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Inter atomic force constants of binary and ternary tetrahedral semiconductors

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In this paper, we present the expressions relating the inter atomic force constants like as bond-stretching force constant (α in N/m) and bond-bending force constant (β in N/m) for the binary (zinc blende structure) and ternary (chalcopyrite structure) semiconductors with the product of ionic charges (PIC) and crystal ionicity (f_i). Interatomic force constants of these compounds exhibit a linear relationship; when plot a graph between Interatomic force constants and the nearest neighbor distance d (Å) with crystal ionicity (f_i), but fall on different straight lines according to the product of ionic charges of these compounds. A fairly good agreement has been found between the observed and calculated values of the α and β for binary and ternary tetrahedral semiconductors.

1. Introduction

Binary tetrahedrally coordinated semiconductors of the chemical formula $A^N B^{8-N}$ have been extensively studied because of their technical and scientific importance. Most of the semiconductors that are used in the modern microelectronic industry have the zinc blende crystallographic structure. The crystals with zinc-blende structure range from raw iron and zinc minerals to man-made GaN and BN semiconductors. The particular omnitriangulated nature in atomic structure gives these materials unique physical properties. A considerable amount of experimental and theoretical work has been done during the last few years on the structural, mechanical and optical properties of zinc blende ($A^{III}B^{V}$ and $A^{II}B^{VI}$) semiconductors [1–4]. Ternary tetrahedrally coordinated semiconductors with the formula $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ such as $CuAlS_2$, $AgAlSe_2$, $AgInTe_2$, $CdSiP_2$ and $ZnSnAs_2$ etc. have been widely studied because of their possible technological applications as photo-voltaic detectors, solar cells, light emitting diodes, modulators, filters and their use in nonlinear optics [5–9]. These semi-conductors crystallize in the chalcopyrite structure, which is deduced from that of zinc blende by the replacement of the cationic sublattice by two different atomic species. The bond-stretching force constant (α in N/m) and bond-bending force constant (β in N/m) of tetrahedral semiconductors have been an important parameter to study because these semiconductors have potential applications in a variety of optoelectronic devices such as integrated circuits, detectors, lasers, light emitting diodes, modulators and filters.

Using the valence-force-field model of Keating [10], the elastic properties of the zinc blende solids with a sphalerite-structure have been analysed by Martin [11] and several other researchers [12,13]. A considerable amount of discrepancies have been obtained between theory and experiment in evaluating vibrational modes on the basis of the model parameters derived from elastic constant data. Presently, more reliable elastic constant data are available which differ partially from those obtained by Martin [11]. According to Martin analysis 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. [14], has pointed out that the Martin relation is incorrect and that the contribution of Coulomb forces to the elastic constants and the transverse optical frequencies must be described in terms of the localized effective charge which differs from the macroscopic effective charge. Neumann [15–19] has extended the Keating 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 [15–19] has taken experimental values of bond ionicity (f_i) [13], to determine the constant associated with the equations. The ab initio calculations for lattice dynamic for BN and AlN semiconductors have been given by Karch and Bechstedt [20]. Kumar [21] has extended the Neumann's model in terms of plasmon energy of the solids, because, plasmon energy $(\hbar\omega_p)$ depends on the number of valence electrons. Theoretical concepts such as valence, empirical radii, electronegativity, ionicity and plasmon energy are then useful [22,23]. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids.

This is due to the fact that the ionic charge depends on the number of valence electrons, which changes when a metal forms a compound. Therefore we thought it would be of interest to give an alternative explanation for the bond-stretching force constant (α in N/m) and bond-bending force constant (β in N/m) of zinc blende and chalcopyrite structured solids.

2. Theory, results and discussion

Bond-stretching (α) and bond-bending (β) force constant depend on nearest neighbour distance obtained from lattice vibration data. Such potentials have the advantage of keeping the repulsive and attractive forces in the same mathematical form. Neumann [15–19] and Harrison [24,25] have been described the simplest form of inter-atomic potential. Both the authors have been assumed that both the repulsive and attractive parts of inter-atomic potential are described by the power law of nearest neighbour distance (d). This form of potential for the total energy per pair of atom can be written as [16],

$$V_1(d) = C/d^m - D/d^n, \tag{1}$$

where C, D, m and n are the constants and d is nearest neighbour distance. These parameters have been estimated for equilibrium condition when the repulsion is half of the attraction i.e. $m = 2n$ [16] and the following equation has been obtained,

$$\alpha = \alpha_0 d^{-x}, \tag{2}$$

where α_0 and x are constants. The other form of potential is based on Morse potential. In this type of potential both the repulsive and attractive terms are described by exponential functions of nearest neighbour distance. The general form of Morse potential is given by [16],

$$V_2(d) = A\exp(-ad) - B\exp(-bd), \tag{3}$$

where A, B, a and b are the constants. Neumann [16–19] has also extended it to ternary chalcopyrites. Solving above Eq. (3) for equilibrium condition $a = 2b$, the following equation has been obtained [16],

$$\alpha = \alpha_1 \exp(-bd), \tag{4}$$

where α_1 and b are constants. In all the above models requires the values of nearest neighbour distance and lattice constants of the semiconductors.

Kumar [21], has shown that the bond-stretching force constant (α) may be determine in terms of plasmon energy by the following form,

$$\alpha = 0.398(\hbar\omega_p)^{1.70} \tag{5}$$

and

$$\alpha = 704.3\exp\left\{-17.41(\hbar\omega_p)^{-2/3}\right\}. \tag{6}$$

In the above Eq. (5) and (6), α is in N/m and $\hbar\omega_p$ in eV. Because, plasmon energy $(\hbar\omega_p)$ depends on the number of valence electrons and ionic charge also depends on the number of valence electrons, which changes when a metal forms a compound.

According to Martin [11] the bond-bending force constant (β) follows the proportionality relation $\beta \propto (1 - f_i)\alpha$, where f_i is the ionicity of the A–B bond in the $A^{III}B^{V}$ and $A^{II}B^{VI}$ semiconductors. Neumann [15] has plotted a graph between β/α and $(1 - f_i)$ 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,

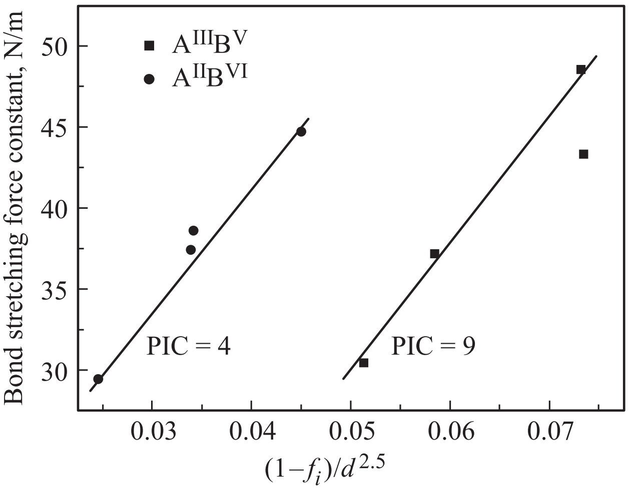

Figure 1. Plot of α (bond stretching force constant) against f_i with d (f_i — crystal ionicity and d nearest neighbour distance of compounds) for $A^{III}B^{V}$ and $A^{II}B^{VI}$ semiconductors. In the plots of α and f_i with d, $A^{III}B^{V}$ semiconductors lie on line nearly parallel to the line for $A^{II}B^{VI}$ semiconductors. In this plot all data are taken from Ref. [15,16].

$$\beta = \beta_0(1 - f_i)\alpha, \tag{7}$$

where $\beta_0 = 0.28 \pm 0.01$ is the proportionality constant.

The bond-stretching force constant (α) of $A^{III}B^{V}$, $A^{II}B^{VI}$ and A–C and B–C bond of $A^{I}B^{III}C_2^{VI}$ and $A^{II}B_{IV}C_2$ semiconductors exhibit a linear relationship when plotted against nearest-neighbour distance (d in Å) with ionicity (f_i), but fall on different straight lines according to the product of ionic charges (PIC) of the compounds, which is presented in Figs 1 and 2. We observe that in the plot of bond-stretching force constant (α) and nearest neighbour distance with ionicity; the $A^{III}B^{V}$ semiconductors lie on line nearly parallel to the line for the $A^{II}B^{VI}$ semiconductors. From the Fig. 1 it is quite obvious that the bond-stretching force constant (α) trends in these compounds decreases with increases nearest neighbour distance and fall on different straight lines according to the product of ionic charges (PIC) of the compounds. We have received similar case for A–C and B–C bond of $A^{I}B^{III}C_2^{V}$ and $A^{II}B^{IV}C_2^{V}$ semiconductors in Fig. 2. If we plot all values with product of ionic charges (PIC) and crystal ionicity with nearest neighbour distance of the compounds, these are presented in Fig. 3 and 4. We found all values close on a single line and found a single relation by curve fitting method. Krishnan-Roy theory [26], Jayaraman et al. [27] and Sirdeshmukh and Subhadra [28] found that substantially reduced ionic charges must be used to get better agreement with experimental values of mechanical properties of solids. Ionic charge depends on the number of valence electrons. Using this idea, we have proposed the expressions for the

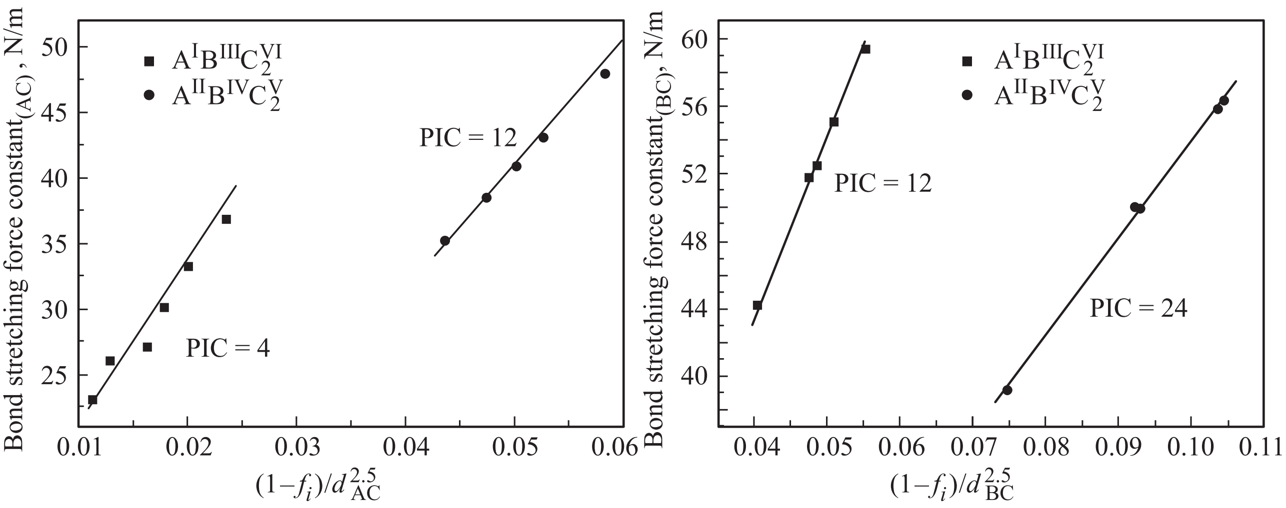

Figure 2. Plot of $\alpha_{(AC)}$ (bond stretching force constant for A–C bond and B–C bond) against f_i with d (f_i — crystal ionicity and d nearest neighbour distance of compounds for A–C bond) for $A^{II}B_{IV}C_2$ and $A^IB^{III}C_2^{VI}$ semiconductors. In the plots of α and f_i with d, $A^{II}B^{IV}C_2^V$ semiconductors lie on line nearly parallel to the line for $A^IB^{III}C_2^{VI}$ semiconductors. In this plot all data are taken from Ref. [29].

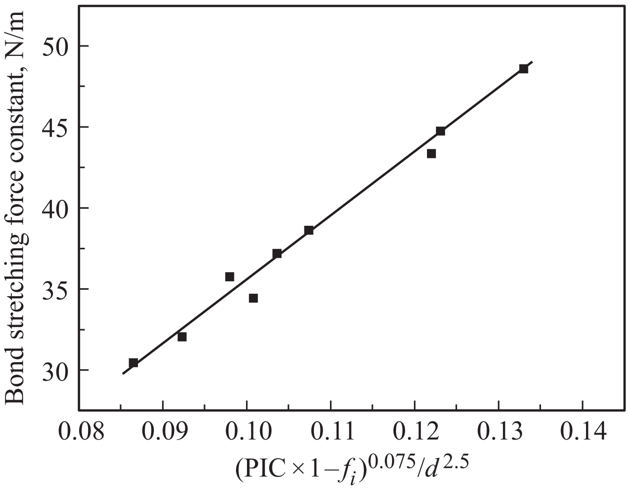

Figure 3. Plot of α (bond stretching force constant) against (PIC×f_i) with d (PIC — Product of ionic charges, f_i — crystal ionicity and d nearest neighbour distance of compounds) for $A^{III}B^V$ and $A^{II}B^{VI}$ semiconductors. In this plot we found all values close on a single line. In this plot all data are taken from Ref. [15,16].

inter atomic force constants like as bond stretching force constant and bond bending force constant by the following relations,

For zinc blende structure:

bond stretching force constant

$$(\alpha \text{ in } N/m) = 365(\text{PIC} \times 1 - f_i)^{0.075}/d^{2.5}, \qquad (8)$$

bond bending force constant

$$(\beta \text{ in } N/m) = 115(\text{PIC} \times 1 - f_i)^{0.075}/d^4. \qquad (9)$$

For Chalcopyrite structure:

$$(\alpha \text{ in } N/m) \text{ for A–C and B–C bond} = 300(\text{PIC}_{XY} \times 1 - f_{iXY})^{0.3}/d^{2.5}_{XY}. \qquad (10)$$

Here XY represents the A–C and B–C bond of $A^IB^{III}C_2^{VI}$ and $A^{II}B_{IV}C_2^V$ semiconductors. The proposed relations (8) to (10) have been applied to evaluate inter atomic force constants like as bond stretching force constant and bond bending force constant values for $A^{III}B_V$, $A_{II}B_{VI}$ and bond stretching force constant for A–C and B–C bond for $A_IB_{III}C_2^{VI}$ and $A_{II}B_{IV}C_2^V$ semiconductors. The values so

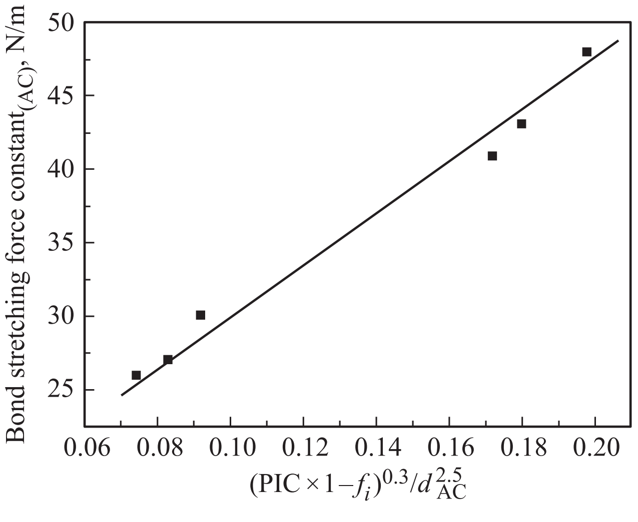

Figure 4. Plot of $\alpha_{(AC)}$ (bond stretching force constant for A–C bond) against (PIC×f_i) with d (PIC — Product of ionic charges, f_i — crystal ionicity and d nearest neighbour distance of compounds for A–C bond) for $A^{II}B^{IV}C_2^V$ and $A^IB_{III}C_2^{VI}$ semiconductors. In this plot we found all values close on a single line. In this plot all data are taken from Ref. [29].

Table 1. Values of bond stretching force constant (α in N/m) and bond bending force constant (β in N/m) for binary tetrahedral semiconductors (Product of ionic charges (PIC) = 4 for $A^{II}B^{VI}$ and PIC = 9 for $A^{III}B^{V}$).

Solids	s (Å) [30]	f_i [30]	$1 - f_i$	(α in N/m) [15,16]	(α in N/m) [21]	(α in N/m) This work	(β in N/m) [15,16]	(β in N/m) [21]	(β in N/m) This work
AlP	2.36	0.307	0.693		48.78	48.9		9.07	11.12
AlAs	2.43	0.274	0.726		44.10	45.6		8.15	10.17
AlSb	2.66	0.426	0.574	35.74	33.77	35.8	6.63	6.15	6.15
GaP	2.36	0.374	0.626	48.57	48.00	48.6	10.4	8.91	10.46
GaAs	2.45	0.31	0.69	43.34	42.04	44.6	8.88	7.74	9.55
GaSb	2.65	0.261	0.739	34.42	32.08	36.8	7.16	5.84	7.27
InP	2.54	0.421	0.579	44.29	39.02	40.2	6.26	7.15	7.44
InAs	2.61	0.357	0.643	37.18	35.52	37.8	5.47	6.49	7.11
InSb	2.81	0.321	0.679	30.44	28.88	31.6	4.73	5.23	5.46
ZnS	2.34	0.623	0.377	44.73	49.09	44.9	4.36	4.54	4.91
ZnSe	2.46	0.676	0.324	38.61	44.26	39.2	4.65	4.05	3.67
ZnTe	2.64	0.546	0.454	32.04	39.02	33.7	4.47	3.52	3.39
CdS	2.52	0.685	0.315		39.63	36.8		3.58	3.28
CdSe	2.62	0.699	0.301		35.22	33.3		3.14	2.73
CdTe	2.81	0.675	0.325	29.44	30.65	28.1	2.48	2.71	2.16
HgS	2.53	0.631	0.369		39.47	36.9		4.18	3.55
HgSe	2.63	0.62	0.38	37.43	30.12	33.6	2.37	3.13	3.09
HgTe	2.8	0.565	0.435	29.32	22.79	29.0	2.54	2.34	2.61

Table 2. Values of bond stretching force constant (α_{XY} in N/m) for A–C and B–C bond of ternary tetrahedral semiconductors.

Solids	d_{AC} [31]	d_{BC} [31]	f_{iA-B} [31]	f_{iB-C} [31]	$1 - f_i$ A-C	$1 - f_i$ B-C	(α_{AC} in N/m) [17]	(α_{AC} in N/m) [29]	(α_{AC} in N/m) This work	(α_{BC} in N/m) [17]	(α_{BC} in N/m) [29]	(α_{AC} in N/m) This work
$CuAlS_2$	2.29	2.29	0.813	0.561	0.187	0.439	33.3	36.82	34.6	62.2	59.34	62.2
$CuAlSe_2$	2.42	2.4	0.817	0.566	0.183	0.434		33.22	30.0	56.6	52.44	55.2
$CuAlTe_2$	2.6	2.56	0.822	0.576	0.178	0.424		27.08	24.9		44.18	46.6
$CuGaS_2$	2.39	2.3	0.816	0.561	0.184	0.439	32.4	32.47	31.0	58.4	58.62	61.6
$CuGaSe_2$	2.49	2.42	0.825	0.567	0.175	0.433	24.7	30.09	27.6	47.8	51.73	54.0
$CuGaTe_2$	2.61	2.59	0.823	0.573	0.177	0.427		26.62	24.6		42.36	45.4
$CuInS_2$	2.49	2.46	0.808	0.569	0.192	0.431	28.1	28.48	28.3	53.1	49.22	51.7
$CuInSe_2$	2.43	2.56	0.817	0.572	0.183	0.428	25.8	32.68	29.7	44.7	42.98	46.7
$CuInTe_2$	2.66	2.7	0.779	0.576	0.221	0.424		25.08	25.1	35.3	37.81	40.8
$AgAlS_2$	2.54	2.26	0.848	0.559	0.152	0.441		28.23	25.1		61.67	64.4
$AgAlSe_2$	2.66	2.36	0.851	0.564	0.149	0.436		26.01	22.3		55.03	57.6
$AgAlTe_2$	2.79	2.57	0.853	0.573	0.147	0.427		22.86	19.7		43.55	46.3
$AgGaS_2$	2.57	2.27	0.849	0.559	0.151	0.441	27.1	27.25	24.4	59.1	61.04	63.7
$AgGaSe_2$	2.66	2.39	0.851	0.566	0.149	0.434	24.9	26.08	22.3	46.9	53.27	55.7
$AgGaTe_2$	2.77	2.6	0.853	0.573	0.147	0.427	22.7	23.48	20.0	35.9	42.15	44.9
$AgInS_2$	2.51	2.47	0.847	0.569	0.153	0.431		29.51	25.9	54.1	48.44	51.2
$AgInSe_2$	2.63	2.58	0.85	0.573	0.15	0.427	24.1	27.25	22.9	43.6	42.90	45.8
$AgInTe_2$	2.79	2.76	0.853	0.578	0.147	0.422	22	23.06	19.7	34.6	35.30	38.6
$ZnSiP_2$	2.375	2.254	0.493	0.2088	0.507	0.7912	45.7	47.93	45.2	57.5	55.79	61.2
$ZnGeP_2$	2.389	2.324	0.493	0.2112	0.507	0.7888	45.8	47.38	45.5	52.9	51.56	56.6
$ZnSnP_2$	2.416	2.485	0.495	0.2162	0.505	0.7838		45.64	44.2		42.59	47.9
$ZnSiAs_2$	2.464	2.35	0.498	0.2122	0.502	0.7878	39.3	43.06	42.1	51.1	49.89	55.1
$ZnGeAs_2$	2.482	2.407	0.499	0.214	0.501	0.786		42.18	41.3		46.69	51.9
$ZnSnAs_2$	2.508	2.557	0.5	0.218	0.5	0.782		40.87	40.2		39.14	44.5
$CdSiP_2$	2.561	2.247	0.502	0.2085	0.498	0.7915	40.3	38.47	38.1	56.3	56.30	61.6
$CdGeP_2$	2.559	2.325	0.502	0.2113	0.498	0.7887	39.8	38.53	38.2	52.7	51.40	56.6
$CdSnP_2$	2.588	2.486	0.504	0.2163	0.496	0.7837	37.8	37.33	37.1	46.7	42.54	47.8
$CdSiAs_2$	2.64	2.348	0.506	0.2202	0.494	0.7798		35.19	35.3		49.99	55.1
$CdGeAs_2$	2.642	2.421	0.506	0.2144	0.494	0.7856	35.7	35.14	35.2	43.7	45.91	51.1
$CdSnAs_2$	2.67	2.572	0.501	0.2184	0.499	0.7816		34.04	34.4		39.49	43.9

obtained are presented in the following Tables 1 and 2 compared with the available experimental and theoretical values. We note that the evaluated values inter atomic force constants like as bond stretching force constant and bond bending force constant by the proposed relations are in close agreement with the values reported by previous researchers so far. The obtained results show that the proposed model is quite reasonable and can give us a useful guide in calculating and predicting the inter-atomic force constants of the binary and more complex class of ternary chalcopyrite semiconductors.

3. Conclusion

We come to the conclusion that product of ionic charges of any compound is a key parameter for calculating the physical properties. Inter atomic force constant of these materials is inversely related to nearest neighbour distance (d in Å) and directly depends on the product of ionic charges. From Figs 1 and 2, we observe that the data points fall on two distinct lines due to their product of ionic charges. This means that ionic binding dominates all these compounds. It is also noteworthy that the proposed empirical relation is simpler, widely applicable and values are in better agreement with experiment data as compared to empirical relation proposed by previous researchers [10–21]. We have been reasonably successful in calculating inter atomic force constants using the product of ionic charges and nearest neighbour distance of the materials for binary and more complex class of ternary chalcopyrite semiconductors.

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