

Lattice properties of heavier halides⁺—I

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The appropriateness of Born's theory as applied to lighter alkali halides and molecules has been further investigated by considering heavier ionic crystals using a modified Born potential energy function. The values of index of repulsive potential, n , the repulsive force parameter λ , lattice energy, compressibility and thermal expansion have been calculated and necessary equations derived. The comparison of the experiment with theory reveals that the present simple and direct approach using modified Born model is quite satisfactory to represent various lattice properties. Also the comparison of the results with those obtained employing other models establishes the superiority of the modified Born model¹

INTRODUCTION

Born (1923, 1927) has formulated a theory to describe the various properties of ionic crystals and molecules on the basis of a very simple form of the function expressing interaction potential energy. The correct representation of the potential energy of a set of atoms as a function of the interatomic distances is of fundamental importance. It is well known that the interaction energy of an ionic crystal, in addition to Coulomb energy, consists of terms involving attractive and repulsive energies. In an ionic crystal the charge distribution on each ion has, approximately, spherical symmetry and 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 the molecules of an inert gas, possessing overlap energy (and Van der Waals energy).

The forces of interaction between ions lead to the formation of the molecules and crystals and at the same time help to determine their properties. For ionic crystals the behaviour of the forces of interaction was studied by Mie (1903), Gruneisen (1912, 1926), Born (1923, 1927), Born & Mayer (1932) and at a later stage by Cubicciotti (1959, 1961), Sharma & Madan (1961, 1962, 1964a, 1964b), Saxena *et al* (1964), Kachhava & Saxena (1965), Gohel & Trivedi (1967), Gupta & Sharma (1969), Chatterjee (1963) and others and has been summarised by Kittel (1956) and Born & Huang (1959). In ionic crystals the interaction consists of (i) an electrostatic term, giving the largest contribution to the total lattice energy (ii) a repulsive term (iii) multipole interactions, like dipole-dipole and dipole-quadrupole interactions, which though small must be taken into account for the sake of completeness and (iv) zero-point energy.

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Many of the properties of liquids and gases have been explained in terms of a commonly used interaction energy function, such as Born potential energy function. This energy function is strictly true for spherical molecules. Thus it is possible to explain a number of properties of ionic crystals on a common basis with the help of this potential energy function. It is reasonable to assume that if we also consider the multipole interactions and zero point energy in conjunction with this potential model (modified Born model) better results may be expected and such an analysis will lead to considerable success.

Now taking into account all the above interactions, the energy of the crystal per unit cell may be expressed as :

$$\psi(r) = -\frac{\alpha e^2}{r} + \frac{\lambda}{r^n} - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon \quad \dots (1)$$

where α is the Madelung constant, e the electronic charge, r the equilibrium interionic distance, λ the repulsive parameter, C the dipole-dipole interaction parameter, D the dipole-quadrupole interaction parameter, ϵ the zero-point energy and n the index of the repulsive term

At this juncture, it may be mentioned that the two types of repulsive functions in vogue are an exponential variation with distance and a simple inverse power variation with distance. The results of quantum-mechanical calculations favour the exponential form which is more cumbersome (Cubicciotti 1959, 1961), whereas, the inverse power form has the advantage of greater simplicity (Chatterjee 1963). The exponential form has been used by Born & Mayer (1932), Huggins (1937), and Cubicciotti (1959, 1961), for lighter alkali halides and by Bleick (1934), Mayer (1933), and Mayer & Levy (1933) for heavier halides. It is, therefore, worthwhile to find out whether the simple inverse power law is equally satisfactory for ionic crystals containing heavier ions as less work has been done on these crystals

In the present work, the inverse power form of repulsive term has been adopted and it has been shown that this modified Born potential energy function, too, is equally satisfactory for metal halides. Besides having the advantage of simplicity, its justification lies in the fact that the interionic distance between two ions remains nearly constant being near the value at the potential minimum.

DETERMINATION OF POTENTIAL PARAMETERS

The well known equilibrium relations, based on certain assumptions by Hildebrand (1931), about the energy of a lattice are:

$$r \left(\frac{d\psi}{dr} \right)_{r=r_0} = \frac{3vT}{\beta} \left(\frac{1}{V} \frac{\partial V}{\partial T} \right)_P \quad \dots (2)$$

and

$$r^2 \left(\frac{d^2\psi}{dr^2} \right)_{r=r_0} = \frac{9v_r F_{TP}}{\beta} \quad \dots (3)$$

where

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

β is the compressibility, $\left(\frac{1}{V} \frac{\partial V}{\partial T} \right)_P$ is the thermal expansion coefficient and v is the volume of the unit cell and is given by $v = kr^3$, where k is the structure constant depending upon the type of crystal lattice.

(a) *The power of repulsive potential*

Combining equations (2) and (3) with equation (1) one obtains,

$$n = \frac{9kr^3}{\beta} F_{T,P} + 2 \frac{\alpha e^2}{r} + 42 \frac{C}{r^6} + 72 \frac{D}{r^8} - 1 \dots \quad (4)$$

$$\frac{\alpha e^2}{r} + \frac{6C}{r^6} + \frac{8D}{r^8} - \frac{3kr^3 T}{\beta} \left(\frac{1}{V} \frac{\partial V}{\partial T} \right)_P$$

From an analysis of the crystal structure data, accurate values of the lattice constant are available from which, using the appropriate structural relationship for different cubic lattices, the nearest neighbour distance r can be obtained. These observed values of r can be substituted in equation (4) to determine the constant n , if we have a knowledge of C and D from other sources. The first term in the numerator and the last term in the denominator are only in the nature of a corresponding term in which experimental values may be used for any selected temperature. If the experimental data for the coefficient of volume expansion, the compressibility and interionic distance be used, the value of n can be computed from equation (4). These values of n for several heavier halides have been reported in table I. The experimental values used for CuCl, CuBr and CuI were obtained from Mayer & Levy (1933), for AgCl, AgBr, AgI, TlCl and TlBr have been taken from Mayer (1933) and for NH_4Cl and NH_4Br from Blicke (1934).

(b) *Repulsive parameter λ*

Once the values of the index of the repulsive term, n , have been evaluated using equation (4), the potential parameters can be evaluated by using the experimental data for different crystal properties.

From equation (1) we at once get

$$\lambda = r^n \left[\psi(r) + \frac{\alpha e^2}{r} + \frac{C}{r^6} + \frac{D}{r^8} - \epsilon \right] \dots \quad (5)$$

Also, combining equations (1) and (2), we obtain

$$\lambda = \frac{r^n}{n} \left[\frac{\alpha e^2}{r} + \frac{6C}{r^6} + \frac{8D}{r^8} - \frac{3kr^3}{\beta} T \left(\frac{1}{V} \frac{\partial V}{\partial T} \right)_P \right] \quad (6)$$

and from equations (1) and (3) we get

$$\lambda = \frac{r^n}{n(n+1)} \left[\frac{9kr^3}{\beta} F_{TP} + \frac{2\alpha e^2}{r} + 42 \frac{C}{r^6} + 72 \frac{D}{r^8} \right]$$

TABLE 1. Potential parameters

Crystal	n		λ		
	Eq (4)	Scitz (1940)	Eq (5)	Eq (6)	Eq (7)
CuCl	9.455	9.000	$5.319 \times 10^{-01.64}$	$7.119 \times 10^{-04.61}$	$7.119 \times 10^{-01.64}$
CuBr	9.704	-	$0.854 \times 10^{-05.03}$	$1.351 \times 10^{-05.03}$	$1.351 \times 10^{-05.03}$
CuI	12.020	-	$0.815 \times 10^{-103.16}$	$1.835 \times 10^{-103.16}$	$1.835 \times 10^{-103.16}$
AgCl	10.009	9.500	$5.973 \times 10^{-00.07}$	$6.952 \times 10^{-00.07}$	$6.952 \times 10^{-00.07}$
AgBr	10.250	-	$0.938 \times 10^{-00.00}$	$1.228 \times 10^{-00.00}$	$1.228 \times 10^{-00.00}$
AgI	10.250	-	$6.762 \times 10^{-00.00}$	$9.822 \times 10^{-00.00}$	$9.822 \times 10^{-00.00}$
TlCl	8.590	10.500	$6.940 \times 10^{-76.72}$	$8.052 \times 10^{-76.72}$	$8.052 \times 10^{-76.72}$
TlBr	8.853	-	$1.230 \times 10^{-77.02}$	$1.409 \times 10^{-77.02}$	$1.409 \times 10^{-77.02}$
NH ₄ Cl	8.811	--	--	$8.189 \times 10^{-78.51}$	$8.189 \times 10^{-78.51}$
NH ₄ Br	8.643	--	--	$9.770 \times 10^{-77.11}$	$9.770 \times 10^{-77.11}$

The values of λ have been computed separately from equations (5), (6) and (7). It is seen from table 1 that there is a good agreement in the values of the repulsive parameter λ obtained by using the value of C from optical data and those obtained by using the experimental values of the lattice energy.

CRYSTAL PROPERTIES

(a) Interaction energy

Using the expressions (1), (6), and (7), the values of the interaction energies have been calculated and presented in table 2 along with the experimental values for the sake of comparison.

The lattice energy can also be calculated using experimental values of reststrahlen frequency ν_0 . This method is supposed to be more realistic and accurate as this involves only two measurable quantities, ν_0 and dielectric constants at static and high frequency regions. If we take the polarization of ions into consideration the equation for force constant can be written as

$$f = \frac{4\pi^2\nu_0^2(\epsilon_0+2)\mu}{(\epsilon_\infty+2)} \quad (8)$$

TABLE 2. Lattice energy and compressibility

Crystal	$\psi(r)$ (K cal./mole)				$\beta(\times 10^{-12} \text{ bars}^{-1})$		
	Observed	Theoretical using eq. (1) and			Calculated Saxena <i>et al</i> (1964)	Observed	Theoretical Using Equation (12)
		λ from Eq (6)	λ from Eq (7)	Eq. (11) and f from Eq. (8)			
CuCl	221.9 ^a	213.5	213.5	209.7	211.0	2.51 ^a	4.13
CuBr	216.0 ^a	204.4	204.4	196.9	201.9	—	—
CuI	213.4 ^a	199.6	199.6	—	195.6	—	—
AgCl	205.7 ^b	200.4	200.4	211.9	197.5	2.40 ^b	3.20
AgBr	201.8 ^b	193.8	193.8	204.6	190.2	2.75 ^b	4.66
AgI	199.0 ^b	188.0	188.0	—	183.9	—	—
TlCl	170.1 ^b	164.7	164.7	—	161.5	4.90 ^b	6.86
TlBr	165.6 ^b	161.2	161.2	—	157.6	5.30 ^b	7.03
NH ₄ Cl	—	160.0	160.0	—	—	—	—
NH ₄ Br	—	152.4	152.4	—	—	—	—

^a Mayer & Levy (1933)^b Mayer (1933)

where μ is the reduced mass per ion pair, c_0 and ϵ_∞ are the static and high frequency dielectric constants, respectively. The experimental values of force constant can be computed using equation (8) if we have a knowledge of experimental values of ν_0 , c_0 and ϵ_∞ . The force constant f can also be written as

$$f = \frac{1}{3} \left[\phi''(r_0) + \frac{2}{r_0} \phi'(r_0) \right] \quad (9)$$

where $\phi'(r_0)$ and $\phi''(r_0)$ are the first and second derivatives of $\phi(r)$ [$\phi(r)$ contains the rest of the energy $\psi(r)$ of equation (1) except the electrostatic term $(-\alpha e^2/r)$].

Using equation (1) for $\phi(r)$ and equation (9) we at once get

$$f = \frac{1}{3} \left[\frac{\lambda}{r^n} \frac{n(n-1)}{r^2} - 30 \frac{C}{r^8} - 56 \frac{D}{r^{10}} \right] \quad (10)$$

Now substituting for λ/r^n from equation (1) in equation (10) and solving for $\psi(r)$ we get

$$\psi(r) = \frac{1}{n(n-1)} \left[3fr^2 - \frac{C}{r^6} (n^2 - n - 30) - \frac{D}{r^8} (n^2 - n - 56) \right] + c_0 - \frac{\alpha e^2}{r} \dots \quad (11)$$

The values of f determined from equation (8) have been used to compute the theoretical values of $\psi(r)$ on the basis of equation (11) and are presented in table 2 only for a few crystals, which verify the suitability of this method.

(b) *Compressibility*

From the knowledge of λ , C , D and the lattice energy, we can derive the crystal compressibility which can be compared with the observed values.

Using equation (3) and solving for β , we get

$$\beta = \frac{9kr^3 f_{T,P}}{-\frac{2\alpha e^2}{r} + n(n+1)\frac{\lambda}{r^n} - 42\frac{C}{r^6} - 72\frac{D}{r^8}} \quad (12)$$

Equation (12) enables us to compute β on substituting the value of λ from equation (5) and the values of C and D from optical data. The values of β thus obtained are given in table 2, where they have been compared with the experimental values of the crystal compressibility.

(c) *Coefficient of thermal expansion*

In a crystal lattice, the ions oscillate about their equilibrium positions and their amplitudes increase with temperature. Hummel (1950) on this basis has explained the thermal expansion as due to the shifting of equilibrium positions of oscillating ions when their amplitudes become sufficiently large. In view of the effect of ionic vibrations on thermal expansion of solids, many workers have correlated this property with vibration characteristics of ions. Weyl (1955), while discussing simple cubic crystals, has pointed out that expansivity should increase with increasing polarisation of ions.

In the present work, the values of coefficient of thermal expansion on the basis of equation (1) have been calculated in two different ways. We shall take up these methods one by one.

(A) Dividing equation (2) by equation (3), we get

$$\alpha_v = \frac{3f_{T,P}}{rT} \frac{(d\psi/dr)}{(d^2\psi/dr^2)} \quad \dots (13)$$

and, for the modified Born potential, equation (13) yields

$$\alpha_v = \frac{3f_{T,P}}{T} \frac{\left[\frac{\alpha e^2}{r} - \frac{n\lambda}{r^n} + \frac{6C}{r^6} + \frac{8D}{r^8} \right] Z}{\left[-\frac{2\alpha e^2}{r} + n(n+1)\frac{\lambda}{r^n} - 42\frac{C}{r^6} - 72\frac{D}{r^8} \right]} \quad \dots (14)$$

In the last equation

$$Z = \frac{Z_c N_c + Z_a N_a}{N_a + N_c}$$

where Z_c , N_c and Z_a , N_a are the charge and number of the cation and anion, respectively. This term has been introduced to account for the polarisation effects. The values of α_v calculated from equation (14), using the values of λ obtained from equation (7), are presented in table 3 along with the experimental values.

TABLE 3. Coefficient of thermal expansion

Crystal	$\alpha_v (\times 10^{-6}$ per degree)			
	Theoretical using			Kumar (1959)
	Observed	Eq. (14)	Eq. (17)	
CuCl	65.40	65.76	--	--
CuBr	62.10	62.30	--	--
CuI	73.50	73.46	--	--
AgCl	98.74	98.73	124.36	94.41
AgBr	104.50	104.38	132.87	95.34
AgI	113.30	113.48	--	--
TlCl	153.80	152.83	181.22	155.40
TlBr	160.40	159.80	--	--
NH ₄ Cl	142.00	141.66	--	--
NH ₄ Br	161.00	161.57	--	--

(B). Kumar (1959, 1960) has developed a simple method for calculating the coefficient of thermal expansion. According to him,

$$\alpha_v = \left(\frac{3C_p}{2E} \right) \left(\frac{n+4}{n} \right) Z^3 \quad \dots (15)$$

where C_p and E are the specific heat at constant pressure and cohesive energy per mole, respectively, and Z is the same as in equation (14).

A more general form of equation (15) is

$$\alpha_v = -\frac{3C_p}{2r_0} \frac{\psi''(r_0)}{[\psi'(r_0)]^2} Z^4 \quad \dots (16)$$

where r_0 is the interionic equilibrium separation distance, $\psi''(r_0)$ and $\psi'(r_0)$ refer to values of third and second derivatives, respectively, of $\psi(r)$ at $r = r_0$.

Thus using equation (1) and substituting for $\psi''(r_0)$ and $\psi'''(r_0)$ we get

$$\alpha_v = -\frac{3}{2} C_p \left[\frac{6 \frac{\alpha e^2}{r} - n(n+1)(n+2) \frac{\lambda}{r^n} + 336 \frac{C}{r^6} + 720 \frac{D}{r^8}}{\left[-2 \frac{\alpha e^2}{r} + n(n+1) \frac{\lambda}{r^n} - 42 \frac{C}{r^6} - 72 \frac{D}{r^8} \right]^2} \right] Zt \dots (17)$$

Using calculated values of λ from equation (7), α_v has been computed only for AgCl, AgBr and TlCl because for other halides the data for C_p is not available in literature.

DISCUSSION

The potential parameters n and λ for the simple modified Born model have been tabulated in table 1. For a single crystal we get three different sets of potential parameter λ calculated from the three conditions. The use of these parameters to calculate lattice properties will throw some light on the accuracy of experimental data used and the assumed potential model.

The present values of repulsive index n agree well with those reported by Seitz (1940). The difference is mainly due to the lattice conditions used (equations (2) and (3)) and data taken and also due to additional terms, *i.e.*, dipole-dipole and dipole-quadrupole interactions. These interactions should always be considered especially in the case of heavier ions (Born & Huang 1954).

Table 2 gives the values of interaction energy calculated for two sets of potential parameter λ (equations (6) and (7)). It can be seen that the results obtained are in excellent agreement with the experimental values. The theoretical values of $\psi(r)$ computed from experimental absorption frequency data compare fairly well with the observed values. The present values of $\psi(r)$ computed from equations (6) and (7) are in much better agreement than those calculated by Saxena *et al* (1964) using exponential energy function. It is, therefore, clear that the inverse power repulsive form can be used to describe successfully all the classical effects associated with ionic crystals. The authors anticipate that, if a more accurate value of F_{TP} , be used in calculating the interaction energy, still better agreement with experiment can be obtained.

The values of the compressibility presented in table 2 are fairly accurate and are nearly of the same order as the experimental values.

The thermal expansion values of the crystals calculated from equation (14) along with the experimental values have been presented in table 3. The table also includes values of α_v calculated from equation (17) for AgCl, AgBr and TlCl and also those reported by Kumar (1959) for these crystals. Values for other crystals could not be given due to nonavailability of experimental data. The present values from equation (14) agree excellently with the experimental values and are better than those of Kumar. However, values calculated presently, from equation (17) following the method of Kumar do not give as good results

for obvious reasons. The agreement between the observed and the theoretical values thus confirms the essential correctness of the theoretical modified Born potential energy model for the ionic lattices.

In view of the simple calculations and the direct approach, it can easily be seen that the modified Born model represents excellently some of the crystal properties reported here and may be considered in preference to the cumbersome models having involved calculations.

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