

# COHESIVE ENERGIES AND OTHER PROPERTIES OF IONIC CRYSTALS—1. ALKALI HALIDES\*

M. N. SHARMA AND M. P. MADAN

DEPARTMENT OF PHYSICS, LUCKNOW UNIVERSITY, INDIA

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**ABSTRACT.** The lattice energies and other properties of ionic crystals have been studied on the basis of a Lennard-Jones (12:6) potential form and the necessary equations derived. Experimental data for the interionic distances and lattice energies for such crystal have been used to give the values of the repulsive force parameter B and the van der Waals Parameter C, which in turn have been utilised to obtain lattice energies, compressibilities and the coefficient of linear expansion. Satisfactory agreement is found between the experimental values and those calculated theoretically.

## INTRODUCTION

The treatment of lattice energy and other properties of ionic crystals was initially given by Born and later developed by Born and Mayer (1932) and others and has been summarised by Born and Huang (1954). The interaction energy of an ionic crystal, in addition to Coulomb energy, consists of an attractive and a repulsive term. The most widely used forms for the repulsive potential have been either the exponential variation of repulsion interaction with distance or simply an inverse power variation. Although the results obtained by considering the Born theory were consistent, there always seemed to be the uncertainty in the magnitude of the force index in the inverse form or the exponent in the exponential form.

In an ionic crystal, the degree of ionization of the constituent atoms is often such that the electronic configuration of all ions correspond to closed electronic shells, as in the case of inert gas atoms. The inert gas atoms have closed shells and the charge distributions are spherically symmetric. We may also expect that the charge distribution on each ion in an ionic crystal may have approximately spherical symmetry and that they interact according to central force law. Thus, it seems reasonable to assume that ions of an ionic crystal are of the same electronic structure as an inert gas, possess overlap energy (and van der Waals energy), following a law with the same interionic distance variation as for two-inert gas atoms, that is, with the same force indices but with different potential parameters.

Many of the properties of gases and liquids have been calculated and explained in terms of a commonly used interaction energy function, such as Lennard-Jones

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(12 : 6) potential. This potential is strictly true for the interaction of spherically symmetric atoms and molecules. It is therefore possible to describe a number of properties of ionic crystals on a common basis with the help of this potential in conjunction with the term for Coulomb energy. This, thus affords a unified approach for evaluating and interpreting the properties of ionic crystals as well as the knowledge about the interaction forces and it is reasonable to assume that such an analysis will achieve considerable success. In the present paper, we have used the Lennard-Jones (12 : 6) form representing the van der Waals energy and the overlap energy. The inclusion of van der Waals energy makes the law applicable more satisfactorily for heavier compounds.

The interionic energies in salt crystals of heavier elements may be assumed to be of the form

$$\phi(r) = A(r) + B(r) \quad \dots (1)$$

in which

$A(r)$  = attractive potential

$B(r)$  = repulsive potential

If we take Lennard-Jones (12 : 6) form in conjunction with the electrostatic energy term, we get the value of  $A(r)$  and  $B(r)$  as

$$A(r) = - \frac{\alpha e^2}{r^6} - \frac{C}{r^6} \quad (2)$$

$$B(r) = \frac{B}{r^{12}} \quad \dots (3)$$

where  $\alpha$  is Madelung's constant (1.7476 for NaCl type, and 1.7626 for the CsCl type) which is characteristic of the type of crystal structure and is independent of the dimensions of the lattice,  $e$  is the electronic charge ( $e = 4.803 \times 10^{-10}$  e.s.u.),  $r$  is the interionic distance,  $C$  is the van der Waals constant and  $B$  is the repulsive parameter which is calculable.

We have taken no account of the overlap potentials between other than nearest neighbours. Born and Huang (1954) have shown that the theoretical estimates are altered on this account by well under 1 per cent.

Cohesive energies for the ionic crystals are between a hundred and thousand times higher than the rare gas crystals and so the zero point energy is comparatively very unimportant for the ionic crystals, still one might take this into account.

If  $\epsilon_0$  is the zero point vibrational energy then the energy per cell in an ionic crystal may be represented as

$$\phi(r) = - \frac{\alpha e^2}{r^6} + \frac{B}{r^{12}} - \frac{C}{r^6} + \epsilon_0 \quad \dots (4)$$



In this equation we have not considered the dipole-quadrupole van der Waals term  $Dr^{-8}$ . However for a check we calculated the effect of this term on lattice energy and the compressibility and found that for lighter alkali halides, contribution due to this term is negligibly small. For higher alkali halides, the deviation is noticeable only in the expression for compressibility, but still is in neighbourhood of 1—2 percent. Therefore estimates of various properties based on (4) should be quite accurate. Equation (4) and the associated expressions can now be used to compute the interionic distances, the lattice energies, the repulsive force constant, the linear expansions and the compressibilities and compare them with experimental determinations as well as with those derived theoretically from other methods.

#### CALCULATION OF POTENTIAL PARAMETERS

The constants in potentials could be assigned values so as to give the best fit for various crystal properties of all the alkali halide lattices in static equilibrium. But, as these quantities for the static lattices are not directly observable, we can assume that at finite temperatures the energy of a lattice consists of two parts, (Hildebrand 1931) one dependent on its volume and the other only on temperature and express the first and second derivatives of the interaction energy in terms of the directly observable quantities. Thus, at equilibrium at zero pressure and at the absolute temperature  $T$ , Huggins (1937),

$$\frac{d\phi(r)}{dr} = \frac{3vT}{r\beta} \left( \frac{1}{V} \frac{\partial V}{\partial T} \right)_P \quad \dots (5)$$

and

$$\frac{d^2\phi(r)}{dr^2} = \frac{9v}{r^2\beta} F_{T,P} \quad \dots (6)$$

where

$$F_{T,P} = 1 + \frac{T}{\beta} \left( \frac{\partial \beta}{\partial T} \right) + \frac{T}{\beta^2 v} \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial \beta}{\partial P} \right)_T + \frac{2T}{3V} \left( \frac{\partial V}{\partial T} \right)_P$$

where  $\beta$  is compressibility,  $\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P$  is thermal expansion coefficient and  $v$  is the volume of the lattice cell. If  $v$  is the molar volume, then  $v = \frac{V}{N} = Kr^3$  in which  $K$  is a constant that is characteristic of the type of the lattice.

#### (a) Repulsive parameter $B$

The potential parameters can be evaluated by using the experimental data for different crystal properties. Using equations (4) and (5), we get

$$B = r^{12} \left[ \left( \frac{\alpha e^2}{12r} + \frac{C}{2r^6} \right) - \frac{3Tv}{12} \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P \right] \quad (7)$$

and also from equation (4)

$$B = -r^{12} \left[ \frac{5}{6} \frac{\alpha e^2}{r} + \phi(r) + \frac{3Tv}{6} \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P - \epsilon_0 \right]. \quad \dots (8)$$

From an analysis of the experimental crystal structure data accurate values for the lattice constant are available, from which using the appropriate structure relationships for cubic lattices, nearest neighbour distance  $r$  can be obtained. These observed values of  $r$  (Huggins 1937) can be substituted in equation (7) to determine the constant  $B$ , if we have a knowledge of  $C$  from other means. The second term in the square bracket is only in the nature of a corresponding term in which experimental values may be used for any selected temperature. If the experimental data for another crystal property, viz, the lattice energy is used in conjunction with the data for  $r$ ,  $B$  could also be computed from equation (8). The values of  $B$  so obtained from both the methods are tabulated in Table I. Mayer's

TABLE I  
Values of the repulsive parameter  $B$

Crystal	$B \times 10^{104}$ (From eqn. 7)	$B \times 10^{104}$ (From eqn. 8)
CsF	72.74	—
CsCl	510.70	531.6
CsBr	817.70	864.6
CsI	1628.00	1496.0
RbCl	184.10	147.8
RbBr	309.20	275.4
RbI	643.60	627.2
KBr	189.90	141.5
KI	404.60	342.7
NaI	163.50	130.6

(1933) estimates of  $C$  obtained from an analysis of optical data were employed while using equation (7). For the sake of comparison few crystals of lighter alkali halides have also been included. It is seen that there is a good agreement in the values of the parameter  $B$ , obtained by using the value of  $C$  from optical data and that obtained by using the experimental values of the lattice energies.

(b) *The van der Waals attraction parameter  $C$*

Values of the lattice energy in conjunction with the experimental values of  $r$ , may be used to determine the attractive parameter  $C$  in a similar manner. The

van der Waal energy increases with the size of the ions and is quite appreciable for crystals of heavier elements. Equations (4) and (5) yield

$$C = -2r^6 \left[ \frac{11}{12} \frac{\alpha e^2}{r} + \phi(r) + \frac{3vT}{12} \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P - \epsilon_0 \right]. \quad \dots (9)$$

The calculated  $C$  values from this equation are given in Table II, where they

TABLE II  
Values of the van der Waals parameter  $C$

Crystal	$C \times 10^{60}$ (From optical data)*	$C \times 10^{60}$ (From equ. 9)
CsF	495	—
CsCl	1590	1766.00
CsBr	2070	2410.00
CsI	2970	2279.00
RbCl	691	97.74
RbBr	898	485.90
RbI	1330	1201.00
KBr	605	—
KI	924	287.90
NaI	482	159.20

\*Mayer (1933)

have been compared with the values estimated by Mayer (1933) from a careful analysis of optical data. The table shows that there is a fair agreement between the two values and can be termed satisfactory, especially as the values of the lattice energies are subject to the possible experimental errors of the order of a few per cent. However, as expected, it may be noticed that the deviations are larger than those in the case of repulsive parameter  $B$ . These deviations are due to the relatively smaller contribution of van der Waals term to the total energy. The experimental lattice energies are tabulated in Table III.

TABLE III  
Calculated and observed values of crystal energies

Crystal	Cohesive Energy $E$ in K Cal/mole.				Calculated (Huggins, 1937)
	Experimental	Calculated (Present Work)	Calculated (Fowler, 1955)	Calculated (Cubicciotti, 1959)	
CsF	—	182.4	176.9	179.2	175.7
CsCl	157.8	156.8	157.3	155.9	153.1
CsBr	152.3	151.6	153.5	151.1	149.6
CsI	145.4 (141.5) <sup>H</sup>	142.9	147.7	143.6	142.5
RbCl	163.6	167.0	165.7	164.3	162.0
RbBr	158.0	162.6	160.6	157.6	156.1
RbI	149.7	150.1	153.5	149.1	148.0
KBr	161.2	165.5	166.3	162.7	161.3
KI	152.8	155.1	158.8	153.4	152.4
NaI	166.3	166.8	170.8	165.9	164.3

(H) Huggins (1937)

Thus, both the potential parameters, repulsive constant  $B$  and the attractive constant  $C$  can be estimated purely from the experimental data and can be used to compute other properties. If we also wish to calculate  $r$  theoretically, this can be done easily from equations (4) and (5) using the values of the potential parameters and solving the equations for  $r$  by any convenient method of successive approximation.

#### CALCULATION OF CRYSTAL PROPERTIES

##### (a) Lattice energies :

Evaluation of the potential parameters from the selected crystal properties, affords a means of calculating other properties of the crystals. As both the distance  $r$  and the energy  $\phi(r)$  have been used to obtain  $B$  and  $C$ , it would be preferable to calculate other properties than these to check the suitability of equation (1). Fortunately, as mentioned earlier,  $C$  can also be obtained separately from the optical data. Therefore, we can determine theoretically, if we use  $B$  as obtained from equation (7), and the experimental values of the constant  $C$  as obtained from the optical data. In Table IV, we have given values of the calculated cohesive energy  $E$  where  $E = -N\phi(r)$  along with the experimental values. In the table are also given values calculated by Fowler (1955) using an inverse ninth power term for the repulsive energy and by Huggins (1937) using an energy function

taking into consideration an exponential expression for the repulsive term along with an additional term for the dipole-quadrupole interaction term. It will be

TABLE IV  
Calculated and observed values of crystal compressibilities

Crystal	$\beta \times 10^{12}$ (bar)		
	Experimental	Calculated (Present work)	Calculated (Present Work)
	(a)	(b)	(c)
CsF	4.25 (4.25)	3.97	—
CsCl	5.95 (5.55)	5.53	5.43
CsBr	7.06 (6.28)	6.39	6.16
CsI	8.57 (7.83)	7.44	8.08
RbCl	6.65 (6.16)	5.45	6.15
RbBr	7.94 (7.38)	6.60	7.05
RbI	9.57 (9.00)	8.57	7.39
KBr	6.70 (6.45)	5.45	—
KI	8.54 (8.07)	7.13	7.82
NaI	7.07 (6.21)	4.68	5.49

(a) Cubicciotti (1959).

(b) Using  $B$  from equation (7).

(c) Using  $B$  and  $C$  from equations (8) and (9) respectively.

seen that the results obtained by us differ very slightly from those obtained by Huggins (1937) and in some cases are even better. Thus, the estimates of the cohesive energy based on equation (1) should be quite adequate.

(b) *Crystal compressibilities*

From the knowledge of  $B$  and  $C$ , we can derive crystal compressibilities which can be compared with observed values. Equation (6) can be written as

$$\beta = \frac{9vF_{T,p}}{\left( -\frac{2\alpha e^2}{r} + 12.13 \frac{B}{r^{13}} - 6.7 \frac{C}{r^7} \right)} \dots (10)$$

The term  $F_{T,p}$  is of the order of a small correcting term which vanishes at 0°K. Using experimental values for this term equation (10) enable to be computed utilizing  $B$  and  $C$  from equation (8) and (9) and also  $B$  from (7) and  $C$  from optical data. In equation (1), the slope of the repulsive term  $Br^{-n}$  ( $n = 12$ ), increases

rapidly as  $r$  diminishes. The effect of this distortion can be corrected, if we replace in  $\frac{d^2\phi(r)}{dr^2}$ , the expression  $n(n+1)$  by  $n^2$  to conform better with the realistic overlap energy (Fowler 1955). The values of  $\beta$  thus obtained are given in Table IV, where they have compared with experimentally observed values of the crystal compressibilities. The agreement is satisfactory.

TABLE V

Calculated and observed values of Coefficient of thermal expansion of crystals

Crystal	$\alpha^1 \times 10^6$		
	Experimental	Calculated (Present Work)	Calculated (Born Model)
NaI	48.3	47.99	42.87
KBr	40.0	37.44	43.08
RbCl	36.0	31.52	41.05
RbBr	38.0	42.61	41.90
CsCl	56.0	55.27	56.18

## OTHER PROPERTIES OF CRYSTAL

Besides the properties discussed in preceding section, many other crystalline properties can be investigated on the basis of the interaction energy form of equation (1), and their calculated values compared with observation. However, we consider here only the coefficient of linear expansion.

The thermal expansion of solids can be qualitatively explained as the result of displacement of the equilibrium positions of the ions due to increase of the amplitude of vibration (Hummel 1950). In view of the influence of the ionic vibration on thermal expansion of solids attempts were made by several workers to correlate this property with vibration characteristics of the ions. An approximate thermodynamic equation for thermal expansion of ionic crystals can be derived and the calculated values of thermal expansion can be compared with the experimental results.

The potential energy at a distance  $r$  can be written as

$$\phi(r) = \phi_0(r) + a(r - r_0)^2 \quad \dots (11)$$

where  $\phi_0(r)$  is the energy at the equilibrium distance  $r_0$ , and

$$a = \frac{1}{2} \left[ \frac{d^2\phi(r)}{dr^2} \right]. \quad \dots (12)$$



Now if  $\alpha^1$  be the thermal expansion,  $C_v$  be the specific heat at constant volume, and  $\nu$  be the frequency of vibration then it can be shown that (Kumar 1959)

$$\alpha^1 = - \frac{C_v}{2ar_0} \left( \frac{1}{\nu} \frac{d\nu}{dr} \right). \quad \dots (13)$$

We know that the frequency of vibration of a simple harmonic oscillator is expressed as

$$\nu = \left( \frac{d^2\phi(r)/dr^2}{4\pi^2 m} \right)^{1/2}, \quad \dots (14)$$

where  $m$  is the reduced mass of the oscillating ions.

At equilibrium position,  $r = r_0$ ,  $\frac{d\phi(r)}{dr} = 0$  and

$$\frac{d\nu}{dr} = \frac{1}{2\pi\sqrt{m}} \frac{1}{2} \left( \frac{d^2\phi(r)}{dr^2} \right)^{-1/2}_{r \sim r_0} \left( \frac{d^3\phi(r)}{dr^3} \right)_{r \sim r_0} \quad \dots (15)$$

We immediately find out, using  $\phi$  and its derivatives obtained from eqn. (4) in (13), that

$$\alpha^1 = \frac{C_v}{2r_0} \frac{\left( 176 \frac{\alpha e^2}{r_0} + 756 \frac{C}{r_0^3} \right)}{\left( 11 \frac{\alpha e^2}{r_0^3} + 36 \frac{C}{r_0^3} \right)^2}. \quad \dots (16)$$

Equation (16), thus derived is nevertheless, subject to certain simplifying assumptions (Kumar 1959). Further, the effect of the polarization of ions has not been considered. Certain empirical changes can be made to account for this effect. Increase in thermal expansion due to polarizability of the ion can be partially accounted for by replacing  $C_v$  with  $C_p$ . Also, on account of polarization, there is an arrangement of charge distributions, and there is some sort of distortion which accompanies the charge. Empirically the effect of this distortion can be taken care of if we rewrite our equation (16) as

$$\alpha^1 = \frac{C_p}{2r_0} S \frac{\left( 176 \frac{\alpha e^2}{r_0} + 756 \frac{C}{r_0^3} \right)}{\left( 11 \frac{\alpha e^2}{r_0^3} + 36 \frac{C}{r_0^3} \right)^2} \quad \dots (17)$$

the correction factor  $S$  is taken to be proportional to polarization  $P$  such that

$$S = (f \times P)$$

where  $P$  is related to the atomic polarizabilities of positive and negative ions in the usual way.  $f$  is given value 0.033 for NaCl type crystals and 0.045 for CsCl type crystals. The results are given in Table V, where they have also been compared with the experimental values. A fair agreement is seen between the two values.

The results of the calculation described above show that the use of the Lennard-Jones (12 : 6) potential form for the ionic crystals is not in conflict with the findings from the use of the original Born equations or its later modifications and describes the crystal properties to practically same degree as the latter, and there is very slight discrepancy between the results from different determinations. The discrepancies become more pronounced as we proceed towards lighter alkali halides. And hence as, for the inert gases and simple near-spherical molecules, different properties can be explained in terms of a single potential in inverse powers of the distance (i.e. L-J 12: 6 potential), it is possible to describe the various properties of ionic crystals, particularly of heavier compounds (high polarizability) by the use of the same simplified potential, even though the absolute computations of properties cannot be termed as better than the previous determinations. The deviation is further reduced if we also consider the dipole-quadrupole term  $D^r^{-8}$ , for these crystals of heavier compounds.

#### A C K N O W L E D G M E N T

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