Indian J. Phys. **77A** (3), 237–241 (2003)

AN INTERNATIONAL JOURNAL IJPA

Interatomic force constants, ionicity and microhardness of binary tetrahedral semiconductors

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Received 29 December 2000, accepted 5 February 2003

Abstract . A simple relation between lattice energy (U), bond stretching and bond bending force constants (α, β), ionicity (f_i) and microhardness (H) developed for $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors. The results are in excellent agreement with the values reported by different investigators

Keywords : Lattice energy, force constants, ionicity, microhardness, tetrahedral semiconductors.

PACS Nos. . 62.20.Qp, 05.50.+q, 34.20.Cf

1. Introduction

During the last few decades, a considerable amount of experimental and theoretical work has been done to understand different properties such as optical, electronic, elastic and thermal properties of binary semiconductors. In the recent past, much attention has been given to the study of binary tetrahedral semiconductors because of their potential applications in the field of linear and non-linear optics, solar cells, light emitting diodes, laser diodes and integrated optical devices such as switches, modulators and filters.

In the valence-force-field model for sphalerite-structure compounds, Martin [1] has introduced two interatomic force constants like bond stretching (α) and bond-bending force constants (β), respectively. The nearest-neighbour bond-stretching central forces have been characterised by the parameters, $\alpha(\mathrm{Nm^{-1}})$ and next-nearest-neighbour bond bending non-central forces by the parameters $\beta(\mathrm{Nm^{-1}})$. In the Martin analysis [1], the contribution of Coulomb force to the elastic constants has been described in terms of the macroscopic effective charge which is responsible for the splitting of transverse and longitudinal optical modes. Lucovsky *et al* [2] have pointed out that the Martin approach [1] is incorrect. The ratio $\beta/\alpha = 0.3\ (1 - f_i)$ measures the importance of covalent bonds in determining the stability of the tetrahedral structures. The overall trend of β/α tends to zero if ionicity f_i tends to unity, *i.e.* for purely ionic crystals. Neumann [3] has extended the Keating [4] model considering localized effective charge to account for long-range Coulomb force and dipole-dipole interaction in analysing the vibrational properties of binary and ternary compounds with a sphalerite-structure. Neumann [5–8] has introduced the experimental values of bond length (d) and spectroscopic bond ionicity (f_i) to determine the constant associated with the above theory. Recently, using plasma oscillations theory of solids, Kumar [9] have developed a simple relation between plasmon energy ($\hbar\omega_p$) and bond length. Kumar *et al* [10] have established a connection

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between α and bond length and β is proportional to α. Thus, β is connected by plasmon energy and the other force constant (α). Reddy *et al* [11–16] and Kumar *et al* [10] have reported a simple correlation between lattice energy U (kcal/mol), plasmon energy ($\hbar\omega_p$) and microhardness H (GPa) for binary tetrahedral semiconductors. Since the optical, structural, stability and other physical properties of semiconducting compounds play important roles in device development and fabrication, it is worthwhile to develop different relations in terms of force constant, microhardness, ionicity and lattice energy. In the present paper, the correlation between lattice energy, bond stretching and bending force constants, ionicity and microhardness have been obtained for $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors.

2. Theory

The nearest-neighbour bond-stretching central forces have been characterized by the parameter α, and next-neighbour bond-bending non-central forces by the parameter β. These parameters depend on interatomic distance obtained from lattice vibration data [10]. The lattice vibration data have been further obtained from various types of two-body interacton potentials given in the literature. Such potentials have the advantage of keeping the repulsive and attractive forces in the same mathematical form. Neumann [5–8] and Harrison [17,18] have attempted to describe these type of potentials. On the basis of repulsive and attractive forces and on Born and Mayer cycle, Ladd and Lee [19] have proposed different potential functions to estimate lattice energies. Interatomic distance, lattice energy, Madelung constant and others are well related by Born-Mayer theory and other potential functions. Reddy *et al* [12] and Kumar *et al* [10] have proposed different relations between lattice energy and plasmon energy. The proposed relations are successfully used for the estimation of lattice energy. The results are in good agreement with the experimental values. Kumar *et al* [20] have also established another relation between microhardness and plasmon energy and bond length and plasmon energy. The above discussion finally suggests that there must be a definite relation between α, β, bond length or interatomic distance, lattice energy, plasmon energy, ionicity and microhardness.

Kumar *et al* [10] have developed the following quadratic relation between lattice and plasmon energies

$$U = a1 + b1(\hbar\omega_p) - c1(\hbar\omega_p)^2. \tag{1}$$

The numerical values for $a1, b1, c1$ are resepctively, 421.224, 27.940 and 0.178 for both II–VI and III–V groups of semiconductors. Reddy *et al* [12] have derived an empirical linear relation between U and $\hbar\omega_p$ in the case of II–VI group semiconductors as

$$U = 381.9 + 24.3\ (\hbar\omega_p). \tag{2}$$

Recently, Kumar [9] have also proposed the following relations :

$$\alpha = 0.398(\hbar\omega_p)^{1.70}, \tag{3}$$

where α and $\hbar\omega_p$ are force constant and plasmon energy respectively. Kumar [9] have given another linear relation which describes the connection between microhardness H and plasmon energy $\hbar\omega_p$:

$$H = K_1(\hbar\omega_p) - K_2, \tag{4}$$

where K_1 and K_2 are constants.

The above equations clearly demonstrate the correlation between lattice energy U, force constant α, microhardness and plasmon energy. To estimate U, α and H, the required parameter is only $\hbar\omega_p$.

Based on the above correlations, the following equation is proposed for the calculation of α :

$$\alpha = m_\alpha U - b_\alpha, \tag{5}$$

where m_α and b_α are constants. α and U are in Nm^{-1} and kcal/mol. The significance and the meaning of α and U are described earlier. In eq. (4), experimental lattice energies are used for the estimation of α. The estimated α values from eq. (5) are in excellent agreement with the literature values and proved its linear nature.

Neumann [5–8] has obtained a relation between bond stretching (α) and bond bending (β) force constants as

$$\beta = \beta_0(1 - f_i)\alpha, \tag{6}$$

where $\beta_0 = 0.28$ and f_i is the ionicity [21].

Similar to eq. (6), the following relation is proposed

$$\beta = m_\beta U - b_\beta, \tag{7}$$

where m_β and b_β are constants.

α and β values obtained from eqs. (5) and (7) are substituted in eq. (6) and then ionicity f_i can be written as

$$f_i = 1 - (\beta / \alpha\beta_0), \tag{8}$$

here $\beta_0 = 0.28$.

Based on the least-square fit of the points between microhardness (H) and lattice energy (U), the following relation has been obtained

$$H = m_H\ U - b_H, \tag{9}$$

where m_H and b_H are constans.

In this model, only lattice energy data is required to estimate α, β, f_i and H values. The computed force constants (α, β), ionicity and microhardness are in good agreement with the literature values [5–9,20,22–24].

3. Results and discussion

The present paper reports different correlations between α, β, f_i and H in $A^{II}B^{V}$ and $A^{III}B^{V}$ semiconductors. The relevant numerical constants used in the above equations are given in Table 1. The calculated values of the above parameters from eqs. (5), (7), (8) and (9) are listed in Tables 2 and 3. A fairly good agreement has been observed between the calculated force constants, ionicity and microhardness with the experimental and literature values [5–9,20,22–24]. The mentioned theory clearly indicates the correlation between lattice energy and α, β, f_i and H. Figures (1–4) shows the trend between present approach and the values obtained by others. A slight deviation has been observed only in the case of ZnSe, ZnTe and CdTe, GaSb for α and β with the results of Neumann [5–8]. This may be due to strong electronegativity values for Se^{-} and Te. The main advantage of the present model is the simplicity of the formulae.

Using eq. (8), the ionicity (f_i) values for $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductors have been calculated. The results are presented in Table 3 together with the values obtained by Biswas *et al* [22] and Kumar *et al* [23]. These values are in consistence with the previous investigations. The calculated

Table 1. Numerical values of the constants m and b.

Parameter	Semiconductors	m	b
α	$A^{II}B^{VI}$	0.2242	139.24
	$A^{III}B^{V}$	0.2422	153.59
β	$A^{II}B^{VI}$	0.0239	15.453
	$A^{III}B^{V}$	0.0491	31.911
H	$A^{II}B^{VI}$	0.01728	11.5707
	$A^{III}B^{V}$	0.006	0.0112

Table 2. Interatomic force constants of binary semiconductors

Compounds	Lattice energy U(kcal/mol) Ref. [10]	α(Nm^{-1}) Eq. [5]	Ref. [9]	Ref. [3–6]	β(Nm^{-1}) Eq [7]	Ref. [9]	Ref. [3–6]
$A^{II}B^{VI}$							
BeS	899	62.648	63.18	–	6.018	6 14	–
BeSe	875	56.967	57.89	–	5 445	5.49	–
BeTe	825	45.755	46.02	–	4.250	4.22	–
MgTe	754	29.834	30.07	–	2 555	2.65	–
ZnO	939	71.318	73.66	–	6.973	7.3	–
ZnS	838	48.67	49.09	44.73	4 561	4.54	4.36
ZnSe	818	44.185	44.26	38.61	4 083	4.05	4.65
ZnTe	795	39.028	39.02	32.04	3 534	3.52	4 47
CdS	798	39.701	39.63	–	3.606	3.58	–
CdSe	778	35.216	35.22	–	3.128	3.14	–
CdTe	756	30.283	30.65	29.44	2.602	2.71	2.48
$A^{III}B^{V}$							
BN	999	88.357	89.58	–	17.179	17.58	–
BP	944	75.037	75.21	–	14.477	14.48	–
BaS	911	67.044	66.94	–	12.855	12 74	-
AlN	969	81.091	81.98	–	15.705	15.87	–
AlP	837	49.122	48.78	–	9.219	9.07	–
AlAs	817	44.278	44.1	–	8.236	8.15	–
AlSb	771	33.137	33.77	35.74	5.975	6.15	6.63
GaN	949	76.248	76.6	–	14.722	14.77	–
GaP	834	48.395	48	48.57	9.071	8.91	10.4
GaAs	808	42.098	42.04	43.34	7.794	7.74	8.88
GaSb	763	31.2	32.08	34.42	5.582	5.84	7.16
InN	884	60.505	60.14	–	11.528	11.35	–
InP	795	38.950	39.02	4.29	7.155	7.15	–
InAs	779	35.075	35.52	37.18	6.369	6.49	5 47
InSb	748	27.567	28.88	30.44	4.845	5.23	4.73
Average deviation		4.58	4.57	–	4.36	12.8	–

Table 3. Ionicity and microhardness of binary tetrahedral semiconductors.

Compounds	Lattice energy U(kcal/mol) Ref. [10]	Ionicity, f_i		Micro hardness, H(Gpa)			
		Eq [8]	Ref. [22,23]	Eq. [9]	Ref. [20]	Ref [24]	Ref. [24]
$A^{II}B^{VI}$							
BeS	899	0.655	0.656	3.964	3.23	-	-
BeSe	875	0 658	0.661	3.549	2.75	-	
BeTe	825	0.667	0.672	2.685	1.8	-	-
MgTe	754	0.693	0.685	4.655	4.05	3.9–4.8	4 6
ZnO	939	0 650	0.646	2.909	2.05	1.7, 2.8, 3.5	3.3
ZnS	838	0.665	0.669	2.564	1.66	1.3–1.8	1 7
ZnSe	818	0.669	0.673	2.166	1.23	0.8–1.1	1 0
ZnTe	795	0 676	0.678	2.218	1.28	1.2	1 1
CdS	798	0.675	0.677	1.873	0.91	0.7–1.2	0 8
CdSe	778	0 682	0.681	1 492	0.53	0 4–0.64	0 5
CdTe	756	0 692	0.684	1.458	0.48	-	-
$A^{III}B^{V}$							
BN	999	0.305	0.299	43.389	26.90	34 3–73 0	45 8
BP	944	0 311	0 312	23 434	20.73	31 4–40	32 3
BaS	911	0.315	0 320	16.193	17.24	19	24 2
AlN	969	0.308	0 306	31 007	23 48	12.3	19 5
AlP	837	0 329	0 336	7.069	9.64	5.5	10 9
AlAs	817	0.335	0.340	5 65	7.67	4.85	6 3
AlSb	771	0.356	0.349	3.375	3 23	4.0	
GaN	949	0.310	0 311	24 78	21.32	-	10 9
GaP	834	0.330	0.337	6.836	9.32	9 45	-
GaAs	808	0.338	0.342	5.109	6.79	7.50	-
GaSb	763	0.361	0.350	3.086	2.48	4 48	-
InN	884	0 319	0.326	11 96	14 40	-	5 3
InP	795	0.344	0.345	4.416	5.50	4.10	-
InAs	779	0.351	0.347	3.692	3.99	3 3	-
InSb	748	0.372	0.353	2.609	1.06	2.20	-
Average deviation		1 23	-	-	-	-	-

values of H obtained from eq. (9) are listed in Table 3 and compared with the values reported by Kumar *et al* [20] and Garbato *et al* [24]. These values are in good agreement with the reported values in literature [20,24]. In most of the cases,

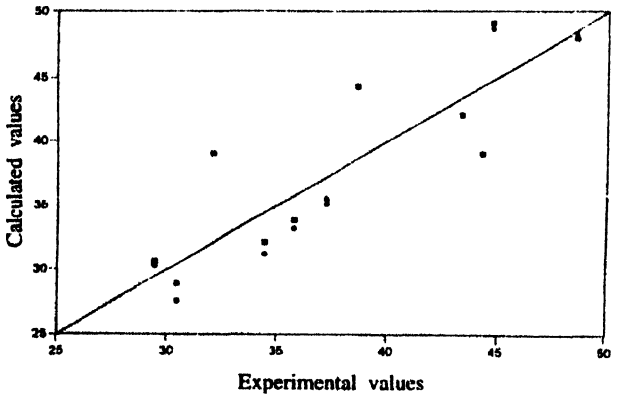

Figure 1. The relationships between the experimental values (Refs. [3–6]) of force constants, α of binary semiconductors and those calculated from lattice energy U (eq. (5)) and plasmon energy, $\hbar\omega_p$ (Ref. [9]). The line is of unit slope. Circle indicates eq. (5) and square indicates $\alpha(\hbar\omega_p)$ (Ref. [9]) of binary semiconductors.

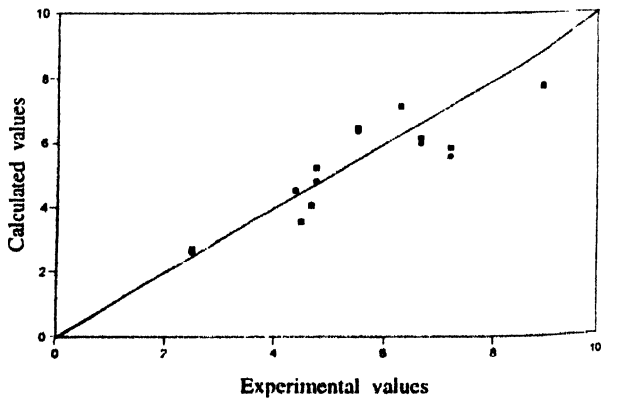

Figure 2. The relationships between the experimental values (Refs [3–6]) of force constants β of binary semiconductors and those calculated from lattice energy U (eq. (7)) and plasmon energy $\hbar\omega_p$ (Ref. [9]) The line is of unit slope. Circle indicates eq. (7) and square indicates $\beta(\hbar\omega_p)$ (Ref. [9]) of binary semiconductors.

the estimated values are in good agreement with the work of Kumar *et al* [9]. Thus, the proposed model has been verified and it agreed well for these semiconductors. It is

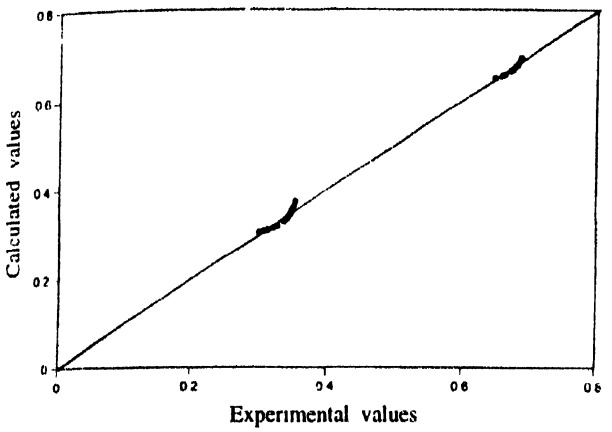

Figure 3. The relationships between the experimental values (Refs [22,23]) ionicity f_i of binary semiconductors and those calculated from lattice energy U (eq. (8)) The line is of unit slope Circle indicates eq (8) of binary semiconductors.

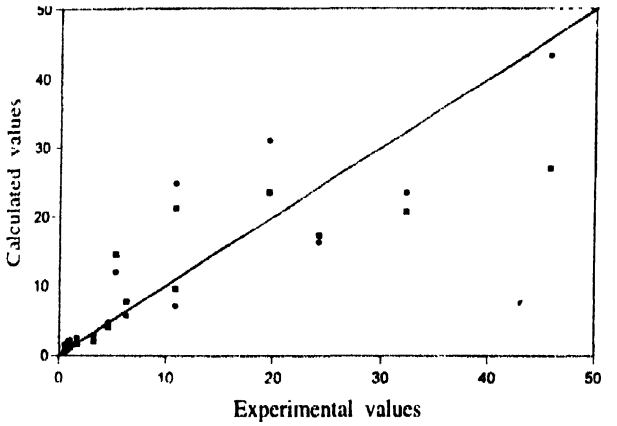

Figure 4. The relationships between the experimental values (Ref. [21]) of microhardness H of binary semiconductors and those calculated from lattice energy U (eq (9)) and plasmon energy $\hbar\omega_p$ (Ref [24]) The line is of unit slope. Circle indicates eq. (9) and square indicates $H(\hbar\omega_p)$ (Ref [24]) of binary semiconductors

concluded from the present study that one can predict the values of α, β, f_i and H for unknown compounds belonging to these groups of semiconductors from their lattice energy.

Average percentage deviation has been computed by considering Neumann [5–8] values as standard ones for the parameters α, β and f_i and are listed at the end of the Tables (2–3).

Microhardness values quoted in the literature are inconsistent with each other. In most of the cases, our estimated values are in fair agreement with Kumar *et al* [20]. Comparing the results between Kumar *et al* [20] and Neumann [5–8], it is noticed that H values are deviating more in the case of ZnO, BN, BP, BaS, GaN and InN. More divergence has been observed with our results. In view of the above, average percentage deviation has not been estimated. Some refinement in the nature of proposed model may yield better results.

Acknowledgments

The support of this research by the University Grants Commission, New Delhi under UGC Career Award (RRR) is gratefully acknowledged.

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