J. Phys. Chem. Solids, 1976, Vol. 37, pp. 395–402. Pergamon Press. Printed in Great Britain

A NEW APPROACH TO REPULSION IN IONIC CRYSTALS

R. NARAYAN and S. RAMASESHAN
Materials Science Division, National Aeronautical Laboratory, Bangalore 560017, India

(*Received* 6 *August* 1975; *accepted* 5 *September* 1975)

Abstract—An empirical approach is attempted to make the repulsion potential of ions in an ionic crystal structure independent and crystal independent so that once the repulsion parameters for an ion are evaluated in one compound, in one structure, they could be used for that ion in any crystal. The repulsion between ions is postulated to be due to the increase in the internal energy of the ions arising from the distortion and the compression at the points of contact with their neighbours. Using an exponential form for the compression energy involving two parameters per ion, a repulsion potential for ionic crystals is proposed which includes the repulsion between nearest and next nearest neighbours. The repulsion parameters for the alkali and halogen ions have been determined to fit the behaviour of 20 alkali halides over the pressure range 0–45 kbars. The r.m.s. percentage deviations from experiment, of the calculated values of lattice spacing and compressibility are respectively 0·997% and 6·76%. The calculated radii of the ions in the various compounds compare well with the experimental values deduced from electron density maps. The advantages of the present form of the repulsion potential over earlier forms are discussed.

1. INTRODUCTION

Properties like ionic radius, ionic polarizability etc., have proved useful in the study of ionic solids. Extending these ideas, one could ask whether the concept of ionic compressibility is meaningful. An ion may be considered to be a soft sphere whose radius is a function of the compressing force acting on it. The ion then has an internal energy which is a function of its size and the repulsion between ions would arise from the increase in their internal energy when compressed together. In this picture, an ion is like a balloon, with an impenetrable surface skin and a compressible interior. This picture is not really defensible from the quantum mechanical point of view according to which the repulsion is caused by the overlap of neighbouring electron clouds. But, the complete quantum mechanical treatment leads to very complicated numerical computation[4] and even in the few cases where this has been carried out, no physical insight seems to be obtained. On the other hand, we know that ions are an experimental fact. Detailed electron density maps of ionic solids[1–3] clearly show that the electrons belonging to different ions are well separated with a region of near zero electron density between them. Further, the Pauli exclusion principle requires that the closed shells of electrons of neighbouring ions resist interpenetration. This lends substance to our empirical approach to the origin of the repulsion between ions.

With the reservations stated above, we propose that the repulsion energy between ions in a binary ionic solid can be written as

$$W_{\text{rep}}(r_+, r_-) = W_+(r_+) + W_-(r_-) \tag{1}$$

where W_+ and W_- are functions of r_+ and r_-, the radii of the two ions. Further, since nearest neighbours are in contact, we get

$$r = r_+ + r_- \tag{2}$$

where r is the nearest neighbour distance. For a given r, there is according to (2) still one internal degree of freedom viz., the radius of one of the ions. This is taken care of by a relation for the internal equilibrium of the lattice obtained by minimising the energy of the crystal with respect to its internal coordinates r_+ and r_-. This gives us the condition

$$\frac{\mathrm{d}W_+(r_+)}{\mathrm{d}r_+} = \frac{\mathrm{d}W_-(r_-)}{\mathrm{d}r_-} \tag{3}$$

Thus, r_+ and r_- are functions of r, W_{rep} is also a function of r and so total derivatives of the form

$$\frac{\mathrm{d}}{\mathrm{d}r} W_{\text{rep}}(r), \quad \frac{\mathrm{d}^2}{\mathrm{d}r^2} W_{\text{rep}}(r),$$

etc. have a meaning.

From the functional form of the repulsion potential (1), two identities can be derived[5], one connecting the lattice spacings of a family of ionic crystals and the other their compressibilities.

Introducing the new repulsion potential (1) into the expression for the total lattice energy per molecule of a binary ionic crystal as given in Born's theory[6], we get

$$W_L(r, r_+, r_-) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_+(r_+) + W_-(r_-). \tag{4}$$

The first three terms on the right hand side of (4) give respectively the Madelung electrostatic energy, the van der Waals dipole-dipole interaction energy and the van der Waals dipole-quadrupole interaction energy. Using relations (2) and (3), it can be shown that

$$\frac{\mathrm{d}W_+(r_+)}{\mathrm{d}r_+} = \frac{\mathrm{d}W_-(r_-)}{\mathrm{d}r_-} = \frac{\mathrm{d}W_L(r)}{\mathrm{d}r} - \frac{\alpha e^2}{r^2} - \frac{6C}{r^7} - \frac{8D}{r^9}$$
$$= f(r) \text{ (say).} \tag{5}$$

Consider four ions A^+, B^+, C^-, D^- and the four crystals they could form

$$\begin{array}{cccc} A^+C^- & A^+D^- & B^+C^- & B^+D^- \\ \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} \end{array} \cdot \tag{6}$$

If these four crystals are subjected to hydrostatic pressures such that the value of $f(r)$ is the same for all four, then postulate (1) for the repulsion potential leads[5] to the identity

$$(r_{\mathrm{I}} + r_{\mathrm{IV}}) - (r_{\mathrm{II}} + r_{\mathrm{III}}) = 0. \tag{7}$$

Differentiating (4) twice with respect to r, we get

$$\frac{1}{\dfrac{d^2W_+(r_+)}{dr_+^{\,2}}} + \frac{1}{\dfrac{d^2W_-(r_-)}{dr_-^{\,2}}} = \frac{1}{\dfrac{d^2W_L(r)}{dr^2} + \dfrac{2\alpha e^2}{r^3} + \dfrac{42C}{r^8} + \dfrac{72D}{r^{10}}} = g(r) \text{ (say)}. \tag{8}$$

Once again, for the four crystals of the type mentioned in (6) under conditions of equal values of $f(r)$, we get the identity

$$\{g(r)_{\mathrm{I}} + g(r)_{\mathrm{IV}}\} - \{g(r)_{\mathrm{II}} + g(r)_{\mathrm{III}}\} = 0. \tag{9}$$

The identities (7) and (9) were tested using the experimental data on the alkali halides[5]. The agreement was quite satisfactory. In fact, even the small deviations of the experimental values from the exact identities could be traced to the fact that the repulsion potential (1) does not take second neighbour repulsions into account. The good agreement was considered to be strong evidence on the validity of the postulate (1).

The repulsion potential (1) does not specify what changes are to be made when an ion occurs in different structures. For this, an additional postulate was proposed[5]. It was suggested that the energy of compression of an ion was local to the points of contact with its neighbours and originated essentially from the local compression and distortion. Thus, the repulsion energy caused by nearest neighbours for a given radius of the ion is directly proportional to the number of nearest neighbours, i.e.

$$W_\pm(r_\pm) = n_1 h_\pm(r_\pm) \tag{10}$$

where n_1 is the number of nearest neighbours and $h_\pm(r_\pm)$ is a unique function for a given ion, independent of the crystal structure. If a substance exists in two different crystal structures (at different pressures) having the same nearest neighbour distance, then (10) implies that

$$\frac{n_1}{n_1'} = \frac{f(r)}{f'(r)} = \frac{g'(r)}{g(r)} \tag{11}$$

where the primes describe quantities in the second phase. The identities in (11) were tested using the experimental data on the potassium and rubidium halides which transform from the NaCl type to the CsCl type structure at higher pressures. The predictions were reasonably well borne out and the small deviations could again be traced to the effect of second neighbour repulsion. This indicated that the postulate (10) is also reasonable.

Encouraged by these favourable indications, we here propose an explicit functional form for the repulsion potential in ionic crystals and fit numerical parameters for the alkali halides. We make an extension of our earlier work[5] by including contributions from second nearest neighbours also.

2. THE REPULSION FUNCTION

Implicit in our description of the origin of repulsion between ions is the assumption that the actual manner of causing the distortion on any ion is immaterial. Thus, the same compression function can be used for nearest as well as next nearest neighbours. The only difference is that the "radius" for the two cases will be different. In fact, for binary ionic crystals of the NaCl or CsCl type structure, next nearest neighbours are identical ions and so, by symmetry, the boundary between them lies at the midpoint between their centres. Thus, the modified repulsion potential in such ionic crystals will be, by (1) and (10)

$$W_{\mathrm{rep}}(r, r_+, r_-) = n_1\{h_+(r_+) + h_-(r_-)\} + n_2\{h_+(\tfrac{1}{2}br) + h_-(\tfrac{1}{2}br)\} \tag{12}$$

where n_2 is the number of next nearest neighbours and br is the distance between next nearest neighbours.

Our approach of using the same function for nearest and next nearest neighbour repulsion is at variance with that of most earlier workers who give different weights to ++, +− and −− interactions. This is done through some "β" factors, first introduced by Pauling[7]. However, since our picture makes no distinction between ++, +− and −− interactions, we do not introduce any such weighting parameters.

As has been shown in the last section, the repulsion potential $W_{\mathrm{rep}}(r, r_+, r_-)$ is ultimately a function of only r. Also, r_+ and r_- can no longer be thought of as the radii of spherical ions. They are only the extension of the ion in the direction of its nearest neighbour. In the direction of the next nearest neighbour, the "radius" is $\frac{1}{2}br$. However, in all later discussion, when we mention the radius of an ion, we mean the quantity $r_\pm$.

It is not possible to obtain from experiment the *functions h* in (12). The best we can do is to propose some simple functional form for h and fit parameters for the ions. Various functional forms (the inverse power law[8], the exponential[9] and a logarithmic[10] form) have been tried for the repulsion potential in the Born theory of ionic solids. In this paper, we try the exponential form for the repulsion function. To be in conformity with (12), we require two different exponentials for the two ions. The specific form we propose for the repulsion potential per molecule in a binary ionic solid is hence

$$\begin{aligned} W_{\mathrm{rep}}(r, r_+, r_-) = {} & n_1\{A_+ e^{-r_+/\rho_+} + A_- e^{-r_-/\rho_-}\} \\ & + n_2\{A_+ e^{-br/2\rho_+} + A_- e^{-br/2\rho_-}\} \end{aligned} \tag{13}$$

where A_+, A_- are the pre-exponential factors for the two ions and ρ_+, ρ_- are their 'hardness' parameters.

It should be emphasized once again that our repulsion potential (13) is valid for all structure modifications. The parameters A_+, A_-, ρ_+, ρ_- are considered unique and entirely structure independent. This we feel is an improvement on the structure dependent parameters introduced by Tosi and Fumi[11, 12]. Also, once the parameters of an ion have been refined in any one crystal or a set of crystals, the same parameters can be used in any other crystal in which it occurs. This versatility of our repulsion potential and some of its advantages will be discussed in Section 5.

3. DATA USED IN THE EVALUATION OF THE REPULSION PARAMETERS

The repulsion parameters for the alkali halides were determined so as to best fit the lattice spacing and the compressibility over a range of pressures. The various data required were obtained as follows. The PV data of Vaidya and Kennedy[13] on the alkali halides were used. The data on each crystal were fitted with the Murnaghan equation of state[14] viz.,

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \tag{14}$$

where V_0 and B_0 are the volume and the bulk modulus at zero pressure and B_0' is the pressure derivative of the bulk modulus. Wherever B_0 was available, B_0' alone was refined. However, for the high pressure phases, both B_0 and B_0' had to be refined simultaneously. V_0 was calculated using the room temperature, atmospheric pressure values of the lattice spacings listed in reference 15. Thus, by equation (14), the nearest neighbour distance r and the compressibility K were obtained over the whole pressure range from 0 to 45 kbars. The PV data for the alkali fluorides appeared to be unreliable and for these compounds, only the atmospheric pressure data were used in the refinement of the repulsion parameters.

The quantity $[\mathrm{d}W_L(r)]/\mathrm{d}r$ (where $W_L(r)$ is the lattice energy per molecule) was calculated using the Hildebrand equation of state[16]

$$\frac{\mathrm{d}W_L}{\mathrm{d}V} = -P + \frac{T\beta}{K} \tag{15}$$

which is easily seen to give

$$\frac{\mathrm{d}W_L}{\mathrm{d}r} = 3xr^2\left(-P + \frac{T\beta}{K}\right). \tag{16}$$

Here β is the volume expansivity, T is the temperature and xr^3 is the volume per molecule. The quantity $[\mathrm{d}^2W_L(r)]/\mathrm{d}r^2$ was calculated from the second Hildebrand equation [16]

$$\frac{\mathrm{d}^2W_L}{\mathrm{d}V^2} = \frac{1}{VK}\left[1 + \frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right] \tag{17}$$

which leads to

$$\frac{\mathrm{d}^2W_L}{\mathrm{d}r^2} = \frac{2}{r}\frac{\mathrm{d}W_L}{\mathrm{d}r} + \frac{9xr}{K}\left[1 + \frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right]. \tag{18}$$

In relations (16) and (18), we need the values of some thermodynamic quantities at high pressures. Since no experimental data are available, these quantities were calculated from the corresponding room temperature atmospheric pressure values by

$$\beta_P = \beta_0\frac{K_PV_0}{K_0V_P} \tag{19}$$

$$\left[\frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right]_P = \frac{\beta_P}{\beta_0}\left[\frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right]_0. \tag{20}$$

Relations (19) and (20) are derived assuming that the Gruneisen's constant $\gamma(= V\beta/C_VK)$ is independent of pressure. The room temperature, atmospheric pressure values of the above thermodynamic quantities were taken from Cubicciotti[17]. For evaluating the van der Waals interaction energy, the van der Waals coefficients C and D for all the alkali halides were obtained respectively from Hajj[18] and Mayer[19].

4. CALCULATION OF THE REPULSION PARAMETERS FOR THE ALKALI HALIDES

The alkali halides family consists of five alkali ions viz., Li^+, Na^+, K^+, Rb^+, Cs^+ and four halogen ions viz., F^-, Cl^-, Br^-, I^-, these ions forming 20 compounds. We have to fit 18 parameters to describe the behaviour of these 20 compounds. A first, rough estimate of the parameters was obtained as follows. In each compound, there are four unknown parameters viz., A_+, A_-, ρ_+ and ρ_-. By using the experimental values of r and $[\mathrm{d}^2W_L(r)]/\mathrm{d}r^2$ at two pressures, one could solve for these four parameters. This turned out to be a highly ill-conditioned problem. However, since any ion occurs in more than one compound, one could search for a set of parameters which give reasonably good overall agreement. The details of these calculation are not being presented here. We finally obtained the set of repulsion parameters listed in Table 1. These parameters served as initial values in the refinement procedures discussed below. Since we did not have high pressure data for the fluorides, these were not included in the above rough estimation of repulsion parameters. As a result we had no initial values for the parameters of the F^- ion.

The repulsion parameters listed in Table 1 were further refined by a least squares procedure. A misfit factor R was defined as

$$R = \sum_{\text{compounds}}\sum_{\text{phases}}\sum_{\text{pressures}}\left[W_r\left(\frac{r_c - r_0}{r_0}\right)^2 + W_c\left(\frac{\left(\frac{\mathrm{d}^2W_L}{\mathrm{d}r^2}\right)_c - \left(\frac{\mathrm{d}^2W_L}{\mathrm{d}r^2}\right)_0}{\left(\frac{\mathrm{d}^2W_L}{\mathrm{d}r^2}\right)_0}\right)^2\right]. \tag{21}$$

Here r_0 and $(\mathrm{d}^2W_L/\mathrm{d}r^2)_0$ are the experimental values. r_c

and $(d^2W_L/dr^2)_c$ are the values calculated with our set of repulsion parameters using the Born theory of ionic crystals[6]. In this theory, the lattice energy per molecule is given by (see eqn (4))

$$W_L(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_{\text{rep}}(r) \tag{22}$$

$W_{\text{rep}}(r)$ is the repulsion energy which in our theory is given by (13). Now, the condition (3) when applied to our repulsion potential gives

$$\frac{A_+}{\rho_+} e^{-r_+/\rho_+} = \frac{A_-}{\rho_-} e^{-r_-/\rho_-} \tag{23}$$

$$\text{i.e. } \frac{r_-}{\rho_-} - \frac{r_+}{\rho_+} = \ln\left(\frac{A_-\rho_+}{A_+\rho_-}\right) \tag{24}$$

This can be solved along with (2) to give

$$r_+ = \frac{\dfrac{r}{\rho_-} - \ln\left(\dfrac{A_-\rho_+}{A_+\rho_-}\right)}{\dfrac{1}{\rho_+} + \dfrac{1}{\rho_-}} \tag{25}$$

$$r_- = \frac{\dfrac{r}{\rho_+} + \ln\left(\dfrac{A_-\rho_+}{A_+\rho_-}\right)}{\dfrac{1}{\rho_+} + \dfrac{1}{\rho_-}}\,. \tag{26}$$

Using (23) and differentiating (22) we have

$$\frac{dW_L(r)}{dr} = \frac{\alpha e^2}{r^2} + \frac{6C}{r^7} + \frac{8D}{r^9} - \frac{n_1A_+}{\rho_+} e^{-r_+/\rho_+} - \frac{bn_2}{2}\left[\frac{A_+}{\rho_+} e^{-br/2\rho_+} + \frac{A_-}{\rho_-} e^{-br/2\rho_-}\right] \tag{27}$$

$$\frac{d^2W_L(r)}{dr^2} = -\frac{2\alpha e^2}{r^3} - \frac{42C}{r^8} - \frac{72D}{r^{10}} + \frac{XY}{X+Y} + \frac{b^2n_2}{4}\left[\frac{A_+}{\rho_+^2} e^{-br/2\rho_+} + \frac{A_-}{\rho_-^2} e^{-br/2\rho_-}\right] \tag{28}$$

where

$$X = \frac{n_1A_+}{\rho_+^2} e^{-r_+/\rho_+} \tag{29}$$

$$Y = \frac{n_1A_-}{\rho_-^2} e^{-r_-/\rho_-}\,. \tag{30}$$

At each pressure of each crystal, r_c was calculated by solving eqn (27) with the help of eqn (25), using the experimental value of $[dW_L(r)]/dr$ (calculated as described in Section 3). Then $\{[d^2W_L(r)]/dr^2\}_C$ was calculated at r_c by eqn (28) making use of eqns (25), (26), (29) and (30). These are the quantities that are involved in the misfit factor R in (21). W_r and W_c are certain weights. W_r was taken as 400 for atmospheric pressure values and 100 for higher pressure values, while the corresponding values of W_c were taken as 4 and 1 respectively. This was to allow for the fact that in our opinion the experimental data at atmospheric pressure are twice as reliable as the data at higher pressures and also that r_0-values are ten times as reliable as the values of $\{[d^2W_L(r)]/dr^2\}_0$. It should be noted that by eqn (18), $[d^2W_L(r)]/dr^2$ is approximately proportional to $1/K$ so that in (21) we are essentially comparing calculated and observed values of lattice spacing and compressibility. In the summations for R, only two pressures were considered for each phase. This was because we felt that any repulsion potential which fitted the experimental data at two sufficiently separated pressures would be equally good in the whole intervening range.

Table 1. Initial estimate of the repulsion parameters for the alkali halides

Ion	A(ergs)	ρ (cm)
Li^+	1.5×10^{-11}	1.5×10^{-9}
Na^+	2.0×10^{-10}	1.6×10^{-9}
K^+	1.0×10^{-9}	1.65×10^{-9}
Rb^+	1.0×10^{-9}	1.7×10^{-9}
Cs^+	2.0×10^{-9}	1.83×10^{-9}
Cl^-	3.9×10^{-9}	1.6×10^{-9}
Br^-	3.8×10^{-0}	1.78×10^{-9}
I^-	3.6×10^{-9}	1.97×10^{-9}

Our aim was to vary the repulsion parameters so as to reduce R to its minimum value. Various non-linear least squares procedures which use the gradient method were tried. But none of these was successful. The reason is that the parameters are coupled to one another to varying degrees. The parameters of two like ions are not coupled at all; the parameters of unlike ions are moderately coupled; whereas the A and ρ of the same ion are very strongly coupled to each other. In the A–ρ space of any ion, the contours of constant R are highly elongated quasi-ellipses. The R-surface is a long valley with very steep walls and a very gentle slope along the valley. In such a case, the usual minimisation procedures which use the gradient method immediately reach the minimum along the local gradient but are extremely inefficient for locating the minimum along the floor of the valley since the gradient in this direction is very small.

The following alternate strategy was therefore used. At each stage, the parameters of one ion alone were refined. R was calculated for various values of A and ρ of the particular ion and the best set was obtained by a graphical method. For a given set of parameters for the positive ions, the negative ion parameters were successively refined. Then, keeping these fixed, the positive ion parameters were refined. This procedure generally converged after two cycles.

The actual details of the procedure adopted were slightly different. The lithium compounds were uniformly very difficult to fit. Hence, in the early stages, only Na^+, K^+, Rb^+, Cs^+, Cl^-, Br^-, I^- were considered. The parameters of these were refined, positives and negatives alternately as mentioned above. At this stage, it was decided to include the fluorides also in the refinement. But we had no estimate for the parameters of F^- for the reason mentioned earlier. However, the values of the parameters of Cl^-, Br^-, I^- suggested the following approximate values

$$A_{F^-} = 5{\cdot}0 \times 10^{-9}\,\text{erg}$$

$$\rho_{F^-} = 1{\cdot}4 \times 10^{-9}\,\text{cm}.$$

Starting off with these values, a thorough grid search was made in the A-ρ space of F^- and finally, the following were seen to be the best values

$$A_{F^-} = 7{\cdot}5 \times 10^{-10}\,\text{erg}$$

$$\rho_{F_-} = 1{\cdot}495 \times 10^{-9}\,\text{cm}.$$

At this stage, the lithium compounds were also included and the complete set of parameters was refined as before. The final "best set" of parameters obtained at the end of the above calculations is listed in Table 2.

Table 2. Final refined values of the repulsion parameters for the alkali halides

Ion	A (ergs)	ρ (cm)
Li^+	7.5×10^{-12}	1.90×10^{-9}
Na^+	6.4×10^{-11}	1.815×10^{-9}
K^+	3.4×10^{-10}	1.848×10^{-9}
Rb^+	2.7×10^{-9}	1.574×10^{-9}
Cs^+	6.5×10^{-9}	1.645×10^{-9}
F^-	6.0×10^{-10}	1.545×10^{-9}
Cl^-	3.0×10^{-9}	1.67×10^{-9}
Br^-	3.0×10^{-9}	1.81×10^{-9}
I^-	3.0×10^{-9}	2.00×10^{-9}

5. DISCUSSION OF THE RESULTS

The calculated values of r (nearest neighbour distance) and d^2W_L/dr^2 (which is proportional to the bulk modulus as shown by eqn (18)) are listed in Table 3. The values of r were obtained by numerically solving the transcendental eqn (27) where $[dW_L(r)]/dr$ was obtained from eqn (16). Then, using this value of r, d^2W_L/dr^2 was calculated through eqn (28). Also listed for comparison in Table 4 are the true experimental values of r and d^2W_L/dr^2. The percentage errors are also listed. The root mean square percentage error in r, calculated for all the compounds at all the pressures listed, is 0·997%. The corresponding value for d^2W_L/dr^2 is 6·755%.

To get an idea of the significance of the above results, we shall compare them with those obtained by earlier workers. The latest and most extensive calculations are those made by Tosi and Fumi[20]. In Table 3, we have listed the values of r and d^2W_L/dr^2 calculated for seventeen compounds at atmospheric pressure on the basis of their repulsion potential. The r.m.s. percentage errors in r and d^2W_L/dr^2 are respectively 1·44% and 15·4% both higher than the corresponding values from the present theory. A detailed comparison of these seventeen cases with the results based on the present theory results in the following. Tosi and Fumi have better agreement with experimental lattice spacings in ten cases and with experimental compressibilities (d^2W_L/dr^2) in eight cases. Hence, on this criterion, the fit with experiment of the two theories is comparable. The significant improvement of the present theory in terms of r.m.s. deviations from experiment is due to the following. Whereas the results of Tosi and Fumi are extremely good for the chlorides, bromides and iodides of sodium, potassium and rubidium, their results are very unsatisfactory in the case of the lithium compounds and the alkali fluorides.

Apart from the improvement of our results over those of Tosi and Fumi, we should note the following further points which make our repulsion potential attractive.

(1) Tosi and Fumi employed 26 parameters viz., 17ρ's and 9 basic radii to describe 17 compounds. On the other hand, in our formulation of the repulsion potential, we have employed only 18 parameters, viz. 9 A's and 9 ρ's to describe 20 compounds.

(2) Tosi and Fumi attempted only the fitting of atmospheric pressure data. Our repulsion parameters fit the alkali halides in the whole pressure range from 0 to 45 kbars. To our knowledge, no attempt has so far been made to fit data over a range of pressures.

(3) When a compound undergoes a phase transition, the procedure of Tosi and Fumi required the refinement of a new set of parameters[11]. We have eliminated this concept of structure dependent parameters and use the same set of parameters in all phases, making only obvious changes in the number of nearest and next nearest neighbours, as explained in Section 2.

(4) The repulsion potential of earlier workers do not have much predictive power. Every time a new compound is encountered, new parameters have to be refined. This is because in their potentials, some of the parameters are crystal dependent. In our formulation of the repulsion potential, the ions are given complete individuality. The repulsion potential in a compound depends only on the ions. So, when a new compound is encountered, if the parameters of the individual ions have already been refined from other compounds, the repulsion potential for the new compound is completely defined. This potential would be valid over a range of pressure. Hence, in theory, all the properties can be calculated.

6. IONIC RADII

The ionic radius is a vital concept in our treatment of ionic solids. It is a variable which varies for an ion from one crystal to the other and with pressure in the same crystal. The repulsion between ions is thought to arise from the increased energy of an ion when constrained to a smaller radius. This dynamic concept of the ionic radius is far removed from the simple pictures of earlier workers where certain *constant* radii were associated with ions and it was shown that the sum of two such constant radii approximately gave the nearest neighbour distance in the corresponding compound. These (constant) ionic radii are further arbitrary to a constant which has to be fixed by some extra relation such as for instance relating the size of an ion to its polarizability.

Table 4 lists the ionic radii of the ions in the various compounds at atmospheric pressure as calculated from

Table 3. Comparison with experiment of the values of r and d^2W_L/dr^2 calculated with the present repulsion potential (13). The values predicted by the potential of Tosi and Fumi[20] are also listed. All deviations are given as percentages of the corresponding experimental values

Crystal	Pressure (kbars)	Structure		Nearest Neighbour Distance (A°)					$\frac{d^2W_L}{dr^2}$ (10^6 erg/cm^2)			
				Present Theory		T.F. Theory			Present Theory		T.F. Theory	
			r_0	r_t	Deviation	r_c	Deviation	$\left(\frac{d^2W_L}{dr^2}\right)_0$	$\left(\frac{d^2W_L}{dr^2}\right)_c$	Deviation	$\left(\frac{d^2W_L}{dr^2}\right)_c$	Deviation
LiF	0	fcc	2.0087	1.9743	-1.715	1.985	-1.179	2.392	2.4681	3.180	2.543	6.313
LiCl	0	fcc	2.570	2.5706	0.024	2.632	2.412	1.3993	1.5142	8.209	1.74	24.348
LiCl	45	fcc	2.4824	2.4897	0.292			2.0808	2.1515	3.396		
LiBr	0	fcc	2.7505	2.7781	1.003	2.812	2.236	1.2118	1.2354	1.949	1.55	27.909
LiBr	45	fcc	2.6339	2.6697	1.360			1.7588	1.9240	9.395		
LiI	0	fcc	3.003	3.0817	2.621	3.059	1.865	0.80052	0.9205	14.993	1.18	47.404
LiI	45	fcc	2.8433	2.9221	2.770			1.4341	1.6787	17.059		
NaF	0	fcc	2.310	2.3236	0.589	2.335	1.082	1.6120	1.594	-1.095	1.589	-1.427
NaCl	0	fcc	2.820	2.8099	-0.360	2.809	-0.390	1.2677	1.160	-8.503	1.20	-5.340
NaCl	45	fcc	2.7048	2.6925	-0.455			1.9478	1.824	-6.342		
NaBr	0	fcc	2.989	2.9584	-1.022	2.987	-0.067	1.0377	1.055	1.626	1.05	1.185
NaBr	45	fcc	2.8494	2.8214	-0.982			1.7595	1.761	0.093		
NaI	0	fcc	3.236	3.2613	0.783	3.243	0.216	0.76933	0.805	4.579	0.75	-2.513
NaI	45	fcc	3.0483	3.0678	0.640			1.4649	1.585	8.188		
KF	0	fcc	2.6735	2.6966	0.865	2.659	-0.542	1.2720	1.197	-5.880	1.250	-1.730
1	2	3	4	5	6	7	8	9	10	11	12	13
KCl	0	fcc	3.147	3.1263	-0.656	3.150	0.095	0.95517	0.922	-3.494	0.94	-1.588
KCl	15	fcc	3.0727	3.0484	-0.792			1.2833	1.2186	-5.043		
KCl	20	sc	3.189	3.2144	0.796			1.2106	1.1950	-1.291		
KCl	45	sc	3.11675	3.1356	0.603			1.7436	1.5660	-10.185		
KBr	0	fcc	3.300	3.261	-1.178	3.305	0.152	0.8325	0.8458	1.597	0.909	9.189
KBr	15	fcc	3.2123	3.1709	-1.287			1.2145	1.1585	-4.611		
KBr	20	sc	3.346	3.3501	0.122			0.9794	1.1389	16.282		
KBr	45	sc	3.2566	3.2620	0.165			1.5960	1.5238	-4.522		
KI	0	fcc	3.533	3.4953	-1.067	3.532	-0.028	0.7339	0.7099	-3.271	0.74	0.831
KI	15	fcc	3.4204	3.3783	-1.230			1.1526	1.0493	-8.966		
KI	20	sc	3.579	3.579	0.009			1.0419	1.0246	-1.658		
KI	45	sc	3.4751	3.4715	-0.103			1.5273	1.4308	-6.315		
RbF	0	fcc	2.820	2.8126	-0.262	2.768	-1.844	1.268	1.3440	5.996	1.303	2.760
RbCl	0	fcc	3.291	3.2735	-0.531	3.293	0.061	0.982	0.9574	-2.508	0.97	-1.222
RbCl	10	sc	3.343	3.3664	0.699			1.0941	1.1232	2.664		
RbCl	45	sc	3.222	3.2486	0.833			1.7977	1.7328	-3.613		
RbBr	0	fcc	3.444	3.4392	-0.140	3.451	0.203	0.8460	0.8315	-1.712	0.82	-3.073
RbBr	5	sc	3.527	3.5611	0.967			0.9251	0.9023	-2.459		
1	2	3	4	5	6	7	8	9	10	11	12	13
RbBr	45	sc	3.3682	3.4079	1.178			1.4889	1.5486	4.008		
RbI	0	fcc	3.671	3.6116	-1.619	3.673	0.054	0.7550	0.7581	0.414	0.74	-1.987
RbI	5	sc	3.769	3.771	0.059			0.8187	0.7991	-2.401		
RbI	45	sc	3.5806	3.5873	0.187			1.5586	1.4724	-5.532		
CsF	0	fcc	3.004	2.9946	-0.314	2.891	-3.762	1.444	1.3416	-7.088	1.660	14.958
CsCl	0	sc	3.571	3.5944	0.655			0.8979	0.8933	-0.516		
CsCl	45	sc	3.3921	3.4241	0.943			1.5688	1.6948	8.033		
CsBr	0	sc	3.720	3.7225	0.066			0.9025	0.8282	-8.233		
CsBr	45	sc	3.5113	3.5322	0.596			1.5554	1.6491	6.021		
CsI	0	sc	3.956	3.8958	-1.522			0.7369	0.7641	3.690		
CsI	45	sc	3.7028	3.6795	-0.6306			1.4428	1.6068	11.367		
			rms		0.997%		1.435%			6.755%		15.404%
			mean absolute		0.788%		0.952%			5.409%		9.046%

our repulsion potential (3). As can be seen, the radius of any ion varies from one compound to the other. Particularly remarkable is the variation in the case of the lithium ion. Also noteworthy is the large change in radius of the Cs$^+$ ion from CsF of *fcc* lattice to CsCl of *sc* lattice.

Table 6 lists the classical ionic radii obtained by Goldschmidt[21], Pauling[22] and Zachariasen[23]. It is difficult to compare them with our radii which are *variables*. However, we have listed in Table 5, the average radii of our ions in their respective compounds at atmospheric pressure. It is noted that our positive ion radii are larger than the classical values while our negative ion radii are smaller. Experimentally, one can get ionic radii from the detailed electron density maps of ionic solids. From the work of Witte *et al.*[1] we get the radii of Na$^+$ and Cl in NaCl to be 1·17 and 1·65 Å respectively. Schoknecht[2] gives almost the same values—1·18 and 1·64 Å. Our ionic radii in NaCl are 1·12 and 1·69 Å which agree much better than the classical values listed in Table 6. Our ionic radii are numbers that have evolved out of the theory without any related information being put in. We consider the close agreement of our radii with the experimental values a strong point in favour of our whole approach. Krug *et al.*[3] have given the electron density map for LiF. Here the overlap is much more and it is difficult to obtain ionic radii. We can, however, approximately estimate the radius of Li$^+$ to be 0·92 Å and *F* to be 1·09 Å. In comparison, our values of 0·70 and 1·28 Å are not too bad. These results are summarized in Table 6.

In addition to the classical ionic radii listed in Table 6, various other attempts have been made to obtain ionic radii from the Born model itself. The ionic radii in the

Table 4. Ionic radii (in Ångstroms) of the alkali and halogen ions at atmospheric pressure calculated from the present theory

	F$^-$	Cl$^-$	Br$^-$	I$^-$
Li$^+$	0.698	0.824	0.863	0.923
	1.276	1.746	1.915	2.159
Na$^+$	1.055	1.122	1.132	1.195
	1.269	1.688	1.826	2.067
K$^+$	1.406	1.442	1.447	1.477
	1.291	1.684	1.815	2.018
Rb$^+$	1.535	1.585	1.603	1.602
	1.277	1.689	1.837	2.009
Cs$^+$	1.729	1.849	1.847	1.846
	1.266	1.745	1.875	2.050

Table 5. Comparison of the classical ionic radii of Goldschmidt[21], Pauling[22] and Zachariasen[23] with those predicted by the present theory. All values are in Ångstroms

Ion	Goldschmidt [21] radii	Pauling [22] radii	Zachariasen [23] radii	Average radii with present potential
Li$^+$	0.78	0.60	0.68	0.83
Na$^+$	0.98	0.95	0.98	1.13
K$^+$	1.33	1.33	1.33	1.44
Rb$^+$	1.49	1.48	1.48	1.58
Cs$^+$	1.65	1.69	1.67	1.82
F$^-$	1.33	1.36	1.33	1.28
Cl$^-$	1.81	1.81	1.81	1.71
Br$^-$	1.96	1.95	1.36	1.85
I$^-$	2.20	2.16	2.19	2.06

Table 6. Comparison of various theoretical ionic radii with the experimental values. All values are in Ångstroms

Crystal	Ion	Experimental radius [1,3]	Goldschmidt radius [21]	Pauling radius [22]	Zachariasen radius [23]	Present theory	Tosi and Fumi radius [20]
NaCl	Na^+	1.17	0.98	0.95	0.98	1.122	1.20
NaCl	Cl^-	1.65	1.81	1.81	1.81	1.688	1.62
LiF	Li^+	0.92	0.78	0.60	0.68	0.698	0.83
LiF	F^-	1.09	1.33	1.36	1.33	1.276	1.19

Huggins–Mayer form of the repulsion potential[24] are indeterminate to a constant which has to be arbitrarily fixed. In the approach of Tosi and Fumi[20], this arbitrariness is apparently removed. But this arises from a weak contribution from second neighbour repulsion. As Douglas[25] has shown, it is possible to get different sets of "basic radii" which would be far different from one another but all of which would describe the family of crystals to the same tolerance. Further, the "basic radii" again suffer from the defect that they are constants. Tosi and Fumi seek to remove this by defining "crystal radii" where the difference between the nearest neighbour distance and the sum of the basic radii is distributed equally between the two ions. But this seems *ad hoc* and would require some justification. It should be mentioned that the crystal radii of Tosi and Fumi agree very well with the experimental values quoted above (see Table 6).

7. CONCLUSION

To summarize, we have postulated that the repulsion between ions in ionic crystals occurs essentially from the distortion and compression of the ions which are considered to be distinct entities. At this stage, there is no theoretical justification for this. By explicitly putting an exponential functional form for the compression energy of individual ions, we have calculated parameters for the ions in the alkali halide family. The resulting repulsion functions describe the alkali halides somewhat better than earlier potentials proposed by other workers. However, the main attraction in the approach lies in the fact that with minor alterations, the same repulsion parameters can be used for an ion in different structures and in different crystals. This makes the present formulation of the repulsion potential very useful. Finally, our approach to repulsion introduces the idea of ionic radius in a very natural way and is capable of predicting the variation in the radius of an ion from one crystal to another and also with pressure in the same crystal.

It should be pointed out that the present empirical approach to repulsion in ionic crystals involves two levels of approximation. In the first level we postulate a specific functional form for the repulsion potential (eqns (1) and (10)). Comparison with experimental results[5] have most favourably verified this level of approximation. In this paper, we have chosen a specific exponential form (eqn (13)) for the repulsion potential. The results are reasonably good. It is quite possible that some other specific function might lead to better agreement with experiment. But this will not basically invalidate our picture of the origin of repulsion between ions.

Acknowledgement—One of the authors (R.N.) wishes to thank the NCERT, India for a fellowship.

REFERENCES

1. Witte H. and Wölfel E., *Z. Physik Chem.* (Frankfurt) [NS] **3**, 296 (1955).
2. Schoknecht G., *Z. Naturforsch.* **12a**, 983 (1957).
3. Krug J., Witte H. and Wölfel E., *Z. Physik Chem.* (Frankfurt) [NS] **4**, 36 (1955).
4. Löwdin P.-O., *Phil. Mag. Suppl.* **5**, 1 (1956).
5. Narayan Ramesh and Ramaseshan S., *Pramāna* **3**, 143 (1974).
6. Tosi M. P., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 16, p. 1. Academic Press, New York (1964).
7. Pauling L., *Z. Krist.* **67**, 377 (1928).
8. Born M., *Atomtheorie des Festen Zustandes.* Teubner, Leipzig (1923).
9. Born M. and Mayer J. E., *Z. Physik.* **75**, 1 (1932).
10. Prakash S. and Behari J., *Ind. J. Pure Appl. Phys.* **7**, 709 (1969).
11. Tosi M. P. and Fumi F. G., *J. Phys. Chem. Solids* **23**, 359 (1962).
12. Tosi M. P., *J. Phys. Chem. Solids* **24**, 1067 (1963).
13. Vaidya S. N. and Kennedy G. C., *J. Phys. Chem. Solids* **32**, 951 (1971).
14. Murnaghan F. D., *Finite Deformation of an Elastic Solid.* Wiley, New York (1951).
15. National Bureau of Standards Circular 539 (1953–1957).
16. Hildebrand J. H., *Z. Physik* **67**, 127 (1931).
17. Cubicciotti D., *J. Chem. Phys.* **31**, 1646 (1959).
18. Hajj F., *J. Chem. Phys.* **44**, 4618 (1966).
19. Mayer J. E., *J. Chem. Phys.* **1**, 270 (1933).
20. Tosi M. P. and Fumi F. G., *J. Phys. Chem. Solids* **25**, 45 (1964).
21. Goldschmidt V. M., *Skrifter Norske Videnskaps-Akad. Oslo, Math.-Nat. Kl.* No. 2 (1926).
22. Pauling L., *Proc. Roy. Soc., London* **A114**, 181 (1927).
23. Zachariasen W. H., reported by C. Kittel, In *Introduction to Solid State Physics* Table 3.5. Wiley, New York (1956).
24. Huggins M. L. and Mayer J. E., *J. Chem. Phys.* **1**, 643 (1933).
25. Douglas T. B., *J. Chem. Phys.* **38**, 2461 (1963).