

A new theory of compressible ions — structures of the alkali halides

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MS received 10 July 1979

Abstract. Ions in ionic crystals are considered to exist in compressible space-filling polyhedral cells analogous to the Wigner-Seitz cell in metals. Repulsion arises from the compression energy of the ions written as a surface integral over the ionic cells. Two adjustable parameters are introduced per ion with the provision that the same parameters can be used in any crystal of any structure in which the ion occurs. The 18 parameters for the 5 alkali and 4 halogen ions have been determined from PV data on the 20 alkali halides. The important successes of the theory are: (i) All the twenty alkali halides are correctly predicted to occur in their observed structures (ii) The thermal transition in CsCl is explained (iii) The pressure transitions in the alkali halides are predicted well (iv) The calculated values of the variation of transition pressures with temperature agree well with experiment. These results are much better than those obtained by earlier theories.

Keywords. Ionic crystals; stability of structures; compressibility; phase transitions.

1. Introduction

Most theories of cohesion in ionic crystals concentrate on calculating the repulsive forces since the attractive interactions in these crystals are well understood. The pioneering studies in this field were by Born (1923) who modelled the repulsion energy in binary ionic crystals by a simple function of the form

$$W_{\text{rep}}(r) = B/r^n, \quad (1)$$

where r is the interionic distance and B and n are adjustable parameters fitted from experimental data on the crystal of interest. Since then, there have been many modifications and extensions (Tosi, 1964 gives a review) which have attempted to study families of ionic crystals simultaneously by requiring certain parameters to be common to more than one crystal. These semi-empirical theories have been successful in fitting the lattice spacings and compressibilities of ionic crystals, notably in the alkali halides. However, none of them has so far explained the observed structures of these crystals. In the well-studied alkali halides, for instance, all semi-empirical theories have two significant discrepancies:

- (i) The crystals CsCl, CsBr and CsI, which are experimentally observed to occur in the CsCl structure, are wrongly predicted to be in the NaCl structure.

- (ii) Further, some of the lithium and sodium halides turn out to be stablest in the ZnS structure (this was recognised recently and pointed out by Narayan 1979).

To resolve the first discrepancy, it has been suggested (e.g., by May 1937, 1938; Jain *et al* 1976; Wallat and Holder 1978) that the van der Waals interaction in the alkali halides may be stronger than hitherto assumed; however, the van der Waals coefficients have to be increased almost three-fold, which is far-fetched. Moreover, this artificial measure does not resolve the second discrepancy (Narayan 1979).

Thus, the problem of the relative stability of the most simple ionic structures still remains unresolved although it has been recognised and attacked since the first theories of ionic crystals were proposed. This is one of the pre-eminent problems in the theory of cohesion of ionic crystals.

In this paper, we present a new theory of ionic crystals which has solved this long-standing problem in the alkali halides. It is a logical extension of our earlier theory of compressible ions (Narayan and Ramaseshan 1974, 1976, 1977) which is briefly recapitulated in § 2. We discuss the modification we have introduced in § 3 and outline the relevant equations for a binary cubic crystal (much of the theoretical derivation is relegated to appendix A). In § 4 we present the results of applying the modified theory to the alkali halides. The most interesting results are:

- (i) All the twenty alkali halides turn out to be most stable in their observed structures.
 (ii) Their pressure and thermal transitions are fairly well explained.

A preliminary account of the present work was recently reported in a letter (Narayan and Ramaseshan 1979).

2. Compressible ion theory

In this approach (Narayan and Ramaseshan 1974, 1976, 1977), we discard the traditional concept of incompressible spherical ions and instead assume that:

- (i) An ion is compressible, with a compression energy which is a function of its size. The repulsion energy in an ionic crystal arises solely from the compression energies of the individual ions. The Born expression for the lattice energy per formula unit in a binary ionic crystal is modified as

$$W_L(r, r_+, r_-) = -ae^2/r - C/r^6 - D/r^8 + W_+(r, r_+) + W_-(r, r_-), \quad (2)$$

where the first three terms are the electrostatic and van der Waals energies, r_+ and r_- are the 'radii' of the ions and $W_+(r, r_+)$ and $W_-(r, r_-)$ are their compression energies. Since nearest neighbours are assumed to be in contact,

$$r = r_+ + r_-. \quad (3)$$

Internal equilibrium further requires that

$$(\partial W_L / \partial r_+)_r = (\partial W_L / \partial r_-)_r. \quad (4)$$

Note that r_+ and r_- are *variables* which depend on the compressing force acting on the ions and so the 'radius' of an ion varies from crystal to crystal and with pressure in the same crystal.

(ii) The compression energy of an ion is taken to be the sum of contributions $A \exp(-r_i/\rho)$ from each contact it makes with its neighbours, where r_i is its 'radius' in the direction of the contact and A and ρ are parameters associated with the ion. For the cation, for instance, we write

$$W_+(r, r_+) = n_1 A_+ \exp(-r_+/\rho_+) + n_2 A_+ \exp(-br/\rho_+), \quad (5)$$

where n_1 and n_2 are respectively the number of nearest and next nearest neighbours and $2br$ is the distance between the ion and its next nearest neighbour. According to this concept, the ion is *not spherical*, its 'radius' being r_+ and br respectively in the direction of unlike nearest and like next nearest neighbours. This picture is strikingly borne out by the electron density maps of NaCl given by Witte and Wölfel (1958).

The theory has two parameters, A and ρ , associated with each ion, thus requiring only 18 parameters for all the 20 alkali halides. Moreover, the parameters that have been determined for an ion from one set of crystal data can be used in any other crystal in which the ion occurs. This lends predictive power to the theory. For instance, the same parameters have been used in both the NaCl and high pressure CsCl phases of alkali halides such as KCl. Moreover, the theory has successfully explained the lattice spacings and compressibilities of a number of perovskite-like crystals (Narayan and Ramaseshan 1978) without introducing any new adjustable parameters, but using only A and ρ values determined from data on other simpler crystals. In fact, the capacity for predictions gives the theory a great advantage over conventional ionic theories which require some of the parameters to be determined only from the experimental data on the crystal of interest, thus ruling out predictions on new systems.

3. The new model of compressible ions

Although the theory discussed above has the unique feature of transferability of parameters from one crystal to another, it fails to solve the problem of the relative stability of different structural modifications of ionic crystals. In a recent paper (Narayan 1979), it has been suggested that a probable reason for these discrepancies is that the simple formula (equation (5)) where the nearest and next nearest neighbour repulsion terms are directly scaled by the number of such neighbours (n_1 and n_2) may be too crude a simplification. One expects that, because of three-body interactions, the repulsion energy at any contact between two adjacent ions is not a function of their separation alone, but is, in fact, reduced by an amount depending on the proximity of other contacts.

Clearly, such an effect favours structures of higher coordination. One rather trivial way of incorporating this effect is through the introduction of more adjustable parameters. However, we present here an alternative physically more pleasing approach which is just an extension of the compressible ion theory discussed earlier and which does not require the introduction of any extra parameters.

In the new picture, we associate a face of contact at each point where two ions

touch. The perpendicular distances to the faces from the ionic centres are the 'radii' which entered the earlier theory. The faces surrounding an ion form a polyhedron and the crystal consists of two kinds of polyhedral cells filling space. This is a natural extension of the Wigner-Seitz cell concept (see e.g. Seitz 1940) to two types of cells associated with two kinds of ions. In fact, when the 'radii' r_+ and r_- in a binary crystal are equal, both polyhedra reduce exactly to the corresponding Wigner-Seitz cell (e.g., the two ionic cells in NaCl reduce to the cell of a simple cubic lattice, CsCl to bcc lattice, ZnS to diamond lattice, etc.). Where two like ions (i.e., next nearest neighbours) touch, the polyhedral face is required by symmetry to be the mid-plane between them. However, where two unlike ions (i.e., nearest neighbours) touch, the position of the plane cannot be fixed *a priori*, since the 'radii' r_+ and r_- are variables and not necessarily equal (though relations (2) and (3) fix r_+ and r_- , once r is given). In fact, the plane would move as a function of pressure and temperature. A few typical ionic polyhedral cells are shown in figure 1.

We now define the compression energy of an ion in a crystal in terms of the polyhedral cell in which it is situated. At each point on the surface of the polyhedron, we associate a compression energy density $(B/2\pi) \exp(-r'/\sigma)$, where r' is the distance of the point from the centre and B and σ are parameters. Thus, the compression energy of the cation, for instance, is the surface integral

$$W_+(r, r_+) = (B_+/2\pi) \iint \exp(-r'(S)/\sigma_+) dS, \quad (6)$$

with a similar expression for the anion (dS is an area element on the surface of the polyhedron at a distance $r'(S)$ from the centre). The above form of the compression energy is by no means unique, but it has the following realistic properties:

(i) $W_+(r, r_+)$ can be written as the sum of compression energies of polyhedral faces. Hence

$$W_+(r, r_+) = n_1 W_{+-} + n_2 W_{++}, \quad (7)$$

where W_{+-} and W_{++} are the energies of nearest and next nearest neighbour faces. Note the similarity to equation (5).

(ii) Each face energy varies approximately exponentially as its 'radius' because the maximum contribution comes from the face centre, reducing rapidly towards the edge. This, in combination with (7), shows that, to a first approximation, (6) is of the form (5), becoming closer at larger values of r .

(iii) The energy per face is reduced compared to that of an infinite plane at the same 'radius' by a quantity which is larger for smaller faces. Thus, the face energy at a given 'radius' is smaller in larger coordination structures. Such an effect is

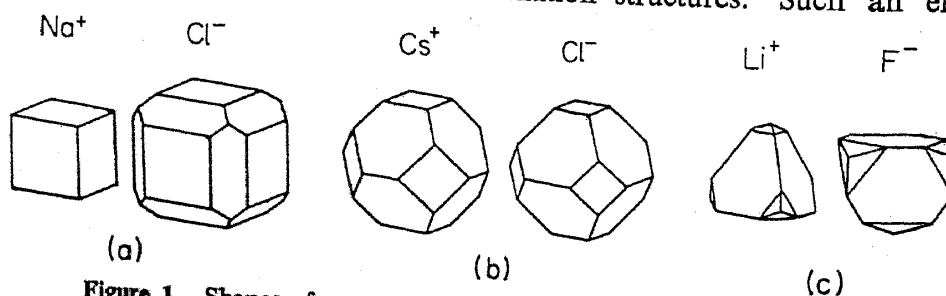


Figure 1. Shapes of some typical ionic cells (a) NaCl (b) CsCl (c) LiF (in a hypothetical ZnS structure).

expected as a result of three-body interactions and this is the crucial feature of the modified theory presented here.

Because of (iii), we expect the expression (6) to be closer to physical reality than the earlier expression (5). We wish to stress that the only modification introduced in this new extension of the theory is in the *form* of the compression energy. All the basic principles of the theory are still retained. We still have only two parameters per ion (B and σ are, in fact, related to the earlier parameters A and ρ). Moreover, we still retain the transferability of ionic parameters from one crystal to another, which is the most important feature of the theory.

At any temperature and pressure, the equilibrium interionic distance r in a crystal is obtained by solving a suitable equation of state. We have employed the equation of Hildebrand (1931) which leads to

$$dW_L/dr = 3x r^2 (-P + T\beta/K), \quad (8)$$

subject to conditions (2) and (3). Here, P is the pressure, T the temperature, B the coefficient of thermal expansivity, K the isothermal compressibility and xr^3 the volume per ion pair. The second derivative of W_L at equilibrium is then related to the compressibility by

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

Equations (8) and (9) require the derivatives of the compression energy (7). Expressions for these can be written down for simple structures with certain approximations and are discussed in appendix A.

4. Results on the alkali halides

4.1 Refinement of parameters

The twenty alkali halides are built out of the nine ions Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , F^- , Cl^- , Br^- and I^- . There are thus 18 adjustable parameters (9 B 's and 9 σ 's) to describe

Table 1. Compression parameters of the alkali and halogen ions

| Ion | B (ergs/cm ³) | σ (Å) |
|---------------|-----------------------------|--------------|
| Li^+ | 5.131×10^{10} | 0.06015 |
| Na^+ | 7.787×10^9 | 0.08501 |
| K^+ | 1.665×10^{10} | 0.09957 |
| Rb^+ | 5.036×10^{11} | 0.08755 |
| Cs^+ | 1.957×10^{11} | 0.10382 |
| F^- | 1.057×10^7 | 0.17322 |
| Cl^- | 3.677×10^7 | 0.18735 |
| Br^- | 4.119×10^7 | 0.19891 |
| I^- | 4.582×10^7 | 0.21473 |

Table 2. Comparison with experiment of the values of r and d^2W_L/dr^2 calculated with the present theory

| Crystal | Pressure | Structure | Nearest neighbour distance r (Å) | | | Ionic radii (Å) | | d^2W_L/dr^2 (10^5 ergs/cm 3) | | | W_{L+PY} (kcal/mole) |
|---------|----------|-----------|------------------------------------|------------|-----------|-----------------|--------|---------------------------------------|------------|-----------|---------------------------|
| | | | Observed | Calculated | Error (%) | r_+ | r_- | Observed | Calculated | Error (%) | |
| | | | | | | | | | | | |
| LiF | 0 | NaCl | 2.009 | 2.0174 | 0.418 | 0.8940 | 1.1234 | 2.391 | 2.3688 | -0.93 | -250.16 |
| LiF | 150 | NaCl | 1.907 | 1.9088 | 0.093 | 0.8680 | 1.0407 | 4.189 | 3.6823 | -12.10 | -218.50 |
| LiCl | 0 | NaCl | 2.570 | 2.5571 | -0.503 | 0.9362 | 1.6209 | 1.399 | 1.4624 | 4.53 | -203.09 |
| LiCl | 40 | NaCl | 2.482 | 2.4734 | -0.346 | 0.9167 | 1.5567 | 2.081 | 2.0278 | -2.56 | -185.36 |
| LiBr | 0 | NaCl | 2.751 | 2.7431 | -0.285 | 0.9497 | 1.7934 | 1.212 | 1.1926 | -1.60 | -190.45 |
| LiBr | 40 | NaCl | 2.634 | 2.6321 | -0.070 | 0.9250 | 1.7072 | 1.759 | 1.7924 | 1.90 | -168.96 |
| LiI | 0 | NaCl | 3.003 | 3.0255 | 0.750 | 0.9746 | 2.0509 | 0.801 | 0.8861 | 10.63 | -173.67 |
| LiI | 40 | NaCl | 2.843 | 2.8622 | 0.676 | 0.9402 | 1.9220 | 1.435 | 1.5365 | 7.07 | -145.72 |
| NaF | 0 | NaCl | 2.310 | 2.3350 | 1.084 | 1.1458 | 1.1892 | 1.612 | 1.6823 | 4.36 | -219.39 |
| NaCl | 0 | NaCl | 2.820 | 2.8227 | 0.094 | 1.1800 | 1.6426 | 1.268 | 1.1876 | -6.34 | -186.29 |
| NaCl | 40 | NaCl | 2.705 | 2.7057 | 0.025 | 1.1449 | 1.5608 | 1.948 | 1.8266 | -6.23 | -162.77 |
| NaBr | 0 | NaCl | 2.989 | 2.9632 | -0.863 | 1.1820 | 1.7812 | 1.038 | 1.0588 | 2.00 | -179.09 |
| NaBr | 40 | NaCl | 2.849 | 2.8246 | -0.855 | 1.1421 | 1.6825 | 1.760 | 1.7204 | -2.25 | -152.16 |
| NaI | 0 | NaCl | 3.236 | 3.2485 | 0.386 | 1.2124 | 2.0361 | 0.769 | 0.8049 | 4.67 | -163.73 |
| NaI | 40 | NaCl | 3.048 | 3.0531 | 0.168 | 1.1590 | 1.8941 | 1.465 | 1.5261 | 4.17 | -129.27 |
| KF | 0 | NaCl | 2.674 | 2.6824 | 0.315 | 1.4594 | 1.2230 | 1.272 | 1.2825 | 0.83 | -194.99 |
| KCl | 0 | NaCl | 3.147 | 3.1686 | 0.686 | 1.4917 | 1.6769 | 0.955 | 0.9761 | 2.21 | -168.82 |
| KCl | 15 | NaCl | 3.073 | 3.0927 | 0.642 | 1.4663 | 1.6264 | 1.283 | 1.2864 | 0.26 | -155.96 |
| KCl | 20 | CsCl | 3.189 | 3.1725 | -0.518 | 1.5055 | 1.6670 | 1.211 | 1.2311 | 1.66 | -151.63 |
| KCl | 40 | CsCl | 3.129 | 3.1103 | -0.597 | 1.4849 | 1.6254 | 1.637 | 1.5197 | -7.17 | -138.19 |
| KBr | 0 | NaCl | 3.300 | 3.3173 | 0.524 | 1.4947 | 1.8226 | 0.833 | 0.8781 | 5.41 | -162.64 |
| KBr | 15 | NaCl | 3.212 | 3.2275 | 0.481 | 1.4657 | 1.7617 | 1.214 | 1.2035 | -0.87 | -147.98 |
| KBr | 20 | CsCl | 3.346 | 3.3181 | -0.833 | 1.5097 | 1.8084 | 0.981 | 1.1325 | 15.45 | -142.88 |
| KBr | 40 | CsCl | 3.271 | 3.2458 | -0.771 | 1.4868 | 1.7590 | 1.472 | 1.4253 | -3.17 | -127.57 |
| KI | 0 | NaCl | 3.533 | 3.5531 | 0.568 | 1.5105 | 2.0426 | 0.734 | 0.7245 | -1.30 | -152.72 |
| KI | 15 | NaCl | 3.420 | 3.4348 | 0.434 | 1.4743 | 1.9605 | 1.153 | 1.0731 | -6.93 | -134.96 |

| | | | | | | | | | | | |
|------|----|------|-------|--------|--------|--------|--------|-------|--------|--------|---------|
| KI | 20 | CsCl | 3.579 | 3.5614 | -0.492 | 1.5304 | 2.0310 | 1.041 | 0.9822 | -5.65 | -127.24 |
| KI | 40 | CsCl | 3.492 | 3.4689 | -0.663 | 1.5026 | 1.9663 | 1.432 | 1.2867 | -10.15 | -108.48 |
| RbF | 0 | NaCl | 2.820 | 3.7930 | -0.958 | 1.5834 | 1.2096 | 1.268 | 1.3752 | 8.45 | -191.56 |
| RbCl | 0 | NaCl | 3.291 | 3.3132 | 0.673 | 1.6223 | 1.6908 | 0.982 | 0.9893 | 0.75 | -163.74 |
| RbCl | 10 | CsCl | 3.343 | 3.3309 | -0.362 | 1.6377 | 1.6931 | 1.091 | 1.1591 | 6.25 | -154.64 |
| RbCl | 40 | CsCl | 3.235 | 3.2309 | -0.126 | 1.6076 | 1.6233 | 1.703 | 1.6805 | -1.32 | -131.68 |
| RbBr | 0 | NaCl | 3.444 | 3.4919 | 1.392 | 1.6333 | 1.8586 | 0.846 | 0.8514 | 0.64 | -155.65 |
| RbBr | 5 | CsCl | 3.527 | 3.5430 | 0.453 | 1.6599 | 1.8831 | 0.928 | 0.9009 | -2.92 | -148.84 |
| RbBr | 40 | CsCl | 3.368 | 3.3901 | 0.658 | 1.6157 | 1.7744 | 1.485 | 1.5275 | 2.86 | -117.41 |
| RbI | 0 | NaCl | 3.671 | 3.6809 | 0.269 | 1.6335 | 2.0474 | 0.755 | 0.7598 | 0.64 | -149.64 |
| RbI | 5 | CsCl | 3.769 | 3.7438 | -0.669 | 1.6649 | 2.0789 | 0.819 | 0.7978 | -2.59 | -141.37 |
| RbI | 40 | CsCl | 3.580 | 3.5602 | -0.553 | 1.6147 | 1.9455 | 1.558 | 1.4367 | -7.78 | -104.73 |
| CsF | 0 | NaCl | 3.004 | 2.9689 | -1.167 | 1.7803 | 1.1886 | 1.444 | 1.3310 | -7.81 | -185.36 |
| CsCl | 0 | CsCl | 3.571 | 3.5850 | 0.391 | 1.8643 | 1.7206 | 0.898 | 0.9253 | 3.04 | -158.92 |
| CsCl | 40 | CsCl | 3.392 | 3.4207 | 0.846 | 1.8084 | 1.6123 | 1.569 | 1.7534 | 11.75 | -122.24 |
| CsBr | 0 | CsCl | 3.720 | 3.7322 | 0.328 | 1.8673 | 1.8649 | 0.903 | 0.8126 | -10.01 | -153.61 |
| CsBr | 40 | CsCl | 3.513 | 3.5385 | 0.727 | 1.8040 | 1.7345 | 1.556 | 1.6307 | 4.80 | -112.73 |
| CsI | 0 | CsCl | 3.956 | 3.9286 | -0.693 | 1.8716 | 2.0570 | 0.737 | 0.7116 | -3.45 | -147.65 |
| CsI | 40 | CsCl | 3.703 | 3.6967 | -0.170 | 1.7997 | 1.8969 | 1.443 | 1.5279 | 5.88 | -100.59 |

5.94

$\langle E^2 \rangle$ 0.622

them. These parameters were determined by least squares fitting the experimental values of r and d^2W_L/dr^2 (which is related to K) of the alkali halides. All the available high pressure data including those available on crystals beyond pressure transitions were included in the calculations. The van der Waals coefficients C and D were taken from Hajj (1966) and Mayer (1933) respectively while the other thermodynamic quantities required in (8) and (9) were taken from Tosi (1964). In certain cases where the small quantities $T\beta/K$ and $T/K [(\partial K/\partial T)_P + \beta/K (\partial K/\partial P)_T]$ were not available, certain reasonable approximations were made (see the appendix in Narayan and Ramaseshan 1978). During the least squares refinement, the weights were adjusted in such a manner that r was fitted 10 times more accurately than d^2W_L/dr^2 , this being our estimate of their relative accuracies. Also, the radius r_+ of Na^+ in NaCl was constrained at the value of 1.18 \AA given by experimental electron density maps (Witte and Wölfel 1958 give 1.17 \AA while Schoknecht 1960 gives 1.18 \AA). This was necessary because unconstrained refinement converged at r_+ about 1.10 \AA which is not good enough.

The parameters B and σ determined by the above procedure are listed in table 1 and the calculated values of r and d^2W_L/dr^2 are compared with the experimental values in table 2. The rms errors in r and d^2W_L/dr^2 are 0.62% and 5.9% respectively. This is better than the fit of 0.71% and 7.4% obtained with the simpler theory (Narayan and Ramaseshan 1977) discussed in §2. Since both theories use the same number of parameters, the better fit we now obtain appears to confirm that the modification we have introduced is in the right direction.

4.2 Stability of structures

Using the parameters of table 1, the free energies of the 20 alkali halides have been calculated in the three competing structures viz., NaCl , CsCl and ZnS at zero temperature and pressure. Apart from the contributions listed in eq. (2) we also included the zero point energy E_{zp} , which was calculated by means of the Debye theory result

$$E_{zp} = 9 k \theta_D/4, \quad (10)$$

where k is the Boltzmann constant and θ_D is the Debye temperature. The Debye temperature was approximately calculated from d^2W_L/dr^2 by the method discussed in appendix B.

When the above calculations are made, *all the 20 alkali halides are correctly predicted to occur in their observed structures*, a result which has been eluding theories of ionic crystals for the last fifty years. For comparison, we show in table 3 the predictions made by other standard potentials. The improvement obtained with the present theory is dramatic.

4.3 Thermal transition in CsCl

Using the high temperature expression for the thermal free energy

$$G_t = 6 k \ln (\theta_D/T), \quad (11)$$

Table 3. Structures predicted for the alkali halides by different theories.

| Crystal | Observed structure | Predicted structure | | | | |
|---------|--------------------|-------------------------|-------|------|-----------------------------|--------|
| | | Semi-empirical theories | | | Quantum mechanical theories | |
| | | HM | TF | PT | LJR | CG |
| LiF | NaCl | ZnS × | ZnS × | NaCl | NaCl | NaCl |
| LiCl | NaCl | ZnS × | ZnS × | NaCl | NaCl | NaCl |
| LiBr | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| LiI | NaCl | NaCl | ZnS × | NaCl | ZnO × | NaCl |
| NaF | NaCl | ZnS × | ZnS × | NaCl | NaCl | NaCl |
| NaCl | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| NaBr | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| NaI | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| KF | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| KCl | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| KBr | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| KI | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| RbF | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| RbCl | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| RbBr | NaCl | NaCl | NaCl | NaCl | NaCl | NaCl |
| RbI | NaCl | NaCl | NaCl | NaCl | NaCl | CsCl × |
| CsF | NaCl | NaCl | NaCl | NaCl | NaCl | — ? |
| CsCl | CsCl | NaCl × | — × | CsCl | CsCl | — ? |
| CsBr | CsCl | NaCl × | — × | CsCl | CsCl | — ? |
| CsI | CsCl | NaCl × | — × | CsCl | CsCl | — ? |

HM — Huggins and Mayer (1933); TF — Tosi and Fumi (1964); PT — Present theory; LJR — Lombardi *et al* (1969); CG — Cohen and Gordon (1975). Crosses are marked against wrong predictions.

given by Weston and Granato (1975), calculations have been made for finite temperatures on the relative stability of structures in the alkali halides. These indicate that CsCl alone will undergo a phase transformation below its melting point. Our calculations predict that it will transform to the NaCl structure at 890°K with a heat of transition of 1.65 kcal/mole. Experimentally also, CsCl is the only alkali halide to show a thermal transition, the observed transition temperature being 752°K and the heat of transition being variously estimated from 0.58 to 1.5 kcal/mole (Kaylor *et al* 1960; Zemczuzney and Rambach 1910; Krogh-Moe 1960; Rao *et al* 1966). The only earlier attempt (Rao *et al* 1966) to explain the thermal transition in CsCl employs adjustable parameters fitted to the transformation data itself.

4.4 Pressure transitions

Using the present theory, the relative stabilities of structures in the alkali halides have been obtained as a function of pressure. The calculated transition pressures are presented in table 4 along with the experimental values. For comparison, the pressures predicted by a typical Born-type theory are also listed. The present results are clearly superior.

The values in columns 3, 5 and 6 of table 4 were actually calculated at 0°K while the experimental values are for 300°K. However, it is experimentally known (Daniels

Table 4. Transition pressures in the alkali halides predicted by different theories.

| Crystal | Observed transition pressure (kbars) | Calculated transition pressures (kbars) | | | |
|---------|--------------------------------------|---|------|-----------------------------|------|
| | | Semi-empirical theories | | Quantum mechanical theories | |
| | | BMJ | PT | LJR | CG |
| LiF | >200 ^a | 300 | 380 | 517 | 2900 |
| LiCl | >200 ^a | 140 | >500 | 231 | 980 |
| LiBr | >200 ^a | 105 | >500 | 189 | 924 |
| LiI | >200 ^a | 68 | >500 | 127 | 184 |
| NaF | >200 ^a | 200 | 124 | 109 | 326 |
| NaCl | <257 ^b | 74 | 167 | 68 | 107 |
| NaBr | >200 ^a | 53 | 197 | 86 | 79 |
| NaI | >200 ^a | 44 | 460 | 78 | 23 |
| KF | 20 ^c | 88 | 59 | 14.1 | 85 |
| KCl | 19.5 ^c | 74 | 22.1 | 16.9 | 34 |
| KBr | 17.6 ^c | 59 | 23.3 | 18.6 | 23 |
| KI | 17.8 ^c | 49 | 36.2 | 16.6 | 3.6 |
| RbF | 6.2 ^c | 68 | 29.5 | 10.3 | 65 |
| RbCl | 4.9 ^c | 39 | 5.8 | 4.3 | 17.1 |
| RbBr | 4.5 ^c | 30 | 10.3 | 5.4 | 9.7 |
| RbI | 4.0 ^c | 22 | 12.1 | 4.8 | <0 |
| CaF | >200 ^a | 35 | >500 | 20.0 | — |

BMJ—Jacobs (1938) using the parameters of Born and Mayer (1932); PT—present theory; LJR—Lombardi *et al* (1969); Cohen and Gordon (1975)

- (a) No transitions have been reported
 (b) Ruoff and Chhabildas (1976)
 (c) Vaidya and Kennedy (1971) and Bridgman (1945)

Table 5. Observed and calculated values of dP_t/dT in the potassium and rubidium halides

| Crystal | dP_t/dT (kbar/°K) | |
|---------|--|------------|
| | Observed Petrunina <i>et al</i> (1972) | Calculated |
| KCl | — | 0.0020 |
| KBr | — | 0.0013 |
| KI | — | -0.0010 |
| RbCl | 0.0033 | 0.0037 |
| RbBr | 0.0020 | 0.0020 |
| RbI | 0.0010 | 0.0010 |

and Skoultchi 1966; Petrunina *et al* 1972) that the transition pressures are quite insensitive to temperature. Rather significantly, our theory also predicts a very small variation of P_t (the transition pressure) with temperature. Table 5 compares our calculated values of dP_t/dT with the experimental values. The agreement is again good. In this connection, the negative value of dP_t/dT predicted by our theory for KI is interesting. Experimental measurements on this crystal would be welcome.

5. Conclusion

To summarise, we view an ionic crystal as a collection of compressible ions in polyhedral, space-filling cells. Repulsion arises solely from the ionic compression energies of the ions, written as an integral over the polyhedral surfaces. The 18 adjustable parameters for the alkali halides have been determined from PV data and these lead to the following results:

- (i) They fit the observed lattice spacings and compressibilities of the alkali halides (including high pressure data) well.
- (ii) All the twenty alkali halides are correctly predicted to occur in their observed structures.
- (iii) The thermal transition in CsCl is explained.
- (iv) The transition pressures in the alkali halides are predicted quite well.

These results are superior to those obtained by earlier theories of ionic crystals. We may mention that, in parallel with the semiempirical approaches, quantum mechanical theories have also been occasionally tried. Tables 3 and 4 present the results obtained by two successful approaches (Lombardi *et al* 1969 and Cohen and Gordon 1975). Unfortunately, the calculations are quite laborious and have to be carried out in great detail (often requiring the inclusion of three body interactions) before good agreement with experiments is obtained. Even then, some of the alkali halides are predicted to occur in wrong structures and the transition pressures in the sodium halides invariably come out far too small. The quantum mechanical approach, because of its complexity, has not often been used, nor has it led to any real advance in our understanding of ionic crystals.

Acknowledgement

The authors wish to thank Dr Rajaram Nityananda for many valuable discussions.

Appendix A: Simplified equations of the theory

A.1 Compression energy of a face

In the present theory, the compression energy associated with an ionic polyhedral face is written in the form

$$W_{\text{rep}} = \iint \frac{B}{2\pi} \exp(-r(S)/\sigma) dS, \quad (\text{A1})$$

where B and σ are the repulsion parameters of the ion, $r(S)$ is the distance of the area element dS from the ion centre and the integral is over the area of the face. This integral, in general, cannot be evaluated analytically for the complicated polygonal faces that arise (see e.g., figure 1). We therefore replace the polygon by a circle of equivalent area (figure 2). Calling the radius of the equivalent circle as r and the distance of the circumference from the ion centre as l , we have

$$l^2 = r_i^2 + r^2 \quad (\text{A2})$$

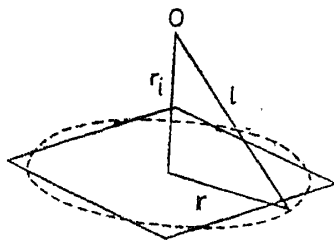


Figure 2. Simplified geometry assumed to minimise the calculations. Each face of an ion is replaced by a circle of equal area with radius r . O is the centre of the ion and r_i is the 'radius' of the ion in the direction of the face.

where r_i is the 'radius' of the ion in the direction of the face, under consideration (figure 2).

Equation (A1) is now simplified to

$$\begin{aligned}
 W_{\text{rep}} &= \int_0^r \frac{B}{2\pi} \exp(-t^2 + r_i^2)^{1/2} / \sigma \cdot 2\pi t dt \\
 &= \int_{r_i}^l B \exp(-u/\sigma) u du, \\
 &= B\sigma [(r_i + \sigma) \exp(-r_i/\sigma) - (l + \sigma) \exp(-l/\sigma)].
 \end{aligned} \tag{A3}$$

A.2 Total compression energy per molecule

Using the expression (A3) and employing a self-evident notation, the repulsion energy per molecule in a NaCl or CsCl lattice (ZnS is a little more complicated and will be considered later) is given by

$$W_{\text{rep}}(r, r_+, r_-) = W_{+-} + W_{-+} + W_{++} + W_{--}, \tag{A4}$$

where $W_{+-} = n_1 B_+ \sigma_+ [(r_+ + \sigma_+) \exp(-r_+/\sigma_+) - (l_{+-} + \sigma_+) \exp(-l_{+-}/\sigma_+)],$ (A5)

$$W_{-+} = n_1 B_- \sigma_- [(r_- + \sigma_-) \exp(-r_-/\sigma_-) - (l_{-+} + \sigma_-) \exp(-l_{-+}/\sigma_-)], \tag{A6}$$

$$W_{++} = n_2 B_+ \sigma_+ [(br + \sigma_+) \exp(-br/\sigma_+) - (l_{++} + \sigma_+) \exp(-l_{++}/\sigma_+)], \tag{A7}$$

$$W_{--} = n_2 B_- \sigma_- [(br + \sigma_-) \exp(-br/\sigma_-) - (l_{--} + \sigma_-) \exp(-l_{--}/\sigma_-)]. \tag{A8}$$

Expressions for the l 's can be worked out in terms of r , r_+ and r_- using the geometry of the polyhedra. These are written down below without derivation.

A.2a. NaCl lattice

(i) $r_+ > r_-$

$$l_{+-} = (2.273240 r_+^2 - 2.546479 r_+ r + 1.273240 r^2)^{1/2}, \tag{A9}$$

$$l_{-+} = 1.507727 r_- \quad (\text{A10})$$

$$l_{++} = (0.450158 r_+ r + 0.274921 r^2)^{1/2}, \quad (\text{A11})$$

l_{--} immaterial since the anion has *no* second neighbour faces.

(ii) $r_- < r_+$

Interchange $+$ and $-$ in equations (A9) to (A11). Now, l_{++} is immaterial.

A.2b. CsCl lattice

(i) $r_-/2 \leq r_+ < 2r_-$

$$l_{+-} = (-0.653987 r_+^2 + 1.653987 r_+ r - 0.275664 r^2)^{1/2}, \quad (\text{A12})$$

$$l_{-+} = (-0.653987 r_-^2 + 1.653987 r_- r - 0.275664 r^2)^{1/2}, \quad (\text{A13})$$

$$l_{++} = (1.909859 r_+^2 - 1.273240 r_+ r + 0.545540 r^2)^{1/2}, \quad (\text{A14})$$

$$l_{--} = (1.909859 r_-^2 - 1.273240 r_- r + 0.545540 r^2)^{1/2}. \quad (\text{A15})$$

For the cases $r_+ < r_-/2$ and $r_- < r_+/2$, a different set of equations are valid. We do not, however, present them here since, in these cases, the stable lattice is never CsCl.

A.2c. ZnS lattice

The expressions for W_{+-} and W_{-+} are similar to (A5) and (A6). However, for W_{++} and W_{--} , there are certain additional complications. Figure 3 shows the shape of the second neighbour face in the ZnS lattice for two different cases. The full lines show the actual shape of the face. When $r_+ < r_-/2$ the anion second neighbour face looks like the polygon ACDFGA in figure 3a (Note that in this case there is no cation second neighbour face). When $r_+ > r_-/2$, then the second neighbour faces of both the cation and the anion look like ABHA in figure 3b. In both figure 3a and 3b, P is the foot of the perpendicular from the ion centre on the face. The problem that arises in the cases considered here is that the faces are no longer symmetrical around P . Thus, it will not be a good approximation to replace the face by an equivalent circle centred at P . Instead, we have made the following decomposition

$$\text{Figure 3a: } ACDFGA = \frac{1}{2} (ACEGA + BCDFGHB), \quad (\text{A16})$$

$$\text{Figure 3b: } ABHA = \frac{1}{2} (ACEGA - BCDFGHB). \quad (\text{A17})$$

Since each of the decomposed polygons is symmetrical around P , each can be replaced by an equivalent circle without much error. Calling the distances of the

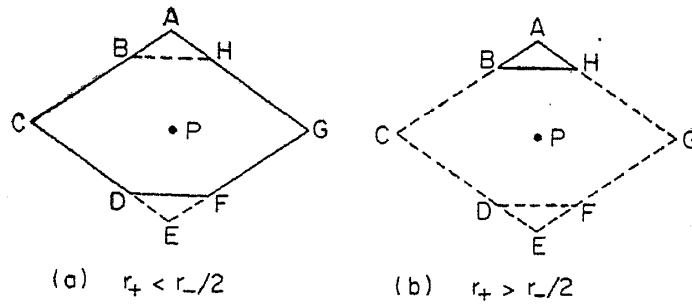


Figure 3. Shape of the second neighbour face in the ZnS lattice (a) when $r_+ < r_-/2$ and (b) when $r_+ > r_-/2$.

corresponding circumferences from the ion centre as l_{1++} for BCDFGHB and l_{2++} for ACEGA, one obtains the following expressions for W_{++} and W_{--}

$$W_{++} = \begin{cases} 0, & r_+ \leq r_-/2 \\ \frac{1}{2} n_2 B_+ \sigma_+ [(l_{2++} + \sigma_+) \exp(-l_{2++}/\sigma_+) - (l_{1++} + \sigma_+) \exp(-l_{1++}/\sigma_+)], & r_+ > r_-/2 \end{cases} \quad (\text{A18})$$

$$W_{--} = \frac{1}{2} n_2 B_- \sigma_- [(1+s)(br + \sigma_-) \exp(-br/\sigma_-) - \{(l_{1--} + \sigma_-) \exp(-l_{1--}/\sigma_-) + s(l_{2--} + \sigma_-) \exp(-l_{2--}/\sigma_-)\}],$$

where $s = \begin{cases} +1, & r_+ \leq r_-/2, \\ -1, & r_+ > r_-/2. \end{cases} \quad (\text{A19})$

The expressions for the l 's in the case of the ZnS structures are:

(i) $r_+ \leq r_-/2$

$$l_{+-} = 2.075566 r_+, \quad (\text{A20})$$

$$l_{-+} = (4.307973 r_-^2 - 6.615947 r_- r + 3.307973 r^2)^{\frac{1}{2}}, \quad (\text{A21})$$

l_{1++} and l_{2++} immaterial,

$$l_{1--} = 0.983245 r, \quad (\text{A22})$$

$$l_{2--} = (-2.700949 r_-^2 + 5.401898 r_- r - 1.734177 r^2)^{\frac{1}{2}}. \quad (\text{A23})$$

(ii) $r_+ > r_-/2$

$$l_{+-} = (-5.615947 r_+^2 + 6.615947 r_+ r - 1.102658 r^2)^{\frac{1}{2}}, \quad (\text{A24})$$

$$l_{-+} = (-5.615947 r_-^2 + 6.615947 r_- r - 1.102658 r^2)^{\frac{1}{2}}, \quad (\text{A25})$$

$$l_{1++} = 0.983245 r, \quad (\text{A26})$$

$$l_{2++} = (-2.700949 r_+^2 + 1.800633 r_+ r + 0.666667 r^2)^{\frac{1}{2}}, \quad (\text{A27})$$

$$l_{1--} = 0.983245 r, \quad (\text{A28})$$

$$l_{2--} = (-2.700949 r_-^2 + 1.800633 r_- r + 0.666667 r^2)^{\frac{1}{2}}. \quad (\text{A29})$$

A.3. Equations for crystal stability

In terms of the quantities described above, the free energy per molecule of a binary ionic crystal at 0°K is given by

$$\begin{aligned} W_L(r, r_+, r_-) = & -ae^2/r - C/r^6 - D/r^8 + W_{+-} + W_{-+} \\ & + W_{++} + W_{--} + xPr^3 + E_{zp}. \end{aligned} \quad (\text{A30})$$

For lattice equilibrium, the above expression should be minimized. This leads to the equations

$$(\partial W_{+-}/\partial r_+) + (\partial W_{++}/\partial r_+) = (\partial W_{-+}/\partial r_-) + (\partial W_{--}/\partial r_-), \quad (\text{A31})$$

$$\begin{aligned} \frac{ae^2}{r^2} + \frac{6C}{r^7} + \frac{8D}{r^9} + \frac{\partial W_{+-}}{\partial r} + \frac{\partial W_{-+}}{\partial r} + \frac{\partial W_{-+}}{\partial r_-} + \frac{\partial W_{++}}{\partial r} + \frac{\partial W_{--}}{\partial r} + \frac{\partial W_{--}}{\partial r_-} \\ + 3xPr^2 = 0, \end{aligned} \quad (\text{A32})$$

subject to the constraint

$$r = r_+ + r_-. \quad (\text{A33})$$

These equations are to be solved numerically. Then, d^2W_L/dr^2 can be obtained either numerically or by writing an expression for it in terms of second partial derivatives (we have done both and verified that they check).

There are a few interesting features in the algorithm used by us to solve the equilibrium equations (A31), (A32) and (A33). We do not discuss these here.

Appendix B: An empirical formula for the Debye temperature

To calculate the zero point energy of the lattice as well as the thermal free energy at finite temperatures (for which we use the expressions given by Weston and Granato 1975), we need the Debye Temperature of the crystal. Since we were able to trace θ_D for only a few of the alkali halides, for the others we used the approximate formula discussed here.

The Debye temperature θ_D is related to a suitable crystal frequency ν_c by means of the relation

$$h \nu_c = k \theta_D, \quad (\text{B1})$$

where h is Planck's constant and k is Boltzmann's constant. Now, in a simple-minded argument, ν_c may be considered to be primarily determined by B , the bulk modulus of the crystal and M , the mass of the atoms in the lattice. Using dimensional considerations, one can therefore write the following approximate expression

$$\theta_D = K \frac{h}{k} (B V^{1/3}/M)^{1/2}, \quad (\text{B2})$$

where V is the volume per atom and K is a dimensionless constant. Using the data given by Gschneidner 1964), K has been separately calculated for 62 elements. The mean value of K so obtained is 0.50 with a r.m.s. scatter of only ± 0.12 . The rather low scatter gives one confidence in the formula (B2).

We have taken the same result (B2) with $K=0.5$ for binary ionic crystals too. Here, V is the volume per ion and M is a mean mass calculated by

$$M = 2 M_a M_b / (M_a + M_b), \quad (\text{B3})$$

where M_a and M_b are the masses of the individual ions (the particular combination (B3) was chosen for M because this is the expression that occurs in the lattice dynamics of a diatomic linear chain).

Using the above formula, we have computed θ_D for all the alkali halides. Table 6 compares the calculated values for NaCl, KCl and KBr with the available experimental ones (Seitz 1940). The agreement is seen to be remarkably good (far better, of course, than the formula would warrant!) This suggests that the result (B2) can be used with some confidence to calculate θ_D in crystals where there is no experimental data available.

Table 6. Experimental and calculated Debye temperatures of some alkali halides.

| Crystal | Debye temperature θ_D (in °K) | |
|---------|--------------------------------------|---|
| | Experimental Seitz (1940) | Calculated from equations (B2) and (B3) |
| NaCl | 281 | 289 |
| KCl | 227 | 226 |
| KBr | 177 | 179 |

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