

Cohesive energy of zincblende ($A^{III}B^V$ and $A^{II}B^{VI}$) structured solids

A S VERMA^{1,*}, B K SARKAR² and V K JINDAL¹

¹Department of Physics, Panjab University, Chandigarh 160 014, India

²Department of Physics, VIT University, Vellore 632 014, India

*Corresponding author. E-mail: ajay_phy@rediffmail.com

MS received 25 August 2009; revised 15 December 2009; accepted 22 December 2009

Abstract. In this paper we present an expression relating the cohesive energy (E_{coh} in kcal/mol) of $A^{III}B^V$ and $A^{II}B^{VI}$ semiconductors with the product of ionic charges ($Z_1 Z_2$) and nearest-neighbour distance d (Å). The cohesive energy values of these solids exhibit a linear relationship when plotted on a log–log scale against the nearest-neighbour distance d (Å), but fall on different straight lines according to the ionic charge product of the solids. A good agreement has been found between the experimental and calculated values of the cohesive energy of $A^{III}B^V$ and $A^{II}B^{VI}$ semiconductors.

Keywords. Cohesive energy; ionic charge; transition metal chalcogenide; pnictides.

PACS No. 62.20.-x

1. Introduction

Cohesive energy is one of the parameters used to understand the nature of chemical bonding and several important parameters can be predicted using it. Its magnitude tells us about the stability and chemical reactivity of solids. Eventually, it is the quantity which determines the structure, because different possible structures would have different cohesive energies [1]. Semiempirical molecular orbitals have been widely and successfully used to develop the solid-state theory. Frequent attempts [2–6] have been made to understand the electronic, mechanical, elastic and optical properties of zincblende ($A^{II}B^{VI}$ and $A^{III}B^V$) semiconductors because of their interesting semiconducting properties and various practical applications in the field of non-linear optics, electronics, photovoltaic detectors, light emitting diodes, solar cells etc. Modern high-speed computer techniques allow researchers to investigate many structural and physical properties of materials by computation or simulation, unlike traditional experiments. Empirical relations have become widely recognized as the method of choice for computational solid-state studies. In many cases empirical relations do not give highly accurate results for each specific

material, but they still can be very useful. Empirical concepts such as valence, empirical radii, electronegativity, ionicity and plasmon energy are useful for the evaluation of solid-state properties [1,7]. 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. Any change in the crystallographic environment of an atom is related to core electrons via the valence electrons. The change in wave function that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between valence, shell and core electrons is changed. This leads to a change in binding energy of the inner electron and to a shift in the position of the absorption edge.

In the previous research [8–12], we have calculated the electronic, mechanical and optical properties of binary and ternary semiconductors with the help of ionic charge theory. 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 that it would be interesting to give an alternative explanation for cohesive energy (E_{coh} in kcal/mol) of zincblende ($\text{A}^{\text{III}}\text{B}^{\text{V}}$ and $\text{A}^{\text{II}}\text{B}^{\text{VI}}$) structured solids.

2. Theory, results and discussion

Aresti *et al* [13] have studied the cohesive energy of zincblende solids and proposed an empirical relation for cohesive energy in terms of the nearest-neighbour distance (d) as follows:

$$E_{\text{coh}} = E_{\text{coh}}(\text{IV}) - B(d, R)\{1 - \Sigma E_{\text{coh}}(i)/E_{\text{coh}}(\text{IV})\}, \quad (1)$$

where $E_{\text{coh}}(\text{IV})$ is the cohesive energy of purely covalent crystals and $B(d, R) = E_{\text{coh}}(\text{IV}) - k(R) \times d(BX)/d$ is now a parameter depending on d and R .

$$k(R) = C \exp\left(\frac{-Z^{1/2}}{4}\right), \quad (2)$$

where C is a constant, which depends on the rows and $Z = Z(A) + Z(B)$ is the sum of atomic number of atoms A and B.

Many theoretical approaches [14–16] have been reported recently to determine the cohesive energy of solid-state compounds. Schlosser [17,18], has studied the cohesive energy trends in rocksalt structure in terms of nearest-neighbour distance using the following relation:

$$E_{\text{coh}} = \frac{\text{constant}}{d}. \quad (3)$$

In a previous work [11], we proposed a simple relation to calculate the dielectric constant of chalcopyrite-structured solids in terms of the product of ionic charges and nearest-neighbour distance by the following relation:

$$\text{Dielectric constant } (\varepsilon_{\infty}) = K(Z_1 Z_2)^S d^2, \quad (4)$$

Cohesive energy of zincblende ($A^{III}B^V$ and $A^{II}B^{VI}$) semiconductors

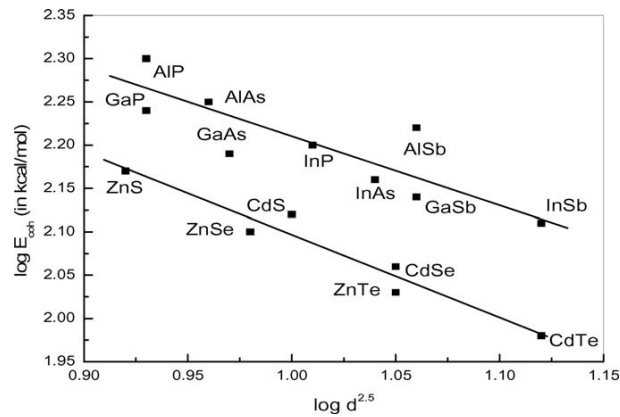


Figure 1. Plot of $\log E_{\text{coh}}$ (kcal/mol) against $\log d^{2.5}$ (nearest-neighbour distance in Å) for transitional metal chalcogenides and pnictides. Plots of $A^{II}B^{VI}$ and $A^{III}B^V$ semiconductors are nearly parallel. All experimental values are from [13].

where Z_1 and Z_2 are the ionic charge on the cation and anion respectively, d is the nearest-neighbour distance in Å and K and S are constants. The cohesive energy of $A^{III}B^V$ and $A^{II}B^{VI}$ semiconductors exhibit a linear relationship when plotted against nearest-neighbour distance, but fall on different straight lines according to the product of the ionic charge of the compounds, which is presented in figure 1. We observe that in the plot of cohesive energy and nearest-neighbour distance, the $A^{III}B^V$ semiconductors lie on a line nearly parallel to the line for the $A^{II}B^{VI}$ semiconductors. The Krishnan–Roy theory [19], Jayaraman *et al* [20] and Sirdeshmukh *et al* [21] found that substantially reduced ionic charges must be used to get better agreement with experimental values. To obtain better agreement between experimental and theoretical data for zincblende-type crystal structure compounds, Schlosser’s relation (3) may be extended as

$$E_{\text{coh}} = \text{constant} \frac{(Z_1 Z_2)^{0.4}}{d^{2.5}}, \quad (5)$$

Z_1 and Z_2 are ionic charges of cation and anion respectively and d is the nearest-neighbour distance in Å. The value of constant for zincblende-type crystal structure is 710. The value of the product of ionic charge is 4 for $A^{II}B^{VI}$ and 9 for $A^{III}B^V$ semiconductors [9]. A detailed discussion about the cohesive energy of these solids has been given elsewhere [13–18] and will not be presented here. The proposed empirical relation (5) has been applied to evaluate $A^{II}B^{VI}$ and $A^{III}B^V$ semiconductors. The results are presented in table 1. The calculated values are in good agreement with the experimental and theoretical values reported by earlier researchers [13].

3. Conclusion

We have presented an empirical expression relating cohesive energy with the product of ionic charges and nearest-neighbour distance. The values obtained from

Table 1. Values of cohesive energy (E_{coh} in kcal/mol) for $A^{\text{III}}B^{\text{V}}$ and $A^{\text{II}}B^{\text{VI}}$ semiconductors.

Solids	d	E_{coh}			% Error (with experimental)
		Exp. [13]	Theor. [13]	This work	
ZnS	2.34	146.6	151.3	147.6	0.7
ZnSe	2.46	124.5	123.7	130.2	4.6
ZnTe	2.64	106.3	108.6	109.2	2.7
CdS	2.52	131.6	134.6	122.6	6.8
CdSe	2.62	113.6	110.3	111.3	2
CdTe	2.81	95.8	95.4	93.4	2.5
HgS	2.53			121.4	–
HgSe	2.63			110.2	–
HgTe	2.80			94.2	–
AlP	2.36	198.0	197.0	199.8	0.9
AlAs	2.43	178.9	177.2	185.8	3.9
AlSb	2.66	165.0	162.4	148.2	10
GaP	2.36	173.8	173.2	199.8	15
GaAs	2.45	154.7	154.6	181.9	17
GaSb	2.65	138.6	140.5	149.6	7.9
InP	2.54	158.6	159.3	166.3	4.9
InAs	2.61	144.3	141.7	155.4	7.7
InSb	2.81	128.5	128.3	129.2	0.5
BA ₅	2.04			287.7	–
BS ₅	2.24			227.7	–
TiP	2.49			175.8	–
TiAs	2.58			159.9	–
TiSb	2.75			136.3	–

the expression for II–VI and III–V semiconductors agree well with the reported experimental values.

Acknowledgements

One of the authors (Dr Ajay Singh Verma, PH/08/0049) is thankful to the University Grants Commission, New Delhi, India for supporting this research under the scheme of UGC Dr D S Kothari Post Doctoral Fellowship.

References

- [1] L Pauling, *The nature of the chemical bond* (Cornell University Press, Ithaca, 1960) 3rd edn
- [2] Y Al-Douri, H Abid and H Aourag, *Mater. Lett.* **59**, 2032 (2005)
- [3] A E Merad, M B Kanoun, G Merad, J Cibert and H Aourag, *Mater. Chem. Phys.* **92**, 333 (2005)

- [4] H M Tutuncu, S Bagci, G P Srivastava, A T Albudak and G Ugur, *Phys. Rev.* **B71**, 195309 (2005)
- [5] S Q Wang and H Q Ye, *J. Phys. Condens. Matter* **17**, 4475 (2005)
- [6] S H Sohn, D G Hyun, M Noma, S Hosomi and Y Hamakawa, *J. Crystal Growth* **117**, 907 (1992)
- [7] V Kumar and B S R Sastry, *J. Phys. Chem. Solids* **66**, 99 (2005)
- [8] A S Verma, *Phys. Scr.* **79**, 045703 (2009)
- [9] A S Verma, *Phys. Lett.* **A372**, 7196 (2008)
- [10] A S Verma, *Phys. Status Solidi* **B246**, 192 (2009)
- [11] A S Verma, *Solid State Commun.* **149**, 1236 (2009)
- [12] A S Verma, *Philos. Mag.* **89**, 183 (2009)
- [13] A Aresti, L Garbato and A Rucci, *J. Phys. Chem. Solids* **45**, 361 (1984)
- [14] L M Liu, S Q Wang and H Q Ye, *J. Phys. Condens. Matter* **17**, 5335 (2005)
- [15] J Haglund, G Grimvall, T Jarlborg and A F Guillermet, *Phys. Rev.* **B43**, 14400 (1991)
- [16] R C Mota, S C Costa, P S Pizani and J P Rino, *Phys. Rev.* **B71**, 224114 (2005)
- [17] H Schlosser, *J. Phys. Chem. Solids* **53**, 855 (1992)
- [18] H Schlosser, *Phys. Status Solidi* **B179**, k1 (1993)
- [19] K S Krishnan and S K Roy, *Proc. R. Soc. London* **210**, 481 (1952)
- [20] A Jayaraman, B Batlogg, R G Maines and H Bach, *Phys. Rev.* **B26**, 3347 (1982)
- [21] D B Sirdeshmukh and K G Subhadra, *J. Appl. Phys.* **59**, 276 (1986)