Force Constant in III-V group of semiconductors

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Abstract: Semiconductors are present in periodic table of group III-V. In this paper, we have calculated values of force constant of III-V group of semiconductors. The value of force constant found corresponding with bond orbital parameter (V_2, V_3), average s-p splitting (V_1^s) and covalency (α_c) used as input data.

Keywords: Semiconductors, bond orbital parameters, s-p splitting, force constant and covalency.

Introduction: We have investigated bonding properties such as force constant for III-V group of semiconductors, by using bond orbital parameters based on tight binding theory with universal parameters. We have reviewed and discussed theoretical formulations for the force constant. Various optoelectronic properties and bond force constant describing the structural behaviour have been studied for the III-V 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 III-V group of semiconductors.

Theory: The bonding properties such as bond length, bond length distortion and bond energy for III-V group of semiconductors studied by Kalyan Singh et al. [1-2] and optoelectronic properties of III-V group of semiconductors studied by V.K. Singh et al. [3-5]. The term bond energy was used by Pauling [6] such that the sum of all bond energies is the energy to separate the system into isolated atoms. In the bond orbital model [7] for polar semiconductors, the bond energy can be approximated by calculating the four major components in the energy as

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

where E_{pro} is promotion energy, E_{sig} is the bond formation energy, E_{over} is the overlap energy and E_{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,

$$|h> = Cos\beta|S> + Sin\beta|P> \quad \text{….(2)}$$

the expectation value of the energy for such hybrid is

$$\left.\begin{aligned} \in_h &= Cos^2\beta \in_s + Sin^2\beta \in_p \\ \in_h &= \frac{\in_s + 3\in_p}{3} \end{aligned}\right\} \quad \text{…. (3)}$$

for an Sp^3 hybrid with $Cos^2\beta = 1/4$, $Sin^2\beta = 3/4$. The formation of hybrids and σ-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 [8,9]

$$V_1 = 1/4\ (\in_s - \in_p) \quad \ldots (4)$$

Where $\in_s$ and $\in_p$ 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 [10]

$$E_{pro} = -\ 2V_1 \quad \ldots. (5)$$

The covalent energy V_2 is given by [10]

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

Where d is the nearest neighbour distance and η 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 [8]. According to Harrison [10], this variation is not important and we can take a approximate value -3.22 for tetrahedral semiconductors. Therefore equation (6) reduces to

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

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

$$E_{sig} = 2V_2 \quad \ldots. (8)$$

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:

$$V_3 = \frac{(\in_h^c - \in_h^a)}{2} \quad \ldots. (9)$$

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

The bond orbital parameters are based upon the tight binding theory, with universal parameters introduced by Harrison [11-14] for the systematic study of properties of semiconductors.

The bond energy E_b, containing promotion energy, σ-bnding energy, overlap interaction effect of metallicity and polarity can be expressed as follows:

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

Where α_m is the metallicity defined as

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

α_p is the polarity defined as

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

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.

$$V_1^a = V_1^c = V_1^s \quad \text{…. (13)}$$

The metallic energy V_1 is given as [8-10]

$$V_1 = \frac{(\in_s - \in_p)}{4} - \frac{\lambda_{sp\sigma}\hbar^2}{3md^2} \quad \text{….(14)}$$

Where $\in_s$ *and* $\in_p$ are the atomic term values. There difference $(\in_s - \in_p)$ has been obtained by Harrison [8-10] by using tight binding theory with universal parameters given as

$$\in_s - \in_p = -\frac{5.55\,\hbar^2}{md^2} \quad \text{…. (15)}$$

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

$$\lambda_{sp\sigma} = -\frac{27\,\pi^2}{256} \quad \text{…. (16)}$$

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

$$V_1 = -1.05\,\frac{\hbar^2}{md^2} \quad \text{…. (17)}$$

using equations (11) (13) and (17) with equation (10), the bond energy E_b can be written as, Kalyan et al. [2]

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

The covalence energy V_2 which is the potential parameter is related with bond length Kalyan et al. [1]

$$d^2 = -\left(\frac{24.532}{V_2}\right) \quad \text{…..(19)}$$

The force constant k for a bond, which is the second derivative of the bond energy with respect to d can be expressed as

$$k = -\frac{8V_2\alpha_c^3}{d^2} + \frac{9\,[(V_1^a)^2 + (V_1^c)^2]}{V_2 d^2}\,(5\alpha_c^2 - 4)\,\alpha_c^5 \quad \text{…. (20)}$$

where α_c is the hybrid covalency and it is defined as

$$\alpha_c = \frac{V_2}{(V_2^2 + V_3^2)^{1/2}} \quad \text{…. (21)}$$

using equation (13), (19) and (21), the expression for force constant (k) i.e. equation (20) can be reduced as

$$k = 0.326V_c^3 - 0.733(V_1^s)^2\ (5\alpha_c^3 - 4)\alpha_c^5 \quad \ldots. (22)$$

We have calculated force constant for III-V group of semiconductors by using equation (22). The input data is given in Table-1. The calculated values of force constant in table-2 and compared with the values obtain by Harrison [10].

Table-1: The values of bond orbital parameters (V_2, V_3) average s-p splitting (V_1^s) and covalency (α_c) of III-V group of semiconductors

Compound	V_2 (ev)	V_3 (ev)	V_1^s (ev)	α_c
BN	-10.35	3.12	1.70	0.91
BP	-6.605	1.20	1.54	1.00
BAs	-6.235	1.07	1.65	1.00
AlN	-7.215	4.09	1.54	0.81
AlP	-4.465	2.17	1.40	0.88
AlAs	-4.205	2.04	1.50	090
AlSb	-3.610	1.48	1.35	0.84
GaN	-7.005	3.92	1.65	0.78
GaP	-4.355	2.00	1.50	0.85
GaAs	-4.100	1.87	1.60	0.87
GaSb	-3.535	1.30	1.44	0.90
InN	-6.285	4.150	1.49	0.77
InP	-3.870	2.23	1.35	0.81
InAs	-3.645	2.10	1.44	0.85
InSb	-3.115	1.54	1.30	0.86

Table-2. The value of force constant (k) (10^5 dyne/cm) for III-V group of semiconductors

Compound	Force Constant (k)	
	Present work equation (22)	Harrison
BN	4.21	-
BP	2.00	-
BAs	1.71	-
AlN	1.51	-
AlP	0.72	-
AlAs	0.66	-
AlSb	0.45	-
GaN	1.30	-
GaP	0.65	-
GaAs	0.61	0.63
GaSb	0.47	-
InN	1.01	-
InP	0.47	-
InAs	0.47	-
InSb	0.35	0.37

Result and Discussion: We have studied the force constant in III-V group of semiconductors. For this purpose we have B-series. Al-series, Ga-series and In-series from III-V group of semiconductors. We have calculated force constant for III-V group of

semiconductors by using equation (22). The input data is given in table-1. The calculated values of force constant are compared with the values obtained by Harrison [10] in table-2. It is found from table-2 that the values of force constant calculated by equation (22), with the results obtained by Harrison. We have also predicted the values of force constant of some semiconductors belonging III-V group of semiconductors, for which values of force constant are not reported so, far in the literature.

References:

1. Kalyan Singh, V.K. Singh, P.K. Sharma, International Journal of Research in Applied Science and Engineering Technology, Vol. 10, Issue VI, 1086 (June 2022).
2. Kalyan Singh, P.K. Sharma, International Journal of Science and Research, Vol. 11, No. 5, 437 (2022).
3. V.K. Singh, Manju Giri and Kalyan Singh, Acta Ciencia Indica Vol. XXXIX P, No. 3, 147 (2013).
4. V.K. Singh, Manju Giri and Kalyan Singh, Acta Ciencia Indica Vol. XXXIX P, No. 3, 141 (2013)
5. V.K. Singh, R.S. Indolia and Kalyan Singh, Acta Ciencia Indica Vol. XXXVI P, No. 2, 245 (2010).
6. L. Pauling, the Nature of the Chemical bond, 3rd ed. Cornell University Press, Ithaca (1960).
7. M. Lannoo, Journal of Phys. C. 17, 3137 (1984).
8. W.A. Harrison, Electronic Structure and Properties of Solids (free man, San Francisco, 1980)
9. W.A. Harrison, Phys. B **24**, 5835 (1981).
10. W.A. Harrison, Phys. Rev. B **27**, 3592 (1983).
11. W.A. Harrison, Phys. Rev. B **8**, 4487 (1973).
12. W.A. Harrison and S. Ciraci, ibid **10**, 1516 (1974)
13. W.A. Harrison, Phys. Rev. B **10**, 767 (1974).
14. W.A. Harrison and J.C. Phillip's Phys. Rev. Letter **33**, 410 (1974).