Note on Structure Parameters of Wurtzite Type Compounds

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Crystal parameters of wurtzite type crystals have been investigated based on the optimized bond orbital model which is known to give the crystal structures of some III-VI compounds as the minimum of bonding energy when bond lengths are fixed. In the case of wurtzite type structures, however, it has become clear that the effect of the change in bond lengths has to be taken into account when minimizing bonding energies.

§1. Introduction

The wurtzite type (B4) structure has tetrahedral covalent bonds between neighbouring atoms. In Fig. 1, we illustrate these bonds and the hexagonal unit cell: We follow conventional notations of structure parameters for these crystals. In a wurtzite type crystal which has perfect tetrahedral bondings, the structure
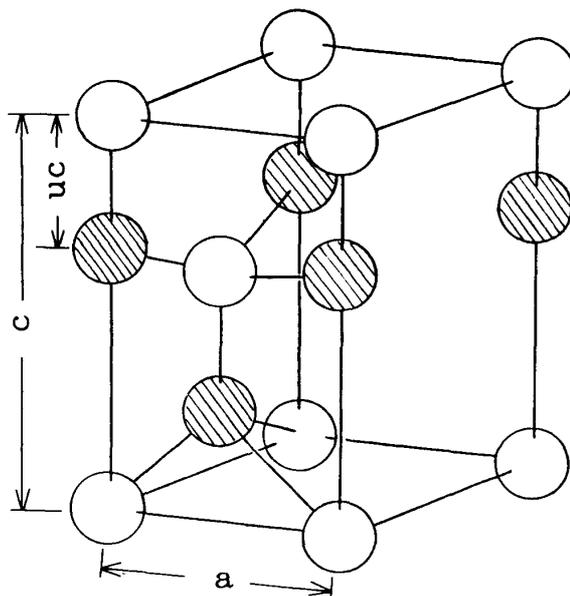

Fig. 1 Wurtzite type structure

parameters satisfy the relations

$$\gamma \equiv c/a = \sqrt{8/3}, \text{ and } u = 0.375.$$

In real B4 type crystals, however, structures are somewhat deviated from the ideal ones. Some examples of wurtzite type crystals are listed in Table I

Table I. Structure parameters of wurtzite type compounds

	$a(\text{Å})$	$c(\text{Å})$	γ	u
ZnO	3.249	5.206	1.6022	0.383
AlN	3.104	4.966	1.600	0.385
CdS	4.137	6.714	1.623	0.378
CdSe	4.30	7.01	1.631	0.377
AgI	4.592	7.508	1.635	0.375
ideal value			1.633	0.375

together with values of structure parameters which have been determined experimentally.[1] In this paper we analyze these deviations on the basis of the optimized bond orbital model proposed by Nakanishi and Matsubara (abbreviated as OBOM hereafter) which gives a satisfactory explanation on the electronic properties of III-VI compounds such as GaS, GaSe, and InSe.[2]

The OBOM is an extention of the bond orbital model due originally to Harrison.[3] In this model, we assume the functional form of sp hybrid orbitals so as to satisfy symmetry and orthogonality requirements and evaluate the electronic energy by minimizing resultant expressions with respect to the parameters included in the hybrid functions.

§2. Optimized Bond Orbital for Wurtzite Type Compounds

We first define sp hybrid orbitals for each anion and cation as follows:

$$|\Psi_0^i> = (1+b_i^2)^{-1/2}\,[b_i\,|s^i> + |p_z^i>],$$

$$|\Psi_1^i> = (1+a_i^2)^{-1/2}\,[|s^i> + a_i(1+c_i^2)^{-1/2}\,(c_i\,|p_x^i> + |p_z^i>)],$$

$$|\Psi_2^i> = (1+a_i^2)^{-1/2}\,[|s^i> + a_i(1+c_i^2)^{-1/2}\,\{\tfrac{1}{2}c_i(\sqrt{3}\,|p_y^i> - |p_x^i>) + |p_z^i>\}],$$

$$|\Psi_3^i> = (1+a_i^2)^{-1/2}\,[|s^i> + a_i(1+c_i^2)^{-1/2}\,\{\tfrac{1}{2}c_i(-\sqrt{3}\,|p_y^i> - |p_x^i>) + |p_z^i>\}],$$

$$(2.1)$$

Here i denotes anion (a) or cation (c) and we take upper and lower signs for cation and anion, respectively. From the orthogonality conditions,

$$<\Psi_s^i \mid \Psi_t^i> = \delta_{st},$$

a_i and b_i are related to c_i by

$$a_i = [2(1 + c_i^2)/(c_i^2 - 2)]^{1/2},$$

$$b_i = [2/(c_i^2 - 2)]^{1/2}. \qquad (2.2)$$

In Fig. 2 we illustrate some of these orbitals in the plane including cation-anion-cation bonds. When $c_i = 2\sqrt{2}$, these sp hybrid orbitals reduce to the well known hybrid orbital of sp^3 type.
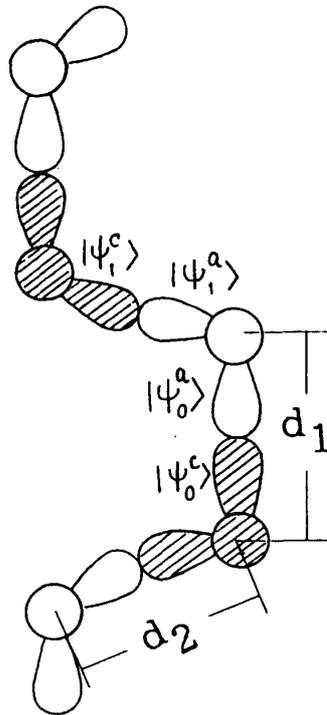

Fig. 2 Hybrid orbitals in the plane including cation-anion-cation bonds.

In the OBOM we construct bond orbitals $| \Psi_{nac}^- >$, $n = 0, 1, 2$, and 3 from $| \Psi_n^a >$ and $| \Psi_n^c >$ shown in Fig. 2. Three orbitals other than $| \Psi_{0ac}^- >$ are equivalent dut to the crystal symmetry. Therefore the electronic energy per molecule may be expressed as

$$E = 6E_1 + 2E_2. \qquad (2.3)$$

The first term on the right hand side of (2.3) represents the energy associated with the bond orbitals of length d_1 with an angle θ to the c-axis. The value of E_1 is given by

$$E_1 = \frac{1}{2}(\varepsilon_{1c} + \varepsilon_{1a}) - (V_2^2 + V_3^2)^{1/2} \qquad (2.4)$$

with

$$V_3 = \frac{1}{2}(\varepsilon_{1c} - \varepsilon_{1a}),$$

$$V_2 = - < \Psi_1^c | H | \Psi_1^a >,$$

$$\varepsilon_{1i} = (1+a_i^2)^{-1} [\varepsilon_{si} + a_i^2 (c_i^2+1)^{-1} (c_i^2 \varepsilon_{pi}^x + \varepsilon_{pi}^z)]. \tag{2.5}$$

Here we have introduced the notations

$$\varepsilon_{si} = < s^i | H | s^i >,$$

$$\varepsilon_{pi}^x = < p_x^i | H | p_x^i >, \quad \text{and} \quad \varepsilon_{pi}^z = < p_z^i | H | p_z^i >. \tag{2.6}$$

The second term on the right oand side of (2.3) is the energy of the bond parallel to the c-axis with the length d_2, and E_2 is given by

$$E_2 = \frac{1}{2} (\varepsilon_{0c} + \varepsilon_{0a}) - (V_2'^2 + V_3'^2)^{1/2}, \tag{2.7}$$

where

$$V_3' = \frac{1}{2} (\varepsilon_{0c} - \varepsilon_{0a}),$$

$$V_2' = - < \Psi_0^c | H | \Psi_0^a >,$$

$$\varepsilon_{0i} = (1+b_i^2)^{-1} [b_i^2 \varepsilon_{si} + \varepsilon_{pi}^z]. \tag{2.8}$$

Using explicit forms (2.1) for orbitals, we rewrite the hybrid covalent energy V_2 as

$$V_2 = - [(1+a_c^2)(1+a_a^2)]^{-1/2} \{ < s^c | H | s^a > - a_c a_a [(1+c_c^2)(1+c_a^2)]^{-1/2}$$

$$\times [c_c c_a < p_x^c | H | p_x^a > + c_c < p_x^c | H | p_z^a > + c_a < p_z^c | H | p_x^a > + < p_z^c | H | p_z^a >]$$

$$+ a_c (1+c_c^2)^{-1/2} [c_c < p_x^c | H | s^a > + < p_z^c | H | s^a >]$$

$$- a_a (1+c_a^2)^{-1/2} [c_a < s^c | H | p_x^a > + < s^c | H | p_z^a >] \}. \tag{2.9}$$

Here, matrix elements such as $< s^c | H | s^a$ and $< p_x^c | H | p_x^a >$ are functions of the anion-cation distance d_1 and are expressed by the Slater-Koster integrals[4] $V_{ss\sigma} (d_1)$, $V_{sp\sigma} (d_1)$, $V_{pp\sigma} (d_1)$ and $V_{pp\pi} (d_1)$ as

$$< s^c | H | s^a > = V_{ss\sigma} (d_1)$$

$$< p_x^c | H | p_x^a > = l^2 V_{pp\sigma} (d_1) + (1-l^2) V_{pp\pi} (d_1),$$

$$< p_x^c | H | p_z^a > = < p_z^c | H | p_x^a > = ln [V_{pp\sigma} (d_1) - V_{pp\pi} (d_1)],$$

$$< p_z^c | H | p_z^a > = n^2 V_{pp\sigma} (d_1) + (1-n^2) V_{pp\pi} (d_1),$$

$$< p_x^c | H | s^a > = - < s^c | H | p_x^a > = - l V_{sp\sigma} (d_1),$$

$$< p_z^c | H | s^a > = - < s^c | H | p_z^a > = - n V_{sp\sigma} (d_1), \tag{2.10}$$

where $l = \sin \theta$, $n = -\cos \theta$, and θ is the cation-anion-cation bond angle.

Similarly, the hybrid covalent energy V_2' is rewritten as

$$V_2' = - < \Psi_0{}^c \mid H \mid \Psi_0{}^a >$$

$$= - [(1+b_c{}^2)(1+b_a{}^2)]^{-1/2} \{b_a b_c < s^c \mid H \mid s^a > + b_c < s^c \mid H \mid p_z{}^a >$$

$$- b_a < p_z{}^c \mid H \mid s^a > - < p_z{}^c \mid H \mid p_z{}^a > \},$$

(2.11)

where

$$< s^c \mid H \mid s^a > = V_{ss\sigma} (d_2)$$

$$< s^c \mid H \mid p_z{}^a > = - < p_z{}^c \mid H \mid s^a > = - V_{sp\sigma} (d_2),$$

$$< p_z{}^c \mid H \mid p_z{}^a > = V_{pp\sigma} (d_2).$$

(2.12)

As interatomic matrix elements such as $V_{ss\sigma}(d)$, we use the universal functional form proposed by Harrison :[5]

$$V_{ss\sigma}(d) = -1.32 (\hbar^2/md^2),$$

$$V_{sp\sigma}(d) = 1.42 (\hbar^2/md^2),$$

$$V_{pp\sigma}(d) = 2.22 (\hbar^2/md^2),$$

$$V_{pp\pi}(d) = -0.63 (\hbar^2/md^2),$$

(2.13)

We take reported values of ε_{si} and ε_{pi} (i = a and c) in Table II and minimize the electronic energy defined in (2.3) with respect to parameters u and γ.

Table II. The list of atomic term values, $-\varepsilon_s(eV)$ and $-\varepsilon_p(eV)$, and covalent radii $R_c(\text{Å})$

	Cd	Zn	Be	Ag	Al	S	Se	O	N	I
$-\varepsilon_s$ [3]	7.70	8.40	8.17	6.41	10.11	20.81	20.32	29.14	23.04	19.42
$-\varepsilon_s$ [3]	3.38	3.38	4.14	2.05	4.86	10.27	9.53	14.13	11.47	9.97
R_c [4]	1.48	1.31	1.06	1.52	1.26	1.04	1.14	0.66	0.70	1.28

§3. Results

We analyze the electronic energy of covalent wurtzite crystals by two different approaches.

First we consider the case where the degree of freedom is limited so that all anion-cation bonds have the same length equal to the sum of covalent radii of an anion and a cation. We fix these bond lengths and find out the lattice constant a which gives the minimum energy. Examples of the calculated results are shown in Figs. 3 (a), (b) and (c). In this case we can get another lattice constant c, parameters γ and u automatically. We note that the results for
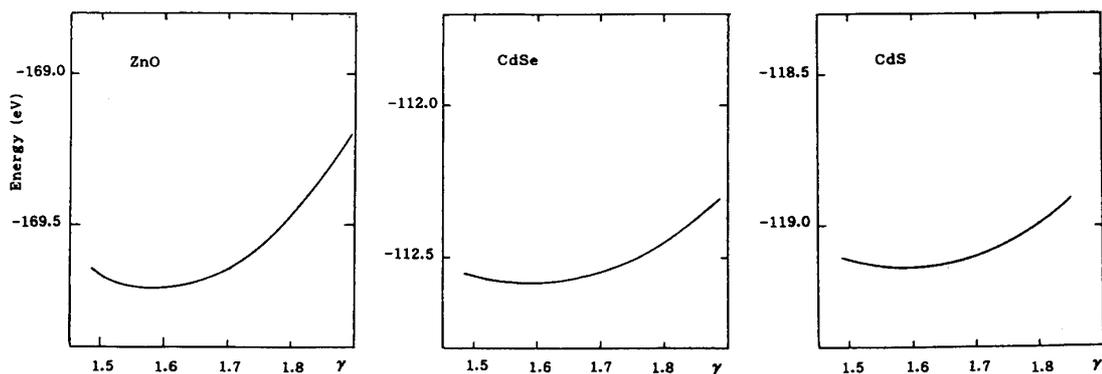
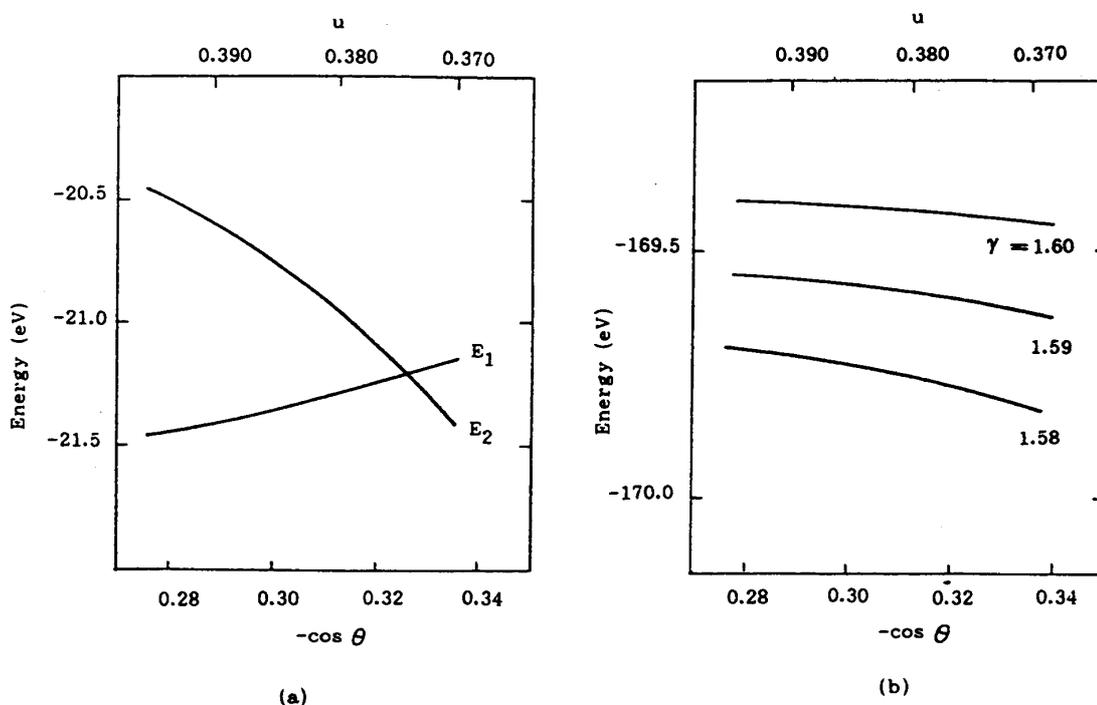Fig. 3. Total bonding energy with fixed bond lengths for (a) ZnO, (b) CdSe, and (c) CdS.

Fig. 4 (a) The θ dependence of E_1 and E_2 for ZnO.

(b) The total bonding energy, $6E_1+2E_2$, for ZnO.

lattice constants are almost identical to experimental values.

Then we assume experimental results for the lattice constant a and try to find out the value of θ which gives minimum electronic energy for given values of parameter γ.

As an example, the results for ZnO are plotted in Figs. 4 (a) and (b). Fig. 4 (a) shows the θ dependence of E_1 and E_2 and Fig. 4 (b) that of $E=6E_1+2E_2$. We see that there are no minima in the total electronic energy E over the range of γ, $1.58 < \gamma < 1.65$, and E decreases with the decrease of γ or the increase of u.
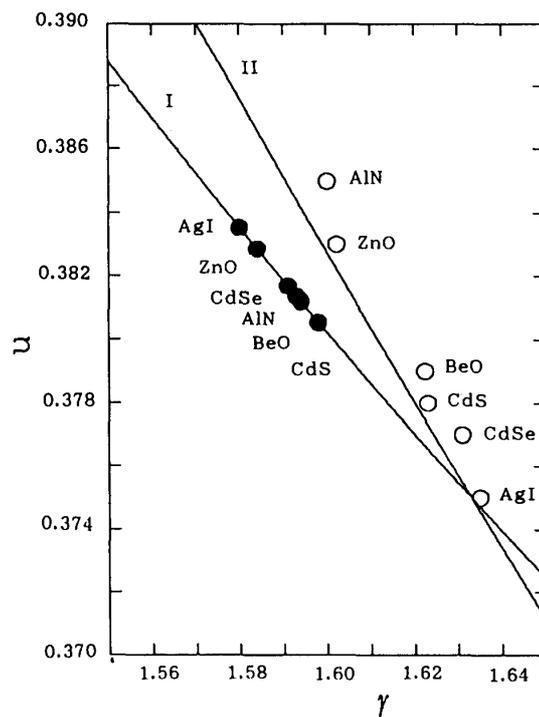
Fig. 5. Comparison between calculated and experimental $u - \gamma$ relations.
●denotes calculated value and ○ denotes experimental value.
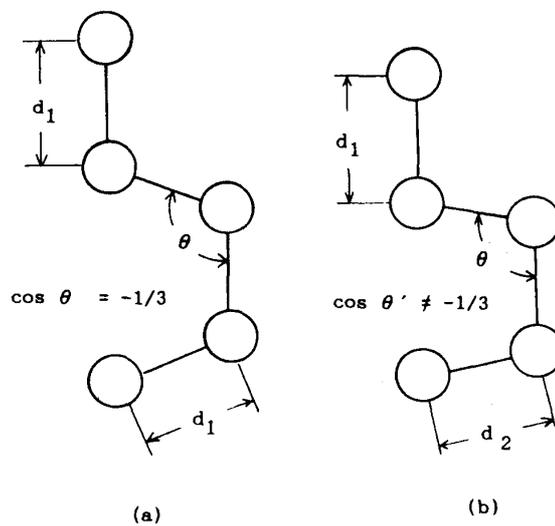The meanings of solid curves are in the text.

Fig. 6. (a) The ideal ionic configuration of B4 structure.
(d) The situation given by $u = \sqrt{3/8} / \gamma$.

Fig. 5 shows these results as the relation between u and γ in comparison with experimental data. Here the solid line (I) expresses the relation

$$1/(3\gamma^2) = u - 0.25,$$

which is derived analytically from the assumption of equal bond length.

In Fig. 5 we also plot another solid line (II)

$$u = \sqrt{3/8} / \gamma .$$

This relation can be obtained by moving the ionic positions along the c-axis under the condition that the bond length parallel to the c-axis is fixed to the ideal value $\sqrt{3/8} \, a$. These processes are shown in Fig. 6.

§4. Discussions

Crystal structure is determined by the stability condition or so as to minimize the total energy of the compound. In the case of compounds with covalent bonding, the electronic bonding energy may be evaluated by an appropriate application of bond orbital models. In fact, as shown in §3, the OBOM approximately reproduces the structure of real wurtzite crystals, when assumption is made on bond lengths from outside of the model.

At the same time, however, it seems that such models fail to give meaningful results when optimized with respect to parameters including bond lengths. This may indicate that we need more accurate estimations of the repulsive part of the interactions between atoms before the first principle calculation of stability of these crystals. In the meantime, the estimation of bond lengths based on covalent radii may be one of ad hoc but useful procedures.

Refences

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4) C. Kittel: *Introduction to Solid State Physics* (John Wiley & Sons Inc. 1976)
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