IS COMPRESSIBILITY AN IONIC PROPERTY ?[*]

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ABSTRACT

A novel approach to the formulation of the repulsion potential of ions in ionic crystals has been attempted. The repulsion potential is postulated to be the sum of contributions from the individual ions, these contributions being proportional to the coordination numbers of the ions. For the specific exponential form of the ionic compression energy [$A \exp(-r/\rho)$] the two parameters A and ρ have been evaluated for 5 alkali and 4 halogen ions to fit the behaviour of 20 alkali halides. Not only is the number of parameters (18) used in this theory less than that (26) in comparable existing ones but the fit also is better. The same parameters fit the data of the alkali halides, (*a*) at atmospheric pressure, (*b*) in the pressure range 0–45 kb wherever data is available and also (*c*) for both the low pressure NaCl and the high pressure CsCl forms when such transformations occur. The important feature in this approach is that the parameters evaluated for an ion in one compound in one crystal structure can be used directly for the same ion in any other crystal of any structure at any pressure.

INTRODUCTION

THE concept of an ion as an incompressible sphere with a specific radius has proved very useful in many fields, particularly so in the crystallography of inorganic substances[1–5]. One is therefore tempted to enquire whether more complex properties like compressibility could also be ion-dependent.

Any crystal is stable because of the balance between attractive and repulsive forces in it. The attractive forces in an ionic crystal mainly consist of electrostatic coulomb forces and dispersion forces arising from van der Waals' dipole-dipole and dipole-quadrupole interactions. The attractive interactions can be calculated fairly accurately. They involve lattice sums for which powerful methods have been evolved (*e.g.*, Ewald[6]). The repulsion forces between ions are known to arise from the overlap of electronic clouds of the neighbouring ions. However, the actual evaluation of these from first principles is extremely difficult and has been rarely attempted[7]. It is therefore customary to use empirical functions to represent the repulsion interaction (*see* Tosi[8] for a review). We can write the lattice energy per molecule of say a binary ionic crystal in terms of the nearest neighbour distance r as

$$W_L(r) = -\frac{ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_{rep}(r) \qquad (1)$$

where the first three terms constitute the attractive energy and describe respectively the Madelung electrostatic, the dipole-dipole and the dipole-quadrupole interaction energies, and $W_{rep}(r)$ is the repulsion energy.

The idea of an ion as a separate entity in an ionic crystal cannot be rigorously justified on the basis of quantum mechanics. But accurate electron density maps of ionic crystals[9–11] clearly show that the electrons of each ion are well separated with regions of near zero electron density between the ions giving a physical substance to the concept of the ionic radius. However, considering the ions as hard incompressible spheres, with fixed radii, is too restrictive. We present here an attempt to widen our concept of the ion and treat it as a compressible sphere.

REPULSION—A RESULT OF IONIC COMPRESSION

The fundamental postulate we make is that the repulsion energy $W_{rep}(r)$ in eqn. (1) can be written as the sum of the contributions from the two ions in the form

$$W_{rep}(r) = W_+(r_+) + W_-(r_-) \qquad (2)$$

where r_+ and r_- are the radii of the two ions. The implications of eqn. (2) are :

(*a*) The ion has an internal energy [*viz.*, $W_+(r_+)$ or $W_-(r_-)$] which is a function of its size, the ion having less energy at large volumes. Figure 1 (full line) shows the type of function that is envisaged for this energy.

(*b*) When the ion is compressed by a pressure, a reaction is set up and the ion reaches an equilibrium size (r_+° in Fig. 1) at which its total energy is minimum.

(*c*) The internal energy of the ion does not depend on the agency that compresses it. For instance, the neighbouring ions of the crystal could be causing the compression. The internal energy of an ion is hence described by the same function in the different crystals in which it occurs [subject to some modifications (discussed later) when the structure type changes].

(*d*) We see from Fig. 1 that a compressed ion reaches an equilibrium size because it resists compression. The basic postulate used in writing down eqn. (2) is that the repulsion between ions arises *solely* from their reaction to compression.

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If the repulsion potential (2) is substituted in the expression (1), the lattice energy of a binary ionic crystal is seen to be a function of three variables, *viz.*, r, r_+ and r_-. However, there are two further relations :

(*a*) Since nearest neighbours are assumed to be in contact

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

(*b*) For any given r, the two ions adjust their sizes so as to minimise their total compression energy. This requires the first differential coefficient of the energies of the two ions to be equal, *i.e.*,

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

or

$$W_+'(r_+) = W_-'(r_-). \tag{4}$$

We can physically picture the neighbouring ions as pushing against each other and so adjusting their radii that the forces they exert on each other are balanced. Equation (4) describes the balancing of the two forces.

Because of eqns (3) and (4), r_+ and r_- are ultimately functions of r and it can be shown that'

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

$f(r)$ has the units of force and is a measure of the compressing pressure acting on the individual ions in the crystal.

$$\frac{dW_L(r)}{dr}$$

is a quantity that can be computed from experimental data (it is proportional to the external pressure applied on the crystal). The next three terms can also be calculated precisely if the constants α, C, D are known, so that $f(r)$ can be calculated for any crystal at any pressure provided the PV data are available.

EXPERIMENTAL JUSTIFICATION OF THE FIRST POSTULATE

In the present picture the ionic radii r_+ and r_- are not *constants* but *variables*. At any given pressure, the ions adjust their radii so as to minimise the total energy given by $W_L(r) + PV$. Even when the externally applied pressure P on the crystal is zero, there is still a pressure acting on the ions [described by $f(r)$] because of the attractive forces among the ions. This attractive force which can be calculated, since all attractive interactions are well understood, varies from one crystal to the other. Even when $P = 0$, the same ion will not have the same radius in two different crystals. This is the basic difference of this theory from the simple hard sphere model. In the present theory, the same ion in two different crystals will have the same radius only when the *internal pressure acting on it* in the two cases are equal. Although the two internal pressures will not normally be equal, it must be possible to select two external pressures P_1 and P_2 such that P_1 acting on the first crystal and P_2 acting on the second crystal both lead to the same internal pressure on the ion. In such a case, the radius of the ion in the two crystals must be equal. This, if verified, will be a strong justification of the postulate that has been made. However, the ionic radius is not an easily accessible quantity even under ordinary conditions, and to obtain it under different pressures would practically be impossible. Fortunately an equally powerful test is possible. Consider four ions A^+, B^+, C^-, D^- and the four crystals they form

$$\underset{\text{I}}{A^+C^-} \qquad \underset{\text{II}}{A^+D^-} \qquad \underset{\text{III}}{B^+C^-} \qquad \underset{\text{IV}}{B^+D^-} \tag{6}$$

Now four pressures P_I, P_{II}, P_{III}, P_{IV} can be calculated such that P_I acting on the crystal I, P_{II} acting on the crystal II, etc., lead to the same internal pressure [*i.e.*, the same value of $f(r)$]. Under these conditions, the ion A^+ has the same radius in crystals I and II, the ion C^- has the same radius in crystals I and III, etc. It is then easy to derive from (3) the relationship between the interionic distances given by

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

Equation (7) can be readily tested as we need only the nearest neighbour distances as a function of pressure in the four crystals. In the case of the alkali halides family of crystals the test shows that the identity (7) is very well satisfied to less than ½% tolerance in fourteen sets of crystals[12].

It is possible to derive another identity similar to (7) connecting compressibilities. The compressibility of an ion depends on the second derivative of its internal energy and is hence a unique function of its radius. This, however, cannot be directly tested since it is not possible to measure the compressibility of an individual ion. What can be measured is the bulk compressibility of the lattice which has contributions from the individual ions *plus* an "attraction contribution" which arises as follows. As the ions get compressed, the interionic distances change, altering, in their turn, the attractive forces. Now define the following function of r for the crystal

$$g(r) = \frac{1}{\dfrac{d^2 W_L(r)}{dr^2} - \dfrac{d^2 W_a(r)}{dr^2}} \tag{8}$$

where

$$\frac{d^2 W_L(r)}{dr^2}$$

is inversely proportional to the compressibility of the crystal and $W_a(r)$ represents the total of the attractive interactions [the first three terms in the R.H.S. of (1)] in the crystal. It can then be shown that for four crystals I, II, III, IV at pressures P_I, P_{II}, P_{III}, P_{IV} as described in (6), the following identity results:

$$[g(r)_I + g(r)_{IV}] - [g(r)_{II} + g(r)_{III}] = 0. \qquad (9)$$

This identity also has been tested on the alkali halides and it checks to about 3%.

The two identities (7) and (9) were derived to be a consequence of the postulate that repulsion arises entirely from the existence of a compression energy for individual ions. Their strong verification may hence be taken to be a fairly good justification of the postulate.

THE EFFECT OF COORDINATION ON THE REPULSION ENERGY

One of the essential features of the present approach is that the functions $W_\pm(r_\pm)$ should be capable of being transferred from one crystal to the other. However, this cannot be done directly when the *structure* changes. If we are to introduce compressibility as a property of the ion irrespective of the structure in which it is situated, we must associate with each ion a unique function which is independent of the symmetry of its environment. We achieve this with a second postulate which states that the compression energy of an ion is directly proportional to the number n of nearest neighbours, *i.e.*,

$$W_\pm(r_\pm) = nh_\pm(r_\pm) \qquad (10)$$

where $h_\pm(r_\pm)$ is a unique function for a given ion, independent of the crystal structure in which it is situated. The relation (10) can be rationalised on the picture that the increase in internal energy arises from the local compression and distortion at the points where an ion "touches" its neighbours. In this picture an ion may be compared to a balloon, with an impenetrable surface skin and a compressible interior. The second postulate implies the following:

(*a*) Suppose a compound exists in two structures having n_1 and n_2 nearest neighbours. Let the nearest neighbour distance r be the same for structure 1 at pressure P_1 and structure 2 at pressure P_2. Then it is easily shown that

$$\frac{n_1}{n_2} = \frac{f_1(r)}{f_2(r)} = \frac{g_2(r)}{g_1(r)} \qquad (11)$$

These identities have been tested on the six compounds KCl, KBr, KI, RbCl, RbBr, RbI which transform from the NaCl to the CsCl structure at high pressures[12]. Here again the results are very encouraging indicating that there is a definite physical basis for the second postulate.

(*b*) We shall show shortly that on the basis of this postulate it is quite straightforward to calculate the contribution to the repulsion from the second neighbour interaction.

THE REPULSION FUNCTION FOR INDIVIDUAL IONS

The next step is to evaluate the function $h(r)$ for different ions. Here again some empiricism is required. The internal energy of the ion has to be represented by a suitable function containing a small number of parameters which have to be refined to fit the data. In our studies we have assumed the following function which would approximate the actual behaviour schematically represented in Fig. 1.

$$h_\pm(r_\pm) = A_\pm e^{-r_\pm/\rho_\pm} \qquad (12)$$

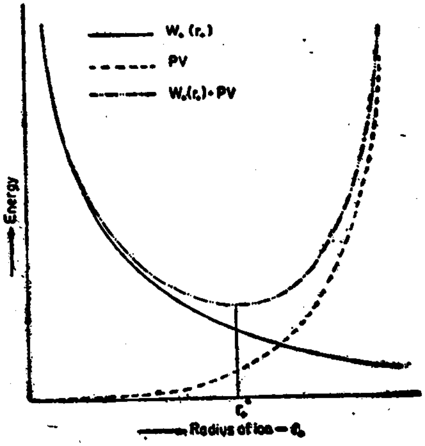

FIG. 1. Schematic graphs of the variation of the internal energy $W_+(r_+)$ of the (positive) ion and the pressure energy PV with r_+ the radius of the ion. The ion takes up a radius r_+° at which the total energy $[W_+(r_+) + PV]$ is a minimum.

where $A_\pm$ and $\rho_\pm$ are the parameters to be refined, the ± standing for the positive and the negative ion respectively. The failure of this approximation will not in any way invalidate the two postulates made earlier. Another model function [*e.g.*, $h_\pm(r_\pm) = A_\pm/r_\pm^{n\pm}$] may possibly give a better description of the ionic compression energy.

Using eqn. (10) we can now write the lattice energy per molecule of a binary ionic crystal as

$$W_L(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + n_1\left[A_+e^{-r_+/\rho_+} + A_-e^{-r_-/\rho_-}\right] + n_2\left[A_+e^{-br/\rho_+} + A_-e^{-br/\rho_-}\right] + PV. \qquad (13)$$

The new term in (11) represents the repulsion energy arising from second neighbours. n_2 is the number of second neighbours and $2br$ is the distance between them. We have used the same compression function for second neighbours also since according to our model, the actual agency compressing an ion is not of consequence. Also we assume that the ionic radius in the direction of the second neighbours is br and so replace $r_\pm$ by br for the second neighbour repulsion terms. This implies that the ion extends to a distance br in the direction of the second neighbours while it extends to r^+ (or r_- as the case may be) in the direction of the first neighbours. In this theory we are compelled to discard the idea of a spherical ion, an aspect strikingly supported by the accurate electron density maps of NaCl obtained by Witte and Wölfel[9] (Fig. 2).

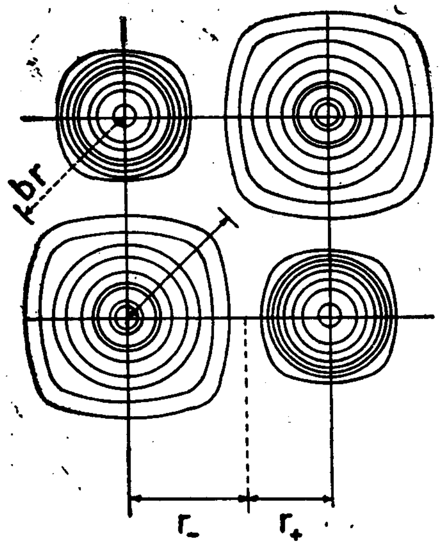

FIG. 2. Electron density plot in the (100) plane of NaCl (after Witte and Wölfel[9]) showing the non-spherical electron distribution in each ion. The ions extend to a distance r_+ and r_- respectively in the direction of the nearest neighbours and to a distance br in the direction of the next nearest neighbours.

The lattice energy function $W_L(r)$ given in (13) was used to fit the repulsion parameters for the five alkali ions Li^+, Na^+, K^+, Rb^+, Cs^+ and the four halogen ions F^-, Cl^-, Br^-, I^-.[13] The available data on the alkali halides were used for this. The lattice energy $W_L(r)$ itself is not very easily measured, neither is it very sensitive to the repulsion function. The equilibrium nearest neighbour distances and the compressibilities which depend on the first and second derivatives of $W_L(r)$ were the data used. These data are available over a range of pressures and the repulsion parameters were refined to fit them over the whole available range. In some cases where there is a phase transformation from NaCl to CsCl structure at high pressures, the data for these new structures were also fitted. This was possible because the second postulate clearly identifies the changes to be made on the repulsion function with change in coordination. Table I gives the final refined parameters for the nine alkali and halogen ions. Table II summarizes the range of validity of these parameters in the alkali halides. The refined parameters fit the experimental data very well justifying the model function used in (10).

TABLE I

Final refined repulsion parameters for the alkali and halogen ions

Ion	A (10^{-9} ergs)	ρ (10^{-9} cm)
Li^+	$7 \cdot 5 \times 10^{-3}$	1 90
Na^+	$6 \cdot 4 \times 10^{-2}$	1·815
K^+	0·34	1·848
Rb^+	2·7	1·574
Cs^+	6·5	1·645
F^-	0·60	1·545
Cl^-	3·0	1·67
Br^-	3·0	1·81
I^-	3·0	2·00

TABLE II

The repulsion parameters listed in Table I fit all the available data for the crystals listed below *

LiF	$\underline{\text{LiCl}}$	$\underline{\text{LiBr}}$	$\underline{\text{LiI}}$
NaF	$\underline{\text{NaCl}}$	$\underline{\text{NaBr}}$	$\underline{\text{NaI}}$
KF	$\boxed{\underline{\text{KCl}}}$	$\boxed{\underline{\text{KBr}}}$	$\boxed{\underline{\text{KI}}}$
RbF	$\boxed{\underline{\text{RbCl}}}$	$\boxed{\underline{\text{RbBr}}}$	$\boxed{\underline{\text{RbI}}}$
CsF	$\underline{\textit{CsCl}}$	$\underline{\textit{CsBr}}$	$\underline{\textit{CsI}}$

* Normal type—only atmospheric pressure data available—NaCl type structure.

Normal type underlined—high pressure data available—NaCl type structure.

Normal type underlined and boxed—high pressure data available on both lower and higher sides of a NaCl to CsCl type transformation.

Italics underlined—high pressure data available—CsCl type structure.

CONCLUSION

The picture of repulsion that we have presented is a simplification of a very complex phenomenon but it is our belief that even so simplistic a model is a first step to get an insight into the phenomena underlying the compressibility of ionic crystals. Even if we disregard the physical basis of our arguments and consider the ionic repulsion function we have proposed as one more of the many empirical functions, it has a number of advantages over the existing ones. These are enumerated below.

(1) The latest and most extensive calculation of the repulsion function in alkali halides is the work of Tosi and Fumi[14]. They have employed 26 parameters in their repulsion functions to describe 17 alkali halides (they did not fit CsCl, CsBr, CsI). We require only 18 parameters (one A and one ρ per ion) to fit all the 20 alkali halides listed in Table II.

(2) The repulsion functions of Tosi and Fumi fit the equilibrium nearest neighbour distances with a r.m.s. deviation of 1·45% and compressibilities with 15·4% r.m.s. deviations. The corresponding values for our theory, *viz.*, 0·997% and 6·76% make a very favourable comparison.

(3) Tosi and Fumi attempted only the fitting of atmospheric pressure data. Our repulsion parameters fit the alkali halides (except the fluorides for which reliable high pressure data are not available) in the whole pressure range from 0 to 45 kbars. To our knowledge, no other attempt has so far been made to fit the data over a range of pressures.

(4) Tosi and Fumi[15] refined a new set of parameters whenever a crystal underwent a phase transition. We have eliminated this concept of structure dependent parameters by using the same set of parameters in all phases. This is significant because the attractive interactions for the new phase can all be calculated (the new C and D coefficients are related to the corresponding values in the old phase). Thus, since the repulsion energy is also known, the theory can predict the properties of the new phase.

(5) In our formulation, if the repulsion parameters of an ion have been determined in one crystal of one structure, they can be used for that ion in any other compound of any other structure. 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, moreover, be valid over a range of pressures. Hence, in principle, all the properties can be calculated. This lends predictive power to our approach. In contrast, almost all earlier attempts fit some crystal-dependent parameters. They can hence never be used to predict the properties of a new system.

(6) As an offshoot of our calculations, we get the "radii" of the ions in the alkali halides. These compare fairly well with the experimental values[13]. Moreover, we also get the variation in the radius of an ion from one crystal to the other and with pressure in the same crystal.

We envisage in the future a number of extensions of the above type of calculations to systems other than the alkali halides. We are in particular considering alkaline earth halides and alkali and alkaline earth oxides and chalcogenides. In this context it would be very interesting to test the claim about the predictive power of this approach [point (5) above]. For instance, the repulsion parameters could be calculated for Ba^{++} from the compressibility data on BaF_2 using the known parameters of F^-. Similarly the parameters of S^{--} could be obtained from the alkali sulphides. Using these new parameters one could check whether the properties of BaS are well described. It is also hoped to extend the calculations to non-cubic structures if the computational problems are not too formidable and also to ionic radicals. Finally, there is the problem of *explaining* phase transitions. For this, more sophisticated models may be necessary.

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