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Research Paper

Interatomic Force Constants, Ionicity and Bulkmodulus of Binary Tetrahedral Semiconductors

Physics

KEYWORDS : Force constants; Ionicity; Bulkmodulus; Plasmon energy

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ABSTRACT

A general linear empirical formula is proposed for calculating bond stretching force constants and bond bending force constants from Plasmon energy of binary tetrahedral semiconductors.The calculated values of bond stretching force constants and bond bending force constants is used to estimate the ionicity of compounds and finally bulkmodulus is calculated from plasmon energy of binary tetrahedral semiconductors.The calculated values are in good agreement with the reported values in the literature. Present study helps in designing novel semiconductor materials and to further explore the mechanical properties of these semiconductors.

1. Introduction

Interest in the study of various properties of binary tetrahedral semiconductors has been increasing in recent years because of their increasing scientific and technological application [1-12]. Interatomic force constants of these materials has, however,not been studied so much.Martin [13] proposed two interatomic force constants like bond stretching (α) and bond bending force constants (β) considering the valence force field model of Keating [14]. In Martin's approach the contribution of Coulomb force to the elastic constants has been explained in terms of the macroscopic effective charge which is responsible for the splitting of transverse and longitudinal modes Lucovsy and coworkers [15] have showed that the Martin's approach is incorrect .The ratio $\frac{\beta}{\alpha}$ measures the strength of covalent bonds to estimate the stability of transverse and longitudinal optical modes. Using the Keating model Neumann [16] analysed the vibrational properties of binary and ternary compounds to account for long range coulomb force and dipole dipole interaction following the localised effective charge.From the theoretical point of view density functional theory (DFT) [17-19] within the local density approximation (LDA) has been shown to be able to describe very accurately the structural and lattice dynamical properties of covalently bonded materials using pseudopotentials and plane wave basis sets.In the frame work of density functional perturbation theory (DFPT) it has been possible to calculate phonon frequencies,dielectic constants, piezoelectric constants, effective charges,interatomic force constants and other properties of elemental and III-V semiconductors. Kagaya and soma [21] proposed some empirical potential in interatomic force constants to analyse lattice dynamics, to obtain phonon dispersion curves for tetrahedral compounds.Vershney and coworkers [20] proposed a complex effective interatomic potential to describe structural phase transition and elastic properties induced by pressure.Considering the interatomic potential described by Neumann [22,23] and Harrison [24] and using Plasmon oscillation theory Kumar [25] reported two empirical relations (expotential as well as power) between interatomic force constants and plasmon energy of binary tetrahedral semiconductors.Reddy and co-workers [26] proposed a linear relation between interatomic force constants and lattice energy and estimated the ionicity as well as microhardness of these semiconductors.An empirical relation, using ionic charge model, was,however proposed by Verma [27] while determining the interatomic force constants of binary tetrahedral semiconductors. Using Plasmon oscillation theory and ionic charge model , Kumar,Reddy and co-workers and Verma established a simple relation between interatomic force constants,Plasmon energy,lattice energy and bulk modulus for binary tetrahedral semiconductors. Since the basic properties of molecules and solids are explained in terms of valence electrons in plasmon energy as well as ionic charge of valence electrons in binary tetrahedral semiconductors ,therefore it is worth while to develop different relations in terms of force constants,ionicity, bulkmodulus and plasmon energy. In this study we have proposed an empirical relation between interatomic force constants with plasmon energy and estimated ionicity and bulk modulus is also estimated from plasmon energy of these materials.

2. Method of calculation

2.1 Correlation between plasmon energy and bond stretching force constants of binary tetrahedral semiconductors.

The nearest neighbour bond stretching central forces have been characterised by the parameter (α).Kumar [25] has shown that the bond stretching force constants (α) may be determine in terms of plasmon energy by the following form

$$\alpha = 0.398(\hbar\omega_p)^{1.0} \qquad (1)$$

and

$$\alpha = 704.3\exp\{-17.41(\hbar\omega_p)^{-2/3} \qquad (2)$$

where equation (1) and (2) α is in N/m and $\hbar\omega_p$ in eV.
In order to estimate the bond stretching force constants α Reddy and coworkers [26] have proposed the linear relation between α and lattice energy as

$$\alpha = m_\alpha U - b_\alpha \qquad (3)$$

where m_α and b_α are constants, α and U are in N/m and Kcal/mol. Their values are 0.2242,139.24 and 0.2422,153.59 respectively for II-VI and III-V semiconductors. Recently Verma [27] has shown that bond stretching force constants (α) of binary tetrahedral semiconductors can be evaluated using their ionic charge by the following relation

$$\alpha = A(Z_1 Z_2)^S / d^3 \qquad (4)$$

where Z_1 and Z_2 are the ionic charge on the cation and anion respectively and d is the nearest neighbour distance respectively in A^0. A and S are constants which depend on their crystal structure and their values are 410 and 0.2 respectively.The results obtained by these authors showed a marked departure from reported as well as experimental values in several other instances [14,16,22,24-26]. However, these results have shown that there must exist some correlation between bond stretching force constants and plasmon energy of materials.Interatomic force constants of a solid is the energy required to separate its constituent ions.In other words it is equal to binding energy of ions in the solid.Higher the value of this energy,tighter will be binding between ions and hence higher will be plasmon energy. These arguments lead to possible correlation between interatomic force constants and plasmon energy. To establish such relationship, a graph has been plotted showing the variation of bond stretching force constants with plasmon energy $\hbar\omega_p$, for II-VI and III-V tetrahedral semiconductors using the experimental values of bond stretching force constants. The plot of α vs $\hbar\omega_p$ for these compounds need Fig. 1 be linear as

$$\alpha = C(\hbar\omega_p) + D \qquad (5)$$

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where C and D have their values 4.2242 and -27.5 for II-VI semiconductors , and 4.8775 and -30.894 for III-V semiconductors respectively.

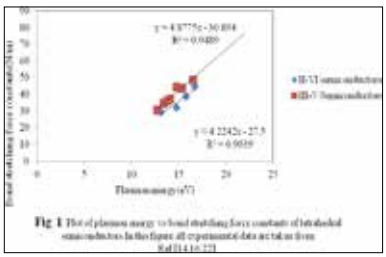

Fig. 1 Plot of plasmon energy vs bond stretching force constants of tetrahedral semiconductors.In this figure all experimental data are taken from Ref [14,16,23].

2.2 Correlation between bond bending force constants and Plasmon energy of binary tetrahedral semiconductors.

According to Martin [13] the bond bending forc onstants (β) follows the proportionality relation $\beta \propto (1-f_i)\alpha$ .Where f_i is the ionicity of the A-B bond in the binary tetrahedral semiconductors.Using the reported values of f_i [5] Neumann [32] has plotted a curve between $\frac{\beta}{\alpha}$ and f_i and a linear relation has been obtained between them.Based on the least square fit of the data points the following relation has been obtained

$$\beta = \beta_0(1-f_i)\alpha \qquad (6)$$

where $\beta_0 = 0.8 \mp 0.0$ [31] is the proportionality constants.Kumar [25] used the calculated values of α from equation (1) and equation (2) to estimate the values of β in which the value of $\beta_0 = 0.8$ has been taken.Considering equation (6) Reddy and coworkers [26] has proposed the following linear empirical relation between lattice energy and bond bending force constants

$$\beta = m_\beta U - b_\beta \qquad (7)$$

where m_β and b_β are constants.The values of constants are 0.0239 and 15.453 for II-VI semiconductors,0.0491 and 31.911 for III-V semiconductors respectively .Based on the concept of ionic charge model of semiconductors, Verma [27] has proposed the following relation

$$\beta = V(Z_1 Z_2)^B / d^3 \qquad (8)$$

where V and B are constants and the value of the constants are 17.6 and 0.85 respectively. Z_1 and Z_2 are the ionic charge of the cation and anion respectively, and d is the nearest neighbour distance in A0 . All the above equations (6-8) depicts that bond bending force constants has direct bearing on plasmon energy,lattice energy ,ionic charge of cation and anion and nearest neighbour distance.To establish such relationship,using the experimental values of bond bending force constants , a graph has been plotted showing the variation of bond bending force constants β with plasmon energy $\hbar\omega_p$, for II-VI and III-V tetrahedral semiconductors. The plot β of vs $\hbar\omega_p$ for these compounds need Fig. 2 be linear as

$$\beta = E(\hbar\omega_p) + F \qquad (9)$$

where E and F are constants and their values are 1.3291and -12.008 for II-VI semiconductors,and 0.4971 and -3.5437for III-V semiconductors respectively. The estimated values of α and β from equation(5) and equation(9) are substituted in equation (6) and ionicity is obtained by the following formula

$$f_i = 1 - \left(\beta / \beta_0\right) \qquad (10)$$

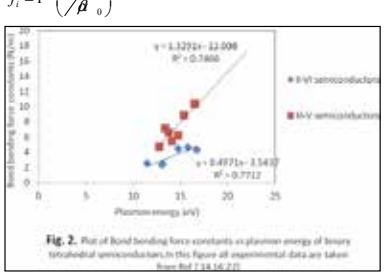

Fig. 2. Plot of bond bending force constants vs plasmon energy of binary tetrahedral semiconductors.In this figure all experimental data are taken from Ref [14,16,23].

2.3. Correlation between bulkmodulus and Plasmon energy of compounds.

The bulk modulus of any material depends on the volume of its constituent atoms. The bulk modulus of any material depends on the valence electron gas pressure completely determine the resistance of atoms to compression. Lam and co-workers [28] and Cohen[29] proposed some simple linear relation between bulkmodulus and bond length.Neumann[16] has developed some empirical relations between bulk modulus, microhardness ionicity.Based on the concept of transition pressure (p_t) Al-Douri and co-workers [30] proposed an empirical relation for bulkmodulus in terms of transition pressure. Kumar and coworkers [34] has proposed power relation between bulkmodulus and plasmon energy of tetrahedral semiconductors. Reddy and co-workers [36] has proposed a simple relation between bulkmodulus and energy gap (E_g) for elemental, compounds and ternary chalcopyrite group of semiconductors and calculated electronic polarisability for compound and ternary chalcopyrite semiconductors.Gorai [12] has given a good account of correlation between bulkmodulus and average principal quantum numberas as well as electronegativity of constituent atoms of compounds and estimated the microhardness of binary tetrahedral semiconductors.Considering the ionic charge model Verma and coworkers [37] has proposed an empirical relation between thermal conductivity and product of ionic charges of cation and anion and also with the nearest neighbour distance (A^0) and also calculated bulkmodulus from thermal conductivity of compound semiconductors. Based on the above relations and our own effort,a relation between bulkmodulus and plasmon energy was established and a graph was plotted given in figure. 3. A graph has been plotted showing the variation of experimental values of bulkmodulus (B) with Plasmon energy $\hbar\omega_p$, for II-VI and III-V tetrahedral semiconductors. The plot of B vs $\hbar\omega_p$ for these compounds need Fig. 3 be linear as

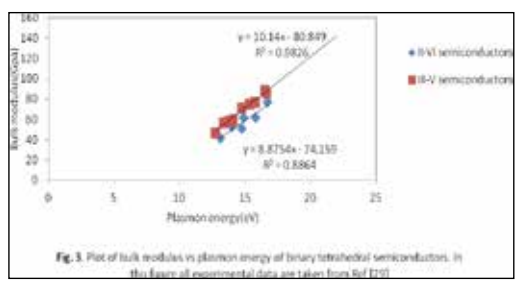

Fig. 3. Plot of bulk modulus vs plasmon energy of binary tetrahedral semiconductors. In this figure all experimental data are taken from Ref [23]

$$B = G(\hbar\omega_p) + H \qquad (11)$$

where G and H are constants and their values 8.8754 and -74.159 for II-VI semiconductors,and 10.14 and -80.849 for III-V semiconductors respectively.

3. Results and discussion

We have proposed four simple linear equations to calculate bond stretching force constants,bond bending force constants,ionicity and bulkmodulus of tetrahedral semiconductors.Using equations (5),(9),(10),(11) the values of bond stretching force constants,bond bending force constants,ionicity and bulkmodulus have been estimated.The estimated values are given in table1-table2.along with the experimental and reported values.Reasonably good agreement has been obtained between the calculated,experimental and reported values.we have calculated the percentage deviation of equations (5),(9),(10),(11) using the relation |experimental value-calculated value|/experimental value and estimated values are shown in table 1 and table 2.Average percentage deviation for α, β, B for II-VI and III-V tetrahedral semiconductors have been found to be respectively 5.16,2.02,14.95,11.83,2.28. For comparison we have also calculated the average percentage deviation of α, β, B for II-VI and III-V group of semiconductors with respect to the values reported by earlier researchers.The minimum average percentage deviation of α is 2.02 has been found in case of bond stretching force constants.The maximum average percentage deviation has been obtained 14.95 slightly higher than Verma[27]. In case of bond bending force constants in all

cases average percentage deviation of our model is better than the models proposed by earlier researchers.Using equation(10) the ionicity f_i values for AIIBVI and AIIIBV semiconductors have been calculated.The results are presented in table 2 together with the values obtained by Biswas and coworkers [33] and Kumar [25].These values are in consistence with the previous investigation.

The calculated average percentage of deviation in the tables shows that our proposed empirical relations give better agreement with the experimental datas compared with values reported by previous researchers.In this case plasmon energy is the only input variable,which do not require any experimental data like bond length,electronic susceptibilities,melting point and lattice parameter of these semiconductors. The inclusion of Plasmon energy has some bearing on the concept chemical bonding. From this study it is possible to correlate bond stretching force constants,bond bending force constants ,ionicity and bulk modulus with the nature of bonding of the materials.This plasmon energy delineates the structure –property relationship in solid state sciences.

Hence it is possible to calculate the values of α, β, f_i, B of AIIBVI and AIIIBV semiconductors and also new type of materials belonging to these group from their plasmon energies.

Table 1. Interatomic force constants of binary semiconductors.

Compounds	Plasmon energy(eV) Ref.[24]	Bond stretching force constants (N/m)					Bond bending force constants (N/m)				
		Expt. Ref. [14,16,22]	Cal. Eqn. (5)	Reported in Ref.[26]	Ref. [25]	Ref. [27]	Expt. Ref. [14,16,22]	Cal. Eqn. (9)	Reported Ref.[26]	Ref. [25]	Ref . [27]
BeS	19.52		54.96	62.648	63.18			6.16			
BeSe	18.39		50.18	56.967	57.89			5.6			
BeTe	16.12		40.59	45.755	46.02			4.47			
ZnO	21.48		63.24	29.834	30.07			7.13			
ZnS	16.71	44.73	43.09	71.318	73.66	42.22	4.36	4.76	4.561	4.54	4.46
ZnSe	15.78	38.71	39.16	48.67	49.09	36.34	4.65	4.3	4.083	4.05	3.84
ZnTe	14.76	32.01	34.85	44.185	44.26	29.4	4.47	3.79	3.534	3.52	3.11
CdS	14.88		35.36	39.028	39.02	33.81		3.85			
CdSe	14.01		31.68	39.701	39.63	30.08		3.42			
CdTe	13.09	29.44	27.79	35.216	35.22	24.38	2.48	2.96	2.602	2.71	2.58
HgS	14.85		35.23					3.84			
HgSe	12.98		27.33				2.37	2.91			3.14
HgTe	11.43		20.78				2.54	2.14			2.61
Average % Deviation			5.16	35.68	37.35	9.26		14.95			14.85
$A^{III}B^{V}$											
BN	24.53		88.75	89.58	88.357			20.59			
BP	21.71		75	75.21	75.037	87.14		16.85			
BAs	20.12		67.24	66.94	67.044	74.95		14.73			
AlN	22.97		81.14	81.98	81.091	97.3		18.52			
AlP	16.65		50.32	48.78	49.122	48.41		10.12			
AlAs	15.75		45.93	44.1	44.278	44.34		8.93			
AlSb	13.72	35.74	36.03	33.77	33.137	33.81	6.63	6.23	5.975	6.15	6.05
GaN	21.98		76.31	76.6	76.248	95.36		17.21			
GaP	16.5	48.57	49.58	48	48.395	48.41	10.4	9.92	9.071	8.91	8.67
GaAs	15.35	43.34	43.98	42.04	42.098	43.27	8.88	8.39	7.794	7.74	7.75
GaSb	13.38	34.42	34.37	32.08	31.2	34.19	7.16	5.78	5.582	5.84	6.12
InN	18.82		60.9	60.14	60.505	70.7		13.01			
InP	14.76	44.29	41.1	39.02	38.95	38.83	6.26	7.61	7.155	7.15	6.95
InAs	14.07	37.18	37.73	35.52	35.075	35.79	5.47	6.69	6.369	6.49	6.41
InSb	12.73	30.44	31.2	28.88	27.567	28.68	4.73	4.91	4.845	5.23	5.14
Average % Deviation			2.02	5.37	6.66	4.03		11.84	12.81	13.7	12.75

Table 2. Bulk modulus and ionicity of binary semiconductors

Bulkmodulus								Ionicity			
Compounds	Plasmon energy(eV)	Expt. Ref [28]	Cal.Eqn. (11)	Ref.[34]	Ref. [29] Ref. [28]	Ref. [30]	Ref.[31]	Eq.(10)	Ref.[25]	Ref. [32,33]	
BeS	19.52		99.09	111.81				0.6	0.655	0.656	
BeSe	18.39		89.06	97.29				0.602	0.658	0.661	
BeTe	16.12		68.91	71.54				0.607	0.667	0.672	

ZnO	21.48		116.48	139.78				0.597	0.646	0.646	
ZnS	16.71	77	74.15	77.8	90	44.7	61	0.605	0.669	0.669	
ZnSe	15.78	62	65.89	68.07	75	39.1	58	0.608	0.673	0.673	
ZnTe	14.76	51	56.84	58.24	59	32.3	54	0.611	0.678	0.678	
CdS	14.88	62	57.91	59.35	69	36.5	66	0.611	0.677	0.677	
CdSe	14.01	53	50.19	51.57	60	32.8	60	0.614	0.681	0.681	
CdTe	13.09	42	42.02	44.01	47	27.5	56	0.619	0.684	0.684	
HgS	14.85		57.64	59.07				0.61			
HgSe	12.98		41.04	51.39				0.619			
HgTe	11.43		27.29	42.15				0.632			
Average % deviation			5.54	6.05	14.93	14.93	14.3				
BN	24.53		167.89					0.171	0.305	0.299	
BP	21.71		139.29					0.198	0.311	0.312	
Bas	20.12		123.17					0.217	0.315	0.32	
AlN	22.97		152.07					0.185	0.308	0.306	
AlP	16.65	86	87.98	87	84	79	86.7	0.282	0.329	0.336	
AlAs	15.75	77	78.86	79	76.1	66	75.3	0.306	0.335	0.34	
AlSb	13.72	58	58.27	57	56.4	61	55.4	0.383	0.356	0.349	
GaN	21.98		142.03					0.195	0.31	0.311	
GaP	16.5	89	86.46	87	84.5	74	89.79	0.285	0.33	0.337	
GaAs	15.35	75	74.8	77	74.5	65	70.6	0.318	0.338	0.342	
GaSb	13.38	57	54.82	58	56.9	59	55.5	0.4	0.361	0.35	
InN	18.82		109.99					0.237	0.319	0.326	
InP	14.76	71	68.82	67	65.6	63	68.7	0.339	0.344	0.345	
InAs	14.07	60	61.82	61	59.5	61	58.19	0.367	0.351	0.347	
InSb	12.73	47	48.23	47	46.7	55	45.05	0.438	0.372	0.353	

Average % deviation		2.28	2.11	2.34

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