Pramāṇa Vol. 3, No. 3, 1974, pp 143–155. © Printed in India.

Compressive energy of ions in ionic crystals

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MS received 24 April 1974; after revision 6 June 1974

Abstract. The possibility of writing the repulsive energy in the Born model of binary ionic crystals as a sum of two separate contributions from the two ions has been investigated. Such an approach leads to two identities, one connecting the lattice spacings of a family of ionic crystals and the other connecting their compressibilities. These identities have been tested on the alkali halide crystals over a range of pressures. The agreement is found to be quite satisfactory. Some further predictions with respect to crystals which exist as two polymorphs have also been tested. In all cases, the deviations of the experimental values from the exact identities can be traced to the fact that second neighbour repulsions in the crystals have been neglected. It is hence concluded that individual compressive energies for ions in ionic crystals is a very attractive possibility.

Keywords. Alkali halides; atomic compression; Born model; ionic crystals; repulsive energy.

Introduction

The introduction of concepts like ionic radius, ionic polarisability, etc., that are dependent on individual ions has proved of immense value in the development of the theory of ionic crystals. In this context it seems relevant to ask whether one could extend these ideas to more complicated properties like compressibility. The concept of ionic compressibility would require two postulates: (*a*) the internal energy of an ion is a function of its size, and (*b*) the repulsive energy in an ionic crystal arises from the increase in the internal energy of the ions when they are compressed. The repulsive energy would then have to be written as the sum of contributions from the two ions as in eq. (1) below. This is a classical picture which would not get theoretical support from the quantum mechanical approach where repulsion is caused by the overlap of neighbouring electron clouds. But then one must note that even the concept of the ionic radius for which there is definite experimental evidence cannot really be justified from the overlap theory. The full quantum mechanical treatment, in fact, leads to very messy numerical computation which has only been carried out approximately for a few compounds, and does not appear to lead to any physical insight. There seems therefore to be some need for postulating empirical functions for the form of the repulsive energy. Almost all earlier workers have tried either the function A/r^n or $b \exp(-r/\rho)$ where r is the interionic distance and have succeeded to some extent in explaining the behaviour of ionic crystals. In this paper, we investigate the consequence of postulating a function of the type in eq. (1). All functions

pro osdpe are only attempted approximations to the true repulsive function. How ever, the function we have proposed, if found acceptable, has some advantages.- Firstly, this would directly lead to a kind of inverse additivity rule for the compressibilities of ions. Further, if we consider a family of binary ionic crystals made up of all combinations of m positive ions and n negative ions, whereas all the earlier approaches mentioned above would require mn functions to be determined, the present alternative would require only $(m+n)$ functions.

In this paper, we test this postulate [(eq. (1)] on the alkali halides. The various attractive forces between the ions have been treated as in the Born model [for a good review of the Born model, *see* Tosi (1964)].

Just from the functional form of the repulsive potential assumed, we are able to derive two identities which have to be satisfied by certain experimentally determinable quantities in sets of crystals. These identities have been tested on the alkali halides. The agreement appears to be satisfactory implying that the concept of individual compressive energy for ions is an attractive possibility worthy of further investigation and evaluation.

Theory

In this paper we investigate the possibility of the repulsive energy being completely separated out into the *sum of contributions from the two ions.* Thus

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

where, W_+ and W_- are functions of r_+ and r_-, the radii of the two ions. The functions W_+ and W_- are presumed to be unique for a given ion and hence transferable from one crystal to another. Geometrically, we can visualize an ion as a soft fluffy sphere, the repulsive energy being produced by compression and distortion at the points of contact with its neighbours. *The repulsive energy in this formulation does not depend on the agency causing the distortion.* It should be noted that in the present formulation r_+ and r_- are *variables* which can vary for a given ion from crystal to crystal and also with pressure in the same crystal.

To keep the discussion as general as possible, we do not specify any particular functional form for W_+ and W_-. We thus write the total lattice energy per molecule of a binary ionic crystal as

$$W = -\frac{ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_+(r_+) + W_-(r_-) \tag{2}$$

where the first three terms on the right hand side give respectively the Madelung electrostatic energy, the van der Waals dipole-dipole interaction energy and the van der Waals dipole-quadrupole interaction energy. As it stands, W is a function of three variables—r, the nearest neighbour distance, r_+, the radius of the positive ion, and r_-, the radius of the negative ion.

Now, in our geometrical picture of the crystal, the nearest neighbours are in contact with one another, so that we immediately have the relation

$$r = r_+ + r_- \tag{3}$$

In addition, we have one further relation expressing the internal equilibrium of the lattice. This arises from the minimisation of the energy of the crystal with

respect to its internal co-ordinates r_+ and r_-. Physically we can picture this as the two ions pushing against each other and so adjusting their radii [subject always to equation (3)] that the forces they exert on each other are balanced. This requires the condition

$$\frac{dW_+(r_+)}{dr_+} = \frac{dW_-(r_-)}{dr_-} \tag{4}$$

Relation (4) like relation (3) is always valid.

Because of relations (3) and (4), r_+ and r_- are functions of r. Thus, in equation (2), *W becomes a function of only r* and we are justified in talking of total derivatives of the type $dW(r)/dr$, $d^2W(r)/dr^2$, etc. Differentiating (2) with respect to r and using relations (3) and (4), we then have

$$W_+'(r_+) = W_-'(r_-) = \frac{dW(r)}{dr} - \frac{\alpha e^2}{r^2} - \frac{6C}{r^7} - \frac{8D}{r^9} = f(r) \tag{5}$$

where for convenience in later discussion, we have called the function on the right $f(r)$. $f(r)$ is a unique function of r for a given crystal though it is, in general, different for different crystals. In the present picture of the crystal, r_+ and r_- are perfectly meaningful physical parameters. The reason why it is necessary to convert back into a description in terms of r is that the various quantities of interest are experimentally determined only as functions of r. All the quantities in $f(r)$ can be calculated from experimental data as will be shown in the next section. Hence, one can calculate the derivative of the two ionic repulsive functions. This derivative varies with the lattice spacing as can be seen from (5), and hence for a range of pressures, one gets a range of values for $W_+'(r_+)$ and $W_-'(r_-)$.

Now suppose we consider the same ion occurring in two different crystals. To fix ideas, let us say the positive ion is common to two crystals. In general, $W_+'(r_+)$ will not be the same for both the crystals. However, it is possible to find two pressures P_1 and P_2 such that the value of $f(r)$ is the same in both the crystals. The function $W_+'(r_+)$, we have assumed, is a property of the ion alone and so is the same in both crystals. Thus, if $W_+'(r_+)$ is a monotonic function of r_+, we can say that the ion has the same radius r_+ in crystal 1 at pressure P_1 and crystal 2 at pressure P_2. This is somewhat similar to the original idea of Goldschmidt (1926) and Pauling (1927) of assigning ionic radii except that in the present treatment, the ionic radii are *variables* and so are equal in two crystals only when $f(r)$ is the same.

Now consider four ions A^+, B^+, C^-, D^- and the four crystals they form

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

Suppose we consider these four crystals under such pressures that the value of $f(r)$ defined in (5) is the same for all four. Then by the above arguments, ion A^+ has the same radius in crystals I and II, ion B^+ the same radius in crystals III and IV, etc., and it is easily shown that

$$(r_{\text{I}} + r_{\text{IV}}) - (r_{\text{II}} + r_{\text{III}}) = (r_+^{\text{A}} + r_-^{\text{C}}) + (r_+^{\text{B}} + r_-^{\text{D}}) - (r_+^{\text{A}} + r_-^{\text{D}}) - (r_+^{\text{B}} + r_-^{\text{C}}) = 0 \tag{7}$$

Equation (7) is an identity among the lattice spacings of any four crystals of the

type (6) considered under conditions of equal $f(r)$. Eq. (7) follows from the original assumption of additivity of separate ionic repulsive energies which we have seen leads to the concept of uniqueness of ionic radius under identical forces, regardless of the actual crystal considered. Hence a verification of (7) may be considered a justification of the assumption.

Now, differentiating (5) with respect to r once again, we have

$$W_+''(r_+)\frac{dr_+}{dr} = W_-''(r_-)\frac{dr_-}{dr} = \frac{d^2W}{dr^2} + \frac{2ae^2}{r^3} + \frac{42C}{r^8} + \frac{72D}{r^{10}} \tag{8}$$

Differentiating (3) with respect to r and solving with the help of (8), we have

$$\frac{dr_+}{dr} = \frac{W_-''(r_-)}{W_+''(r_+) + W_-''(r_-)} \tag{9}$$

and a similar expression for dr_-/dr. Substituting back in (8) and inverting the whole equation, we have

$$\frac{1}{W_+''(r_-)} + \frac{1}{W_-''(r_-)} = \frac{1}{\frac{d^2W}{dr^2} + \frac{2ae^2}{r^3} + \frac{42C}{r^8} + \frac{72D}{r^{10}}} = g(r) \tag{10}$$

where, for convenience, we have called the function on the right $g(r)$. The left hand side of (10) is again the sum of two terms each of which is exclusively the function of one of the ions. Hence, exactly as before, if we consider four crystals of the type (6) under conditions of equal values of $f(r)$, we have

$$\{g(r)_{\mathrm{I}} + g(r)_{\mathrm{IV}}\} - \{g(r)_{\mathrm{II}} + g(r)_{\mathrm{III}}\} = 0 \tag{11}$$

$g(r)$ is related to the compressibility through d^2W/dr^2 [eqs (10) and (15)] and hence (11) is essentially an identity among the compressibilities of the crystals I to IV. The verification of (11) may be considered another justification for the additivity of ionic repulsive energies assumed in (1).

It should be noted that in eqs (7) and (11), the four crystals compared have to be of the same crystal structure. This is an obvious precaution since the repulsive potential is a function of the co-ordination number. However, we could correct for the change in crystal structure by postulating that the repulsive potential is directly proportional to the number of nearest neighbours n, *i.e.*,

$$W_\pm(r_\pm) = nh_\pm(r_\pm) \tag{12}$$

where $h_\pm(r_\pm)$ is a unique function for a given ion, independent of the crystal structure. This seems reasonable in our geometrical picture of the repulsive potential arising from the distortion and compression of the spherical ion at the points of contact with its neighbours. Thus, if a crystal exists in two different structures (at different pressures, of course) having the same nearest neighbour distance, then (12) implies that

$$\frac{n_1}{n_2} = \frac{f_1(r)}{f_2(r)} = \frac{g_2(r)}{g_1(r)} \tag{13}$$

This is yet another result that can be tested.

It should be mentioned that the results (7), (11) and (13) cannot be exact if second neighbour repulsions are also present. This is because second neighbour repulsion cannot be separated into two functions of r_+ and r_- alone, but depends

on the inter-ionic spacing $r (= r_+ + r_-)$. Thus, the expression (2) for the lattice energy does not include the contribution from second neighbour repulsion.

Results

The above identities, eqs (7), (11) and (13), have been tested for the alkali halides. The experimental values for the calculations were taken from the following sources. The room temperature atmospheric pressure lattice spacings were taken from NBS (1953–1957). For variations of r with pressure, the compressibility data of Vaidya and Kennedy (1971) were used. The van der Waals coefficients C and D were taken from Mayer (1933). For dW/dr and d^2W/dr^2, the Hildebrand (1931) equations of state were used

$$\frac{dW}{dV} = -P + \frac{T\beta}{K} \tag{14}$$

$$\frac{d^2W}{dV^2} = \frac{1}{VK}\left[1 + \frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right] \tag{15}$$

where P is the pressure, V is the volume per molecule, T is the temperature, β is the isobaric volume expansivity $1/V\ (\partial V/\partial T)_P$ and K is the isothermal compressibility $-1/V\ (\partial V/\partial P)_T$. The room temperature, atmospheric pressure values of the thermodynamic quantities were taken from Cubicciotti (1959, 1960, 1961). Since there are no experimental data at high pressures, the following approximate relations were used:

$$\beta_P = \beta_0 \frac{K_P V_0}{K_0 V_P} \tag{16}$$

$$\left[\frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right]_P = \frac{\beta_P}{\beta_0}\left[\frac{T}{K}\left\{\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right\}\right]_0 \tag{17}$$

where K_P, the compressibility at pressure P was obtained from the PV data of Vaidya and Kennedy (1971). Relations (16) and (17) were derived assuming that the Grüneisen's constant $\gamma\ (= V\beta/C_V K)$ is independent of pressure. It should be mentioned that the approximations (16) and (17) are not very important since the corresponding terms in (14) and (15) are only in the nature of small corrections.

Using the above values, the quantity $f(r)$ was calculated as a function of pressure for 15 alkali halides, *viz.*, the chlorides, bromides and iodides of lithium, sodium, potassium, rubidium and caesium. The fluorides were not included because, in many cases, sufficiently reliable high pressure data were not available. Taking the crystals in groups of four as in (6), the quantity

$$\Delta r = (r_{\mathrm{i}} + r_{\mathrm{iv}}) - (r_{\mathrm{ii}} + r_{\mathrm{iii}}) \tag{18}$$

was calculated for a range of common value of $f(r)$. The mean results are tabulated in table 1. It is seen that $\langle \Delta r \rangle$ is not exactly zero as expected by eq. (7) but is invariably a small negative quantity. The significance of this is discussed in the next section. The r.m.s. deviations of Δr, also given in table 1, are seen to be of the order of 0·0020 Å (r is of the order of 3 Å).

Table 1. Testing relation (7) among lattice spacings and relation (11) among compressibilities for sets of alkali halides

Type of structure	Combination of Alkali Halides	Δr (Å)		Δg (10^{-6} cm²/erg)	
		$\langle \Delta r \rangle$	r.m.s. deviation	$\langle \Delta g \rangle$	r.m.s. deviation
NaCl	LiCl, LiBr, NaCl, NaBr	−0·0048	0·0010	+0·134	0·002
	LiCl, LiI, NaCl, NaI	−0·0116	0·0012	+0·133	0·12
	LiBr, LiI, NaBr, NaI	−0·0064	0·0010	−0·121	0·15
	NaCl NaBr, KCl, KBr	−0·0147	0·0005	−0·310	0·021
	NaBr, NaI, KBr, KI	−0·0128	0·0008	−0·718	0·013
CsCl	KCl, KBr, RbCl, RbBr	−0·0065	0·0007	+0·180	0·13
	KCl, KI, RbCl, RbI	−0·0123	0·0010	−0·080	0·07
	KBr, KI, RbBr, RbI	−0·0060	0·0003	−0·190	0·065
	KCl, KBr, CsCl, CsBr	−0·0121	0·0009	−0·169	0·204
	KCl, KI, CsCl, CsI	−0·0344	0·0019	+0·160	0·171
	KBr, KI, CsBr, CsI	−0·0213	0·0030	+0·329	0·083
	RbCl, RbBr, CsCl, CsBr	−0·0071	0·0023	−0·353	0·11
	RbCl, RbI, CsCl, CsI	−0·0208	0·0024	+0·180	0·084
	RbBr, RbI, CsBr, CsI	−0·0131	0·0041	+0·505	0·058

In a similar manner, at constant $f(r)$, the quantity Δg given by

$$\Delta g = \{g(r)_{\mathrm{I}} + g(r)_{\mathrm{IV}}\} - \{g(r)_{\mathrm{II}} + g(r)_{\mathrm{III}}\} \tag{19}$$

was also calculated for the same groups of crystals. The mean results are tabulated in table 1. The r.m.s. deviations of Δg are seen to be of the order of 0·15 $\times 10^{-6}$ cm²/erg. (g is of the order of 5×10^{-6} cm²/erg).

To get a better idea of the quantities entering in the calculations above, a few sample tables and graphs are shown in Appendix 1.

Equation (13) was tested in the case of potassium and rubidium halides which exist in a NaCl type structure ($n_1 = 6$) at low pressures and a CsCl type structure

Table 2. Testing relation (13) (ligancy effect) for potassium and rubidium halides

Crystal	$\frac{n_2 f_1(r)}{n_1 f_2(r)}$		$\frac{n_2 g_2(r)}{n_1 g_2(r)}$	
	$\left\langle \frac{n_2 f_1(r)}{n_1 f_2(r)} \right\rangle$	r.m.s. deviation	$\left\langle \frac{n_2 g_2(r)}{n_1 g_1(r)} \right\rangle$	r.m.s. deviation
KCl	0·026	0·002	0·895	0·005
KBr	0·894	0·003	0·905	0·025
KI	0·830	0·002	0·854	0·007
RbCl	0·974	0·001	0·986	0·017
RbBr	0·948	..	1·00	..
RbI	0·897	..	0·939	..

($n_2 = 8$) at high pressures. The quantities $n_2 f_1(r)/n_1 f_2(r)$ and $n_2 g_2(r)/n_1 g_1(r)$ have been calculated for these crystals for a range of common values of r and the mean values are tabulated in table 2. The deviations of these quantities from the expected value of 1·0 are discussed in next section.

Discussion of the results and effect of second neighbour repulsion

Tables 1 and 2 show that the relations (7), (11) and (13) are not exactly satisfied. It is possible to explain the deviations as due to the effect of second neighbour repulsions which have been neglected in the above theory. The effect of second neighbour repulsion is to increase the total repulsive potential and thus to shift the equilibrium to larger inter-ionic distances. Whereas this effect is present in all the crystals, the effect can be expected to be much larger in those cases where the ions are of widely differing sizes. In table 1, the crystals have been arranged so that crystal II has the largest disparity in the sizes of the ions. Thus, the increase in r_{II} would be expected to be much larger than the increase in r_I, r_{III} or r_{IV} and hence $\triangle r$ is expected to be always negative, as indeed it is in table 1. There are some further trends which strengthen the belief that second neighbour repulsions might be responsible for the deviations. The deviations in $\triangle r$ would be expected to be greater where there is greater disparity in size between the largest and smallest ion in a group. This is verified in table 1 where $\triangle r$ is larger whenever Cl^- and I^- are compared than when Cl^- and Br^- or Br^- and I^- are compared; so too, $\triangle r$ is larger whenever K^+ and Cs^+ are compared than when K^+ and Rb^+ or Rb^+ and Cs^+ are compared. Further, $\triangle r$ is in general larger in CsCl type structures than in NaCl type structures which is explained by the fact that second neighbour distances are much smaller in the former type ($r' = 1{\cdot}154r$) than in the latter ($r' = 1{\cdot}414r$).

The values of $\triangle g$ in table 1, however, do not show any systematic deviations. The agreement with eq. (15) is fairly good — $\triangle g$ which is the difference of two quantities of the order of 10 is of the order of 0·2. It is not very obvious how second neighbour repulsion will affect the function $\triangle g(r)$ and so no explanation of the deviations is attempted.

Considering the values calculated in table 2, it is seen that they deviate from the theoretically expected value of 1·0. Again the deviations can be traced to second neighbour repulsion which increases $f(r)$ and decreases $g(r)$, the changes being more in CsCl type structures than in NaCl type structures (due to the reason discussed above). Thus, we expect all the quantities to be less than 1·0 and this is so. Also, the deviations are proportional to the disparity in the sizes of the ions as expected, being largest for KI and smallest for RbCl.

As regards the sensitivity of the above tests, we can make the following remark. In calculating $\triangle r$, we take crystals I to IV at four pressures. The maximum difference in pressure, *viz.*, $(P_{IV} - P_I)$ is about 10–25 kbar. We could determine the $\triangle P$ which has to be made on any of the pressures, say P_{IV}, which will bring $\triangle r$ to the expected value of 0. Such a check is meaningful only where the second neighbour repulsion is minimum since the major deviations have any way been traced to it. Thus, if we consider the most favourable case of LiCl, LiBr, NaCl, NaBr, $(P_{IV} - P_I)$ is about 25 kbar whereas a change in P_{IV} of $-1{\cdot}5$ kbar causes

Δr to become 0. But, apart from this, the very fact that the deviations are so systematic and are amenable to a consistent explanation is itself a pointer to the plausibility of the approach taken in this paper.

Corrections for second neighbour repulsion

It is not possible to develop a theory with a general repulsive function with second neighbour repulsions also included. However, an approximate correction has been attempted as follows. In the repulsive potential of Tosi and Fumi (1964), we note that there are two terms, one for nearest neighbour repulsion and the other for next nearest neighbour repulsion. It is assumed here that this potential function does indeed describe how the two contributions are split up [there is no justification for this, since in the procedure of Tosi and Fumi (1964) it is only the total function that has been made to fit the experimental data]. Then eq. (5) is modified to

Table 3. Testing relation (7) among lattice spacings and relation (11) among compressibilities for sets of alkali halides after applying correction for second neighbour repulsion.

Type of structure	Combination of Alkali Halides	Δr (Å)	
		$\langle \Delta r \rangle$	r.m.s. deviation
NaCl	LiCl, LiBr, NaCl, NaBr	+0·0127	0·0021
	LiCl, LiI, NaCl, NaI	+0·0210	0·0010
	LiBr, LiI, NaBr, NaI	−0·0150	0·0024
	NaCl, NaBr, KCl, KBr	−0·0003	0·0005
	NaCl, NaI, KCl, KI	+0·014	..
	NaBr, NaI, KBr, KI	+0·0133	0·0013
CsCl	KCl, KBr, RbCl, RbBr	−0·0025	0·0008
	KCl, KI, RbCl, RbI	+0·0050	0·0
	KBr, KI, RbBr, RbI	+0·0074	0·0005

Table 4. Testing relation (13) (ligancy effect) for potassium and rubidium halides after applying correction for second neighbour repulsion.

Crystals	$\frac{n_2 f_1(r)}{n_1 f_2(r)}$		Crystals	$\frac{n_2 f_1(r)}{n_1 f_2(r)}$	
	$\left\langle \frac{n_2 f_1(r)}{n_1 f_2(r)} \right\rangle$	r.m.s. deviation		$\left\langle \frac{n_2 f_1(r)}{n_1 f_2(r)} \right\rangle$	r.m.s. deviation
KCl	1·06	0·0	RbCl	1·12	..
KBr	1·03	0·006	RbBr	1·08	..
KI	0·99	0·006	RbI	1·04	..

$$W_+'(r_+) = W_-'(r_-) = \frac{dW}{dr} - \frac{\alpha e^2}{r^2} - \frac{6C}{r^7} - \frac{8D}{r^9} + \frac{dW_{2rep}}{dr} \tag{20}$$

where dW_{2rep}/dr, the derivative of the second neighbour repulsive energy, is calculated from the potential of Tosi and Fumi (1964).

Table 3 shows the mean values of $\triangle r$ calculated after applying this correction. All the combinations in table 1 could not be corrected since Tosi and Fumi (1964) have not given their repulsive potential for the caesium halides. It is seen that $\triangle r$ in table 3 has become positive in most cases showing that the correction for second neighbour repulsion is in the right direction. There is, however, an over-correction in most cases which is probably due to our questionable procedure of splitting the potential of Tosi and Fumi (1964) into two parts and attaching a physical significance to each.

Table 4 shows the values of $n_2 f_1(r)/n_1 f_2(r)$ calculated after applying the correction (20). Again it is seen that the values are pulled towards the expected value of 1·0, although over corrected in some cases.

The above corrections for second neighbour repulsion are not meant as any quantitative checks. Their chief function is to illustrate that corrections for second neighbour repulsion do alter the values in tables 1 and 2 in the required direction.

Conclusion

Starting from the physically pleasing postulate [equation (1)] that the repulsive potential is the sum of two contributions, one from each ion, we have derived certain results which have been verified numerically for the family of alkali halides. It has been possible to explain the deviations consistently in terms of second neighbour repulsions. By putting in an explicit functional form for the individual ionic repulsive potentials, it would then be possible to include second neighbour repulsions directly in the theory.

If we introduce two parameters for each repulsive function (as has been done by most earlier workers) then, in the above approach, we would require sixteen parameters to describe the set of alkali halides considered. For the same alkali halides, the original approach of Born requires thirty parameters whereas the Tosi and Fumi approach requires twenty-three. Also, some of the above tests seem to indicate that we might expect the same parameters to describe a crystal over a range of pressures and even in two different structures. This means we could do away with the idea of structure-dependent parameters introduced by Tosi and Fumi (1962).

We should mention that recently Smith (1972) has postulated atom dependent potentials to account for the repulsive potential of *rare-gas atoms* in binary collisions. His approach seems to lead to better results in that problem.

Appendix

To facilitate a better appreciation of the quantities entering in the analysis, we present here a few sample calculations and results. Table 5 shows the quantities entering in the calculation of $f(r)$ and $g(r)$ for the crystal LiCl at various pressures from 0 to 45 kbar. Figure 1 shows $f(r)$ plotted as a function of r for the four

Table 5. Details of calculations of $f(r)$ and $g(r)$ for the crystal LiCl.

P (kbar)	r (Å)	K (10^{-12} cm², dyne^{-1})	β (10^{-4} deg^{-1})	dW/dr	ae^2/r^2	$6C/r^7$	$8D/r^9$	$f(r)$
				(10^{-5} erg cm^{-1})				
0	2·570	3·36	1·22	4·32	61·0	9·16	1·70	−67·5
5	2·557	3·11	1·15	2·41	61·7	9·49	1·78	−70·6
10	2·545	2·90	1·08	0·456	62·2	9·80	1·86	−73·4
15	2·533	2·73	1·04	−1·37	62·8	10·1	1·94	−76·2
20	2·522	2·59	1·00	−3·21	63·4	10·4	2·02	−79·0
25	2·511	2·46	0·958	−5·04	63·9	10·8	2·10	−81·8
30	2·501	2·33	0·918	−6·82	64·5	11·1	2·17	−84·6
35	2·491	2·21	0·881	−8·58	65·0	11·4	2·25	−87·2
40	2·482	2·11	0·851	−10·3	65·4	11·7	2·33	−89·7
45	2·473	2·02	0·823	−12·0	65·9	12·0	2·40	−92·3

P (k bar)	$\frac{T}{K}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]$ (10^{-2})	d^2W/dr^2	$2ae^2/r^3$	$42C/r^8$	$72D/r^{10}$	$g(r)$ (10^{-6} cm², erg^{-2})
		10^5 erg cm^{-2}				
0	−0·805	1·40	0·475	0·249	0·065	4·53
5	−0·759	1·49	0·482	0·260	0·068	4·35
10	−0·713	1·57	0·489	0·270	0·071	4·17
15	−0·686	1·65	0·496	0·280	0·075	4·00
20	−0·660	1·72	0·503	0·290	0·078	3·86
25	−0·632	1·79	0·509	0·300	0·082	3·73
30	−0·606	1·87	0·515	0·310	0·085	3·60
35	−0·582	1·95	0·522	0·320	0·088	3·47
40	−0·562	2·02	0·527	0·330	0·092	3·37
45	−0·543	2·09	0·533	0·339	0·095	3·27

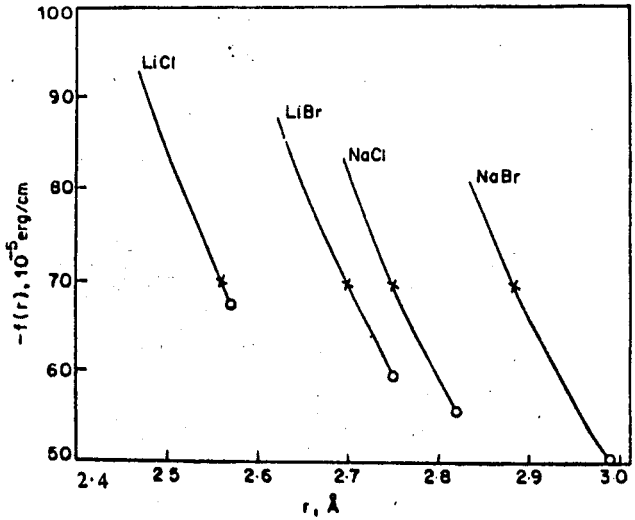

Figure 1. Curves of $f(r)$ vs r for LiCl, LiBr, NaCl and NaBr to test relation (7) among their lattice spacings.

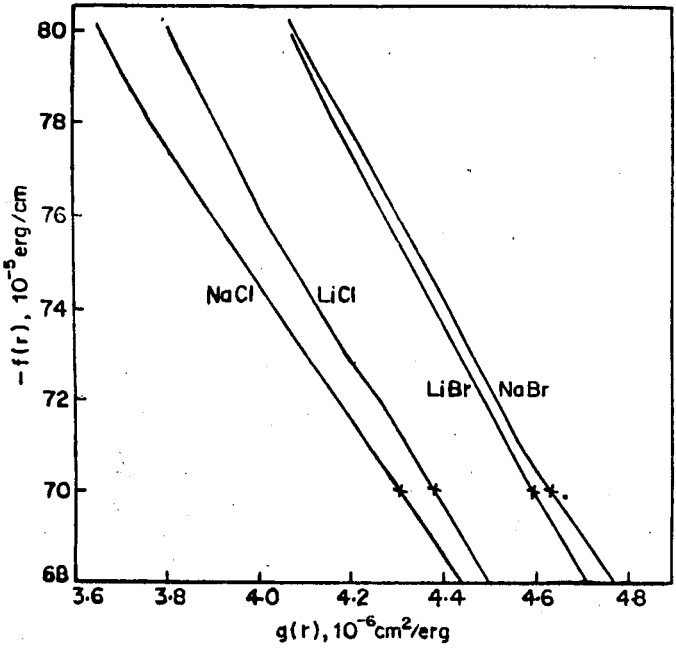

Figure 2. Curves of $f(r)$ vs $g(r)$ for LiCl, LiBr, NaCl and NaBr to test relation (11) among their compressibilities.

Table 6. Testing relation (7) among lattice spacings and relation (11) among compressibilities for the set of alkali halides: LiCl, LiBr, NaCl, NaBr.

$-f(r)$ (10^{-5} erg. cm^{-1})	r_{LiCl}	r_{LiBr}	r_{NaCl}	r_{NaBr}	Δr	$\lvert \Delta r - \langle \Delta r \rangle \rvert$	g_{LiCl}	g_{LiBr}	g_{NaCl}	g_{NaBr}	Δg	$\lvert \Delta g - \langle \Delta g \rangle \rvert$
	All values in 10^{-8} cm						All values in 10^{-6} cm^2/erg					
68	2·568	2·709	2·758	2·892	−0·007	0·0022	4·50	4·71	4·44	4·77	0·12	0·014
69	2·564	2·704	2·753	2·888	−0·005	0·0002	4·44	4·65	4·37	4·70	0·12	0·014
70	2·560	2·699	2·749	2·883	−0·005	0·0002	4·38	4·59	4·30	4·63	0·12	0·014
71	2·555	2·694	2·744	2·879	−0·004	0·0008	4·32	4·54	4·23	4·57	0·12	0·014
72	2·551	2·689	2·740	2·874	−0·004	0·0008	4·26	4·49	4·17	4·51	0·11	0·024
73	2·547	2·684	2·736	2·870	−0·003	0·0018	4·19	4·44	4·10	4·46	0·11	0·024
74	2·542	2·680	2·732	2·866	−0·004	0·0008	4·13	4·38	4·03	4·42	0·14	0·006
75	2·538	2·676	2·728	2·861	−0·005	0·0002	4·07	4·33	3·97	4·36	0·13	0·004
76	2·534	2·671	2·724	2·857	−0·004	0·0008	4·01	4·27	3·90	4·30	0·14	0·006
77	2·530	2·667	2·720	2·853	−0·004	0·0008	3·96	4·22	3·84	4·25	0·15	0·016
78	2·526	2·663	2·716	2·848	−0·005	0·0002	3·91	4·17	3·77	4·19	0·16	0·026
79	2·522	2·658	2·712	2·844	−0·004	0·0008	3·86	4·12	3·71	4·13	0·16	0·026
80	2·518	2·654	2·708	2·840	−0·004	0·0008	3·81	4·07	3·66	4·08	0·16	0·026
				$\langle \Delta r \rangle = -0{\cdot}0048$						$\langle \Delta g \rangle = 0{\cdot}134$		
					$[\langle \Delta r^2 \rangle - \langle \Delta r \rangle^2]^{\frac{1}{2}} = 0{\cdot}0010$						$[\langle \Delta g^2 \rangle - \langle \Delta g \rangle^2]^{\frac{1}{2}} = 0{\cdot}002$	

crystals LiCl, LiBr, NaCl, NaBr. With respect to this figure we can distinguish between our additivity of ionic radii and the classical approach of Pauling (1927) and Goldschmidt (1926). In the classical approach, the comparison is made among the lattice spacings corresponding to the circled points in figure 1 (which are the atmospheric pressure values). In our approach on the other hand we are comparing r-values at constant $f(r)$ as for instance the set of points marked with a cross in figure 1. Figure 2 similarly shows $g(r)$ against $f(r)$. Again, the additivity between the four values of $g(r)$ occurs at constant $f(r)$, for instance at the points marked with a cross. The above comparisons are made at various constant values of $f(r)$. Table 6 gives the results for the set of crystals LiCl, LiBr, NaCl, NaBr. The mean values $\langle \Delta r \rangle$, $\langle \Delta g \rangle$ and their root mean square deviations have been calculated as shown. It is these quantities for various sets of crystals that are tabulated in table 1.

References

Cubicciotti D 1959 *J. Chem. Phys.* **31** 1646

Goldschmidt V M 1926 *Skrifter Norske Videnskaps—Akad. Oslo, Math.-Nat. Kl.* No. 2

Hildebrand J H 1931 *Z. Physik.* **67** 127

Mayer J E 1933 *J. Chem. Phys.* **1** 270

National Bureau of Standards Circular 539 (1953–1957)

Pauling L 1927 *Proc. Roy. Soc., London* **A 114** 181

Smith F T 1972 *Phys. Rev.* **A 5** 1684

Tosi M P 1964 'Cohesion of ionic solids in the born model' *Solid State Physics*, Vol. 16 ed F. Seitz and D. Turnbull

Tosi M P and Fumi F G 1962 *J. Phys. Chem. Solids* **23** 359

Tosi M P and Fumi F G 1964 *J. Phys. Chem. Solids* **25** 45

Vaidya S N and Kennedy G C 1971 *J. Phys. Chem. Solids* **32** 951