Van der Waals contribution to the lattice potential in alkali halides

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Van der Waals (VdW) interactions constitute a rather small component in the cohesive energy of ionic crystals. The contributions of the VdW and the short range repulsion becomes more and more predominant at successive differentiations of the lattice energy as compared to the coulomb contributions because of their particular nature of dependence on the lattice parameter. The complete Van der Waals (VdW) contributions to the equilibrium condition and the second order elastic constant for NaCl and CsCl structure alkali halides have been derived in this paper.

1. Theory

Van der Waals (VdW) interactions constitute a rather small component in the cohesive energy of ionic crystals. The only terms contributing significantly are the dipole-dipole (dd) and the dipole-quaderpole (dq) terms varying as $1/r^6$ and $1/r^8$ respectively, r being the lattice parameter. This functional dependence renders the potential a short range character. This is why this potential is often implicitly included in the short range repulsion usually represented as a potential with two disposable parameters. However, when a study is directed to establishing the relationships between properties related to different order derivatives of the lattice energy it becomes necessary to retain the separate potential components with their known functional forms.

The contributions of the VdW and the short range repulsion becomes more and more predominant at successive differentiations of the lattice energy as compared to the coulomb contributions because of their particular nature of dependence on the lattice parameter. Thus even in the case of second order elastic constants (SOEC) which involves the second derivatives of the lattice energy the VdW contribution acquires a numerical magnitude which is of the same order as that due to the Coulomb term. It is obvious that the Van der Waals potentials should necessarily be included explicitly in the lattice energy in the studies of physical properties like the third and fourth order elastic constants (TOEC and FOEC) related to the first and second order pressure derivatives of the bulk modulus respectively, piezoelectric and photoelastic properties and the like which involved higher order derivatives of the energy function.

Recent studies (1-3) have proved that even in ionic solids the Van der Waals energy is not as insignificant as was believed earlier. Numerical values for the parameters of this potential evaluated through expressions derived from fundamental considerations are now available (3) and have proved useful in several studies (4,5). Contributions of the potential to the equilibrium conditions and the SOEC necessary for lattice dynamical studies have been derived by Sangster and Dixon (6) and used by Singh and Sanyal (7). However, this analysis assumes the nearest neighbour and the next nearest neighbour VdW contributions included in the short range repulsion term and hence is not quite useful for studies of physical properties related to higher derivatives like the TOEC and FOEC.

The VdW potential per unit cell for binary solids can be expressed in the form

$$\Phi^V = \sum \left[\frac{C_{+-}}{r^6(0+,1-)} + \frac{1}{2} \frac{C_{++}+C_{--}}{r^6(0+,1+)} + \frac{D_{+-}}{r^8(0+,1-)} + \frac{1}{2} \frac{D_{++}+D_{--}}{r^8(0+,1+)} \right] \quad (1)$$

where the indices +, - indicate the sign of charge of the ions, the C and D coefficients are the Van der Waals constants, 1 is the cell index and r represents the distance between the ions indicated by the suffix pairs inside the associated brackets. The evaluation of these potentials and their contributions to the equilibrium condition and the elastic constants demands the knowledge of several lattice sums. These sums are of the form

$$S_n^{P_1,P_2,P_3}(kk`) =$$
$$a^{P_1+P_2+P_3-n} \sum_l [(X_1^{P_1} . X_2^{P_2} . X_3^{P_3})/r^n]_{(0k,1k`)} \quad (2)$$

where a is a lattice parameter equal to half the edge length of the unit cube, X_i (i=1,2,3) are the cartesian components of the vector **r**, k, k` are the indices indicating the charge of the ions (i.e. +,-), $P_1$, $P_2$, $P_3$ are even integers including zero and n is another integer such that $n > P_1 + P_2 + P_3 + 6$. The subscript (0k, 1k`) to the bracket under the summation sign indicates that the coordinates inside represent the separation between the atoms 0k and 1k`. These lattice

sums can be reduced to combinations of sums over cubic Bravais lattices (8) and therefore can be obtained from the tables published by Born and Mishra (9). The sums needed in the present calculations are listed below in the Table 1.

Table 1. Lattice sums required in the present work.

Sum	Lattice		
	s.c.	f.c.c.	b.c.c.
S_6^{000}	8.4019	1.8067	0.45383
S_{10}^{220}	0.1914	0.1409	0.03746
S_{10}^{400}	2.4178	0.3204	0.07636
S_8^{000}	6.9458	0.80012	0.12784
S_{12}^{220}	0.7818	0.06458	0.01140
S_{12}^{400}	2.1589	0.13754	0.01982

The calculations for the NaCl and CsCl structures follow;

2. NaCl structure

From equations 1 and 2, we can write

$$\Phi^V = (1/a^6)[(S_6^{000}(\text{s.c.}) - S_6^{000}(\text{f.c.c.})C_{+-} + (1/2)S_6^{000}(\text{f.c.c.})(C_{++} + C_{--})]$$
$$+ (1/a^8)[(S_8^{000}(\text{s.c.}) - S_8^{000}(\text{f.c.c.})D_{+-} + (1/2)S_8^{000}(\text{f.c.c.})(D_{++} + D_{--})]$$

or $\Phi^V = (C/a^6) + (D/a^8)$ (3)

where $C = 6.5952C_{+-} + 0.9039(C_{++} + C_{--})$ (4)

$D = 6.1457D_{+-} + 0.4001(D_{++} + D_{--})$ (5)

Assuming the total lattice potential to be

$$\Phi = (\alpha_M e^2/a) + 6\Phi^R(a) + \Phi^V(a) \quad (6)$$

The first term on the right hand side is the long range electrostatic Madeling energy term, the second term represents the short range overlap repulsive interactions; and the last term represents the VdW interactions. We obtain the equilibrium condition in the form

$$B = (2\alpha_M/3) + (2V/e^2)\{(C/a^8) + (4/3)(D/a^{10})\} \quad (7)$$

With

$$B = (2V/e^2)(1/r)(d\Phi^R(r)/dr)_{r=a} ; V = 2a^3$$

The expressions for the second order elastic constants can be derived following either the method of finite deformation or that of the long wavelength limit. We obtain

$$C_{11} = (e^2/4a^4)(-5.112 + A)$$
$$+ [(1/Va^6)\{87.485C_{+-} + 5.883(C_{++} + C_{--})\} + (1/Va^8)\{145.320D_{+-} + 4.435(D_{++} + D_{--})\}]$$

$$= (e^2/4a^4)(-5.112 + A) + C_{11}^V \quad (8)$$

$$C_{12} = (e^2/4a^4)(0.226 - B)$$
$$+ [(1/Va^6)\{15.614C_{+-} + 5.188(C_{++} + C_{--})\} + (1/Va^8)\{17.477D_{+-} + 3.650(D_{++} + D_{--})\}]$$

$$= (e^2/4a^4)(0.226 - B) + C_{12}^V \quad (9)$$

$$C_{44} = (e^2/4a^4)(2.556 + B)$$
$$+ [(1/Va^6)\{-10.766C_{+-} + 1.575(C_{++} + C_{--})\} + (1/Va^8)\{-15.301D_{+-} + 1.516(D_{++} + D_{--})\}]$$

$$= (e^2/4a^4)(2.556 + B) + C_{44}^V \quad (10)$$

where the last term with the square bracket in each expression represents the VdW Contribution and can be denoted by C_{ij}^V. The repulsive force parameter B is already defined and

$$A = (2V/e^2)(d^2\Phi^R(r)/dr^2)_{r=a}$$

One can prove from equations (9), (10) and (7) that $C_{12} = C_{44}$ as should be the case for a central potential. One can also prove that the bulk modulus K derived from potential (6) is given by

$$K = V(d^2\Phi/dV^2) = (1/3)(C_{11} + 2C_{12})$$

as obtained from equation (8) and (9).

The differences between the numerical coefficients in our equations and in the corresponding equations of Sangster and Dixon (6) are easily accounted for. The reason for these differences has been already explained.

3. CsCl structure

In case of the CsCl structure solids also we choose the edge length of the cubic unit cell equal to 2a. With this choice the VdW potential parameters are

$$C = 0.3226C_{+-} + 0.0656(C_{++} + C_{--}) \quad (11)$$

$$D = 0.1007D_{+-} + 0.0136(D_{++} + D_{--}) \quad (12)$$

The total potential per unit cell can again be expressed by

$$\Phi = (\alpha_M e^2/a) + 8\Phi^R(a\sqrt{3}) + (C/a^6) + (D/a^8) \quad (13)$$

The equilibrium condition is given by

$$B = (\alpha_M/3) + (V/4e^2)\{(C/a^8) + (4/3)(D/a^{10})\} \quad (14)$$

and the elastic constants by

$$C_{11} = (e^2/4a^4)(0.701 + (A + 2B)/6)$$
$$+ [(1/4Va^6)\{4.827C_{+-} + 3.102(C_{++} + C_{--})\} + (1/4Va^8)\{2.570D_{+-} + 1.205(D_{++} + D_{--})\}]$$

$$= (e^2/4a^4)(0.701 + (A + 2B)/6) + C_{11}^V \quad (15)$$

$$C_{12} = (e^2/4a^4)(-0.690 + (A - 4B)/6)$$
$$+ [(1/4Va^6)\{9.199C_{+-} + 0.812(C_{++}$$
$$+ C_{--})\} + (1/4Va^8)\{4.623D_{+-}$$
$$+ 0.194(D_{++} + D_{--})\}]$$
$$= (e^2/4a^4)(-0.690 + (A - 4B)/6) + C_{12}^V (16)$$

$$C_{44} = (e^2/4a^4)(-0.350 + (A + 2B)/6)$$
$$+ [(1/4Va^6)\{4.038C_{+-} - 0.2380(C_{++}$$
$$+ C_{--})\} + (1/4Va^8)\{2.476D_{+-}$$
$$- 0.096(D_{++} + D_{--})\}]$$
$$= (e^2/4a^4)(-0.350 + (A + 2B)/6) + C_{44}^V (17)$$

The repulsive potential parameters A and B in these equations are defined by

$$A = (V/e^2)(d^2\Phi^R(r)/dr^2)_{r=a\sqrt{3}}$$
$$B = (V/e^2)(1/r)(d\Phi^R(r)/dr)_{r=a\sqrt{3}} ; V = 8a^3$$

Equations (7 to 10) represent the equilibrium condition and expressions for the three elastic constants for the rigid ion or a simple shell model of the NaCl structure solids. Equations (14 to 17) are the corresponding equations for the CsCl structure.

4. Discussion

The three body modifications of these equations can be obtained in a straightforward manner by simply adding the VdW terms to the corresponding expressions of the three body force rigid ion model or the three body force shell model equations. This is a welcome situation since it enables us to express the higher order elastic constants or other properties depending on higher order derivatives of the lattice potential without introducing any new disposable parameters. In particular we can follow the scheme proposed by Garg et al (10) in which now the elastic constants would have to be effectively replaced by

$$C_{ij} - C_{ij}^V \text{ or } C_{ijk} - C_{ij\,k}^V \text{ etc.}$$

This scheme is certainly superior to Sangster and Dixon's as in their case the short range parameters are derived from a potential obtained by adding the NN and NNN VdW terms to the usual Born-Mayer potential. Such a situation doesn't allow us to obtain a simple relationship between the short range force parameters derived from say the third and fourth order derivatives as for example used by Garg et al. We therefore, expect that our scheme will prove quite useful in studies of the TOEC, FOEC and hence of the pressure derivatives of the SOEC as also of the piezoelectric and photoelastic behaviors of ionic solids.

5. Numerical applications

Numerical application of the equations given above yield good values for the cohesive energies and to some extent for the pressure derivatives of the bulk modulus also with certain significant limitations related to the values of the individual elastic constants. As a matter of fact the VdW parameters themselves show wide variations in calculations based on different physical conditions (1-3). If one uses the recent most values of VdW parameters C_{++}, C_{--} and C_{+-} determined by Shankar et al (3) to evaluate C_{44} one obtains large negative contributions leading to negative values for the shear modulus for many of the alkali halides. This is obviously impossible. The theory is therefore not capable of yielding accurate values of B_0, $B_0^{`}$ and $B_0^{``}$ etc from either fundamental or phenomenological calculations. The equations derived above should thus be used for determining the potential parameters from the knowledge of $B_0$, $B_0^{`}$ and $B_0^{``}$ as derived from the P-V data.

6. Conclusion

The complete Van der Waals (VdW) contributions to the equilibrium condition and the second order elastic constant for NaCl and CsCl structure alkali halides have been derived in this paper. Our expressions have the advantage that they can be directly added to the corresponding expressions derived for the rigid ion or shell models of ionic solids with or without the three body interactions to obtain the correct expressions for models based on the lattice energy including the VdW potential explicitly.

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