

## The Nature of the Ionic Bond\*

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### Abstract

A new model to describe interionic binding in diatomic crystals is proposed. With the inclusion of an overlap repulsion of logarithmic form along with charge-charge and van der Waals interaction terms, the model is found to yield improved values for the cohesive energy and other parameters of alkali halide crystals. Unlike previous forms for the interionic binding in an LiF crystal, in which the potential is negative at distances much smaller than the distance of closest approach of  $\text{Li}^+$  and  $\text{F}^-$  ions, the present model tends to infinity in the positive energy region before such distances are approached.

### 1. Introduction

The nature of the binding in diatomic ionic crystals has been a subject of extensive study over the past six decades. A number of attempts have been made to approximate the interionic potential in such crystals by assuming them to be composed of completely ionized atoms, and earlier models along these lines have been proposed by Born and Lande (1918), Born and Mayer (1932), Rittner (1951), Varshni and Shukla (1961) and Patel *et al.* (1967). These models have been accepted as being reasonably successful in describing the ionic bond in diatomic molecules and crystals. Reviews of the progress in this field have been made by Sherman (1932), Waddington (1959) and Ladd and Lee (1964), while recent developments are described by Kachhava and Saxena (1963, 1965), Mathur and Singh (1967), Pandey (1969, 1970a), Pandey and Saxena (1969), Barr and Lidiard (1970) and Redington (1970).

In models for the interionic binding, the potential function is represented by a large number of terms, but only the following ones are important:

- (i) the charge-charge interaction term ( $-Ae^2/r$ ),
- (ii) the dipole-dipole and dipole-quadrupole interaction terms ( $-C/r^6$  and  $-D/r^8$  respectively),
- (iii) the zero-point energy term, and
- (iv) a short-range repulsive term.

The existence of hyperpolarizability in atoms and molecules has been established theoretically (Sewell 1949; Coulson *et al.* 1952; Buckingham *et al.* 1956), and Lawley (1961) has included this effect in his study of the properties of ion pairs.

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It may be shown from Lawley's theory that the leading term in the hyperpolarizability contribution to the interaction potential between an unlike ion pair is of the form  $-Le^2/r^{10}$ , where

$$L = 2\alpha_1\alpha_2(\alpha_1 + \alpha_2) - e^2(B_1^2/2\alpha_1 + B_2^2/2\alpha_2). \quad (1)$$

Here  $\alpha_1$  and  $\alpha_2$  are the polarizabilities of the ions and  $B$ , which is the leading hyperpolarizability contribution governing the change in polarizability caused by the field gradient of the neighbouring ion, is given by

$$B = -\frac{4}{5}se^3(\theta|r^4|0)/V^2, \quad (2)$$

where the suffixes 1 and 2 distinguishing between ions have been omitted. In this expression  $s$  is the number of electrons in the group of degenerate orbitals of highest energy,  $\theta$  is the ground state wavefunction and  $V$  is the effective excitation energy for the particular perturbation. It is difficult to obtain an accurate evaluation of  $B$ . Lawley (1961) gave the probable lower limit as

$$B = -\frac{9}{5}\alpha^2/es, \quad (3)$$

$s$  being the number of electrons in the outermost shell. For this value of  $B$  the expression for  $L$  reduces to

$$L = \alpha_1^2(2\alpha_2 - 1.62\alpha_1/s_1^2) + \alpha_2^2(2\alpha_1 - 1.62\alpha_2/s_2^2). \quad (4)$$

The interaction term  $-Le^2/r^{10}$  due to the presence of hyperpolarizability in a single  $\text{Na}^+\text{Cl}^-$  bond may be generalized for a sodium chloride crystal so that, together with additional geometric factors, the hyperpolarizability per ion pair in the crystal is thus the sum of the infinite series

$$\begin{aligned} \frac{Le^2}{r^{10}} \left( 6 - \frac{12}{2^{10/2}} + \frac{8}{3^{10/2}} - \frac{6}{4^{10/2}} + \frac{24}{5^{10/2}} - \frac{24}{6^{10/2}} + \dots \right) \\ = 5.6566561 Le^2/r^{10} = KLe^2/r^{10}. \end{aligned} \quad (5)$$

The constant  $K$  (analogous to the Madelung constant for charge-charge interaction) is a characteristic for the particular lattice, its value depending on the geometry.

The hyperpolarizability term for diatomic alkali halide molecules has been considered only by a few authors (Varshni and Shukla 1965; Pandey 1970*b*) since it contributes less than 0.01% to the total energy. However, it cannot be neglected in any study of binding at separations less than the equilibrium ionic distance, as it plays an important role in this region.

## 2. Previous Potential Models

With the inclusion of terms for the various interactions noted above, the forms proposed in previous models of the interionic potential energy function  $\phi(r)$  for an ion pair interacting with each other and with the rest of the lattice are as follows.

Born and Landey (1918; BL model),

$$\phi(r) = -Ae^2r^{-1} - Cr^{-6} - Dr^{-8} - KLe^2r^{-10} + Br^{-m} + \varepsilon; \quad (6)$$

Born and Mayer (1932; BM model),

$$\phi(r) = -Ae^2r^{-1} - Cr^{-6} - Dr^{-8} - KLe^2r^{-10} + Q_1 \exp(-r/q_1) + \varepsilon; \quad (7)$$

Varshni and Shukla (1961; VS model),

$$\phi(r) = -Ae^2r^{-1} - Cr^{-6} - Dr^{-8} - KLe^2r^{-10} + Q_2 \exp(-q_2 r^2) + \varepsilon; \quad (8)$$

Patel *et al.* (1967; PGT model),

$$\phi(r) = -Ae^2r^{-1} - Cr^{-6} - Dr^{-8} - KLe^2r^{-10} + Q_3 \exp(-q_3 r^{3/2}) + \varepsilon. \quad (9)$$

In equations (6)–(9),  $A$  is the Madelung constant,  $B$ ,  $m$ ,  $Q_i$  and  $q_i$  are potential parameters and the remaining terms have their usual meaning. These model potentials, without the hyperpolarizability term, have been widely used (e.g. Ladd and Lee 1958; Saxena and Kachhava 1966; Dheer and Sharan 1967; Cleaver *et al.* 1972; Lal and Spencer 1973; Shukla *et al.* 1973). We shall now examine the validity of the models (6)–(9) for the case of diatomic ionic crystals.

For all of the above models we have\*

$$\lim_{r \rightarrow 0} \phi(r) = -\infty, \quad (10)$$

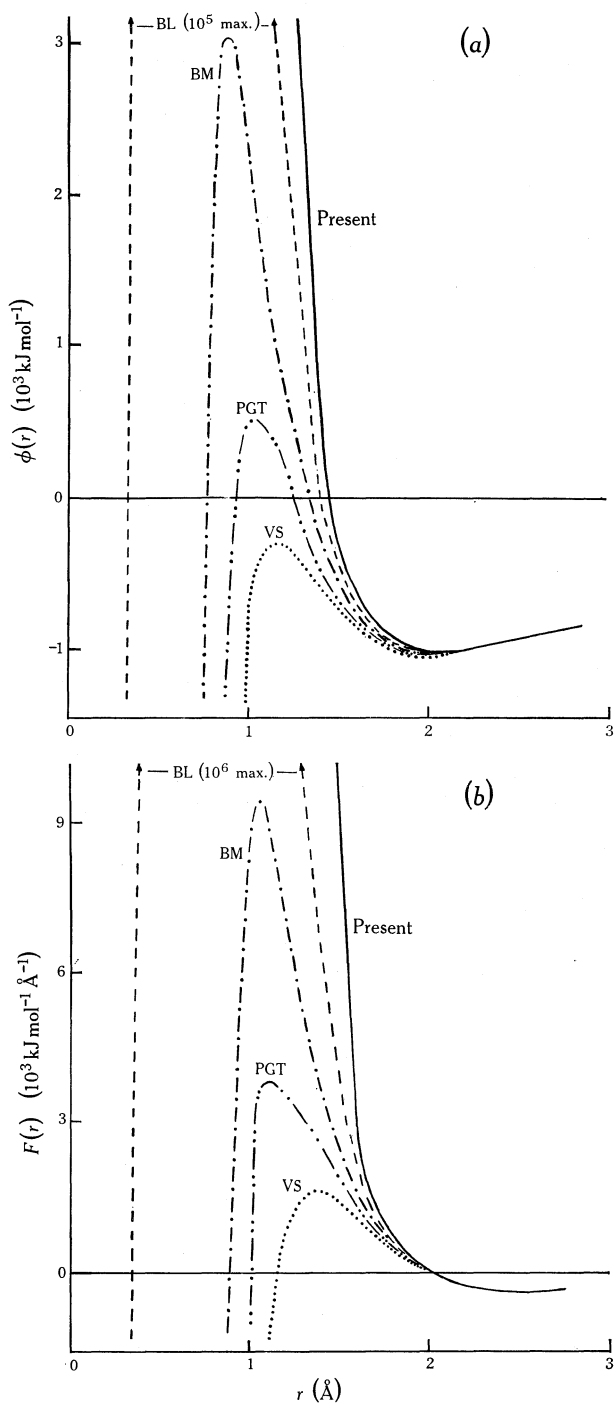
and thus the potential energy curves will approach infinity in the negative energy region. The exponential repulsion terms suffer from the fundamental physical drawback that they give a constant finite value for  $r = 0$ . The forms of the pair potential for an LiF crystal as predicted by the models (6)–(9) are shown in Fig. 1a, where it is seen that, after the usual minimum at the equilibrium ionic separation  $r_0$ , the curves have a maximum in the region  $r < r_0$  and tend to infinity as  $r \rightarrow 0$ . The height of the potential barrier for the BL model is about  $10^5$  kJ mol<sup>-1</sup>, very much greater than for the other models.

The potential energy curves in Fig. 1a as predicted by the previous models are not satisfactory. Since there must be a finite probability for penetration of ions in each direction through the potential barrier (Bohm 1951; Harmony 1972), under these conditions a crystal would not remain stable and could either collapse or contain heavier nuclei formed by fusion following such tunnelling. There is no evidence to show that diatomic ionic crystals have these characteristics.

The force  $F(r) = -d\phi(r)/dr$  between an ion pair, as given by the models (6)–(9), is plotted as a function of the ionic separation  $r$  in Fig. 1b. Again the curves are not satisfactory since they all give  $F(r)$  zero for two values of  $r$ , indicating a stable crystal for two values of ionic radius, together with the possibilities of crystal collapse and the formation of heavier nuclei by the application of an external force equal to the height of the force curve.

It is obvious that the presence of attractive terms proportional to  $r^{-6}$ ,  $r^{-8}$  and  $r^{-10}$ , when considered with charge-charge interaction and the previous forms of the repulsive terms, reduce the height and thickness of the potential barrier. It may also be shown that there are additional attractive terms due to dispersion effects (Curtiss 1967) and proportional to higher inverse powers of  $r$  which must further reduce the barrier, and thus increase the probability of penetration. A further difficulty with the previous potential forms is that they exist as a negative function at small separations (Fig. 1a). Since, for an LiF crystal, the electronic shells of the ions will have

\* The property (10) is true for the BL model only for  $m < 10$ , but this holds for most of the alkali halides.



**Fig. 1.** Comparison of the behaviour of (a) the pair potential  $\phi(r)$  and (b) the interionic force  $F(r)$ , for an LiF crystal, according to the present potential model and the corresponding curves for the previous models discussed in the text.

overlapped long before the interionic separation has been reduced to  $1\text{Å}$ ,  $\text{Li}^+$  and  $\text{F}^-$  ions cannot exist in this region, and an interionic potential as such cannot be defined here. Essentially then there are two main regions to consider: (I)  $0 < r < r_x$  (where  $r_x$  is the interionic distance at which the electronic shells come into contact), in which entirely different concepts must be introduced to deal with the internuclear forces, and (II)  $r > r_x$ , in which anions and cations can exist in their normal state. Obviously a realistic model for the interionic potential should be confined to region II.

For predicting the form of the potential energy curve then, from the above discussion the BL model is the most successful of the previous models. However, in other respects an inverse power function is not as good a representation of the repulsive term as an exponential function (Born and Mayer 1932; Rice and Klemperer 1957; Varshni 1957; Seitz 1940). One argument that has been frequently advanced in support of the exponential function is that such a term is predicted by quantum mechanical calculations. Theoretical treatments of the repulsive force between closed shell anions and point cations (e.g. Unsold 1927; Bruck 1928) and between inert-gas atoms (e.g. Slater 1928; Bleicke and Mayer 1934; Kunimune 1950; Sakamoto and Isiguro 1956) have tended to support the assignment of an exponential term. However, several of the theoretical results are in serious disagreement with the experimental data (Sakamoto and Isiguro). Thus the available evidence suggests that present quantum mechanical treatments cannot be applied to the representation of the binding in diatomic ionic crystals. Finally, as Dobbs and Jones (1957) remark, 'The exponential form for the repulsive potential makes calculations of the lattice properties rather complicated and, in any case, is, perhaps, not valid in the region near the minimum of the total potential which is of course the essential part in considering the properties of the lattices'.

### 3. A New Potential Model

Until a complete quantum mechanical treatment of ions in close contact is available, the overall effect of the short-range forces can only be represented by an empirical term in any model of the potential energy. As demonstrated in Section 2, however, existing models are not entirely satisfactory and it would seem worth while to consider an alternative form for the repulsive potential term. It is accepted that this term will only be an adequate representation within the region II defined above. Also, since the adjustable parameters in the empirical model will normally be based on compressibility data which involve distortions of not more than 1% in most cases, the model can only be expected to be valid for a comparable range of displacements.

In accordance with the Pauli principle, the short-range repulsion should become infinite when the closed-shell electron clouds of the anion and cation overlap and, taking account of this, the following logarithmic form for the repulsive potential is proposed:

$$\psi(r) = P \log(1 + p'r^{-n}), \quad (11)$$

where  $P$ ,  $p'$  and  $n$  are constants. With the inclusion of terms for the other interactions, as discussed in Section 1, the final form for the potential energy of an ion pair is then

$$\phi(r) = -Ae^2r^{-1} - Cr^{-6} - Dr^{-8} - KLe^2r^{-10} + P \log(1 + p'r^{-n}) + \epsilon. \quad (12)$$

The last two terms of this equation may be combined to give

$$P \log(1 + p'r^{-n}) + \varepsilon = P \log(a + pr^{-n}), \quad (13)$$

where  $\varepsilon = P \log a$  now represents the zero-point energy and  $p = ap'$ . This particular form of representation of the zero-point energy is a convenient one since  $a$  turns out to have a constant value of 0.988435 for all crystals.

**Table 1. Calculated values of potential parameters for alkali halide crystals**

Crystal	$-P$ (kJ mol <sup>-1</sup> )	$-p'$ (Å <sup>6</sup> )	$r_0^A$ (Å)	$r_x$ (Å)	$(r_+ + r_-)^B$ (Å)
LiF	9609.31	1.73	2.014	1.0959	1.585
LiCl	927.00	46.37	2.570	1.8953	1.950
LiBr	644.59	89.10	2.751	2.1134	2.075
LiI	509.34	169.47	3.000	2.3524	2.260
NaF	936.04	26.70	2.317	1.7288	1.985
NaCl	548.41	119.21	2.820	2.2185	2.350
NaBr	389.41	209.78	2.989	2.4375	2.475
NaI	319.45	373.74	3.237	2.6839	2.660
KF	471.94	100.96	2.674	2.1578	2.295
KCl	320.86	321.37	3.147	2.6172	2.660
KBr	286.95	447.00	3.298	2.7023	2.785
KI	239.52	730.28	3.533	3.0009	2.970
RbF	391.81	152.38	2.815	2.3111	2.430
RbCl	261.90	467.95	3.291	2.7813	2.795
RbBr	251.23	619.45	3.445	2.9196	2.920
RbI	209.42	981.14	3.671	3.1516	3.105
CsF	278.17	271.91	3.004	2.5453	2.565
CsCl	176.41	935.01	3.571	3.1271	2.930
CsBr	155.31	1256.41	3.720	3.2849	3.055
CsI	143.15	1872.52	3.956	3.5107	3.240

<sup>A</sup> From Pandey (1970a).

<sup>B</sup> From Huggins and Mayer (1933).

Application of crystal stability and compressibility conditions to equations (12) and (13) yields the following expressions for the potential parameters:

$$P = \frac{x^2}{(n+1)x-y}, \quad p' = r_0^n \left( \frac{(n+1)x-y}{y-x} \right), \quad \log a = \frac{(n+1)x-y}{x^2}, \quad (14)$$

where

$$x = Ae^2 r_0^{-1} + 6Cr_0^{-6} + 8Dr_0^{-8} + 10KLe^2 r_0^{-10} \quad (15)$$

and

$$y = 9k_1 r_0^3 \beta^{-1} + 2Ae^2 r_0^{-1} + 42Cr_0^{-6} + 72Dr_0^{-8} + 110KLe^2 r_0^{-10}, \quad (16)$$

with  $\beta$  the compressibility and  $k_1$  the crystal parameter which depends upon the particular structure of the crystal.

The above model is investigated here for a parameter value of  $n = 6$ . The potential energy and force curves for an LiF crystal from equation (12) are included in Figs 1a and 1b respectively. The form of the present potential function is satisfactory since, unlike the previous curves, it has a single turning point at  $(-\phi(r_0), r_0)$  and tends to infinity in the positive energy domain *outside* region I.

Also unlike the previous models, it is found that equation (12) is not affected by the inclusion of higher inverse power terms. The particular value  $r_x$  of the ionic separation at which both the potential energy and force become infinite is given by

$$r_x = (-p/a)^{1/n} = (-p')^{1/n},$$

which is positive since both  $p$  and  $p'$  are negative. Thus  $r_x$  may be interpreted as the minimum possible separation between unlike ions in a vacuum at which their normal electronic configuration is preserved.

Calculated values of the potential parameters  $P$ ,  $p'$  and  $r_x$  for alkali halide crystals are listed in Table 1. Values of the equilibrium interionic distance  $r_0$  and the sum of the ionic radii ( $r_+ + r_-$ ) are also listed for comparison with  $r_x$ . It can be seen that  $r_x$  is always less than  $r_0$  and very nearly equal to  $(r_+ + r_-)$ . Since ionic radii vary substantially with the coordination in solids (Shannon and Prewitt 1969), it is reasonable to take  $r_x$  as equivalent to the sum of the ionic radii.

Having now defined our potential model, we proceed to test it by computing several properties of alkali halide crystals. The particular properties we shall examine are those which make use of the first, second, third and fourth order derivatives of the potential energy. In the following calculations, values of the parameters  $r_0$ ,  $\beta$  and  $\varepsilon$  have been taken from Pandey (1970a) and  $C$  and  $D$  from Born and Huang (1955).

#### 4. Evaluation of Proposed Model

##### (a) Crystal Energies

The cohesive energy per mole,  $W$ , of a crystal is simply related to the potential energy by

$$W = -N\phi(r_0), \quad (17)$$

where  $N$  is Avagadro's number. Once the values of  $W$  are known, the atomization energy  $E_a$  may be easily obtained (Sinha and Thakur 1974). The calculated values of  $W$  and  $E_a$  from the present model are compared with experimental data in Tables 2a and 2b. It can be seen that there is generally good agreement. Corresponding theoretical values for the previous models are also included for comparison in Table 2. For all the models the average percentage deviations of the predictions from experiment have been calculated, and the results (listed in the table) show that the present model compares more than favourably with the previous ones.

##### (b) Grüneisen and Anderson-Grüneisen Parameters

The Grüneisen parameter  $\gamma$ , which has been previously computed by several authors (Dugdale and Macdonald 1955; Blackman 1957; Yates and Ponter 1962; Kachhava and Saxena 1966; Mishra and Sharma 1972), has been recalculated for the present potential model with the help of the relation (Sharma and Jain 1973)

$$\gamma = -\frac{1}{6}r_0 \phi'''(r_0)/\phi''(r_0), \quad (18)$$

where the primes denote derivatives with respect to  $r$ .

Table 2. Cohesive energy and atomization energy for alkali halide crystals

(a) Cohesive Energy  $W$ 

Crystal	Exp. $W^A$ (kJ mol <sup>-1</sup> )	Calculated $W$ (kJ mol <sup>-1</sup> ) from models				
		Present	BL <sup>B</sup>	BM <sup>B</sup>	VS <sup>B</sup>	PGT <sup>A</sup>
LiF	1004.6	1009.5	1041.0	1009.5	1037.0	1057.8
LiCl	843.1	853.0	828.0	827.9	840.3	840.6
LiBr	801.2	805.5	786.0	782.0	794.3	790.4
LiI	753.1	759.6	731.7	727.7	748.3	727.7
NaF	892.9	898.5	907.3	911.5	928.3	945.0
NaCl	772.8	781.8	781.8	777.9	790.1	765.3
NaBr	736.0	739.8	736.0	736.0	744.4	732.0
NaI	695.8	701.6	686.0	689.8	674.3	677.6
KF	792.0	799.5	811.2	810.9	823.8	819.5
KCl	702.1	712.4	702.7	702.7	711.1	698.4
KBr	677.8	681.7	677.4	677.4	685.8	668.9
KI	639.3	645.8	635.7	635.8	643.9	627.1
RbF	759.8	768.3	781.8	781.9	790.5	773.1
RbCl	684.5	689.4	681.6	681.8	690.0	673.1
RbBr	661.1	672.1	652.4	656.4	660.8	639.9
RbI	626.3	632.9	619.1	623.0	627.3	606.3
CsF	726.8	736.5	745.8	744.2	752.7	736.1
CsCl	660.2	660.9	652.2	652.5	660.7	623.2
CsBr	637.2	646.3	627.1	623.2	631.5	602.1
CsI	608.4	615.5	589.5	598.0	602.3	564.7
Average error (%):		0.9	1.5	1.3	1.8	2.6

(b) Atomization Energy  $E_a$ 

Crystal	Exp. $E_a^C$ (kJ mol <sup>-1</sup> )	Calculated $E_a$ (kJ mol <sup>-1</sup> ) from models				
		Present	BL	BM	VS	PGT
LiF	849.4	816.6	848.1	806.6	844.1	864.9
LiCl	690.4	686.2	686.1	661.1	673.5	673.7
LiBr	623.4	580.7	561.2	557.3	569.5	565.6
LiI	539.7	549.3	521.4	517.4	538.0	517.4
NaF	757.3	729.8	738.6	742.8	759.5	776.2
NaCl	640.2	639.1	639.2	635.3	647.4	622.6
NaBr	581.6	539.2	535.4	577.2	589.4	564.6
NaI	502.1	515.5	499.9	503.7	488.2	497.5
KF	732.2	707.9	719.5	729.2	732.1	727.9
KCl	648.5	646.8	637.1	637.1	645.5	622.9
KBr	594.1	558.2	553.9	553.9	562.3	545.5
KI	523.0	536.8	526.7	526.8	534.9	518.1
RbF	711.3	692.5	706.0	706.0	714.6	697.5
RbCl	635.9	639.6	631.8	632.0	640.2	623.3
RbBr	585.8	564.4	544.8	548.7	553.2	522.2
RbI	518.8	539.7	525.9	529.8	534.1	513.1
CsF	686.2	690.1	697.4	695.8	704.2	687.7
CsCl	631.8	638.5	629.9	630.2	638.3	600.9
CsBr	585.8	566.0	546.9	547.0	551.2	521.8
CsI	523.0	549.7	523.7	532.2	536.5	528.9
Average error (%):		3.0	2.7	2.8	2.3	3.7

<sup>A</sup> Pandey (1970a).<sup>B</sup> Kachhava and Saxena (1965).<sup>C</sup> Sanderson (1967).



Table 3. Grüneisen and Anderson-Grüneisen parameters for alkali halide crystals

(a) Grüneisen Parameter  $\gamma$

Crystal	Exp. $\gamma^A$	Calculated $\gamma$ from models				PGT <sup>c</sup>
		Present	BL <sup>B</sup>	BM <sup>C</sup>	VS <sup>C</sup>	
LiF	1.99	1.97	2.20	1.79	1.80	2.54
LiCl	1.54	1.62	2.19	1.97	1.70	1.45
LiBr	1.70	1.81	2.16	2.04	1.66	1.39
LiI	—	1.70	2.30	2.09	1.69	1.37
NaF	1.57	1.65	2.20	1.99	1.63	1.49
NaCl	1.43	1.52	2.34	2.28	1.76	1.63
NaBr	1.55	1.63	2.41	2.21	1.80	1.69
NaI	1.59	1.65	2.48	2.27	1.87	1.26
KF	1.48	1.59	2.37	2.17	1.73	1.64
KCl	1.34	1.48	2.49	2.28	1.88	1.68
KBr	1.43	1.51	2.53	2.33	1.91	1.78
KI	1.58	1.65	2.60	2.40	1.97	1.92
RbF	1.28	1.39	2.44	2.24	1.81	1.80
RbCl	1.25	1.34	2.58	2.02	1.93	1.82
RbBr	1.27	1.35	2.58	2.26	1.95	1.81
RbI	1.50	1.62	2.66	2.25	2.01	1.88
CsF	—	1.72	—	—	—	—
CsCl	1.97	1.81	2.83	2.25	2.13	2.20
CsBr	—	2.01	—	—	—	—
CsI	—	2.13	—	—	—	—

(b) Anderson-Grüneisen Parameter  $\delta$

Crystal	Exp. $\delta^A$	Calculated $\delta$ from models				PGT
		Present	BL	BM	VS	
LiF	3.98	3.94	4.40	3.58	3.60	5.08
LiCl	3.08	3.24	4.38	3.94	3.40	2.90
LiBr	3.40	3.62	4.32	4.08	3.32	2.78
LiI	—	3.40	4.60	4.18	3.38	2.74
NaF	3.14	3.30	4.40	3.98	3.26	2.98
NaCl	2.86	3.04	4.68	4.56	3.52	3.26
NaBr	3.10	3.26	4.82	4.42	3.60	3.38
NaI	3.18	3.30	4.96	4.54	3.74	2.52
KF	2.96	3.18	4.74	4.34	3.46	3.28
KCl	2.68	2.96	4.98	4.56	3.76	3.36
KBr	2.86	3.02	5.06	4.66	3.82	3.58
KI	3.16	3.30	5.20	4.80	3.94	3.82
RbF	2.56	2.78	4.88	4.48	3.62	3.60
RbCl	2.50	2.68	5.16	4.04	3.86	3.64
RbBr	2.54	2.70	5.16	4.52	3.90	3.62
RbI	3.00	3.24	5.32	4.50	4.02	3.76
CsF	—	3.44	—	—	—	—
CsCl	3.94	3.62	5.66	4.50	4.26	4.40
CsBr	—	4.02	—	—	—	—
CsI	—	4.26	—	—	—	—

<sup>A</sup> Born and Huang (1955).

<sup>B</sup> Kachhava and Saxena (1966).

<sup>C</sup> Mishra and Sharma (1972).

The Anderson–Grüneisen parameter  $\delta$  has also been computed using Chang's (1967) formula connecting  $\gamma$  and  $\delta$ , which he derived on the basis of the relation between  $\gamma$  and the change of compressibility with volume given by Dugdale and Macdonald (1955).

The results thus obtained for  $\gamma$  and  $\delta$  are listed in Tables 3a and 3b, together with the experimental values of Born and Huang (1955) and the values calculated from the previous models. The predictions of the present model are seen to be generally in better agreement with experiment.

**Table 4. Reststrahlen frequency and anharmonicity for alkali halide crystals**

The values of the reststrahlen frequency  $\nu_0$  are in units of  $10^{-12}$  Hz and the anharmonicity factor  $\bar{c}$  is in  $\text{kJ mol}^{-1} \text{\AA}^{-4}$

Crystal	Exp. $\nu_0^A$	Calculated $\nu_0$ from models					Calc. $\bar{c}$ (present model)
		Present	BL <sup>B</sup>	BM <sup>C</sup>	VS <sup>D</sup>	PGT <sup>D</sup>	
LiF	9.12	7.98	8.40	19.35	20.83	18.68	582.429
LiCl	5.12	6.10	6.40	10.89	14.82	12.96	246.402
LiBr	5.13	5.42	5.66	9.48	12.84	11.75	201.672
LiI	4.32	4.56	4.77	8.25	11.16	10.25	143.338
NaF	7.38	6.89	6.53	7.80	13.10	10.49	429.387
NaCl	4.92	4.93	5.55	6.60	8.19	7.35	306.589
NaBr	4.05	4.03	6.09	5.34	6.74	6.31	183.315
NaI	3.51	3.48	3.45	4.62	5.75	5.37	139.860
KF	5.76	5.64	—	7.59	9.00	8.29	297.854
KCl	4.32	4.24	4.48	5.25	6.25	5.89	165.097
KBr	3.48	3.49	3.94	4.14	4.76	4.50	140.795
KI	3.03	3.31	3.37	3.57	3.86	3.49	164.682
RbF	4.80	4.72	—	6.36	8.59	7.85	260.793
RbCl	3.57	3.52	3.57	4.26	5.08	4.79	158.077
RbBr	2.70	2.66	2.85	3.09	3.69	3.48	126.244
RbI	2.25	2.36	2.03	2.94	2.87	2.72	107.432
CsF	—	3.62	—	6.24	8.32	6.64	254.622
CsCl	2.97	2.95	2.64	—	4.61	4.29	162.906
CsBr	2.22	2.22	2.45	—	3.09	2.88	161.439
CsI	—	2.12	—	—	2.27	2.30	121.478

<sup>A</sup> Dixit and Sharma (1972).

<sup>B</sup> Srivastava *et al.* (1967).

<sup>C</sup> Pandey and Gupta (1969).

<sup>D</sup> Thakur and Thakur (1976).

### (c) Anharmonicity and Reststrahlen Frequency

When the lattice formed by a cation is displaced by a small distance  $z$  ( $z \ll r_0$ ) with respect to the anion lattice, the potential energy per ion pair may be expressed in the form

$$U = U_0 + az^2 + cz^4 + \dots, \quad (19)$$

where the constants  $a$  and  $c$  determine respectively the frequency of oscillations and the anharmonic contribution. Terms in odd powers of  $z$  are absent from equation (19) owing to the centre of symmetry of lattice points in alkali halide crystals (Krishnan and Roy 1951; Dixit and Sharma 1972).

The numerical procedures involved in going from  $\phi(r)$  to the frequency of oscillations  $\nu_0$  and the average value  $\bar{c}$  of  $c$  over all directions have been discussed fully by Krishnan and Roy (1951), and their method has been followed here. The

results obtained for  $v_0$  and  $\bar{c}$  are given in Table 4, where they are compared with experimental values of  $v_0$  and previous model predictions for this quantity. Once more it can be seen that the present model gives generally better agreement with experiment. The validity of the calculated values of  $\bar{c}$  cannot be tested owing to lack of experimental data, but the results are in the same range of magnitude as those computed with other models (Krishnan and Roy 1951).

## 5. Discussion

We have seen that previously proposed models for the potential energy function in an ionic crystal are not entirely satisfactory, in that they are defined for a region (denoted as region I above) where normal ionic forces no longer control the interaction between ions, and the form of the potential energy and force curves is unacceptably modified by the presence of the attractive terms for the theoretically established dipole-dipole, dipole-quadrupole and hyperpolarizability forces, for almost all leading repulsive interaction terms. In order to overcome these difficulties a new model has been proposed in which the interionic potential energy tends to infinity in the positive energy domain and has imaginary values in region I. It has been found that the new model gives a better representation of the experimental data for the cohesive energy, the Grüneisen and Anderson-Grüneisen parameters and the reststrahlen frequency than previous models, and is comparable in its predictions of the atomization energy.

Although the earlier models do not give realistic forms for the potential energy and force curves, they still yield satisfactory results for the various crystal parameters. However, this is because they are constrained by known crystal stability and compressibility conditions and thus all have a minimum at  $r_0$  etc. Under these conditions any reasonable potential model can be made to yield more or less acceptable values for crystal properties, particularly in view of the uncertainties in the experimental data, and for a model to be reliable it must be able to also predict satisfactory forms for the potential energy and force curves. Obviously this is the fundamental requirement, for once a model has this merit it will automatically predict accurate values of the crystal properties. The form for the potential proposed here is an improvement on previous models and, although far from perfect, it may help in obtaining a better understanding of the nature of the ionic bond.

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