

SUBSTITUTION AND SOLUTION ENERGIES FOR ORTHORHOMBIC COMPOUNDS SEMICONDUCTING A⁴B⁶

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Cohesive energies and force constants of the bonds for GeS, GeSe, SnS and SnSe crystals, as well as the energies of substitution by formation of solid solutions and the heat of mixing is calculated. It is shown that the main contribution to the heat of mixing comes from the energy of elastic deformation due to the difference in the bond lengths in the components of solid solutions.

1. Introduction

The tight-binding theory, based upon universal parameters and energies of separate bonds corrected form interaction between nearest neighbors was successfully applied to diamond-like A³B⁵ and A²B⁶ compounds by Harrison and Kraut for calculation of the cohesive energy, force constants of the bonds, as well as the energy of substitution and the heat of dissolving [1].

In the present paper we modify the technique developed in [1] taking into account structural peculiarities of the orthorhombic layered A⁴B⁶ crystals. We calculate cohesive energies and force constants of the bonds for GeS, GeSe, SnS and SnSe crystals, as well as the energies of substitution by formation of solid solutions based on these crystals and the heat of mixing. We show that, similarly to the case of diamond-like compounds, the main contribution to the heat of mixing comes from the energy of elastic deformation due to the difference in the bond lengths in the components of solid solutions.

2. Cohesive energy of the orthorhombic A⁴B⁶ crystals.

According to [1] cohesive energy is the sum of the following energies: promotion energy, bond-formation energy, overlap energy or energy of repulsion, and energy of metallization. Below we give the expressions for each of these contributions in the total bond energy. The promotion energy is the energy necessary for the transfer of the *s*-electron of cation and anion into *p*-state and transfer of one *p*-electron from anion to cation with the formation of a hybrid state. To calculate this energy one has to sum the energies of hybrid states of cation and anion and subtract the energies of free atoms.

The energy of a hybrid state has the following form:

$$\varepsilon_i^k = (1 - N_{ik}^2)\varepsilon_s^k + N_{ik}^2\varepsilon_p^k, \quad (1)$$

where *k* denotes the cation (*c*) or anion (*a*), *i*=*l* or *h* for the corresponding bond, *N_{ik}* are the normalizing factors for hybrid orbitals [2].

It is known [2] that in the structure of A⁴B⁶ orthorhombic crystals there are two types of bonds: *l*-type - two "horizontal" bonds and *h*-type - one vertical bond. Normalizing factors are determined by the angles between bonds:

$$N_{hk}^{-2} = 1 - \frac{\cos^2 \beta_k}{\cos \alpha} \quad (2)$$

$$N_{lk}^{-2} = 1 - \cos \alpha \quad (3)$$

Here α is the angle between two *l*-bonds, β_k is the angle between *l*- and *h*-bonds, respectively at the anion and cation.

The fourth hybrid state at the cation and anion contains an lonely pair of electrons. The normalizing factor for this state is related to the normalizing factors *N_{ik}* by the universal relation:

$$N_{4k}^2 + 2N_{1k}^2 + N_{hk}^2 = 3 \quad (4)$$

Taking into account all mentioned above for the promotion energy we get:

$$E_{pro} = \varepsilon_p^c - \varepsilon_p^a + N_{4c}^2(\varepsilon_p^c - \varepsilon_s^c) + N_{4a}^2(\varepsilon_p^a - \varepsilon_s^a) \quad (5)$$

In this expression the first term corresponds to the transfer of one *p*-electron from anion to cation, the second and the third term correspond to the hybridization of *s*- and *p*-electronic states of the cation and anion, respectively. The values of *E_{pro}* calculated with the use of (5) are given in the table 1.

Table 1. Promotion energy *E_{pro}*, bond formation energy *E_{BF}*, metallization *E_{met}*, overlap energy *E_{over}*, and the total binding energy *E_{tot}*, parameters of repulsive potential η_l and η_h , force constants of bonds for orthorhombic A⁴B⁶ compounds.

	GeS	GeSe	SnS	SnSe
<i>E_{pro}</i> , eV	13,30	11,37	12,65	10,81
- <i>E_{BF}</i> , eV	29,38	25,36	27,46	23,76
- <i>E_{met}</i> , eV	0,88	0,88	0,69	0,62
<i>E_{over}</i> , eV	8,74	8,07	6,61	6,26
η_l	2,33	2,55	2,40	2,62
η_h	2,08	2,26	2,11	2,28
- <i>E_{tot}</i> , kcal/mol	190,5	157,1	203,5	167,7
- <i>E_{coh}</i> , kcal/mol [4]	169,8	160,6	163,6	138,8
<i>C_l</i> , N/m	18,1	17,6	10,4	10,4
<i>C_h</i> , N/m	50,9	44,5	25,6	23,7
$\theta_{r,r}$, N/m [5]	36,3	-	-	-

For the calculation we used the values of s - and p -states of valence electrons of atoms, that form the compounds [1]. The magnitudes of the angles between bonds are given in [3].

Now let us consider the bond-formation energy. This is the energy required for the transfer of an electron from a bonding state into an antibonding one. Since in our case there are two bonds of l -type and one-bond - of h -type then the formation energy E_{BF} is equal to

$$E_{BF} = -2\sqrt{V_{2h}^2 + V_{3h}^2} - 4\sqrt{V_{2l}^2 + V_{3l}^2} \quad (6)$$

where

$$V_{3i} = \frac{\epsilon_i^c - \epsilon_i^a}{2} \quad (7)$$

$$V_{2i} = N_{ic} \{ N_{ia} 1.32(N_{ic}^{-2} - 1)^{1/2} (N_{ia}^{-2} - 1)^{1/2} + 1.42[(N_{ic}^{-2} - 1)^{1/2} + (N_{ia}^{-2} - 1)^{1/2}] + 2.22 \} \frac{\hbar^2}{m\alpha_i^2} \quad (8)$$

The meaning of the above expressions is explained in [2]. The values of the bond-formation energy calculated with use of (6) are given in Table 1.

The most time-consuming is the calculating of the energy of metallization, that is the correction to the energy of sepa-

rate bonding orbitals due to overlapping with the neighbor antibonding orbitals of the same atom. In our case the energy of metallization contains the following six contributions:

1) the interaction of bonding h -orbital with the neighbor antibonding l -orbital at the cation:

$$(1 - \alpha_p^h)(1 + \alpha_p^l)(1 - N_{hc}^2)(1 - N_{lc}^2) \frac{(\epsilon_p^c - \epsilon_s^c)^2}{(\epsilon_b^h - \epsilon_a^l)} \quad (9)$$

2) the interaction of the bonding l -orbital with the antibonding h -orbital at the cation:

$$(1 - \alpha_p^l)(1 + \alpha_p^h)(1 - N_{hc}^2)(1 - N_{lc}^2) \frac{(\epsilon_p^c - \epsilon_s^c)^2}{(\epsilon_b^l - \epsilon_a^h)} \quad (10)$$

3) the interaction of the bonding l -orbital with the antibonding l -orbital at the cation:

$$(1 - \alpha_p^l)(1 + \alpha_p^l)(1 - N_{lc}^2)^2 \frac{(\epsilon_p^c - \epsilon_s^c)^2}{(\epsilon_b^l - \epsilon_a^l)} \quad (11)$$

4) the interaction of the bonding h -orbital with the antibonding l -orbital at the anion:

$$(1 - \alpha_p^h)(1 + \alpha_p^l)(1 - N_{ha}^2)(1 - N_{la}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\epsilon_b^h - \epsilon_a^l)} \quad (12)$$

5) the interaction of the bonding l -orbital with the antibonding h -orbital at the anion:

$$(1 + \alpha_p^l)(1 - \alpha_p^h)(1 - N_{ha}^2)(1 - N_{la}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\epsilon_b^l - \epsilon_a^h)} \quad (13)$$

6) the interaction of the bonding l -orbital with the antibonding l -orbital at the anion:

$$(1 + \alpha_p^l)(1 - \alpha_p^l)(1 - N_{la}^2)^2 \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\epsilon_b^l - \epsilon_a^l)} \quad (14)$$

Here

$$\alpha_p^i = \frac{V_{3i}}{\sqrt{V_{2i}^2 + V_{3i}^2}} \quad (15)$$

and the expressions for ϵ_b^i and ϵ_a^i are given in [1].

Summing up the contributions of the all above given expressions (9)-(14), we obtain the energy of metallization, as shown in Table 1.

The energy of repulsion, E_{over} , corresponds to the overlapping of the wave functions of the atoms that form the bond and it is determined, in accordance with [1], by the following expression:

$$E_{over} = \eta \frac{2V_2^2}{\epsilon_h^c + \epsilon_h^a} \quad (16)$$

where ϵ_h^c and ϵ_h^a are the energies of hybrid states of the cation and anion, respectively, V_2 is the covalence energy, η is an empirical parameter defined from the condition of minimization of the total binding energy at given bond length.

In our case, taking into account the existence of two l -bonds and one h -bond per molecule of A^4B^6 , we have:

$$E_{over} = 2\eta_h \frac{V_{2h}^2}{\epsilon_h^c + \epsilon_h^a} + 4\eta_h \frac{V_{2l}^2}{\epsilon_l^c + \epsilon_l^a} \quad (17)$$

By minimizing E_{tot} with respect to d_h and d_l , we determine η_h and η_l . The Table 1 compiles the magnitudes of these parameters, as well as the values of the total binding energy for four A⁴B⁶ compounds with orthorhombic lattice. The experimental values of the heat of atomization taken from [4] are given in the same Table.

The force constants of the bonds are determined by the second derivation of total binding energy with respect to the bonds length. After neglecting the small contribution of the energy of metallization into the total binding energy we obtain simple expressions for force constants of l - and h -bonds:

$$C_i = \frac{8}{d_i^2} \frac{V_{2i}^4}{(V_{2i}^2 + V_{3i}^2)^{3/2}} \quad (18)$$

Calculated magnitudes of C_l and C_h are also given in Table 1. In spite of the closeness of the bond lengths for l - and h -bonds the force constants differ drastically. This fact indicates the different nature of l - and h -bonds. In particular,

$$\Delta E_{pro} = (\epsilon_p^{Sn} - \epsilon_p^{Ge})(1 + N_{4c}^2) - N_{4c}^2(\epsilon_s^{Sn} - \epsilon_s^{Ge}) \quad (19)$$

i.e., we replace single-electron energies of atoms of Ge by corresponding energies for atoms of Sn.

In the same way we calculate the changes in the bond-formation energy and the overlap energy, i.e. we replace in the expressions for V_{3h} and V_{3l} the single-electron atomic energies for Ge by the ones for Sn.

At the same time we do not touch the covalence energy, V_{2i} , assuming that there are no relaxation effects.

Instead of η_h and η_l , the expressions for the overlap energy one has to substitute the geometric means of these parameters for corresponding components of the solid solutions.

The calculation of the changes in the energy of metallization is slightly more complicated, although the principle of the account for changes in the energy by substitution holds, i.e. we replace only the single-electron atomic energies.

For the cationic substitution, $\Delta E(c)$, the formulas (9)-(11) continue to hold with the only difference that every-

the latter is characterized by almost complete absence of hybridization at the cation. In [5] the authors, basing on the assumption of the equality of force constants for l - and h -bonds for GeS obtained the estimate of 36.3 N/m, that is close to our result 34,5 N/m, averaged over both types of bonds.

3. Energy of substitution for solid solutions of A⁴B⁶ compounds.

The substitution energy is defined as the energy required for the removal of one atom from a semiconducting compound and the replacement of this atom by an atom of other element. Here we consider only isovalence substitution. To calculate the energy of substitution we consider the change in each of the above listed contributions into the total energy as at the cationic, as the anionic substitution. We begin with the cationic substitution. If, for example, we substitute atom Ge by the atom Sn in GeS crystal, then in accordance with (5), we obtain the following change in the promotion energy:

where ϵ_p^{Ge} and ϵ_s^{Ge} are replaced by ϵ_p^{Sn} and ϵ_s^{Sn} , respectively. Since α_p^i also depend on ϵ_p^c and ϵ_s^c , by means of V_{3i} , they also change. The same is true with respect to ϵ_b^i and ϵ_a^i . Now consider expression (12). This expression takes into account the interaction between the bonding h -orbital and the antibonding l -orbital at the anion. Here, three cases of the location of anion with respect to cation are possible: 1) anion is located at h -bond with the replaced atom Ge by Sn, and the antibonding l -orbital corresponds to the Ge-anion bond; 2) anion is located at the h -bond with Ge, and the antibonding orbital also corresponds to the Ge-anion bond; 3) anion is located at the h -bond with Ge, and the antibonding orbital corresponds to the Sn-anion bond.

Finally, the expression (12) takes the form:

$$\begin{aligned} & \frac{1}{2} (1 + \bar{\alpha}_p^h)(1 - \alpha_p^i)(1 - N_{ha}^2)(1 - N_{la}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\epsilon_b^h - \epsilon_a^i)^2} + \\ & + \frac{1}{4} (1 + \alpha_p^h)(1 - \alpha_p^i)(1 - N_{ha}^2)(1 - N_{la}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\epsilon_b^h - \epsilon_a^i)^2} + \\ & + \frac{1}{4} (1 + \alpha_p^h)(1 - \bar{\alpha}_p^l)(1 - N_{ha}^2)(1 - N_{la}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\epsilon_b^h - \epsilon_a^{-l})^2} \end{aligned} \quad (20)$$

Here the dash over α_p^i and ϵ_b^i , ϵ_a^i denotes replacement of the cation, i.e. in the corresponding expressions atomic energies of Ge were substituted for those of Sn.

Similar reasoning leads to the following expressions instead of (13) and (14):

$$\begin{aligned} & \frac{1}{2} (1 + \alpha_p^1)(1 - \bar{\alpha}_p^h)(1 - N_{ha}^2)(1 - N_{1a}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\bar{\epsilon}_b^1 - \bar{\epsilon}_a^h)} + \\ & + \frac{1}{4} (1 + \alpha_p^1)(1 - \alpha_p^h)(1 - N_{ha}^2)(1 - N_{1a}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\bar{\epsilon}_b^1 - \epsilon_a^h)} + \\ & + \frac{1}{4} (1 + \bar{\alpha}_p^1)(1 - \alpha_p^h)(1 - N_{ha}^2)(1 - N_{1a}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\bar{\epsilon}_b^1 - \bar{\epsilon}_a^h)} \end{aligned} \quad (21)$$

and

$$\begin{aligned} & \frac{1}{2} (1 + \bar{\alpha}_p^1)(1 - \alpha_p^1)(1 - N_{1a}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\bar{\epsilon}_b^1 - \epsilon_a^1)} + \\ & + \frac{1}{4} (1 + \alpha_p^1)(1 - \alpha_p^1)(1 - N_{1a}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\bar{\epsilon}_b^1 - \epsilon_a^1)} + \\ & + \frac{1}{4} (1 + \alpha_p^1)(1 - \bar{\alpha}_p^1)(1 - N_{1a}^2) \frac{(\epsilon_p^a - \epsilon_s^a)^2}{(\bar{\epsilon}_b^1 - \bar{\epsilon}_a^1)} \end{aligned} \quad (22)$$

In the case of anionic substitution, $\Delta E(a)$ the expressions (12)-(14) hold with the only difference that everywhere the single-electron atomic energies are replaced by the corresponding atomic energies of the substituting atom. And the expressions (9)-(11) take the form similar to (20)-(22) with the obvious replacing of cation for anion.

Calculated values of the energy of substitution are given in Table 2.

Table 2. Energy of substitution, heat of mixing and misfit energy for solid solutions of A^4B^6 .

	GeS	GeSe	SnS	SnSe
$\Delta E(c)$, eV	-0,67	-0,58	0,8	0,67
$\Delta E(a)$, eV	1,27	-1,28	1,43	-1,44
$\Omega(c)$, eV	0,06	0,04	0,06	0,04
$\Omega(a)$, eV	0,00	0,00	0,00	0,00
$\Omega_{misfit}(c)$, eV	0,03	0,03	0,03	0,03
$\Omega_{misfit}(a)$, eV	0,01	0,01	0,01	0,01

To compare with the experiment it is worth to calculate the values of the heat of mixing with the use of these data. The heat of mixing is defined by the average enthalpy of the solution for the both solid solutions.

Thus, for example, for GeS-GeSe:

$$\Omega = \frac{1}{2} [\Delta E(\text{GeS} / \text{Se}) + \Delta E(\text{GeS} / \text{Se})] \quad (23)$$

$$\Omega_{misfit} = \frac{3}{32} (C_{1h} + C_{2h})(h_1 - h_2)^2 + \frac{6}{32} (C_{1l} + C_{2l})(l_1 - l_2)^2 \quad (25)$$

The values of the energy of misfit calculated with the use of (25) are given in Table 2. Because of the lack of experimental data on the heat of mixing of solid solutions based on A^4B^6 we cannot compare our results with the experiment. However, the comparison with the corresponding data for A^3B^5 given in [1] shows that these values are usually small and make hundredths of eV. The calculated values of the heat of mixing for A^4B^6 have the same order of magnitude.

The values of Ω are also given in Table 2. All of them are positive or equal to zero, which indicates that the energy is to be transferred to system from outside.

In [1] it has been shown that for isovalence solid solutions of A^3B^5 and A^2B^6 the main contribution to the heat of mixing comes from the energy of the misfit related to the difference in the interatomic distances in the components of the solid solutions. Our estimates of the misfit energy for A^4B^6 confirm this viewpoint. For this purpose let us consider a cluster of 10 atoms: 1 - substituted atom, 3 - its nearest neighboring and 2 - each neighbors of nearest neighborhoods of the substituted atom. In accordance with [1], the elastic energy corresponding to the change of one bond length is equal to:

$$\frac{1}{2} \left[\frac{C_1 + C_2}{2} \left(\frac{d_1 - d_2}{2} \right)^2 \right] \quad (24)$$

Here C_1 and C_2 are the force constants of the bonds for each component of the solid solution, d_1 and d_2 are the lengths of these bonds.

In our case we have three bonds of h -type and six bonds of l -type. The total energy of the misfit, Ω_{misfit} , is equal to:

4. Conclusion.

In summary the tight-binding theory developed by Harrison for calculation the cohesive energy, force constants of bonds and energy of substitution is applied for the first time to A^4B^6 layered crystals with orthorhombic structure. In spite of substantial difference in bonding features from tetrahedral bonds compounds, Harrison's method describes correctly above mentioned crystal properties for A^4B^6 .

- [1] *W.A.Harrison, E.A.Kraut. Phys. Rev.*, 1988, B37, № 14, p. 8244-8256.
- [2] *F.M. Gashimzade, D.A. Guseinova. Inorganic Materials*, v. 32, № 9, p.955-959.
- [3] *H.Wiedemeier, H. von Schnering. Zeitschrift fur Kristallographic*, 1978, 148, p. 295-303.
- [4] *N.Ch.Abrikosov, B.F.Bankina, L.V.Parichkaya, E.V.Skudnova, L.E.Shelimova. Poluprovodnikoviye soyedineniya, ich polucheniye i svoystva*, M. "Nauka", 1967, s. 176.
- [5] *W. Kress, A. Frey, B. Dorner, W. Kaiser. Proceeding of the Conference on Neutron Scattering, Gatlinburg, Tennessee, USA, 1976, June 6-10, v. 1, p. 216-222.*

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ORTOROMBİK A⁴B⁶ YARIMKEÇİRİCİLƏRİNDƏ ƏVƏZLƏNMƏ VƏ HƏLL OLMA ENERJİLƏRİ

GeS, GeSe, SnS və SnSe kristalları üçün rabitə enerjisi və rabitələrin qüvvə sabitləri, həmçinin bərk məhlulun əmələ gəlməsiylə əlaqədar əvəzləmə enerjisi və həll olma istiliyi hesablanmışdır. Həll olma istiliyinin əsasən elastiki deformasiya enerjisi ilə əlaqədar olduğunu göstərilmişdir. Bu deformasiya bərk məhlulun komponentlərində rabitələrin uzunluqlarının fərqlənməsi ilə izah olunur.

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ЭНЕРГИИ ЗАМЕЩЕНИЯ И РАСТВОРЕНИЯ ДЛЯ ОРТОРОМБИЧЕСКИХ ПОЛУПРОВОДНИКОВЫХ СОЕДИНЕНИЙ A⁴B⁶

Рассчитаны энергии сцепления и силовые постоянные связей для кристаллов GeS, GeSe, SnS, и SnSe. Также вычислены энергии замещения при образовании твердых растворов и теплоты смещения. Показано, что основной вклад в теплоту смещения связан с энергией упругой деформации обьязанной различию длин связей в компонентах твердых растворов.

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