

## Theory of divalent ions in crystals

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**Abstract.** The divalent ions in alkaline earth chalcogenides are viewed as compressible objects and are treated within a purely ionic model. As in earlier studies on the alkali and ammonium halides, the ions are taken to be in the form of space-filling polyhedral cells and the compression energy, which is the source of repulsion, is written as a surface integral over the cell faces. A simple method of computing the repulsion energy in any crystal lattice of arbitrary symmetry is proposed and the repulsion parameters  $B$  and  $\sigma$  are refined for the divalent ions under study. The theory explains the predominant occurrence of the NaCl structure in the alkaline earth chalcogenides. Hard sphere radii are estimated for the tetravalent cations  $Ti^{4+}$ ,  $Sn^{4+}$  and  $Pb^{4+}$  using the repulsion parameters of  $O^{2-}$  ion and the data on the corresponding rutile structure oxides. These radii are seen to be consistent with the measured interionic distances in several compounds occurring in the perovskite structure. The free transfer of repulsion parameters among several structures, which is a key feature of the present approach to repulsion, is confirmed to be valid by the present study.

**Keywords.** Divalent ions; compressible ion theory; repulsion parameters; hard sphere radii.

### 1. Introduction

In a series of papers, Narayan and Ramaseshan (1976, 1978, 1979a, b) developed a compressible ion model of repulsion in ionic crystals. The theory treats compressibility as an ionic property and associates the repulsion energy between two ions with the compression energies of the individual ions. An early version (Narayan and Ramaseshan 1976, 1978), where the compression energy per bond was represented by a simple exponential function of the ionic radius, was later modified (Narayan and Ramaseshan 1979a, b) to empirically include many-body interactions. In this latter approach the ions are viewed as polyhedral, space-filling cells with the repulsion arising from the increased compression at the cell faces. This theory explained for the first time the structures of all the alkali halides and has, more recently, worked well in the ammonium halides (Raghurama and Narayan 1983b).

In view of its successes, it appeared worthwhile to extend the theory to other ions and crystals. In the present paper we study the alkaline earth chalcogenides, which are generally considered to be amenable to an ionic theory. At room temperature and pressure these compounds crystallize in the NaCl-type structure, except MgTe which occurs in the wurtzite structure. With a view to later extending the theory to more complicated structures, it was felt that a simpler formulation of the compressible polyhedral cell theory would be welcome. Section 2 presents such a formulation which is then used in § 3 to derive the repulsion parameters,  $B$  and  $\sigma$ , for the

divalent ions. A study of the structural stability of alkaline earth chalcogenides is carried out in § 4, where the theory is found to correctly predict the predominant occurrence of the NaCl structure. In § 5, the theory is extended to the noncubic rutile structure and hard sphere radii for tetravalent ions are derived. The radius of  $\text{Ti}^{4+}$  ion is found to be consistent with the experimental electron density map. Also, the radii of  $\text{Ti}^{4+}$  and  $\text{Sn}^{4+}$  fit the lattice spacings of several perovskite type crystals.

## 2. Simplified area theory

In the compressible ion model (Narayan and Ramaseshan 1979 a, b) a radius is associated with an ion in the direction of each of its nearest and next nearest neighbours. The ion is then pictured to be in the form of a polyhedron whose faces are perpendicular to the interionic bonds at distances from the ion centre equal to the corresponding radii. For each bond the sum of the radii of the ions is taken to be equal to the bond length and so the whole crystal is made up of space-filling polyhedra. The compression energy at the face  $i$  of an ion of polyhedral shape is assumed to be of the form

$$W_{\text{rep}} = \frac{B}{2\pi} \int \int \exp(-r'(s)/\sigma) ds, \quad (1)$$

where  $r'(s)$  is the distance from the centre of the cell to an area element  $ds$  on the face and the integral is over the face area.  $B$  and  $\sigma$  are the repulsion parameters for the ion under consideration. The cell face can be approximated to a circle of equal area (Narayan and Ramaseshan 1979b) and we can then write the compression energy of the  $i$ th face as

$$W_{\text{rep},i} = B\sigma [(r_i + \sigma) \exp(-r_i/\sigma) - (l_i + \sigma) \exp(-l_i/\sigma)], \quad (2)$$

where  $r_i$  is the distance to the  $i$ th face from the ion centre (referred to as the 'radius' of the ion) and  $l_i$  is the distance to the circumference of the corresponding circular cell face. The  $l_i$ 's depend on the interionic distance  $r$  as well as the crystal structure. Detailed formulae are given by Narayan and Ramaseshan (1979b) for the NaCl, CsCl and ZnS structures. However, the labour involved in deriving exact formulae for the different  $l_i$  can become quite excessive when one deals with other lower symmetry structures and this would defeat the very purpose of the present approach which seeks to develop a simple semi-empirical theory of repulsion. We present here an alternative simplified approach, where  $l_i$  is computed in terms of only the co-ordination number and ionic radii.

If there are  $n$  faces symmetrically disposed at equal distances from the ion centre, the solid angle subtended by each face at the centre is  $\phi = 4\pi/n$ . If the  $n$  faces are at different distances  $r_i$  from the centre, we may define a weighted average distance  $r_{\text{av}}$  as

$$r_{\text{av}} = \frac{1}{n} \sum_i r_i. \quad (3)$$

If  $r_i < r_{av}$ , the solid angle subtended by such a face will be greater than  $4\pi/n$  while the reverse will be true when  $r_i > r_{av}$ . Motivated by this we approximately write

$$\phi_i = 4\pi \left\{ 1/n + K/2 [1 - (r_i/r_{av})] \right\}, \quad (4)$$

where we have written  $\phi_i$  in a form which ensures that  $\sum_i \phi_i = 4\pi$ .  $K$  is a suitable constant which has to be determined. It can be easily shown that (4) leads to the following relation for  $l_i$

$$l_i = \frac{r_i}{1 - 2/n + K(r_i/r_{av} - 1)}. \quad (5)$$

The constant  $K$  has been estimated to be 0.85 by a least squares fit to the known exact values of the  $l_i$ 's (Narayan and Ramaseshan 1979b) in the NaCl, CsCl and ZnS structures.

The main advantage of relation (5) is that the only inputs required for the calculation of  $l_i$  are the number of nearest and next nearest neighbours and the corresponding radii. This formula, when applied to the alkali halides, reproduces the interionic distances and compressibilities with RMS deviations of only 0.23% and 0.47% respectively from the exact results of Narayan and Ramaseshan (1979b).

### 3. Repulsion parameters for divalent ions

Using the experimental data on the lattice spacings and compressibilities of the alkaline earth chalcogenides as a function of pressure, we have refined the parameters  $B$  and  $\sigma$  for all the constituent ions.

The free energy per molecule of the crystal is given by

$$W_L = -\frac{Ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_{rep} + PV, \quad (6)$$

where  $r$  is the nearest neighbour distance,  $P$  the pressure and  $V$  the volume per molecule. The Madelung constant  $A$  is known for the structures of interest (Tosi 1964). The van der Waal's coefficients  $C$  and  $D$  can be calculated (Narayan and Ramaseshan 1978) in terms of the polarisabilities of the ions and the effective number of participating electrons (Kim and Gordon 1974). However, we have recently shown (Raghurama and Narayan 1983a) that the polarisabilities of the chalcogen ions cannot be considered to be constants but must be taken to vary in the form

$$\alpha_{anion} = \alpha_0 (r/3)^n, \quad (7)$$

where the  $n$  value is 0.9. The effect is quite considerable and has to be taken into account.

In our calculations on the alkaline earth chalcogenides, the repulsion energy was computed using the simplified formulae (5). The actual procedure of optimising

the repulsion parameters  $B$  and  $\sigma$  is explained elsewhere (Narayan and Ramaseshan 1976, 1979b). In table 1 we give the refined parameters of the divalent ions. During the refinement, we included data on Pb, Sm, Eu and Yb chalcogenides and the parameters of these ions are also given. The RMS error between the calculated and observed interionic distances  $r$  in all the crystals included in the refinement is 0.76% while for  $d^2 W_L/dr^2$  it is  $\sim 17\%$ . The comparatively large error in the second differential (which is essentially proportional to the bulk modulus) could perhaps imply that our purely ionic model of these crystals is an over simplification.

Using the repulsive parameters of the chalcogen ions, we can determine repulsion parameters for other divalent cations. However, considering the low compressibility of cations compared to anions, we can assume the cations to be hard spheres to a first approximation. Then we have only one parameter per ion, the hard sphere radius, which can be fitted to reproduce the experimental interionic distances of the corresponding chalcogenides. The results for  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  are given in table 2.

#### 4. Structural stability studies

The compressible ion theory has been shown to satisfactorily explain the structures of the alkali and ammonium halides as well as the pressure and thermal transitions

Table 1. Repulsion parameters of divalent ions.

| Ion              | $B$ (ergs/cm <sup>2</sup> ) | $\sigma$ (Å) |
|------------------|-----------------------------|--------------|
| $\text{Mg}^{2+}$ | $9.832 \times 10^{10}$      | 0.0750       |
| $\text{Ca}^{2+}$ | $6.827 \times 10^{11}$      | 0.0784       |
| $\text{Sr}^{2+}$ | $2.271 \times 10^{11}$      | 0.0900       |
| $\text{Ba}^{2+}$ | $9.110 \times 10^{10}$      | 0.1050       |
| $\text{Pb}^{2+}$ | $5.176 \times 10^{10}$      | 0.1060       |
| $\text{Sm}^{2+}$ | $5.985 \times 10^{12}$      | 0.0769       |
| $\text{Eu}^{2+}$ | $1.432 \times 10^{14}$      | 0.0662       |
| $\text{Yb}^{2+}$ | $3.840 \times 10^{15}$      | 0.0556       |
| $\text{O}^{2-}$  | $9.672 \times 10^8$         | 0.2179       |
| $\text{S}^{2-}$  | $9.445 \times 10^8$         | 0.2646       |
| $\text{Se}^{2-}$ | $7.959 \times 10^8$         | 0.2867       |
| $\text{Te}^{2-}$ | $9.865 \times 10^8$         | 0.2933       |

Table 2. Hard sphere radii of some divalent ions.

| Ion              | Hard sphere radius (Å) |
|------------------|------------------------|
| $\text{Cd}^{2+}$ | 1.297                  |
| $\text{Mn}^{2+}$ | 1.127                  |
| $\text{Fe}^{2+}$ | 1.075                  |
| $\text{Co}^{2+}$ | 1.064                  |
| $\text{Ni}^{2+}$ | 1.033                  |

in these crystals, (Narayan and Ramaseshan 1979a, b; Raghurama and Narayan 1983b). We have carried out a similar study on the alkaline earth chalcogenides.

Experimentally, the most stable structure here happens to be the NaCl type, except for MgTe which exhibits a wurtzite type structure. The calculated free energies at 0°K of the various dichalcogenides were compared with the NaCl, CsCl and ZnS structures. The results showed that all the chalcogenides prefer the NaCl structure—even MgTe is predicted to occur in this phase. Thus, while the theory correctly identifies the NaCl structure as being the most likely, it appears to overestimate the stability of this phase. We note that the energy differences between the three structures is only about 1% of the total lattice energy. Apart from the Coulomb interaction, the other contributions to the free energy have been calculated through empirical models which could be in error. For instance, an error in the evaluation of the van der Waal's interaction cannot be ruled out. Also, we have completely neglected any possible covalency. At this stage, it is difficult to identify the precise source of the trouble.

### 5. Extension to rutile structure

One of the attractive features of the compressible ion theory is that the repulsion parameters are structure-independent and depend only on the ions concerned. Once the parameters  $B$  and  $\sigma$  of an ion have been determined from any set of experimental data the same parameters can be used for that ion in any other crystal in which it occurs. Thus, having obtained the parameters of the  $O^{2-}$  ion, we are now in a position to use them in other oxides. An interesting class of crystals are dioxides in the rutile structure. Calculations with these crystals would be an ideal opportunity to test the theory in a non-cubic structure.

Rutile has a tetragonal lattice with two molecules per cell (Wyckoff 1963). The atomic positions are (see figure 1)

$$\begin{aligned} \text{Ti}^{4+}: & (0, 0, 0) \\ & (0.5, 0.5, 0.5) \\ \text{O}^{2-}: & \pm(x, x, 0) \\ & \pm(0.5 + x, 0.5 - x, 0.5) \end{aligned} \quad (8)$$

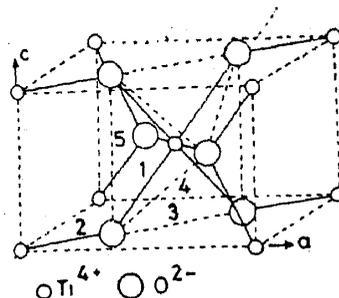


Figure 1. The unit cell of the tetragonal crystal rutile. The numbers refer to the bond types referred to in the text.

The  $x$  value is  $\sim 0.305$  in the oxides of interest to us. Each cation is held in a distorted oxygen octahedron, two oxygens being at a slightly different distance compared to the other four. The anion sites are non-centrosymmetric and thus the electric fields at these locations are non-zero. This leads to induced dipoles on the oxygen ions and thereby an additional polarisation energy. Though this contribution is not very significant (Bertaut 1978), for completeness we have included it in the free energy. Hence, we have per molecule

$$W_L(r) = -\frac{Ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + 2 [W_{\text{rep}} - \frac{1}{2} \alpha E^2], \quad (9)$$

where the first term is the Coulomb attraction which we have calculated by the method of non-overlapping charges (Bertaut 1978), the second and third terms represent the van der Waal's attraction, and  $W_{\text{rep}}$  is the compression energy per anion. We take the cation to be a hard sphere and hence there is no corresponding contribution to  $W_{\text{rep}}$ . The last term in (9) represents the polarisation energy, where  $\alpha$  is the anion polarisability [see equation (7)] and  $E$  is the magnitude of the electric field at the oxygen site. The factor of 2 accounts for two anions per molecule. The magnitude of the electric field at the anion site can be written as

$$E = S_E e/r^2,$$

where  $S_E$  is a lattice sum which we have evaluated using the method of Bertaut (1978). To make the treatment simple, the position parameter  $x$  in (8) is fixed at 0.305 and the  $c/a$  ratios in the various crystals are taken to be the experimentally observed values. The coefficients  $C$  and  $D$  are given in terms of the appropriate lattices sums  $S_{ij}$  and  $T_{ij}$  as

$$\begin{aligned} C &= c_{+-} S_{+-} + c_{++} S_{++} + c_{--} S_{--}, \\ D &= d_{+-} T_{+-} + d_{++} T_{++} + d_{--} T_{--}, \end{aligned} \quad (10)$$

where  $c_{ij}$  and  $d_{ij}$  are ion-dependent coefficients. The lattice sums of interest could not be found in the literature and were computed by summing in direct space (table 3).

We have studied three oxides *viz*  $\text{TiO}_2$ ,  $\text{PbO}_2$  and  $\text{SnO}_2$ . The polarisabilities of the cations  $\text{Ti}^{4+}$ ,  $\text{Pb}^{4+}$  and  $\text{Sn}^{4+}$  were taken to be 0.185, 1.12 and 3.4  $\text{\AA}^3$  respectively (Tessman *et al* 1953; Shanker and Verma 1976). The repulsion energy associated with the anion compression was computed using (2) and (5). Each anion has 3 surrounding cations. In  $\text{TiO}_2$ , two of the  $\text{Ti}^{4+}$  ions are at a shorter distance (Ti-O bonds marked 1 in figure 1) compared to the third (Ti-O bond, 2 in figure 1). The situation is reversed in  $\text{SnO}_2$  and  $\text{PbO}_2$ . There are a total of 11 next nearest neighbours around each  $\text{O}^{2-}$  ion. These are distributed in groups of 1, 8 and 2 ions (the corresponding O-O bonds are marked 3, 4 and 5 in the figure). Thus the compression energy of each anion is

$$W_{\text{rep}} = 2W_{-+}^{(1)} + W_{-+}^{(2)} + W_{--}^{(3)} + 8W_{--}^{(4)} + 2W_{--}^{(5)}, \quad (11)$$

Table 3. Calculations on oxides in the rutile structure.

|   | TiO <sub>2</sub> | SnO <sub>2</sub> | PbO <sub>2</sub> |
|---|------------------|------------------|------------------|
| Input Data  |                  |                  |                  |
| <i>a</i> (Å)  | 4.593            | 4.737            | 4.946            |
| <i>c</i> (Å)  | 2.959            | 3.186            | 3.379            |
| <i>r</i> (Å)  | 1.948            | 2.060            | 2.171            |
| <i>A</i>  | 19.099           | 19.129           | 19.025           |
| <i>S<sub>E</sub></i>  | 0.736            | 0.428            | 0.320            |
| <i>S<sub>+−</sub></i>   | 6.318            | 6.657            | 6.788            |
| <i>S<sub>++</sub></i>   | 0.230            | 0.238            | 0.241            |
| <i>S<sub>−−</sub></i>   | 1.655            | 1.780            | 1.828            |
| <i>T<sub>+−</sub></i>   | 5.861            | 6.272            | 6.435            |
| <i>T<sub>++</sub></i>   | 0.072            | 0.073            | 0.073            |
| <i>T<sub>−−</sub></i>   | 0.725            | 0.804            | 0.835            |
| Results   |                  |                  |                  |
| Cation radius<br><i>r<sub>+</sub></i> (Å)   | 1.196            | 1.340            | 1.348            |
| <i>d<sup>2</sup> W<sub>L</sub>/dr<sup>2</sup></i><br>(10 <sup>8</sup> erg/cm <sup>2</sup> ) |                  |                  |                  |
| Calculated  | 2.350            | 2.213            | 2.072            |
| Experimental  | 2.18             | ...              | ...              |

where the superscripts describe which type of contact is involved (figure 1 gives the code). Each term in (11) can be written in terms of  $B_{-}$  and  $\sigma_{-}$  using (2) and (5). The total free energy (9) is minimised with respect to the shortest interionic distance  $r$ . The equilibrium condition at temperature  $T$  is given by (Hildebrand 1931),

$$\frac{dW_L(r)}{dr} = \frac{3V}{r}(T\beta/K), \quad (12)$$

where  $\beta$  is the coefficient of thermal expansion and  $K$  is the compressibility. The experimental values of  $\beta$  and  $K$  were taken from Krishna Rao (1973), Ming and Manghani (1979) and Hazen and Finger (1981).

The radius of the tetravalent cation was optimised in each of the three dioxides studied so as to fit the experimentally observed interionic distance. The input data are given in table 4 along with the results. The calculated radii are much larger than the standard values. For example, we obtain a radius of 1.2 Å for Ti<sup>4+</sup> ion which is almost double the value (0.76 Å) quoted by Shannon (1976). From the available electron density map of TiO<sub>2</sub> (Baur 1956), we deduce the 'experimental' radius of Ti<sup>4+</sup> to be  $\sim 1.15$  Å. We consider this a strong experimental confirmation of our calculated radii. Moreover, our predicted compressibility of TiO<sub>2</sub> is within 8% of the measured value, again establishing the validity of our theory.

Another way to check the tetravalent cation radii is to predict the interionic distances in other structures where these ions may occur; e.g. the perovskite family. The results in table 4 show that the RMS error in the predicted cell dimensions in a

Table 4. Predictions on crystals in the perovskite structure.

| Crystal              | Cubic cell parameter (Å) |              |         | $d^2 W_L/dr^2$ ( $10^5$ ergs/cm <sup>2</sup> ) |              |         |
|----------------------|--------------------------|--------------|---------|--|--------------|---------|
|                      | Calculated               | Experimental | % error | Calculated                                     | Experimental | % error |
| BaTiO <sub>3</sub> * | 4.049                    | 4.012        | 0.92    | 7.63   | 5.99         | 27.4    |
| CaTiO <sub>3</sub>   | 3.908                    | 3.840        | 1.77    | 7.69   | ...          | ...     |
| SrTiO <sub>3</sub>   | 3.958                    | 3.904        | 1.38    | 7.75   | 6.34         | 22.0    |
| BaSnO <sub>3</sub>   | 4.155                    | 4.117        | 0.92    | 6.99   | ...          | ...     |
| SrSnO <sub>3</sub>   | 4.089                    | 4.033        | 1.39    | 6.81   | ...          | ...     |

\*at  $T = 474$  K; other data are at 300 K.

number of ABO<sub>3</sub> perovskites is only  $\sim 1.3\%$ . This again confirms that the radii of the tetravalent ions as well as the  $B$ ,  $\sigma$  values of the divalent ions are reliable and meaningful parameters describing the properties of these ions quite adequately. The bulk modulus agrees to within  $\sim 25\%$  in BaTiO<sub>3</sub> and SrTiO<sub>3</sub>, for which values could be traced (Huibregtse *et al* 1959; Okai and Yoshimoto 1975). This must be considered satisfactory in view of the long chain of calculations from the alkaline earth chalcogenides to rutile to the perovskites.

## 6. Conclusion

The compressible ion theory of repulsion has been applied to the alkaline earth chalcogenides using a simplified formulation of the polyhedral cell approach. The theory correctly shows that most of the crystals should occur in the NaCl structure. The repulsion parameters of the chalcogen ions have been used to derive hard sphere radii for a few divalent ions. Also, the theory has been extended to the rutile and perovskite structures where the interionic distances and compressibilities are satisfactorily predicted. These results indicate that the theory, which is based on a purely ionic picture, is quite valid for divalent ions in crystals. However, there is a mild discrepancy in the matter of the relative stability of different crystal structures. The present approach appears to overestimate the stability of the NaCl structure and underestimate the binding energies of the competing ZnO (or ZnS) and CsCl structures. The presence of covalency might possibly explain the discrepancy.

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