

Van der Waals coefficients and cohesive energies of lead chalcogenides

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Abstract. The cohesive energies of PbS, PbSe and PbTe, having NaCl type of crystal structure, are calculated using the generalized Huggins-Mayer form (GHM) for the Born repulsion energy. The van der Waals interactions (VDW) are estimated from the London and Mayer formulae and compared with those estimated from the Slater-Kirkwood variational method. The cohesive energies calculated adopting the VDW coefficients calculated from the later method are in good agreement with the experimental values. The difference between the experimental cohesive energies and the calculated, assuming variational method, are 2.26, 2.97 and 3.75 eV respectively for PbS, PbSe and PbTe which are in good agreement with the reported values for the covalent bonding correction using Heitler-London-Lowdin method (HLL) which are respectively 2.1, 2.9 and 3.3 eV (Tanaka and Morita 1979).

Keywords. Lead chalcogenides; van der Waals interactions; variational method; Huggins-Mayer form of Born repulsion; cohesive energy; covalent bonding.

1. Introduction

The present paper attempts in evaluating the VDW coefficients and the cohesive energies of PbS, PbSe and PbTe by the London and Mayer formulae (Tosi 1964) for VDW coefficients assuming electronic polarizabilities and the excitation energies (for the anions electron affinities and for the cation the 3rd ionization potential) for the ions. The VDW coefficients are also computed from the variational method (Margenau 1971, Narayan 1977 and Jain and Jaishankar 1979). The repulsive parameters for each crystal are calculated employing the two sets of VDW coefficients, adopting Huggins-Mayer form for the determination of Born repulsive energy. The cohesive energies calculated by both the methods are compared with the experimental values reported. It is observed that the cohesive energies calculated from the variational method are in good agreement with the experimental values. In lead chalcogenides the VDW interactions are found to contribute significantly to the cohesion in these crystals.

2. The cohesive energy equation

The cohesive energy of ionic crystalline solids can be written as:

$$W_L \text{ (kcal/mole)} = 10^{-10} (N/J) (\phi + \psi), \quad (1)$$

$$\phi = -a (ze)^2/r - C/r^6 - D/r^8 + b \beta_{+-} M \exp [(r_+ + r_- - r)/\rho] + \frac{M'}{2} b \{ \beta_{++} \exp [(2r_+ - \sqrt{2r})/\rho] + \beta_{--} \exp [(2r_- - \sqrt{2r})/\rho] \}, \quad (2)$$

The symbols in these equations have the same significance as reported by Huggins and Sakamoto (1957) and the zero-point energy per molecule, $\psi = 9/4 h\nu_{\max}$, is computed from the Debye temperature. The Pauling coefficients, $\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}$ where z 's are the valencies and n 's are the number of outer shell electrons of the i th and j th ions, and it is assumed that $\beta_{+-} = 1$, $\beta_{++} = 1.5$ and $\beta_{--} = 0.5$.

3. Van der Waals interactions

3.1 Van der Waals coefficients using London and Mayer formulae

The VDW coefficients C and D can be calculated from the pair of interaction coefficients c_{ij} and d_{ij} given by

$$c_{ij} = \frac{3}{2} a_i a_j \frac{E_i E_j}{E_i + E_j}, \quad (3)$$

$$d_{ij} = \frac{9}{4} \frac{c_{ij}}{e^2} \left[\frac{a_i E_i}{P_i} + \frac{a_j E_j}{P_j} \right], \quad (4)$$

where the a 's are the polarizabilities, the E 's are the excitation energies of the ions and the P 's are the effective number of outer shell electrons. Assuming the P 's each equal to 5.5 (Huggins and Sakamoto 1957) the c 's and d 's are calculated and thus C and D are calculated using the appropriate lattice sums (Tosi 1964). The results are shown in table 2 from the data of table 1.

3.2 Van der Waals coefficients by variational method

The pair interaction coefficients can also be expressed, following the variational method based on the Slater-Kirkwood variational method (Margenau 1971; Narayan 1977; Jain and Jaishankar 1979), as

$$c_{ij} = 3/2 \frac{e\hbar}{m^{1/2}} a_i a_j / [(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}], \quad (5)$$

$$d_{ij} = \frac{27}{8m} \hbar^2 a_i a_j [(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}]^2 / \left[\frac{\alpha_i}{N_i} + \frac{20}{3} \frac{\alpha_i \alpha_j}{N_i N_j} + \frac{\alpha_j}{N_j} \right], \quad (6)$$

where N 's are the effective number of electrons in the two ions participating in the interactions and are taken from Scott and Scheraga 1965. The VDW coefficients calculated from equations (5) and (6) are shown in table 2.

Table 1. Crystal data for lead chalcogenides at room temperature.

	PbS	PbSe	PbTe
Interionic distance r (Å)	2.968 (a)	3.074 (a)	3.225 (a)
Elastic constants (10^{11} dynes/cm ²)			
c_{11}	12.40 (a)	12.37 (a)	10.72 (a)
c_{12}	3.30 (a)	1.98 (a)	0.768 (a)
c_{44}	2.30 (a)	1.59 (a)	1.30 (a)
Compressibility K (10^{-12} cm ² /dyne)	1.580*	1.850*	2.450*
Polarizability (Å ³)	5.460 (b)	7.210 (b)	10.65 (b)
	4.90 (c)		
Electron affinity E (kcal/mole)	99.0 (d)	117.0 (d)	97.0 (d)
3rd ionization energy of Pb (kcal/mole)	736.4 (e)		
Volume thermal expansion β ($10^{-4}/^{\circ}\text{C}$)	0.608 (f)	0.582 (f)	0.594 (f)
Pauling crystal radii (Å)			
r_-	1.84 (g)	1.98 (g)	2.21 (g)
r_+	1.21 (g)		
Debye temperature θ (°K)	227.0 (i)	138.0 (i)	125.0 (i)
Effective number of electrons			
N_-	15 (h)	21 (h)	29 (h)
N_+	49 (h)@		

*Compressibility is computed from the elastic data of Jogi and Tripathi 1975.

@ N_+ , the effective number of electrons for the lead ion which contribute to the polarization is taken from the graph of Scott and Scheraga (1965) by extrapolation of the graph while N_- are directly read from it.

(a) Jogi and Tripathi 1975, (b) Agrawal *et al* 1978, (c) Tessman *et al* 1953, (d) Huggins and Sakamoto 1957, (e) Harvey and Porter 1972, (f) Novikova and Abikosov 1964, (g) Dekker 1969, (h) Scott and Scheraga 1965, (i) Parkinson and Quarrington 1954.

4. Born repulsion parameters

The repulsion parameters for the Huggins-Mayer form of the Born repulsive energy can be determined from the solid-state data in standard thermodynamic conditions by solving the equation for the cohesive energy together with the equation of state of various crystals and its volume derivative at constant pressure in the vibrational Hilderbrand form:

$$r = r_+ + r_- + \rho \ln \left\{ 6 \beta_{+-} b \frac{r}{\rho} \right. \\ \left. 1 + \sqrt{2} \left[\frac{\beta_{++}}{\beta_{+-}} \exp\left(\frac{r_+ - r_-}{\rho}\right) + \frac{\beta_{--}}{\beta_{+-}} \exp\left(\frac{r_- - r_+}{\rho}\right) \right] \exp\left(\frac{(1 - \sqrt{2})r}{\rho}\right) \right\}, \quad (7)$$

$$\frac{\left(\frac{r}{\rho} \frac{\tau}{\sigma} - 1\right)}{\left(\sqrt{2} \frac{r}{\rho} \frac{\tau}{\sigma} - 1\right)} = -\sqrt{2} \left[\frac{\beta_{++}}{\beta_{+-}} \exp\left(\frac{r_+ - r_-}{\rho}\right) + \frac{\beta_{--}}{\beta_{+-}} \exp\left(\frac{r_- - r_+}{\rho}\right) \right] \\ \exp\left[\frac{(1 - \sqrt{2})r}{\rho}\right], \quad (8)$$

Table 2. The calculated values of the VDW coefficients, repulsion parameters and the cohesive energies [the upper number is the calculated value using equations (3) and (4) and the lower one is obtained by using variational method equations (5) and (6)].

	PbS	PbSe	PbTe
VDW 'c' coefficients c_{++}	921·196 955·074	921·196 955·074	921·196 955·074
(10^{-80} erg/cm ⁶) c_{--}	151·768 621·549	316·890 1115·973	573·214 2354·316
c_{+-}	243·287 736·944	371·667 992·070	466·073 1423·9210
C	2575·595 6284·535	3569·643 8413·779	4423·820 12380·574
'd' coefficients (10^{-76} erg/cm ⁶) d_{++}	8191·809 456·161	8191·809 456·161	8191·809 456·161
d_{--}	204·839 566·384	658·790 987·639	1459·339 2154·888
d_{+-}	1243·769 529·209	2038·873 656·288	2665·581 1047·069
D	11003·329 3661·537	16071·425 4611·066	20243·245 7479·706
Repulsion parameters ρ (Å)	0·402 0·427	0·431 0·456	0·485 0·505
b (10^{-12} erg/molecule)	1·279 1·856	1·331 2·053	1·053 1·534
Madelung energy W_e (kcal/mole)	-781·901	-754·939	-719·591
Dipole-dipole interaction energy W_{dd} (kcal/mole)	-54·238 -132·342	-60·899 -188·137	-56·601 -158·407
Dipole-quadrupole interaction energy W_{dq} (kcal/mole)	-26·304 -8·753	-29·016 -8·325	-24·903 -9·202
Repulsion energy W_b (kcal/mole)	152·127 221·517	175·923 269·440	171·356 248·623
Zero point energy W_0 (kcal/mole)	1·637	0·992	0·899
Cohesive energy W_1 (kcal/mole) ($W_1 = W_e + W_{dd} + W_{dq} + W_0 + W_b$)	-708·679 -699·842	-667·919 -680·968	-628·840 -637·678

$$\text{where } \tau = \frac{\alpha (ze)^2}{r} + \frac{6C}{r^6} + \frac{8D}{r^8} - \frac{6r^3 \beta T}{K}, \quad (9)$$

$$\sigma = \frac{2\alpha (ze)^2}{r} + \frac{42C}{r^6} + \frac{72D}{r^8} + \frac{18r^3}{K} F(T, P), \quad (10)$$

$$F(T, P) = 1 + \frac{T}{K} \left[\left(\frac{\partial K}{\partial T} \right)_P + \frac{\beta}{K} \left(\frac{\partial K}{\partial P} \right)_T \right] + \frac{2}{3} \beta T. \quad (11)$$

τ and σ are computed using the two sets of calculated values of C and D from (9) and (10). While evaluating $\sigma F(T, P)$ is assumed to be unity. ρ is determined by assuming Pauling crystal radii for the ions using (8) and then the energy parameter b is determined from (7) for each crystal. The repulsion parameters and the various energy terms obtained by the two methods *viz.* using (3) and (4), and by the variational method equations (5) and (6), are shown in table 2.

5. Discussion

The interaction coefficients d 's obtained by (3) and (4) are seen to be larger compared to those obtained by the variational method, while the c 's are relatively smaller, as is evident from table 2. However, it has been earlier reported (for a good review see Tosi 1964; Waddington 1959 and Jain and Jaishankar 1979) that the former method is subjected to considerable uncertainties. The justification in the reliability of the calculated values of c 's and d 's from (5) and (6) is that the assumptions regarding the excitation energies is removed. The elimination of E 's from (3) with the help of the one level formula for polarizability $\alpha = Ne^2 h^2/mE^2$ leads to (5) and a similar approach to (6). From the calculations it is seen that the van der Waals energy significantly contributes to the cohesive energy of these crystals. The Born repulsion coefficients calculated on the basis of variational method ρ and b are larger compared to those obtained from London and Mayer formulae. ρ varies from 0.427 to 0.505 from sulphide to telluride.

Comparison of the cohesive energies of lead chalcogenides calculated from (1) with the experimental values shows that the difference between experimental and the theoretical one on the basis of ionic approximation increased from PbS to PbTe. Thus from the difference it can be said that PbS is more ionic and the covalent contribution increases from PbS to PbTe.

Recently the cohesive energies of PbS, PbSe and PbTe have been reported by Tanaka and Morita (1979) which are shown in table 3. His calculations are based on the Heitler-London-Lowdin treatment modified so as to include the effect of covalent bonding. The covalent bonding correction for PbS, PbSe and PbTe on the basis of HLL treatment is given in table 3, which is in good

Table 3. Cohesive energies of PbS, PbSe and PbTe.

Crystal	Present work		Tanaka and Morita 1979		W_L (Expt.)— W_L (variational method) (eV)
	London Mayer formulae for VDW (kcal/Mole)	Variational method (kcal/Mole)	Experimental (as reported) (kcal/Mole)	Covalent bonding correction based on the quantum theory (eV)	
PbS	-708.679	-699.842	-751.854	2.1	2.26
PbSe	-667.919	-680.968	-749.548	2.9	2.97
PbTe	-628.840	-637.678	-724.178	3.3	3.75

agreement with the difference of cohesive energies calculated on the basis of the variational method in the determination of c 's and d 's (present calculations) and the experimental values.

Finally, the Huggins-Mayer form of the Born repulsion which assumes a constant value of ρ for different pairs of ions leads to the cohesive energies which are in good agreement with those evaluated on the basis of quantum theory (HLL-treatment) on an ionic approximation, when the repulsion parameters for each crystal are evaluated from the calculated values of the VDW coefficients on the basis of variational method.

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