsilon}_s + 3\overline{\varepsilon}_p)/4. \tag{4}$$

The values of ε_h, ε_s, ε_p for crystals differ slightly from those for molecules [10].

Ionicity appears only for the bonds between atoms of different types, A and B, or atoms of the same type but in different states in a crystal lattice. The values of ε_s and ε_p are known for all the atoms of the elements of the Periodic Table [8—13]. These values for the elements of semiconductor crystals can also be found in reference books [7, 10].

Metallic bonds appear due to the difference of energies in ε_s and ε_p states which results from the Pauli principle and is determined as follows:

$$E_m = V_m = -\langle h_s^1|H|h_p^1\rangle = \frac{-1}{4}(\varepsilon_p - \varepsilon_s) = -\frac{1}{4}\cdot\Delta\varepsilon_{sp}. \tag{5}$$

For two- or multicomponent compounds, we have

$$\overline{\varepsilon_s} = \frac{1}{n}\sum_i^n \varepsilon_s^i = \frac{1}{2}\left(\varepsilon_s^1 + \varepsilon_s^2\right),$$

$$\overline{\varepsilon_p} = \frac{1}{n}\sum \varepsilon_p^i = \frac{1}{2}\left(\varepsilon_p^1 + \varepsilon_s^2\right). \tag{6}$$

As is known, the values of ε_s are twice and more as large as the values of ε_p and increase monotonically from group I to group VIII for the same row. On the other hand, they slightly decrease with increase in the number of a row in the Periodic Table (by about 1.5 times passing from row 1 to row 6). Semiconductor materials are located in the columns of the middle part of PTE (IV, III—V, II—VI). In this region, the values of metallic bonds V_1 are nearly constant (Fig. 3) [10]:

$$E_m = V_m \approx -(1.8 \pm 0.25)\,\text{eV} \approx \text{const}. \tag{7}$$

On the other hand, the "factor of metallicity" depends substantially on L:

$$\alpha_m = V_m/\left(V_v^2 + V_i^2\right)^{\frac{1}{2}} \approx V_m/V_v \approx$$

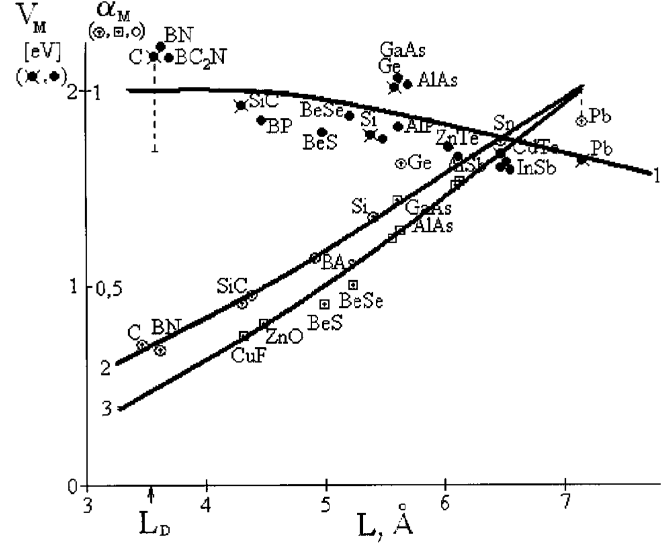

Fig. 3. Metallic bond matrix element energy, V_m, (circles), the degree of metallicity, $\alpha_m = V_m / V_v$ (tailed black circles), and the factor of metallicity, $\alpha_m = V_m/\left(V_v^2 + V_p^2\right)^{1/2}$ (crossed black dots) as functions of L. (The dots have been calculated using the formula [10] $V_m = (\varepsilon_p - \varepsilon_s)/4 \approx (1.8 \pm 0.2)$ eV, the solid line - by the expression $\alpha_m \approx (L/2L_D)^2$)

$$\approx 1.1\,(L/2L_D)^2 \approx L^2 \approx d^2 \tag{8}$$

(the last is true for nonpolar crystalls, when V_i=0 or is a lower value in comparison to V_v). Hence, the metallicity factor α_m of nonpolar or weakly polar materials can be therefore expressed by a simple quadratic function of the lattice constant L only: $\alpha_m \approx C''L^2$, where $C'' \approx 1.1\,(2L_D)^{-2}$, α_m increases proportionally to L^2 up to $\alpha_m \to 1$ for the materials with large interatomic distances, d, as shown in Fig. 3 (solid lines are theoretical curves at $C'' = (1/2\ L_D)^{-2}$, and the dots are calculated basing on the data on ε_s and ε_p from [10]).

The latter leads to the important prediction that the monotonous dependence of the energy gap on L is always observed for single-component semiconductor crystals with both the direct and indirect structures of electron bands, with only one parameter known, $C'' = (1/2\ L_D)^{-2}$:

$$E_g \approx 1.2E_v\,(1 - \alpha_m) = \frac{A}{L^2}\left(1 - 1.1\frac{L^2}{4L_D^2}\right),$$

$$A = 1.2 \times 7.6\,\text{eV}/\text{Å}^2. \tag{9}$$

As the metallicity reduces the energy of valence bonds, the value of α_m has to be subtracted in

formula (9). In particular, for large $L \sim 2L_D$ (L_D being the lattice constant of diamond), the factor $\left[1-\left(\frac{L}{2L_D}\right)^2\right] \to 0$, which leads to zero-gap materials. At $L > 2L_D$, the materials can even have "negative gaps" (see Fig. 2).

For the materials consisting of atoms of different types, the diagonal matrix elements of the Hamiltonian differ, and the heteropolar (ionic, polar) bonds appear. The energy of ionic bonds is equal to half the difference between the energies of anion, $\varepsilon_s^1, \varepsilon_p^1$, and cation states, $\varepsilon_s^2, \varepsilon_p^2$:

$$V_i^p = \frac{1}{2}\left(\varepsilon_p^1 - \varepsilon_p^2\right), \quad V_i^s = \frac{1}{2}\left(\varepsilon_s^1 - \varepsilon_s^2\right),$$

$$V_i^h = \frac{1}{2}\left(\varepsilon_h^1 - \varepsilon_h^2\right), \tag{10}$$

where V_l^h are the energies of the ionic bonds of hybridized orbits

$$\varepsilon_h = \frac{1}{4}(\varepsilon_s + 3\varepsilon_p). \tag{11}$$

The polarity of bonds is caused by the asymmetric redistribution of the wave functions of neighboring atoms, which is absent, of course, in single-component crystals with $\varepsilon_h^1 = \varepsilon_h^2$. A redistribution of the charge between the neighboring atoms is more substantial for the atoms with small radii than that for the atoms in the lower rows of PTE. The influence of polarity also becomes less important (Fig. 4) with increase in L. The values of V_p have to be added to the bonding (ε_b) energies and be substracted from the antibonding (ε_a) ones of valence bonds:

$$\varepsilon_b = \varepsilon_h - \left(V_v^2 + V_i^2\right)^{1/2}, \tag{12}$$

$$\varepsilon_a = \varepsilon_h + \left(V_v^2 + V_i^2\right)^{1/2}, \tag{13}$$

which results in the additional splitting of the conduction and valence bands [10,11]. So, the resulting energy gap has the following form [10, 11]:

$$E_g = \varepsilon_a - \varepsilon_b = 1.1\alpha\left(V_v^2 + V_i^2\right)^{1/2}(1 - 1.1\alpha_m). \tag{14}$$

The degree of covalence, metallicity, and ionicity (polarity) can be defined as follows:

$$\alpha_v = V_v/\left(V_v^2 + V_i^2\right)^{1/2}, \quad \alpha_i = V_i/\left(V_v^2 + V_i^2\right)^{1/2},$$

$$\alpha_m = V_m/\left(V_v^2 + V_i^2\right)^{1/2}. \tag{15}$$

The degree of the covalence of bonds can be expressed as

$$\alpha_v^2 + \alpha_i^2 = 1. \tag{16}$$

Both of these values can be calculated for various compounds, using the energies of atomic terms, $\varepsilon_s, \varepsilon_p$, which only slightly differ from these values for free atoms [10]. From this, it is possible to calculate the energy gap E_g for cubic crystals (i.e. the edge of optical absorption E_0 for direct-gap semiconductors) in the general case which includes three types of bonds, namely valence V_v, ionic (polar) V_i, and metallic V_m bonds [10,11] (Fig. 2):

$$E_g = 1.2V_v\left[1 + \frac{\alpha_i^2}{(1-\alpha_i)^2}\right]^{1/2}(1 - 1.1\alpha_m). \tag{17}$$

The degree of ionicity can also be presented in a simpler way using the Pauling principle for the difference of electronegativities, $\Delta X = X_A - X_B$ [7]. The table of X for different elements is well known, which allows us to calculate the ionicity of chemical bonds quite easily as

$$i = \left[1 - \exp\left(-\Delta X_{AB}/2\right)^2\right] \approx \Delta X^2/4, \tag{18}$$

$$\alpha_p = \sqrt{i} = \frac{\Delta X}{2}. \tag{19}$$

The general formula for the calculation of energy gaps can be represented in a rather simple analytic form as a function of L (or the interatomic distance) with only two parameters, L_D and ΔX:

$$E_{g\Sigma} = AV_v\left(1 + \alpha_i^2/(1-\alpha_i)^2\right)^{1/2}(1 - 1.1\alpha_m) \approx$$

$$\approx E_{gD}\left(\frac{L_D}{L}\right)^2\left(1 + i/\left(1 - i^{1/2}\right)^2\right)^{1/2}\left[1 - \left(\frac{L}{2L_D}\right)^2\right], \tag{20}$$

$i = \left(\frac{\Delta X}{2}\right)^2$ at $\Delta X \le 1$.

The correction factor A (due to the approximations used) was estimated to be $A \sim (1.2 \div 1.25)$ [10].

In the general case, the materials produced of elements belonging to different rows of the Periodic Table have larger polarity of bonds. If the value of α_i is rather small, $\alpha_i \le 0.4$, the correction in the term $\left(V_{2v}^2 + V_{3p}^2\right)$ is also comparatively small, about 10—15%. For greater values of α_i, $\alpha_i \ge 0.65 - 0.75$, the contribution of polarity in the formulas for the energy gap, E_g, becomes substantial, amounting to about 100% or even more (e.g., for CdTe, BeO, Cu-haloids, etc.). In the middle part of this figure, the data obtained using both approaches nearly coincide, $\alpha_i \sim 0.5 \pm 0.1$.

ISSN 0503-1265. Ukr. J. Phys. 2005. V. 50, N 10

3. Comparison with Experimental Data

Fig. 2 demonstrates the comparison of the results of calculations of the energy gap for more than 50 most important semiconductors (compounds of groups IV, III—V, and II—VI) using the general formula (17).

The crystals with small polarity, α_i, have always a monotonic dependence of the band gap on L close to that theoretically predicted. Selected points of the crystals with large polarity and rather small metallicity factor are located in the upper part of the figure, even higher than the curve obtained for the energy of covalent bonds, $V_v \sim 1/L^2$ (Fig. 2, curve *1*). In the region of intermediate values of α_i, the value of E_g follows approximately curve *2*:

$$E_g = V_v^D \left(L_D/L\right)^2 .$$

The comparison of the values of α_i calculated according to ε_s, ε_p (V_m, V_v, V_i) from the data on electronegativity as well as from differences of the radii of atoms ($r_a - r_k$) is shown in Fig. 4 versus ΔX. Besides α_i calculated by the general Pauling formula, the values of α_i calculated on the base of electron hybrid terms (the dashed line in Fig. 4) are presented for different semiconductor materials with cubic lattice. The compounds with a strong degree of metallicity have the smallest values of α_i (e.g., for InSb, $\alpha_i \sim 0.13$, $\alpha_m \sim 0.8$, etc.), while the large polarity is typical of semiconductors with a low degree of metallicity (e.g., for LiBr and AlN, $\alpha_i \sim 0.6{-}0.7, \alpha_m < 0.4$). The dependence V_i on L is more complex than that for the valence and metallicity components ($\sim L^n$) demonstrated above. Only for crystals with the same anion component, a rather slow monotonous decay $\alpha_i \sim 1/L^n$, $n < 1$, takes place, i.e. the behavior of $\alpha_i(L)$ is much more slower than those of $V_v(L)$ and α_m (L). Hence, for this group of crystals, the influence of polarity on the chemical bond energy becomes larger with increase in L. But, for the set with the same cations, the opposite dependence takes place. Hence, the universal dependences for α_i and V_i as functions of L do not exist, and these values have to be calculated from formula (18) or be taken from Fig. 5. In the middle part of this figure, the data obtained by both approaches almost coincide, and $\alpha_i \sim 0.5 \pm 0.1$).

Figs. 1—3 demonstrate the comparison of the general theoretical curves and experimental data for E_g.

Basic parameters of cubic crystals

Material	R_v, Å	L, Å	E_g, eV (E_{gv})	X, eV	H, GPa	ω_0, meV	T_m, K
β-C	$0,77 \times 2$	3,4	5,5	$\pm 0,5$	100	145	4300
Si	$1,18 \times 2$	5.4	1.1	4.3	18	30	1700
Ge	$1,39 \times 2$	6.0	0.7	4.6	12	25	1200
β-SiC	1.95	4.3	2.5	2.0	40	55	3000
GeC	2.6	4.8	1.5	4.0	25	40	2550
SiGe	2.57	5.7	0.9	4.4	14	28	1400
SiCGe	2.22	5.1	1.5	4,2	20	35	2100
SiC_2Ge	2.00	4.9	1.7	4,0	22	42	2500
Si_3N_4	1.8	4.1	3.5	2	55	55	3800
Si_2N_4Ge	1.8	4.3	2.4	4.1	40	55	3000
SiN_4Ge_2	2.16	5	1.2		21	36	2150
BN	1.68	3.75	4.2	+1	70—80	70	3600
β-BC_2N	1.61	3.6	6 (9)	$0 \div 1$	85—90	75—80	4000
β-BC_4N	1.60	3.55	5.8	0	90	80	4200
β-C_3N_4	~ 1.46	3.2	7(10)	–1.5	140—170	95	5000
GaAs	2.6	5.75	1.4(1.0)	4,5	12	30	1500
GaCAs	2.2	5.1	1.8(1.5)	4.2	22	35	2000
GaC_2As	2.0	4.9	2 (1.7)	4.0	28	40	2300
InAs	2.8	6.1	0.35—(0.3)	4.6	8	15—20	1200
InCAs	2.5	5.6	1.2 (1)	4.4	12	28	1700
InC_2As	2.2	5.1	1.8(1.5)	4	22	35	2000
AlAs	2.7	5.8	2.15(2)	4.6	11	45	2000
AlCAs	2.3	5.2	1.6 (1.4)	4.2	16	30	1900
AlC_2As	2.1	5	1.7(1.3)	3.9	20	35	2100
$SiC_{1,2,3}Ge$	2.2	5.2	2.0— 1.4	3.5	30	45	2800
$Si_{1,2,3}N_4Ge_{3,2,1}$	1.9—2	4.8	1.8	3.8	25	45	2700
$In_{1,2,3}N_4As_{3,2,1}$	2.1	5	1.4	3.7	27	40	2800
$Ga_{1,2,3}N_4As_{3,2,1}$	1.9	4.8	1.6	3.8	30	45	2600
$Al_{1,2,3}N_4As_{3,2,1}$	2	4.9	1.7	4.0	28	40	2500

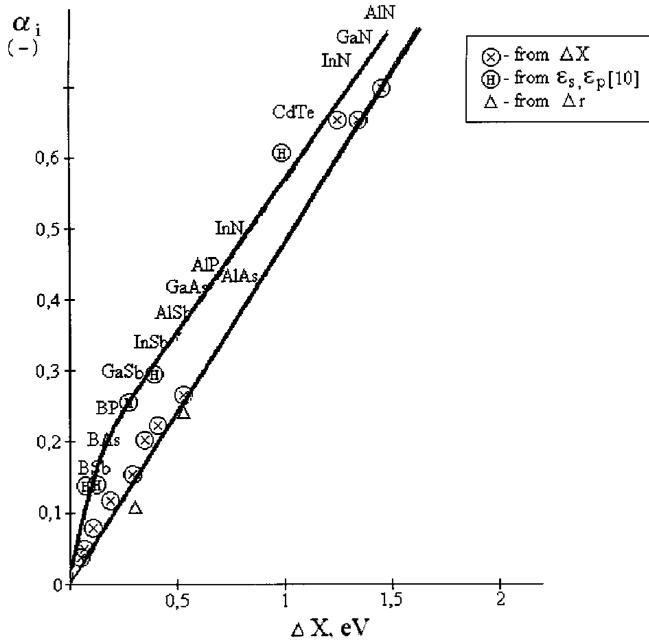

Fig. 4. Ionicity degree $\alpha_i = (i)^{1/2} = V_i / \left(V_v^2 + V_i^2\right)^{1/2}$ and ionicity matrix elements $V_i = \frac{1}{2}\left(\varepsilon_h^1 - \varepsilon_h^2\right)$ calculated from the energies $\varepsilon_s \varepsilon_p$ of different elements [10] or using the Pauling electronegativity factor X and the ionicity $i = [1 - e^{-(\Delta X/2)^2}]^{1/2} \approx \Delta X/2$ (crosses) and from the Δr relation as functions of the electronegativity difference for elements of AB compounds, $\Delta X = (X_A - X_B)$. For the middle of ΔX in the region $(0.5 \leq \Delta X \leq 2)$ which is typical of semiconductor compounds, and the values of α_i are in the range of $0.4 \leq \alpha_p \leq 0.7$

Formulas (9, 20) predict a rather monotonous dependence of the energy gap E_g on the lattice constant L for the majority of practically important semiconductors with cubic configuration and both the direct and indirect band gap structures. It is important to note that the energy for the direct transitions (Γ-point) is independent of the component of both the metallic and polar bonds and reveals the monotonous dependence, $E_g \sim V_v = A/L^2$ (Fig. 2, curve *1*). For group-IV crystals, this fact is illustrated by the transitions $\Gamma_{25'} - \Gamma_{2'}$.

Probably, in the case of a constant wave vector, $\Delta k = 0$, $k = 0$, the electron transitions occur so quickly that the polarization and metallicity become not substantial.

Let us consider a more complicated case of two (or more) atomic components for a tetrahedral configuration in cubic crystals (even belonging to the same group of PTE, like SiGe, SiC, SiCGe, etc.). We note that the influence of other mechanism of bonding, namely of that through the ionic component, should be taken into

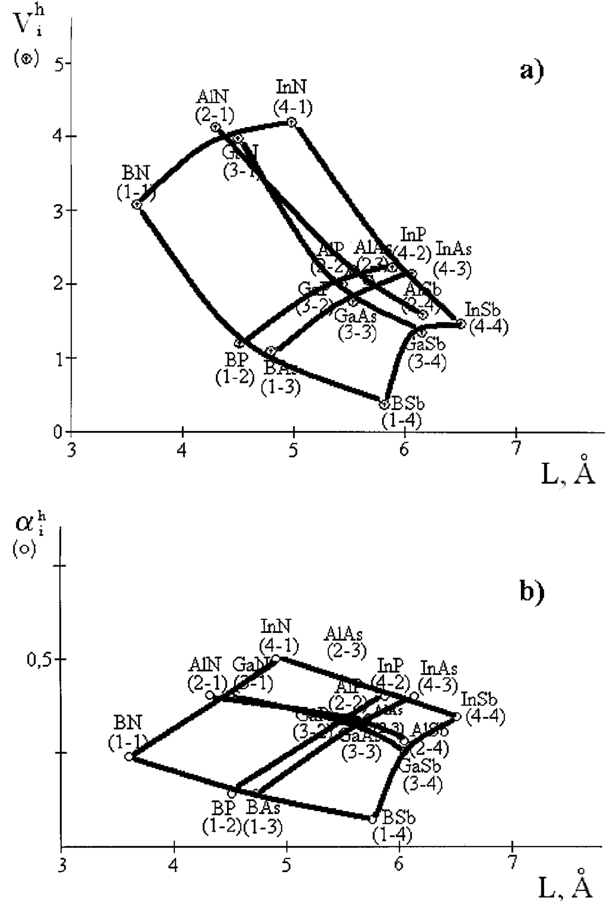

Fig. 5. Dependences of the ionicity matrix element energy, V_i, and the degree of ionicity, α_i, on the lattice constant L for intermetallic zinc blend crystals made of elements from different sets of PTE

account. The estimations can be performed with a reasonable accuracy by basing on the phenomenological Pauling principle and using the known values of the electronegativity of elements [7]. Moreover, the energy gap of many tetrahedral cubic materials is described by the above-presented formulas (18) and (20).

It can be seen that the normalized value

$$E_g / \left(1 + \alpha_i^2 / (1 - \alpha_i)^2\right)^{1/2} =$$

$$= E_{gD} \left(\frac{L_D}{L}\right)^2 \left(1 - \left(\frac{L}{2L_D}\right)^2\right) \quad (21)$$

depends monotonously on the lattice constant L for all the cubic semiconductor crystals.

The ionicity (in contrast to the metallicity) leads to an increase in the energy band gap. For typical

semiconductor compounds of groups III-V, the values of α_i do not exceed 35%, and the correction factor, $(1+\alpha_i^2)^{1/2}$, has the same order of magnitude. If the extreme differences of the ionicity are as large as $\sim 50\%$, the ionic bonds dominate. In this case, the valence bond approximation is no valid.

Similar to the previous publications [10, 16—18], we can state that the dependence of the melting temperature, T, and the optical phonon frequency, ω_{LO}, on L will be approximately the same as that of the V_v (since the mentioned characteristics strongly correlate with the energy bond parameters):

$$T_m, \omega_{L0} \sim C/L^2. \tag{22}$$

The hardness H depends on L more sharply [18]:

$$H \sim C^1/L^n, \quad n \sim (3.5 \div 5). \tag{23}$$

The band structure scheme presented in [8–10] yields the universal relation between $E_g(L)$ and the electron affinity (optical work function), X_0, [15—18]

$$E_g(L) + X_0(L) = 5.35 + \Delta E_v(L) \approx 5.5\,\text{eV}, \tag{24}$$

where $\Delta E_v \approx (2L_D - L)/L < 1$ eV is a relatively small correction which arises due to a small change of the valence band edge $E_v(L)$ under variation in the value of L,. Therefore, knowing the value of E_g, one may determine the work function X_0 for the discussed class of semiconductor crystals and vice versa (Fig. 1):

$$X_0 \equiv W_0(L) = 5.35 + \Delta E_v - E_g(L) \approx$$

$$\approx 5.35\left[\left(\frac{L_D}{L}\right)^2\left[\left(\frac{L}{2L_D}\right) - 1\right] + 1\right] \tag{25}$$

(in particular, $\Delta E_v \cong 0.5\,\text{eV}$ for Ge and Si, and $\Delta E_v = 0$ for Sn).

The calculated curves for X_0 and the comparison with experimental data are illustrated by Fig. 1. Besides, we present the table with the main characteristics of tetrahedral cubic crystals calculated by the proposed formulas. The part of parameters in the table has well-known values, but the other (marked by bold letters) was calculated for the first time in the framework of the model described above (see the Table). It is easy to see that formula (25) predicts very small (or even negative) values of the electron work function for the wide-gap fcc semiconductor crystals, while X for the narrow-gap crystals has large enough values ($\gtrsim 4.5 \div 5.5$ eV). The data obtained are in the qualitative accordance with the novel calculations for alloys with the tetrahedral configuration in the approximation of a virtual crystal with the corrections on the local deformation potential and the composition disorder [19].

Solid materials with nanostructures which represent a new class of materials with specific parameters rouse a particular interest.

For quantum-size (QZ) structures, formula (25) predicts a very remarkable decrease of the work function due to the increase of E_g, which was demonstrated previously both theoretically and experimentally [16—18]. For example, under a reasonable increase of E_g due to the quantization, $\Delta E_g \sim 2 \div 3$ eV, the value of X_0 drastically decreases down to $2 \div 2.5$ eV. This effect is important for different kinds of electron emission phenomena and devices. Since the band gap of QZ structures is a definite function of the size parameter d, the new values of X_0 can be calculated from the values of E_g. They decrease with the diameter d, as shown in Fig. 1. Relation (1) for QZ structures can be rewritten as follows:

$$\left(E_{g0} + A/d^2\right) + \left(X_0 - B/d^2\right) = 5,3 - \delta E\,(L, d) \approx \text{const.} \tag{26}$$

Therefore, it seems to be possible to create new crystalline materials with small or even negative values of the optical work function, X_0.

4. Conclusion

Similarly to the Periodic Table of elements, it is useful to propose a scheme systematizing the crystalline materials or, at least, some types of crystal structures. In the present paper, we have discussed the variant of such a scheme for diamond-like fcc crystals which include a wide range of semiconductors: IV-group elements (C, Si, Ge, Sn, SiGe, SiC, etc.), a number of compounds of groups III—V (GaAs, AlAs, InSi, etc.), some of compounds of groups II—VI, as well as three- and four-component crystals made of elements belonging to PTE middle columns. The system discussed allows one to calculate such parameters as the forbidden gap energy, E_g, electron affinity (optical work function), X_0, hardness, H, and melting temperature, T_m. The analysis performed in the framework of the theory of tight-binding bands has demonstrated the dependence of the mentioned parameters on the lattice constant of crystals, L, whose values have been calculated using the valence atomic radii, r_{AB}, or determined experimentally. It has been shown that the quantum-size structures can be analyzed within the same approach

as well. The analysis performed for the QZ structures has allowed us to predict a substantial decrease of the work function, which is rather promising for the study and application of the electron emission from nanostructures. In conclusion, we note that the internal local deformations are negligible for diamond-like and zinc blend structures, whereas the change of the energy parameters is substantial for wurtzite-like structures.

This work was supported by the INTAS grant, the grant of the Ministry of Science and Education of Ukraine, and the Project of the National Academy of Sciences of Ukraine.

I would like to express my deep thanks to Profs. V.N. Dobrovolskii and F.T. Vasko for the helpful discussions.

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Received 24.04.05

ВИЗНАЧЕННЯ БАЗОВИХ ПАРАМЕТРІВ НАПІВПРОВІДНИКОВИХ КУБІЧНИХ КРИСТАЛІВ ЧЕРЕЗ СТАЛУ ГРАТКИ

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Р е з ю м е

Розроблено метод розрахунку електронних параметрів кубічних алмазоподібних кристалів. Метод базується на запропонованій аналітичній залежності цих параметрів від відстані між сусідніми атомами в кристалі або від пропорційної їй масштабної характеристики — сталої гратки L. Використовуючи цей підхід, були визначені такі параметри електронної структури, як енергія забороненої зони E_g, ступені ковалентності, металічності та іонності хімічного зв'язку, проведена оцінка електронної спорідненісті X_0 (оптичної роботи виходу), температури плавлення $T_{\text{пл}}$. З отриманих залежностей можна також передбачити параметри деяких нових кристалів, які можуть бути сконструйовані. Зокрема, були визначені параметри нових надтвердих матеріалів, таких, як кубічний нітрокарбон C_3N_4, боронітрокарбон BCN, параметри деяких нових вузькозонних багатокомпонентних напівпровідників (типу SiGaPb, SiGeSn) та ін. Проаналізовано також деякі властивості нанорозмірних матеріалів.