

# Pressure dependence of energy gap of III–V and II–VI ternary semiconductors

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Received: 3 February 2012 / Accepted: 30 March 2012 / Published online: 19 April 2012  
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**Abstract** A general expression for the pressure dependence of the energy gap of a series of group III–V and group II–VI ternary semiconductors have been derived based on Van Vechten’s dielectric theory. The results obtained are in good accord with the available experimental data. The trends in the variation of the pressure dependence of the energy gap with the nearest neighbor distance and Phillips ionicity are explored qualitatively.

## Introduction

Semiconductor ternary compounds have been widely used because of the ability to tailor their optoelectronic properties, in particular, the band gap, with composition. For instance,  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  has become a well-established material for UV light emitters and UV detectors due to the fact that its band gap covers a broad range [1] of wavelengths in the ultraviolet.  $\text{ZnS}_x\text{Se}_{1-x}$  has been widely used for optoelectronic applications in blue–green spectral region [2] and  $\text{CdS}_x\text{Se}_{1-x}$  plays an important role in semiconductor doped glasses [3]. Along with these applications, significant interests and efforts have been directed towards their fundamental material properties. One such example is the interest in pressure dependence of the band gaps of these ternary compound semiconductors. In general, there has been very little data on the pressure dependence of the energy gap of ternary compound semiconductors and even within the limited available experimental data, there is a significant variation. For example, the pressure coefficient

of the band gap of  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ , reported by Hakki et al. [4] is 13 meV/kbar, in contrast with the 8.4 meV/kbar obtained by Chen et al. [5]. Thus, a theoretical approach is required to analyze the problem.

In condensed matter physics, ab initio methods have been used to predict the pressure coefficients of the energy gap of some ternary compounds. However, possibly due to the approximations and assumptions made in these calculations, the results are not always reliable. In general, ab initio calculations are complex and require significant efforts. Therefore, empirical approaches have been developed to address some of these problems. The transition from binary compound semiconductors to ternary compound semiconductors requires the understanding of the bowing parameter [6]. Fundamentally, the bowing parameter is the result of the deviation of the energy gap of the ternary compound from that of the alloy system comprising of the two binary compounds. Mathematically, the bowing parameter of a ternary compound  $\text{AB}_xC_{1-x}$  is expressed by the following equation:

$$E_g(x) = xE_g^{\text{AB}} + (1-x)E_g^{\text{AC}} - c_{\text{ABC}}x(1-x) \quad (1)$$

where,  $x$  is the composition in the compound  $\text{AB}_xC_{1-x}$ ,  $E_g^{\text{AB}}$  and  $E_g^{\text{AC}}$  are the energy gaps of binary compounds AB and AC, respectively and  $c_{\text{ABC}}$  is the bowing parameter. Hill [6] has ascribed the physical meaning of the bowing parameter to the nonlinear dependence of the crystal potential on the properties of the component ions and derived the following expression:

$$c_{\text{ABC}} = \frac{Zer_{\text{BC}}}{4\pi\epsilon_0} \left[ \frac{1}{r_{\text{B}}} - \frac{1}{r_{\text{C}}} \right]^2 \exp\left(-\frac{1}{2}sr_{\text{BC}}\right) \quad (2)$$

in which  $Z = Z_{\text{B}} = Z_{\text{C}}$  is the valence number of ions B and C,  $r_{\text{B}}$  and  $r_{\text{C}}$  are the covalent radii of B and C,

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$r_{BC} = r_B + r_C$  and  $s = 0.25$  is a screening constant. Differentiating Eq. (2) with respect to pressure, Hill and Pitt [7] obtained the following expression:

$$\frac{dc_{ABC}}{dP} = \frac{1}{2\sqrt{3}} \frac{c_{ABC}}{r_B - r_C} \left[ \frac{r_C}{r_B} a_{AB} \chi_{AB} - \frac{r_B}{r_C} a_{AC} \chi_{AC} \right] \quad (3)$$

where,  $a_{AB}$ ,  $a_{AC}$  and  $\chi_{AB}$ ,  $\chi_{AC}$  are lattice constants and compressibilities of compounds AB and AC, respectively. Based on this model, Hill and Pitt [7] calculated the pressure coefficients of the bowing parameters for a number of ternary semiconductors. However, in order to calculate the pressure dependent band gap of ternary semiconductor  $AB_xC_{1-x}$  using this model, one has to use the experimental data for band gap pressure coefficients of binary compounds AB and AC, because, in general,:

$$\frac{dE_g(x)}{dP} = x \frac{dE_g^{AB}}{dP} + (1-x) \frac{dE_g^{AC}}{dP} - \frac{dc_{ABC}}{dP} x(1-x). \quad (4)$$

Van Vechten [8, 9] proposed a dielectric theory for tetrahedral compounds based on Phillips' spectroscopic theory of electronegativity difference [10]. The theory was successfully applied and generalized to a variety of areas in materials science including band structures, alloy bowing parameters, elastic constants etc. Camphausen et al. [11] used this model to calculate the pressure coefficients of band gaps of nineteen binary semiconductors and appear to yield good agreement between theoretical expectations and experimental results.

In this study, we use Van Vechten's model to calculate a number of group III–V and II–VI zincblende ternary semiconductors. Necessary modifications are made to the theory. Predicted results are compared with all the available recently measured experimental data and those calculated by other methods and the results are generally in good agreement. The trends in the variation in the energy gap and its pressure coefficient with respect to the nearest neighbor distance and Phillips' ionicity [10] are explained.

### Generalized expressions for ternary compounds

In Van Vechten's dielectric theory [8, 9], the energy gap between the minimum conduction band and the maximum valence band, if the effect of  $d$ -state core is involved, is expressed as:

$$E'_g = [E_{g,h} - (D_{av} - 1)\Delta E_g][1 + (C/E_{g,h})^2]^{1/2}. \quad (5)$$

In this expression,  $E_{g,h}$  is the homopolar gap for transition corresponding to particular energy gap and is assumed to be a power function of the nearest neighbor distance  $r$  given by  $E_{g,h} \propto r^{s_1}$ , where,  $s_1 = -2.75$ .  $D_{av}$  is

the factor that describes the lowering of  $s$ -like conduction band states caused by the effect of  $d$ -states and the value is the skewed average of  $D$  values of the crystals containing the constituent atoms and the atom from the same row in the periodic table. For the first three rows in the periodic table,  $D_{av}$  is unity and Eq. (5) reduces to Phillips' pseudo potential theory [10].  $\Delta E_g$  is the correction related factor given by  $\Delta E_g \propto r^{s_2}$ , where  $s_2 = -5.07$ .  $C$  is the heteropolar gap produced by the anti-symmetric potential in the corresponding binary compounds. For binary compound AB,  $C$  is given by [8]:

$$C = be^2 \left[ \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right] \exp(-k_s r) \quad (6)$$

For a ternary compound  $AB_xC_{1-x}$ , it can be generalized as follows:

$$C = be^2 \left[ \frac{Z_A}{r_A} - x \frac{Z_B}{r_B} - (1-x) \frac{Z_C}{r_C} \right] \exp(-k_s r) \quad (7)$$

where, the pre-factor  $b$  is a constant around 1.5,  $Z_A$ ,  $Z_B$ ,  $Z_C$  are the valence numbers for ions A, B, and C respectively,  $r_A$ ,  $r_B$ ,  $r_C$  are the corresponding covalent radii [8] for ions A, B, and C.  $k_s$  is the radius-dependent Thomas–Fermi screening wave number,  $r = r_A + xr_B + (1-x)r_C$  is the nearest neighbor distance.

From Eqs. (5)–(7), the pressure coefficients of the energy gap are given by:

$$\begin{aligned} \frac{dE'_g}{dP} &= [1 + (C/E_{g,h})^2]^{1/2} \\ &\times \left[ \frac{dE_{g,h}}{dP} - \Delta E_g \frac{d(D_{av} - 1)}{dP} - (D_{av} - 1) \frac{d\Delta E_g}{dP} \right] \\ &+ \left[ \frac{E_g}{1 + (E_{g,h}/C)^2} \right] \left[ \frac{1}{C} \frac{dC}{dP} - \frac{1}{E_{g,h}} \frac{dE_{g,h}}{dP} \right]. \quad (8) \end{aligned}$$

This expression (8) is the same as the one derived by Camphausen et al. [11] and is applicable to both binary and ternary compounds. Camphausen et al. [11] have proved that, even in non-ionic materials,  $dC/dP$  is sufficiently small and can be considered to be negligible while compared with the other terms in the expression. They further pointed out the expression for the correction term to be  $D_{av} - 1 \propto r^y(1-f)^z$ , in which,  $f = C^2/(E_h^2 + C^2)$  is the Phillips' ionicity [10].  $E_h$  is the average homopolar energy gap given as  $E_h \propto r^{s_3}$ , where  $s_3 = -2.48$ .  $s_1$ ,  $s_2$ , and  $s_3$  are constants determined from experimental values of two group IV elements [9]. Camphausen et al. [11] found that  $y = 13$  and  $z = 2.4$  by fitting the pressure coefficient of the energy gap of Ge.

In their later study, Van Vechten and Bergstresser [12] pointed out that the bowing parameter  $c_{ABC}$  of ternary compound  $AB_xC_{1-x}$  comprises of two parts. This first part, intrinsic bowing parameter,  $c_i$ , originates from the variation

of the average crystal potential under virtual crystal approximation which assumes periodic potential in the crystal. If one calculates the energy difference using Eq. (5), the result,  $E_g^{ABC}$ , will be different from the compositionally weighted average energy of the corresponding two binary compounds. This difference is the intrinsic bowing parameter. Another part,  $c_e$ , the extrinsic bowing parameter, arises from the real short range aperiodicity, and is the small deviation of real potential from virtual periodic potential. In terms of this theory, the real energy gap in Eq. (5) becomes the following:

$$E_g(x) = E_g^{ABC} - c_e x(1 - x) \tag{9}$$

where, the intrinsic bowing parameter is included in the first term; the extrinsic bowing parameter is proposed by Van Vechten and Bergstresser as [12]:

$$c_e = \frac{C_{BC}^2}{A} \tag{10}$$

$$C_{BC} = be^2 \left| \frac{Z_B}{r_B} - \frac{Z_C}{r_C} \right| \exp(-k_s r) \tag{11}$$

In the above Eq. (10), the bandwidth parameter  $A$  is a constant for all compounds and found to be 0.98 eV by fitting the extrinsic bowing parameter with  $C_{BC}$  for the ZnS-Te system.  $C_{BC}$  is the fluctuation of the actual potential in the virtual crystal approximation which is different from  $C$  in Eq. (7).

By summarizing the aforementioned equations, we obtain the expression for the pressure dependent band gap of ternary semiconductor  $AB_xC_{1-x}$  as:

$$\begin{aligned} \frac{dE_g(x)}{dP} = & \frac{1}{3B} \left\{ \left[ 1 + (C/E_{g,h})^2 \right]^{1/2} \right. \\ & \times \left[ s_1 E_{g,h} - (D_{av} - 1) \Delta E_g \left( y + \frac{2zs_3}{1 + (E_h/C)^2} + s_2 \right) \right] \\ & \left. - \frac{s_1 E_g(x)}{1 + (E_{g,h}/C)^2} - 2x(1-x)c_e r \left( \frac{1}{b} \frac{db}{dr} - \frac{k_s}{4} - \frac{1}{r} \right) \right\}. \end{aligned} \tag{12}$$

In the above expression, the first two terms on the right hand side stem from the pressure dependence of the band gap in virtual crystal approximation. The last term is the pressure dependence of the extrinsic bowing parameter.  $B$  is the bulk modulus of the ternary compound semiconductor.

### Results and discussion

The bowing parameter, energy gap and their pressure coefficients of III–V and II–VI ternary semiconductors, calculated from the above theory, are listed in Table 1

together with other parameters that are relevant for the present calculations. Comparisons show good accord between the calculated results and experimental data.

#### Dependence of pre-factor $b$ on pressure

In Van Vechten’s dielectric theory [8], the pre-factor,  $b$ , is introduced to balance the overestimate of the Thomas–Fermi effect on dielectric screening at short distances. The dependence of this pre-factor on pressure, i.e.,  $(r/b)db/dr$ , was proved to be approximately 2.0–2.5 for materials with ionicity larger than 0.93, while, for partial covalent materials ( $f_i < 0.9$ ), this dependence is much weaker. Since for all the ternary compounds considered in this study, ionicity is  $< 0.72$ , we assume  $(1/b)db/dr = 0$  throughout the entire calculations.

#### Bulk moduli of ternary compound semiconductors

Cohen et al. [13] proposed a simple power rule to calculate the bulk moduli of compound semiconductors based on Phillips’ theory of average homopolar energy gap [10]. This semi-empirical power rule is given by:

$$B = kr^{-3.48} \tag{13}$$

where,  $B$  is the bulk modulus,  $r$  is the nearest neighbor distance and  $k$  is a constant of proportionality. In order to obtain the bulk moduli of ternary compound semiconductors, we fit this model to all the available experimental data of binary compounds in the same group as those of the ternaries. For group III–V ternary semiconductors, we found that the coefficient  $k = 1726$  while, for group II–VI,  $k = 1491$ , in units corresponding to Eq. (13). From the above equation, it is seen that the bulk modulus is inversely proportional to the nearest neighbor distance.

#### Trends in pressure coefficients of energy gap

For the common-cation system, for example, Ga-InP, Ga-InAs, Ga-InSb (Ga:In::0.5:0.5), the pressure coefficient of the band gap increases with increasing nearest neighbor distance (Columns 13 and 2, respectively, in Table 1). In Eq. (12), the pressure coefficient of the band gap is inversely proportional to the bulk modulus which according to Eq. (13), is inversely proportional to the nearest neighbor distance. Thus, the pressure coefficient of the band gap will increase with increasing nearest neighbor distance due to the decrease in the bulk modulus. In general, pressure will cause a dilation of the lattice and will lead to changes in its potential energy resulting in the overlap of the energy levels which will subsequently lead to change in the energy gap. However, for the common-anion system, this trend is not so significant. For instance,

**Table 1** Calculated properties of III–V and II–VI ternary semiconductors for  $x = 0.5$ 

Alloy	$r[8]$ (Å)	$D_{av}[9]$	$C$ (eV)	$c_c$ (eV)	$c_{ABC}$ (eV)	$c_{ABC}(exp)$ (eV)	$f_i$	$E_g$ (eV)	$E_g(exp)$ (eV)	$dc_{ABC}/dP$ (meV/kbar)	$dc_{ABC}/dP$ [7] (meV/kbar)	$dE_g/dP$ (meV/kbar)	$dE_g/dP(Exp.)$ (meV/kbar)
GaP-As	2.404	1.183	3.090	0.186	0.399	0.175–0.21 [24] 0.54 [24]	0.319	2.217	2.048 [26] 2.15 [27]	0.523	0.4	9.005	
GaP-Sb	2.508	1.223	2.327	1.647	2.768	2.7 [24]	0.247	1.244	0.845 [28] 1.06 [26]	3.486	2.5	9.736	
GaAs-Sb	2.552	1.266	2.159	0.802	1.093	1.0–1.2 [24] 1.42–1.44 [24]	0.235	1.031	0.81 [29] 0.763 [26]	2.726	2.5	11.400	12.25 [43]
InP-As	2.586	1.308	3.445	0.119	0.174	0.09–0.38 [24]	0.455	1.039	0.819 [26]	–0.620	0.3	10.623	
InP-Sb	2.678	1.345	2.725	1.294	1.814	1.2–2.0 [24]	0.384	0.478	0.48 [30] 0.36 [26]	3.423	1.2	11.277	
InAs-Sb	2.712	1.388	2.758	0.774	0.89	0.58–0.7 [24]	0.405	0.319	0.12 [26]	4.505	–1.0	12.271	
Ga-InP	2.456	1.203	3.333	0.315	0.737	0.39–0.76 [24]	0.378	2.026	1.98 [27] 1.9 [26]	–2.026	0.3	8.939	8.4 [5] 8.8 [44]
Ga-InAs	2.534	1.288	3.198	0.307	0.527	0.32–0.6 [24]	0.395	1.056	2.19 [31] 0.813 [32]	1.165	0.3	10.880	13 [4] 10.95 [45]
Ga-InSb	2.730	1.366	1.827	0.177	0.283	0.36–0.43 [24]	0.235	0.587	0.75 [26] 0.34 [26] 0.43 [33]	1.649	–0.6	13.894	16 [46]
Al-GaN	1.964	1.070	10.624	0.097	4.051	0.25–1.78 [24]	0.670	8.358	4.48 [34] 3.12 [35]	–1.131		3.607	3.24 [35] 4 [34]
Al-GaP	2.361	1.070	3.215	0.009	–0.031	0, 0.49 [24]	0.317	4.051	3.34 [26] 2.38 [36]	–0.339		5.608	
Al-GaAs	2.441	1.173	2.795	0.014	0.0126	–0.127–1.183 [24]	0.293	2.337	2.94 [26] 2.158 [37]	0.654		8.887	9.15 [14] 10.85 [47]
ZnS-Se	2.398	1.153	5.885	0.349	0.506	0.456–0.68 [24]	0.627	3.743	3.08 [26]	3.118	0.8	6.180	
ZnS-Te	2.493	1.169	4.905	2.476	3.144	2.4–3 [25], 3.75 [26]	0.586	2.626	2.36 [38] 2.061 [26]	7.387	6.6	5.633	
ZnSe-Te	2.549	1.191	4.623	1.041	1.189	1.23–1.7 [25]	0.584	2.606	2.3 [39] 2.12 [26]	4.658	1.6	6.920	7.6 [48]
CdS-Se	2.590	1.247	6.416	0.291	0.399	0.53 [25]	0.745	2.670	2.25 [40] 1.95 [26]	–0.997	1.6	5.576	4–6 [49]
CdS-Te	2.674	1.265	5.511	2.345	2.696	1.73–1.84 [25]	0.716	1.810	1.58 [26]	6.212	2.3	4.751	6.2 [50]
CdSe-Te	2.722	1.287	5.159	1.001	1.04	0.755 [25] 0.87 [25]	0.708	1.864	1.047 [26] 1.48 [41]	2.453	0.3	6.221	
Cd-ZnS	2.442	1.179	6.524	0.170	0.491	0.3, 0.6 [25] 0.83 [26]	0.693	3.611	2.89 [26]	–0.809		5.792	5.3 [51]

**Table 1** continued

Alloy	$r$ [8] (Å)	$D_{av}$ [9]	$C$ (eV)	$c_e$ (eV)	$c_{ABC}$ (eV)	$c_{ABC}(exp)$ (eV)	$f_i$	$E_g$ (eV)	$E_g(exp)$ (eV)	$dc_{ABC}/dP$ (meV/kbar)	$dc_{ABC}/dP$ [7] (meV/kbar)	$dE_g/dP$ (meV/kbar)	$dE_g/dP(Exp.)$ (meV/kbar)
Cd-ZnSe	2.546	1.223	5.801	0.136	0.36	0.3-0.35 [25] 0.387 [26]	0.687	2.775	2.1 [26]	0.584		6.579	
Cd-ZnTe	2.725	1.255	4.086	0.090	0.197	0.153–0.463 [25]	0.604	2.113	1.85 [42] 1.7 [26]	–0.646		8.356	

$r$  is the nearest neighbor distance,  $D_{av}$  is the  $d$ -state effect parameter,  $C$  is the ternary's heteropolar energy gap calculated using Eq. (7),  $C_e$  is the extrinsic bowing parameter,  $f_i$  is the Phillips' ionicity,  $E_g$  is the ternary energy gap and  $dE_g/dP$  is the pressure coefficient of band gap for  $x = 0.5$

the pressure coefficient increases in group III–V in the following order of common group V elements: (GaP-As, InP-As), (GaP-Sb, InP-Sb), (GaAs-Sb, InAs-Sb) while it decreases in group II–VI in the following order of common group VI elements: (ZnS-Se, CdS-Se), (ZnS-Te, CdS-Te), (ZnSe-Te, CdSe-Te). As discussed earlier, the decrease in bulk modulus will result in an increase in the pressure coefficient of the energy gap. In their studies on the predicted pressure coefficient of the energy gap, Wei and Zunger [14] have found that the  $s$ – $s$  and  $p$ – $p$  coupling will enhance while  $p$ – $d$  coupling will reduce the pressure coefficients of the energy gap. Thus, we may conclude that the trend in group III–V common-anion system is because the effect of  $s$ – $s$ ,  $p$ – $p$  coupling and bulk modulus is stronger than the effect of  $p$ – $d$  coupling, and vice versa for group II–VI common-anion system.

Another trend is that the pressure coefficient of the band gap decreases with increasing ionicity (Columns 13 and 8, respectively, in Table 1). In order to verify this correlation, we compare compounds with similar bulk moduli due to similar nearest-neighbor distance (Column 2 in Table 1), for example, GaP-As (2.404 Å) with ZnS-Se (2.398 Å). For GaP-As and ZnS-Se, the corresponding ionicities are 0.319 and 0.586 and pressure coefficients are 9.005 and 6.18 meV/kbar, respectively. Similar trends are also found in other comparisons. Combining these results with the above analysis, this trend also indicates [14] that coupling effects could be reflected from ionicity.

Exceptions to the trend in the variation in the pressure coefficient of the energy gap with ionicity and nearest neighbor distance appear in zinc and cadmium chalcogenide common-anion systems. This is due to the large bowing parameter (Column 6 in Table 1) and its pressure coefficient (Column 11 in Table 1) of ZnS-Te and CdS-Te. The pressure coefficient of the bowing parameter is 7.387 meV/kbar in ZnS-Te compared with 3.118 and 4.658 meV/kbar in ZnS-Se and ZnSe-Te systems, respectively. Similarly, the bowing parameter pressure coefficient for CdS-Te is 6.212 meV/kbar compared with –0.997 meV/kbar for CdS-Se and 2.453 meV/kbar for CdSe-Te. These exceptions reflect the importance of bowing parameters in determining the electronic properties of ternary compounds and the invalidity of the well accepted Vegard's law [15] which can be used to obtain the physical properties of ternary compounds from the linear interpolation of two binary compounds.

#### Comparison with experiments and other calculations

The agreement between the calculated results and the experimental data are generally good. All the calculations, presented in this study, have been performed for composition  $x = 0.5$ . However, some experimental values are only available for other compositions. We list these

**Table 2** Comparison between calculated pressure coefficients of band gap for some ternary compounds for compositions  $\neq 0.5$  and Al-compounds

	x	$dE_g/dP$ (meV/kbar)	$dE_g/dP$ (Exp) (meV/kbar)
Cd <sub>x</sub> Zn <sub>1-x</sub> Se	0	7.564	7.2–7.5 [18], 7.0 [19]
	1	5.886	5.8 [18], 5.5 [14]
	0.73	6.586	3.54 [16]
ZnS <sub>x</sub> Te <sub>1-x</sub>	0	8.606	10.5 [52], 11.5 [18]
	1	6.355	5.8 [18], 6.4 [19], 6.7 [53]
	0.3	5.732	6.2 [21]
GaAs <sub>x</sub> Sb <sub>1-x</sub>	0	13.552	14.0 [18]
	1	10.61	8.5–12.6 [18]
	0.88	11.516	9.5 [22]
Al <sub>x</sub> Ga <sub>1-x</sub> N	0	5.224	3.6 [14], 4.0 [54]
	1	1.423	4.7 [14]
	0.5	3.607	3.24 [35], 4 [34]
Al <sub>x</sub> Ga <sub>1-x</sub> P	0	7.662	9.7 [18]
	1	3.385	11.1 [14]
	0.5	5.608	
Al <sub>x</sub> Ga <sub>1-x</sub> As	0	10.61	8.5–12.6 [18]
	1	7.49	10.2 [18]
	0.5	8.887	9.15 [14], 10.85 [47]

experimental values and compare them with the calculated results for the corresponding compositions in Table 2. For example, Zhao et al. [16] found that the pressure coefficient of band gap for Cd<sub>0.73</sub>Zn<sub>0.27</sub>Se is 3.54 meV/kbar and our calculation at this composition is about 6.586 meV/kbar. This difference may arise from the wurtzite structure of their experimental sample while all our calculations assume zincblende structures. The mechanisms for the influence of structure on the pressure coefficients of the band gap are not yet theoretically well understood. However, the available data show that the pressure coefficients for materials with wurtzite structure are generally less than those of zincblende structure. For example, the experimental pressure coefficient for wurtzite ZnSe is around 4.5 meV/kbar [17] while, for zincblende ZnSe, the available data is 7.0–7.5 meV/kbar [18, 19] and our calculated result is 7.564 meV/kbar. The pressure coefficient of the band gap for wurtzite CdSe is around 4.3 meV/kbar [20] and, for zincblende structure, it is around 5.8 meV/kbar [14, 18] and our calculation yields a value of 5.886 meV/kbar. The results of the experiment by Zhao et al. for the band gap pressure coefficient of wurtzite CdSe is  $2.84 \pm 0.6$  meV/kbar. This is much smaller than the generally accepted results in the literature. From the perspective of the above analyzed trends with respect to nearest neighbor distance and ionicity in the order of CdZnS, CdZnSe, CdZnTe, our result is also reasonable. For ternary

compound ZnS<sub>0.3</sub>Te<sub>0.7</sub>, Fang et al. [21] found that the band gap pressure coefficient is about 6.2 meV/kbar. From their graph, the pressure coefficient is almost constant with respect to composition. We calculate for this material at  $x = 0.3$  and find the value to be 5.732 meV/kbar which is very close to the value of Fang et al. [21] within experimental uncertainty. Moreover, the band gap pressure coefficient for GaAs<sub>0.88</sub>Sb<sub>0.12</sub> is reported by Prins et al. [22] to be 9.5 meV/kbar and our calculations show value of 11.516 meV/kbar, close to that of GaAs.

In Table 2, our calculated Al-GaN pressure coefficient of the band gap of 3.607 meV/kbar is very close to the reported experiment values of 3.24 and 4 meV/kbar. However, our calculated value for the pressure coefficient of AlN of 1.423 meV/kbar, is smaller than Wei's [14] first principle calculation of 4.7 meV/kbar. Similarly, our value for AlP is 3.385 meV/kbar compared with Wei's [14] value of 11.1 meV/kbar and, for AlAs, we get 7.49 meV/kbar while the available experimental [18] value is 10.2 meV/kbar. The reason for this discrepancy has not yet been understood.

A closer investigation of our calculated energy gaps (Column 10 in Table 1) will find that they are, in general, larger than the experimental values and this discrepancy is even larger for group II–VI than group III–V semiconductors. One possible origin for this result is the expressions for  $E_{g,h}$  and  $\Delta E_g$  in Eq. (5) are obtained by fitting to the experimental data of non-ionic group IV materials [9]. The data shows that the energy gap, in general, increases with decreasing nearest neighbor distance and increasing ionicity. Since the ionicity increases from group IV to III–V to II–VI, the calculated values of the band gap of these III–V and II–VI ternary semiconductors will be enhanced and larger than experimental values. The ionicity of group III–V ternary compounds is in the range 0.23–0.45, and the difference between our calculated results and the experimental data is approximately in the range of 0–0.25 eV. The ionicity of group II–VI ternary compounds is around 0.58–0.72 and, correspondingly, the energy gap discrepancy is about 0.3–0.8 eV.

We have discussed the model proposed by Hill and Pitt [6, 7] in the first section. Their calculated results for pressure coefficients of the bowing parameter are listed in Table 1 (Column 12) and comparisons show that their results are generally much smaller than ours. This may be because they take the screening wave number in Eq. (2) as a constant, 0.25, which may not affect the accuracy of calculation of the bowing parameters but will affect the accuracy of pressure coefficients of the bowing parameters. We also note that Hill and Pitt [6, 7] consider a set of approximations in their calculations which may result in this difference. The reason that they could fit their results to

Ga-InP system is because the pressure coefficient of bowing parameter in this system, as described in Eq. (4), is much smaller than the band gap coefficients of the binaries which the authors take from experiments.

#### Temperature coefficients of ternary compounds

Methods that are similar to this theory cannot be applied to temperature coefficients of ternary compounds by relating it to thermal expansion coefficients. This is because the temperature coefficient can be expressed as two terms: the effect of volume expansion which could be similarly derived from this theory and explicit temperature coefficient at constant volume which has to be calculated by other means. Yu and Cardona [23] have shown that the first term only takes less than 20 % of the total temperature coefficients.

#### Conclusions

The pressure dependence of the energy gap of a series of group III–V and II–VI ternary semiconductor compounds have been calculated in terms of a generalized expression of Van Vechten's dielectric theory. The agreement of our calculations with the available experimental data and other calculations are quite good. Our calculations show the following: (I) The pressure coefficient of the energy gap increases with increasing nearest neighbor distance in common-cation system. (II) In general, the pressure coefficient of the energy gap decreases with increasing ionicity. (III) The energy gap increases with decreasing nearest neighbor distance and increasing ionicity. (IV) The theory shows certain discrepancy in calculating energy gap due to its built-in assumptions.

#### References

- Gil B (1998) Group III nitride semiconductor compounds: physics and applications. Clarendon, Oxford
- Lomascolo M, Li GH, Syassen K, Cingolani R, Suemune I (1994) Phys Rev B 50:14635
- Nmec P, Maly P (2000) J Appl Phys 87:3342
- Hakki BW, Jayaraman A, Kim CK (1970) J Appl Phys 41:5291
- Chen J, Sites JR, Spain IL, Hafich MJ, Robinson GY (1991) Appl Phys Lett 58:744
- Hill R (1974) J Phys C 7:521
- Hill R, Pitt GD (1975) Solid State Commun 17:739
- Van Vechten JA (1969) Phys Rev 182:891
- Van Vechten JA (1969) Phys Rev 187:1007
- Phillips JC (1973) Bonds and bands in semiconductors. Academic, New York
- Camphausen DL, Neville Connell GA, Paul W (1971) Phys Rev Lett 26:184
- Van Vechten JA, Bergstresser TK (1970) Phys Rev B 1:3351
- Cohen ML (1985) Phys Rev B 32:7988
- Wei SH, Zunger A (1999) Phys Rev B 60:5404
- Vegard L (1921) Z Phys 5:17
- Zhao Z, Zeng J, Ding Z, Wang X, Hou J (2007) J Appl Phys 102:053509
- Cardona M (1963) J Phys Chem Solids 24:1543
- Madelung O, Schulz M (1987) Numerical data and functional relationships in science and technology, new series, group III, vol 22. Springer-Verlag, Berlin
- Reimann K, Haselhoff M, Rubenacke St, Steube M (1996) Phys Status Solidi B 198:71
- Shan W, Walukiewicz W, Ager JW, Yu KM, Wu J, Haller EE (2004) Appl Phys Lett 84:67
- Fang ZL, Li GH, Liu NZ, Zhu ZM, Han HX, Ding K (2002) Phys Rev B 66:085203
- Prins AD, Dunstan DJ, Lambkin JD, O'Reilly EP, Adams AR, Pritchard R, Truscott WS, Singer KE (1993) Phys Rev B 47:2191
- Yu PY, Cardona M (1970) Phys Rev B 2:3193
- Vurgaftman I, Meyer JR (2001) J Appl Phys 89:5815
- Hernandez-Calderon I (2002) Optical properties and electronic structure of wide band gap II–VI semiconductors. Taylor and Francis, New York
- Adachi S (2009) Properties of semiconductor alloys: Group-IV, III-V and II–VI semiconductors. Wiley, New York
- Nicklas JW, Wilkins JW (2010) Appl Phys Lett 97:091902
- Shimomura H, Anan T, Sugou S (1996) J Cryst Growth 162:121
- Tsang WT, Chiu TH, Chu SNG, Ditzenberger JA (1985) Appl Phys Lett 46:659
- Dreus D, Schneider A, Werninghaus T, Behres A, Heuken M, Heime K, Zahn DRT (1998) Appl Surf Sci 123/124:746
- Alibert C, Bordure G, Laugier A, Chevallier J (1972) Phys Rev B 6:1301
- Alavi K, Aggarwal RL, Groves SH (1980) Phys Rev B 21:1311
- Desplanque L, Vignaud D, Godey S, Cadio E, Plissard S, Wallart X, Liu P, Sellier H (2010) J Appl Phys 108:043704
- Shan W, Ager JW, Yu KM, Walukiewicz W, Haller EE, Martin MC, Mckinney WR, Yang W (1999) J Appl Phys 85:8505
- Dridi Z, Bouhafs B, Ruterana P (2002) New J Phys 4:94
- Chen A, Woodall JM (2009) Appl Phys Lett 94:021102
- Bosio C, Stachli JL, Guzzi M, Burri G, Logan RA (1988) Phys Rev B 38:3263
- Yang XD, Xu ZY, Sun Z, Sun BQ, Li GH, Sou IK, Ge WK (2005) Appl Phys Lett 86:052107
- Seong MJ, Alawadhi H, Miotkowski I, Ramdas AK, Miotkowska S (1999) Solid State Commun 112:329
- Murali KR, Thilagavathy, Vasantha S, Gopalakrishnan, Oommen PR (2010) Sol Energy 84:722
- Muthukumarasamy N, Balasundaraprabhu R, Jayakumar S, Kannan MD (2007) Mater Sci Eng 137:1
- Olego DJ, Faurie JP, Sivananthan S, Raccach PM (1985) Appl Phys Lett 47:1172
- Teissier R, Sicault D, Harmand JC, Ungaro G, Le Roux G, Largeau L (2001) J Appl Phys 89:5473
- Uchida K, Yu PY, Noto N, Weber ER (1994) Appl Phys Lett 64:2858
- Lambkin JD, Dunstan DJ (1988) Solid State Commun 67:827
- Bouarissa N, Aourag H (1995) Infrared Phys Tech 36:973
- Adachi S (1994) GaAs and related materials: bulk semiconducting and superlattice properties. World Scientific, Singapore
- Wu J, Wwalukiewicz W, Yu KM, Shan W, Ager JW III, Haller EE, Miotkowski I, Ramdas AK, Su CH (2003) Phys Rev B 68:033206
- Azhniuk YM, Lopushansky VV, Hutych YI, Prymak MV, Gomonnai AV, Zahn DRT (2011) Phys Status Solidi B 248:674
- Zerroug S, Sahraoui FA, Bouarissa N (2007) Eur Phys J B 57:9

51. Beliveau A, Carlone C (1989) *Semicond Sci Technol* 4:277
52. Gil B, Dunstan DJ (1991) *Semicond Sci Technol* 6:428
53. Gonzalez J, Perez FV, Moya E, Chervin JC (1995) *J Phys Chem Solids* 56:335
54. Teisseyre H, Kozankiewicz B, Leszczynski M, Grzegory I, Suski T, Bockowski M, Porowski S, Pakula K, Miesz PM, Bhat IB (1996) *Phys Status Solidi B* 198:235