



# Bond energy in II-VI group of Semiconductors

Kalyan Singh<sup>1</sup>, V.K. Singh<sup>2</sup>, Arun Sharma<sup>3</sup>

<sup>1,3</sup>Deptt. of Applied Science, IIMT College of Engineering, Greater Noida

<sup>2</sup>D.S. College, Aligarh

Email: dr.ksrajpoot@gmail.com

**Abstract:** Semiconductors are presenting periodic table of group II-VI, in this paper, we have calculated values of bond energy of II-VI group of semiconductors. The value of bond energy found corresponding with bond orbital parameter ( $V_2$ ,  $V_3$ ), average s-p splitting ( $V_1^s$ ) and polarity ( $\alpha_p$ ) used as input data.

**Keywords:** Semiconductors, bond orbital parameters, s-p splitting and polarity.

**Introduction:** We have investigated bonding properties such as bond energy for II-VI group of semiconductors, by using bond orbital parameter based on tight binding theory with universal parameters. We have reviewed and discussed theoretical formulations for the bond energy. Various optoelectronic properties and bond energy describing the structural behaviour have been studied for the II-VI group of semiconductors. Some useful relationships have been obtained by making some theoretical assumptions for s-p splitting of the anion and cation, in the tight binding theory with universal parameters, which yield consistent results for bonding properties of II-VI group of semiconductors.

**Theory:** The bonding properties and bond length distortion of II-VI group of semiconductors studied by Kalyan Singh et al. [1] and optoelectronic properties of II-VI group of semiconductors studied by V.K. Singh et al. [2-4]. The term bond energy was used by

Pauling [5] such that the sum of all bond energies is the energy to separate the system into isolated atoms. In the bond orbital model [6] for polar semiconductors, the bond energy can be approximated by calculating the four major components in the energy as

$$E_{\text{bond}} = E_{\text{pro}} + E_{\text{sig}} + E_{\text{over}} + E_{\text{met}} \quad \dots (1)$$

where  $E_{\text{pro}}$  is promotion energy,  $E_{\text{sig}}$  is the bond formation energy,  $E_{\text{over}}$  is the overlap energy and  $E_{\text{met}}$  is the metallization energy. There are two aspects to the bond orbital approximation. First is the neglect of coupling between two hybrids on the same atom, but directed into different bonds. Second is the neglect of coupling between one hybrid and a hybrid on a neighbouring atom, but directed into a different bond.

A general sp-hybrid is a normalized sum of an S and P state which can be written,

$$|h\rangle = \text{Cos}\beta|S\rangle + \text{Sin}\beta|P\rangle \quad \dots(2)$$

the expectation value of the energy for such hybrid is

$$\left. \begin{aligned} \epsilon_h &= \text{Cos}^2\beta\epsilon_s + \text{Sin}^2\beta\epsilon_p \\ \epsilon_h &= \frac{\epsilon_s + 3\epsilon_p}{3} \end{aligned} \right\} \quad \dots (3)$$

for an  $Sp^3$  hybrid with  $\text{Cos}^2\beta = 1/4$ ,  $\text{Sin}^2\beta = 3/4$ . The formation of hybrids and  $\sigma$ -bond orbital are characterized by the bond orbital parameters  $V_1$ ,  $V_2$  and  $V_3$  which are in fact the metallic, covalent and polar energies respectively.

The metallic energy  $V_1$  for  $sp^3$  hybrids is given by [7,8]

$$V_1 = 1/4 (\epsilon_s - \epsilon_p) \quad \dots (4)$$

Where  $\epsilon_s$  and  $\epsilon_p$  are the free atom energies for S and P states,  $V_1$  is the principal term which gives the valency bonds and conduction bonds their width, but it does not affect the total energy in the bond orbital approximation. For this case promotion energy, which is the energy required to promote every electron from its atomic orbital to hybrid orbital is given by

[9]

$$E_{\text{pro}} = -2V_1 \quad \dots (5)$$

The covalent energy  $V_2$  is given by [9]

$$V_2 = \frac{\eta \hbar^2}{md^2} \quad \dots (6)$$

Where  $d$  is the nearest neighbour distance and  $\eta$  remains constant over the entire range of interest -3.19, -3.26 and -3.22 respectively, for  $sp$ ,  $sp^2$  and  $sp^3$  hybrids obtained using Harrison universal parameters [7]. According to Harrison [9], this variation is not important and we can take a approximate value -3.22 for tetrahedral semiconductors. Therefore equation [6] reduces to

$$V_2 = -\frac{3.22 \hbar^2}{md^2} \quad \dots (7)$$

The coupled hybrids from bonding and anti-bonding states of energy  $\epsilon_h \pm V_2$  and the gain in energy, called the  $\sigma$ -bonding energy and is given per bond by

$$E_{\text{sig}} = 2V_2 \quad \dots (8)$$

Since there are two electrons for each bond. In a polar bond the two hybrids forming the bond have different energy. The polar energy or hybrid ionic energy  $V_3$  is defined to be the half the difference as follows:

$$V_3 = \frac{(\epsilon_h^c - \epsilon_h^a)}{2} \quad \dots (9)$$

Where  $\epsilon_h^c$  and  $\epsilon_h^a$  are cation and anion hybrid energy respectively.

The bond orbital parameters are based upon the tight binding theory, with universal parameters introduced by Harrison [10-13] for the systematic study of properties of semiconductors.

The bond energy  $E_b$ , containing promotion energy,  $\sigma$ -bonding energy, overlap interaction effect of metallicity and polarity can be expressed as follows:

$$E_b = V_2 (1 - \alpha_m) + 3 [(V_1^a)^2 + (V_1^c)^2] (1 - \alpha_p^2)^{3/2} / 4V_2 \quad \dots (10)$$

Where  $\alpha_m$  is the metallicity defined as

$$\alpha_m = \frac{2V_1}{V_2} \quad \dots (11)$$

$\alpha_p$  is the polarity defined as

$$\alpha_p = \frac{V_3}{(V_2^2 + V_3^2)^{1/2}} \quad \dots (12)$$

$V_1^a$  and  $V_1^c$  are the s-p splitting of the anion and cation respectively, we assumed that

$V_1^a$  and  $V_1^c$  can be taken equal to  $V_1^s$  which is the average s-p splitting i.e.

$$V_1^a = V_1^c = V_1^s \quad \dots (13)$$

The metallic energy  $V_1$  is given as [7-9]

$$V_1 = \frac{(\epsilon_s - \epsilon_p)}{4} - \frac{\lambda_{sp\sigma} \hbar^2}{3md^2} \quad \dots (14)$$

Where  $\epsilon_s$  and  $\epsilon_p$  are the atomic term values. Their difference  $(\epsilon_s - \epsilon_p)$  has been obtained by

Harrison [7-9] by using tight binding theory with universal parameters given as

$$\epsilon_s - \epsilon_p = -\frac{5.55 \hbar^2}{md^2} \quad \dots (15)$$

and parameter  $\lambda_{sp\sigma}$  is given as

$$\lambda_{sp\sigma} = -\frac{27 \pi^2}{256} \quad \dots (16)$$

using equations (14) to (16) the metallic energy  $V_1$  can be written as

$$V_1 = -1.05 \frac{\hbar^2}{md^2} \quad \dots (17)$$

using equations (11) (13) and (17) with equation (10), the bond energy  $E_b$  can be written as

$$E_b = 0.347 V_2 + 3V_1^s (1 - \alpha_p^2)^{3/2} / 2V_2 \quad \dots (18)$$

We have calculated bond energy for II-VI group of semiconductors by using equation (18). The input data is given in Table-1. The calculated values of bond energy are compared with the available experimental values [9] as well as with the values obtained by Harrison [9] in Table-2.

Table-1. The values of bond orbital parameters ( $V_2$ ,  $V_3$ ) average s-p splitting ( $V_1^s$ ) and polarity ( $\alpha_p$ ) of II-VI group of semiconductors.

Compound	$V_2$ (ev)	$V_3$ (ev)	$V_1^s$ (ev)	$\alpha_p$
BeS	-6.360	-	1.54	0.21
BeSe	-5.860	-	1.65	0.32
BeTe	-4.920	-	1.49	0.00
ZnO	-7.625	6.62	1.65	0.70
ZnS	-4.510	4.13	1.50	0.73
ZnSe	-4.140	3.80	1.60	0.72
ZnTe	-3.430	3.04	1.44	0.72
CdS	-4.110	4.22	1.35	0.77
CdSe	-3.770	3.88	1.44	0.77
CdTe	-3.120	3.13	1.30	0.76
MgTe	-3.440	3.38	1.35	0.67

Table-2. The value of bond energy  $E_b$  (ev) for II-VI group of semiconductors

Compound	$E_b$		
	Present work equation (18)	Expt. values	Harrison values
BeS	-2.73	-	-
BeSe	-2.63	-	-
BeTe	-2.16	-	-
ZnO	-2.84	-	-
ZnS	-1.80	-	-
ZnSe	-1.75	-1.29	-0.93
ZnTe	-1.49	-	-
CdS	-1.60	-	-
CdSe	-1.52	-	-
CdTe	-1.31	-1.03	-0.67
MgTe	-1.52	-	-

**Result and Discussion:** We have studied the bond energy in II-VI group of semiconductors. For this purpose we have B-series, Al-series, Ga-series and In-series from II-VI group of semiconductors. We have calculated bond energy for II-VI group of semiconductors by using equation (18). The input data is given in table-1. The calculated values of bond energy are compound with available experimental values [9] as well as with the values obtained by Harrison [9] in table-2. It is found from table-2 that the values of bond energy obtained by Harrison are far from the experimental values in most of semiconductors in comparison to our results. It shows improvement over the work of Harrison. We have also predicted the

values of bond length of some semiconductors belonging II-VI group of semiconductors, for which values of bond energy are not reported so, far in the literature.

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