

## A new logarithmic form of overlap repulsion for the heavier salts

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The various lattice properties of metal halides containing heavier ions have been studied on the basis of a modified new logarithmic form  $1 \log(1 + B/\rho^n)$  for overlap repulsion. The necessary equations for the potential parameters  $A$  and  $B$  have been derived using the room temperature lattice conditions. These parameters have been utilized to compute the cohesive energies, force constants, reststrahlen frequencies and Debye characteristic temperatures. It is inferred that the theoretical values of these lattice properties compare well with observed values and are much better than the other computed values reported earlier. The present approach serves to justify the adequacy of the chosen potential energy function for the heavier salts also.

### INTRODUCTION

The theory of ionic crystals was first developed by Born and later extended by Born & Mayer (1932) and others. The cohesive energy of ionic crystals consists of the Coulomb interaction which gives rise to Madelung's energy, the short range repulsive potential energy, the dipole-dipole and dipole-quadrupole interaction energies and the zero point energy.

The need for a repulsive potential in order to maintain a stable crystal was recognized long before the advent of quantum mechanics and in order to facilitate the computation of cohesive energy of ionic crystals, Born and other workers adopted an empirical repulsive potential of the form  $\lambda/r^n$ , where  $\lambda$  and  $n$  are constants to be determined by the condition of thermodynamic equilibrium of the crystal lattice.

After the advent of quantum mechanics Born & Mayer (1932) introduced an exponential form  $\lambda \exp(-r/\rho)$  where  $\lambda$  and  $\rho$  were taken as potential parameters. These forms for repulsive potential are not quite adequate. The Born form is a fair approximation for short range of  $r$  only, whereas in the Born & Mayer (1932) form  $\rho$  is chosen quite arbitrarily for different crystals and the constant  $\lambda$  has ionic radii dependence. Keeping in view the limitations of these repulsive potential forms, Prakash & Behari (1969) have recently suggested a new logarithmic form for repulsive potential and successfully calculated the cohesive energies of alkali halide crystals at 0°K. In the present work we have modified the logarithmic form of the overlap repulsion by taking into account

the dipole-quadrupole interaction energy term, because Van der Waal's potential shows a systematic tendency to increase for salts of heavier ions

#### EVALUATION OF POTENTIAL PARAMETERS

Taking into account all the above interaction energy terms, the cohesive energy per unit cell in an ionic crystal may be written as

$$\psi(r) = -\frac{\alpha e^2}{r} + A \log_e \left(1 + \frac{B}{r^9}\right) - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon \quad (1)$$

where  $\alpha$  is the Madelung's constant,  $e$  the electronic charge,  $r$  the interionic distance,  $A$  and  $B$  the potential parameters.  $C$  and  $D$  Van der Waal's interaction constants and  $\epsilon$  the zero point energy

The potential parameters  $A$  and  $B$  are evaluated from the room temperature equilibrium lattice conditions due to Hildebrand (1931).

$$\left(r \frac{d\psi}{dr}\right)_{r=r_0} = \frac{3vT\alpha_v}{\beta} \quad (2)$$

and

$$\left(r^2 \frac{d^2\psi}{dr^2}\right)_{r=r_0} = \frac{9v}{\beta} F_{T,P} \quad (3)$$

where  $\beta$  is the compressibility,  $\alpha_v$  the thermal expansion,  $T$  the absolute scale room temperature and  $v$  the volume per ion pair given by  $v = V/N = kr_0^3$  in which  $k = 2$  for f.c.c. crystals,  $k = 1.54$  for b.c.c. crystals and  $k = 3.2$  for crystals having zinc blende structure.  $F_{T,P}$  is a correction term which is taken to be equal to unity due to non-availability of data required for its computation.

Equations (1), (2) and (3) give

$$A = \frac{1}{9} \left( \frac{\alpha e^2}{r_0} + \frac{6C}{r_0^6} + \frac{8D}{r_0^8} - \frac{3vT\alpha_v}{\beta} \right) \left(1 + \frac{r_0^9}{B}\right) \quad (4)$$

and

$$B = \frac{8\alpha e^2 r_0^7 + 18Cr_0^2 + 8D - 3vr_0^8(10T\alpha_v + 3)/\beta}{\frac{\alpha e^2}{r_0^2} + \frac{36C}{r_0^7} + \frac{64D}{r_0^6} + \frac{3v}{\beta r_0}(T\alpha_v + 3)} \quad (5)$$

#### COMPUTATION OF CRYSTAL PROPERTIES

##### (1) Cohesive energies

The values of  $A$  and  $B$  computed on the basis of equations (4) and (5) have been utilized for the theoretical determination of  $\psi(r)$  from equation (1) which are presented in table 1.

Table 1 Values of Cohesive Energies

Crystal	$\psi(r)$ (K cal/mol)			
	Expt.	Theor. eq. (1)	Theor. (c)	Theor. (d)
NH <sub>4</sub> Cl	—	164.1	—	—
NH <sub>4</sub> Br	—	156.9	—	—
CuCl	221.9 <sup>a</sup>	214.9	211.0	216.9
CuBr	216.0 <sup>a</sup>	204.8	201.9	—
CuI	213.4 <sup>a</sup>	197.2	195.6	194.5
AgCl	205.7 <sup>b</sup>	200.6	197.5	197.9
AgBr	201.8 <sup>b</sup>	193.3	190.2	190.5
AgI	199.0 <sup>b</sup>	186.9	183.9	—
TlCl	170.1 <sup>b</sup>	166.8	161.5	168.2
TlBr	165.6 <sup>b</sup>	169.2	167.6	162.4

(a) Mayer & Levy (1933)

(b) Mayer (1933).

(c) Saxena & Kachhava (1961)

(d) Mathur & Singh (1967)

(2) *Reststrahlen frequencies*

Krishnan & Roy (1951) and Born & Huang (1954) have given the following relation for the force constant in terms of potential parameters,

$$f = \frac{1}{3} \left[ \phi''(r_0) - \frac{2}{r_0} \phi'(r_0) \right] \tag{6}$$

in which  $\phi'(r)$  and  $\phi''(r)$  are the first and second derivatives of  $\phi(r)$ , ( $\phi(r)$  contains the rest of energy in  $\psi(r)$ , except the Coulombian term  $-ae^2/r$ ). Using equation (6) in conjunction with equation (1), the expression for the force constant can be derived as

$$f = \frac{3AB(8r_0^9 - B)}{r_0^2(B + r_0^9)^2} - \frac{10C}{r_0^8} - \frac{56D}{3r_0^{10}} \tag{7}$$

Now if we consider the polarization of positive ions with respect to the lattice of negative ions, the reststrahlen frequency can be computed from the equation

$$\nu = (2\pi)^{-1} [f(\epsilon_\infty + 2)]^{1/2} [\mu(\epsilon_0 + 2)]^{-1/2} \tag{8}$$

where  $\mu$  is reduced mass per ion pair,  $\epsilon_0$  and  $\epsilon_\infty$  are the static and high frequency dielectric constants, respectively. The calculated values of  $f$  from equation (7) have been used to compute  $\nu_0$  on the basis of equation (8) and are tabulated in table 2.

Table 2. Values of Force Constants and Reststrahlen Frequencies

Crystal	$f \times 10^{-4}$ Eq. (7)	$\nu_0 \times 10^{-12}$ cm/sec.		
		Expt.	Theor. eq. (8)	Theor. <sup>(c)</sup>
NH <sub>4</sub> Cl	2.756	—	4.26	—
CuCl	9.065	5.67 <sup>a</sup>	5.31	5.344
CuBr	8.137	5.27 <sup>a</sup>	4.67	4.692
AgCl	7.095	3.09 <sup>b</sup>	3.99	4.168
AgBr	6.422	2.40 <sup>b</sup>	3.06	3.086
TlCl	3.241	1.89 <sup>b</sup>	1.85	1.909
TlBr	3.089	1.43 <sup>b</sup>	1.38	1.591

(a) Born &amp; Huang (1954)

(b) Jones *et al* (1961).

(c) Srivastava &amp; Madan (1967)

## (3) Debye Characteristic Temperature

A number of relations have been given for  $\Theta_D$  in terms of compressibility and lattice energy by Joshi & Mitra (1960) and Srivastava & Madan (1967). It is seen that their results are at variance when compared with experimental results. However, in the present work a relation has been suggested for  $\Theta_D$  in terms of the various lattice properties. If the value of force constant  $f$  is computed from equation (7), the value of  $\Theta_D$  can be easily obtained from the equation

$$\Theta_D = h(2\pi k)^{-1} [f(\epsilon_\infty + 2)]^{1/2} [\mu(\epsilon_0 + 2)]^{-1/2} \quad (9)$$

where  $h$  is the Planck's constant and  $k$  the Boltzmann's constant. The theoretical values of  $\Theta_D$  for a few metal halides have been presented in table 3, where these

Table 3. Values of Debye Characteristic Temperatures

Crystal	$\Theta_D$ in °K				
	Expt.	Theor. eq. (9)	Theor. <sup>(a)</sup>	Theor. <sup>(b)</sup>	Theor. <sup>(c)</sup>
NH <sub>4</sub> Cl	—	204	—	—	—
CuCl	—	255	255	—	—
CuBr	—	224	222	—	—
AgCl	183	191	198	136	—
AgBr	144	147	147	128	—
TlCl	—	89	89	—	167, 123, 125, 164.
TlBr	—	66	65	109	123, 114, 117

(a) Sharma (1969).

(b) Reddy (1963).

(c) Mitra &amp; Joshi (1960).

have been compared with the experimental values as well as with the calculated values from other methods. The present values of  $\Theta_D$  are in excellent agreement with observed values and are in a much better fit with the values obtained from other determinations.

#### DISCUSSIONS

The theoretical values of  $\psi(r)$  (table 1) using the logarithmic form of repulsion interaction in terms of various lattice properties are in excellent agreement with the experimental results when compared with the theoretical values of Saxena & Kachhava (1964) who employed the Born-Mayer potential energy function, and with those of Mathur & Singh (1967) using Varshni & Shukla (1961) potential model which neglect the dipole-dipole and dipole-quadrupole interactions.

The computed values of  $\nu_0$  (table 2) show a superiority over the theoretical values of Srivastava & Madan (1967) employing the repulsion interaction term of the form  $\lambda e^{-r/\rho}$ , neglecting the contribution of dipole-dipole and dipole-quadrupole interaction terms, which are quite important for crystals containing heavier ions, when compared with observed values of  $\nu_0$ . In view of the present simple approach using a more accurate potential model, the present results are comparable to the results obtained from the study of frequency *versus* wave vector dispersion curves.

The calculated values of  $\Theta_D$  for AgCl, AgBr are in better agreement with the observed values of  $\Theta_D$  as compared with the calculated values of Reddy (1963). Unfortunately for other crystals observed data are not available, therefore we can predict the correctness of theoretical values of  $\Theta_D$  for  $\text{NH}_4\text{Cl}$ , CuCl, CuBr, TlCl, and TlBr on this basis. The authors feel that the old and incomplete experimental data for  $\Theta_D$  need thorough revision for these crystals. The salts considered here have different characteristics from the alkali halides. These salts have a high value of attractive Van der Waal's potential so that the contribution due to dipole-quadrupole interaction is quite significant for them.

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