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Semi-quantitative theory of the structures of simple ionic crystals

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Abstract. A simple theory is developed which shows that the regions of stability of the CsCl, NaCl and ZnS structures can be demarcated in a two-dimensional plot of the radius ratio versus the strength of the van der Waals interaction. There is good agreement with experiment. The effect of pressure on these structures is explained qualitatively. The increased occurrence of the ZnS structure and the decreased stability of the CsCl structure in the A^{2+} B^{2-} crystals compared to the A^+B^- crystals is also explained. Finally it is shown that the radius ratio and the polarizabilities of the ions are the important factors that determine the structures of AB_2 crystals.

Keywords. Ionic crystals; crystal structures; repulsion potential; van der Waals interactions.

1. Introduction

A very interesting problem in solid state physics is to understand from first principles the underlying reasons for the various observed crystal structures. One tries to explain why a compound exists in one structure and not in any one of the numerous other structures it could have taken. Among the various types of crystals *e.g.*, ionic, covalent, metallic, molecular, etc., the problem appears to be most tractable in the case of the ionic crystals since the major interactions in these systems are fairly well understood. The binding energy per molecule of a simple *AB* type ionic crystal can be written in the form

$$W_L(r) = -\frac{\alpha Z^2 e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_{\text{rep}}(r), \tag{1}$$

where r is the interionic distance between nearest neighbours, α is a lattice sum called the Madelung constant, $\pm Ze$ are the charges on the ions, C and D are the van der Waals dipole-dipole and dipole-quadrupole interaction coefficients and $W_{\text{rep}}(r)$ is the repulsion potential. The Coulomb interaction term $-\alpha Z^2 e^2/r$, which is about ten times larger than the other terms in (1), can be calculated with great precision. Despite this favourable circumstance, theories of ionic crystals have had very little success in explaining their crystal *structures*. The most successful theory to date is that of Narayan and Ramaseshan (1979) which has provided a complete explanation for the structures and structural transformations of the alkali halides. No detailed theories are available for any of the other crystals* though there have been many

*There are more than five hundred crystals which are more or less ionic and which have simple crystal structures (Wyckoff 1971).

semiquantitative attempts at understanding crystal structures (*e.g.*, Kjekshus and Pearson 1964; Phillips and Van Vechten 1969; Simons and Bloch 1973; St. John and Bloch 1974).

At a qualitative level, an elegant picture, called the radius ratio approach (reviewed by Evans 1964), has been very popular. This method makes the following extreme approximations in an attempt to simplify the problem.

(a) Only the Madelung energy is considered when comparing different possible structures for a given compound.

(b) The van der Waals interactions are completely neglected.

(c) The repulsion energy is also neglected. However, the presence of repulsion is recognized by treating ions to be impenetrable hard spheres of characteristic radii (r_+ for the cation and r_- for the anion). Under normal circumstances (see (d) below for exceptions), the interionic distance is given by r_0, the sum of the radii,

$$i.e., \qquad r = r_0 = r_+ + r_-, \tag{2}$$

Thus, the lattice energy is approximated by $-\alpha Z^2e^2/(r_+ + r_-)$, suggesting that the structure with the largest α (*e.g.*, the CsCl structure among AB compounds) should be most stable.

(d) A study of the packing of ions in the various crystal lattices shows that sometimes, when the two ions are very dissimilar in size, next nearest neighbours may come into contact, resulting in r being greater than r_0

$$i.e., \qquad r > r_+ + r_-. \tag{3}$$

Because of this effect, it can be shown that, when the radius ratio r_+/r_- (for which we use the symbol $r_{+/-}$) is smaller than 0·73 or greater than 1·37, the NaCl structure is more stable than the CaCl structure. There is similarly a crossover from the NaCl to the ZnS structure at $r_{+/-} = 0{\cdot}41$.

The radius ratio method is based on a pleasing geometrical picture and makes apparently reasonable approximations. Unfortunately, the results are not very encouraging. Table 1 compares the observed structures (Wyckoff 1971) of 24 monovalent A^+B^- crystals and 64 divalent $A^{2+}B^{2-}$ crystals* with those predicted by the radius ratio method using the radii of Narayan (1979). (If we use the ionic radii given by others, the details change but the agreement continues to be poor). The theory seems

Table 1. Comparison of the number of compounds observed in the three simple AB structures with the predictions of the radius ratio method.

	A^+B^- Crystals		$A^{2+}B^{2-}$ Crystals	
Structure	Experiment	Radius ratio theory	Experiment	Radius ratio theory
CsCl	6	16	1	49
NaCl	18	6	57	12
ZnS	0	2	6	3

*Crystals such as ZnS, which are believed to have a high degree of covalency, have been left out. No distinction has been drawn between the ZnS and ZnO structures. Also, crystals with ionic radicals have not been included.

to grossly overestimate the stability of the CsCl structure. It is also unable to account for the curious reduction in the number of CsCl structures from the monovalent crystals (6 CsCl structures in 24 crystals) to the divalent crystals (1 CsCl structure in 64 crystals.)

In short, the simple radius ratio method is incapable of reliably predicting the structures of ionic crystals whereas the detailed theories, though adequate in principle, have not yet been developed to the stage where they can be routinely applied. There is therefore a need for intermediate theories which, while being more sophisticated than the radius ratio method, are still sufficiently simple and straightforward. We present such a theory in this paper. The main emphasis here is on AB type crystals. We show that the structure adopted by an AB compound depends on its location in a two-dimensional plot (figures 2 and 3). We further explain the differences between monovalent and divalent crystals and also the effect of pressure on these crystals. The present theory shows that the van der Waals interactions are very important in determining the crystal structure. This explains partly why the radius ratio method is inadequate. At the end of the paper it is argued that the polarization energy associated with permanent electric dipoles is an important factor in AB_2 crystals (Bertaut 1978). This leads to an empirical two-dimensional plot (figure 4) which seems to efficiently separate the structures of AB_2 crystals.

2. Theory

2.1 *Reference lattice*

We introduce a series of approximations to simplify the theory without losing any of the essential physics. We first introduce the ' reference lattice ' which we take to be the NaCl structure with no van der Waals interactions and where each ion experiences repulsion only with six nearest neighbours (*i.e.*, no second neighbour repulsion). If the radii of the ions are r_+ and r_- in this ideal lattice, then the lattice energy is

$$W_0(r_0) = -\frac{a_0 Z^2 e^2}{r_0} + 6A \exp(-r_0/\rho), \tag{4}$$

$$r_0 = r_+ + r_-, \tag{5}$$

where a_0 is the Madelung constant of the NaCl lattice and we have adopted the common exponential form of repulsion (see (10) below). The equilibrium condition on the lattice gives

$$(dW_0/dr)_{r=r_0} = \frac{a_0 Z^2 e^2}{r_0^2} - \frac{6A}{\rho}\exp(-r_0/\rho) = 0. \tag{6}$$

Equation (4) therefore simplifies to

$$W_0(r_0) = -\frac{a_0 Z^2 e^2}{r_0} + \frac{a_0 Z^2 e^2}{r_0}(\rho/r_0). \tag{7}$$

In the actual crystal of interest, a might be different from a_0, there would be van der Waals interactions and the repulsion would be different from that in (4). Consequently, the equilibrium nearest neighbour distance r_{eq} would be different from r_0. The lattice energy at equilibrium of such a crystal is

$$W_L(r_{eq}) = -\frac{a Z^2 e^2}{r_{eq}} - W_{vdW}(r_{eq}) + W_{rep}(r_{eq}). \tag{8}$$

As shown in (ii) below, the repulsion energy can be written in the form $n_{eff} A \exp(-r/\rho)$, where n_{eff} is the effective number of 'nearest' neighbours. Moreover, in general, r_{eq} is not very different from r_0. Hence, since r_{eq} is a true minimum of $W_L(r)$, we see that $W_L(r_0)$ and $W_L(r_{eq})$ differ only in second order terms, which we neglect. The lattice energy of a real crystal can then be written in the approximate form

$$W_L(r_{eq}) \simeq W_L(r_0) = -\frac{a Z^2 e^2}{r_0} - W_{vdW}(r_0) + \frac{n_{eff}\, a_0 Z^2 e^2}{6 r_0}(\rho/r_0), \tag{9}$$

where the last term is obtained through (7).

2.2 *Repulsion and effective number of nearest neighbours*

The commonly adopted Born and Mayer (1932) repulsion potential can be written in the form*

$$W_{rep}(r) = n_1 c \exp[(r_+ + r_- - r)/\rho] + \tfrac{1}{2} n_2 c [\exp(2r_+/\rho) + \exp(2r_-/\rho)] \exp(-2br/\rho), \tag{10}$$

where n_1 and n_2 are the numbers of nearest and next nearest neighbours around an ion, c is a constant and $2br$ is the distance between next nearest neighbours. The second term in (10), which is the repulsion arising from next nearest neighbour contacts, is in general significant only between the larger ions. Hence, if $r_- > r_+$, then we can drop the $+ +$ term (*viz.*, $\exp(2r_+/\rho)$ in (10) and vice versa. Identifying $c \exp[(r_+ + r_-)/\rho]$ as A, we can then write the repulsion energy at r_0 in the form (compare with (4))

$$W_{rep}(r_0) = n_{eff} A \exp(-r_0/\rho), \tag{11}$$

$$n_{eff} = n_1 + \tfrac{1}{2} n_2 \exp\left[\left(\frac{1}{r_{+/-} + 1} - b\right)\frac{2r_0}{\rho}\right], \tag{12}$$

where $r_{+/-}$ is the radius ratio r_+/r_- and we have assumed $r_- < r_+$. For the case $r_+ > r_-$, $r_{+/-}$ should be replaced by $1/r_{+/-}$ in (12). Apart from the obvious dependence of n_{eff} on the structural constants n_1, n_2 and b, we note that it also depends on

*We have omitted the β factors of Pauling (1928).

$r_{+/-}$ and r_0/ρ (which we call the hardness parameter). The dependence of n_{eff} on $r_{+/-}$ is a more quantitative version of the basic radius ratio theory. However, the dependence on the hardness parameter is new and interesting. The value of r_0/ρ varies from one crystal to the other. However, one can broadly divide the AB crystals into two classes—the monovalent A^+ B^- crystals with an average value of $r_0/\rho = 9{\cdot}7$ and the divalent $A^{2+}B^{2-}$ crystals with an average $r_0/\rho = 6{\cdot}8$ (from Narayan 1979). One sees that, unlike in the radius ratio method, in the present theory, monovalent and divalent crystals may be expected to behave differently. This is further discussed in § 3.

Figure 1 shows the variation of n_{eff} with $r_{+/-}$ for monovalent and divalent crystals in the CsCl, NaCl and ZnS lattices. It is reassuring that n_{eff} in the CsCl lattice increases rapidly for $r_{+/-}$ in the region of 0·73, the critical value in the radius ratio method. This shows that we have made the rigid radius ratio approach more quantitative without losing any of the physics. In the process, we have also introduced some new effects through the dependence of n_{eff} on r_0/ρ.

For convenience we have used the Born-Mayer form of the repulsion potential for the discussion in this paper. However, the results do not change qualitatively even if we use any of the other standard forms *e.g.*, the improved potentials of Narayan and Ramaseshan (1976, 1977, 1979).

2.3 *Van der Waals interactions*

In this theory, we entirely drop the van der Waals dipole-quadrupole term since this

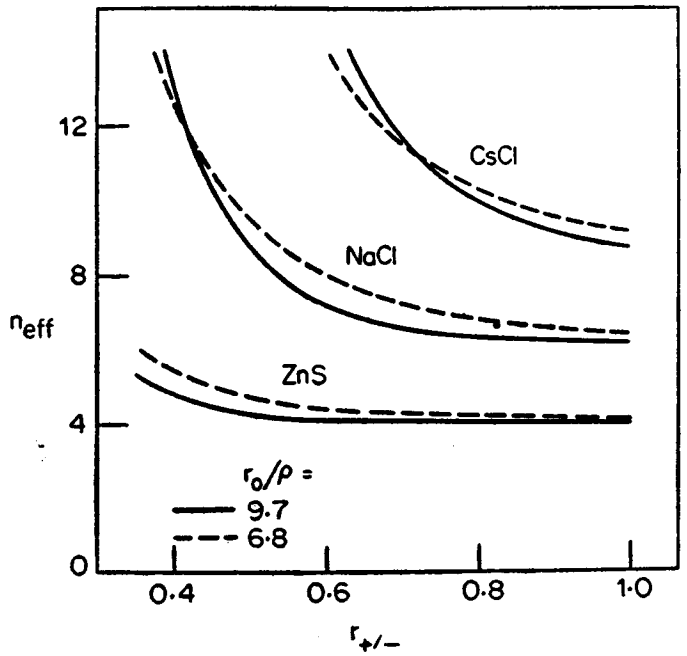

Figure 1. Variation of the effective number of neighbours with the radius ratio in the CsCl, NaCl and ZnS structures. The solid lines correspond to monovalent crystals (A^+B^-) with $r_0/\rho = 9.7$ and the dashed lines to divalent crystals ($A^{2+}B^{2-}$) with $r_0/\rho = 6{\cdot}8$.

is invariably much smaller than the dipole-dipole term. The dipole-dipole coefficient C in (1) can be written in the form

$$C = \beta c_{+-} + \gamma(c_{++} + c_{--}), \tag{13}$$

where β and γ are lattice sums and c_{+-}, c_{++}, c_{--} are pair-wise van der Waals interactions between cations and anions, cations and cations, etc. Since β is usually much larger than γ, we make the further approximation of dropping the second term in (13). Thus, we take the van der Waals interaction term in the form

$$W_{vdW}(r_0) = \beta c_{+-}/r_0^6, \tag{14}$$

2.4 *Relative stability of structures*

We are now in a position to approximately calculate the lattice energies $W_{L1}(r_0)$ and $W_{L2}(r_0)$ of a compound in two competing structures. Using (9) and (14), the marginal case of equal stability of the two structures leads to the equation

$$-\frac{a_1 Z^2 e^2}{r_0} - \frac{\beta_1 c_{+-}}{r_0^6} + \frac{n_{\text{eff}1}\, a_0 Z^2 e^2}{6r_0}(\rho/r_0) = -\frac{a_2 Z^2 e^2}{r_0}$$

$$-\frac{\beta_2 c_{+-}}{r_0^6} + \frac{n_{\text{eff}2}\, a_0 Z^2 e^2}{6r_0}(\rho/r_0), \tag{15}$$

$$i.e., \left[(a_2 - a_1) + \frac{a_0}{6}\left(\frac{\rho}{r_0}\right)(n_{\text{eff}1} - n_{\text{eff}2})\right] Z^2 e^2 = (\beta_1 - \beta_2)\frac{c_{+-}}{r_0^5}. \tag{16}$$

We notice that, for a given value of r_0/ρ, the left side of (16) is a function of only the radius ratio $r_{+/-}$ while the right side depends only on c_{+-}/r_0^5. Hence, the solution to (16) is a line in the $(r_{+/-})$ *vs* (c_{+-}/r_0^5) plane. This line would separate the regions of stability of structures 1 and 2. Figures 2 and 3 show the theoretically predicted regions of stability of the CsCl, NaCl and ZnS structures for the monovalent $(r_0/\rho = 9{\cdot}7)$ and divalent $(r_0/\rho = 6{\cdot}8)$ crystals.

3. Discussion of the results

The values of $r_{+/-}$ and c_{+-}/r_0^5 of a number of AB type crystals are plotted in figures 2 and 3. The radii r_+ and r_- of many ions have been tabulated by Narayan (1979). These were used to compute $r_{+/-}$. For some divalent cations, radii were not available and were therefore estimated from observed nearest neighbour distances using the known radii of the divalent anions. The van der Waals coefficient c_{+-} was computed for each crystal by means of the following variational formula due to Slater and Kirkwood (1931)

$$c_{+-} = \frac{3}{2}\frac{e\hbar}{m^{1/2}}\frac{a_+ a_-}{(a_+/N_+)^{1/2} + (a_-/N_-)^{1/2}}. \tag{17}$$

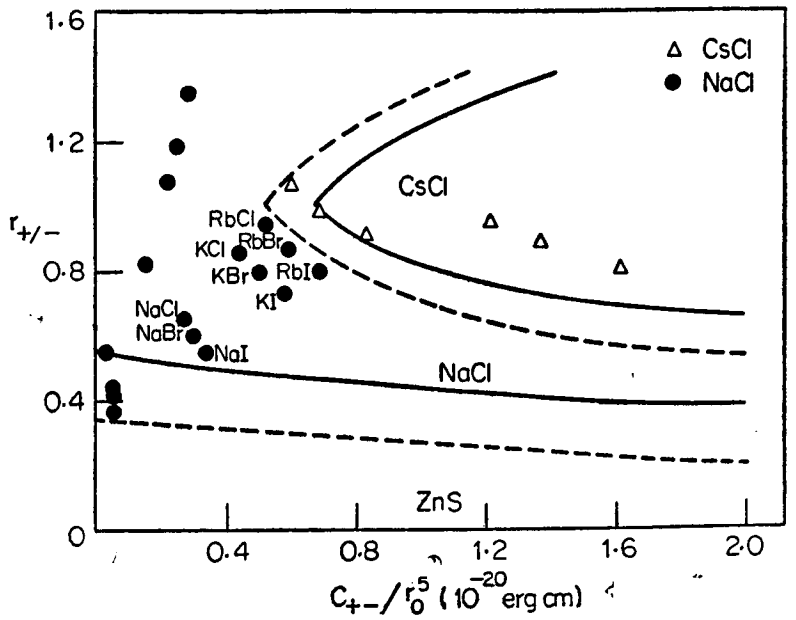

Figure 2. Areas of stability of the CsCl, NaCl and ZnS structures among monovalent AB crystals in the $(r_{+/-})$ *vs* (c_{+-}/r_0^5) plane. The solid lines are given by theory while the dashed lines have been empirically drawn for perfect separation of the observed structures.

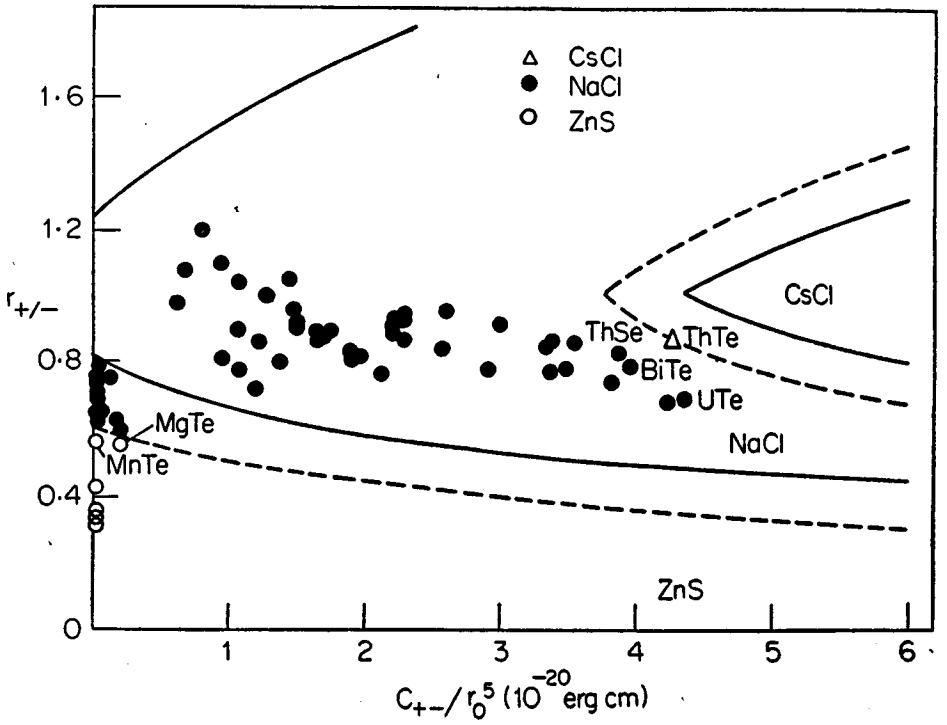

Figure 3. Areas of stability of the CsCl, NaCl and ZnS structures among divalent AB crystals in the $(r_{+/-})$ *vs* (c_{+-}/r_0^5) plane. The solid lines are given by theory while the dashed lines have been empirically drawn for perfect separation of the observed structures.

Here α_+ and α_- are the polarizabilities of the two ions, N_+ and N_- are the effective numbers of electrons participating in the interaction, e is the electronic charge, $\hbar$ is Planck's constant and m is the electronic mass. The polarizabilities are available for many ions and were estimated for the rest using the empirical trends in the variation of $\alpha_\pm$ along the periodic table of elements. The effective numbers of electrons were obtained for closed shell ions from Pitzer (1959) and were estimated for the others by interpolation.

Figures 2 and 3 show that the observed structures closely follow the demarcations obtained from theory. There are, of course, a few exceptions which are to be expected after making so many approximations. The general trend is however very clear. In fact, the empirical dashed lines in figures 2 and 3 separate the three structures perfectly.

The present theory shows that the van der Waals interaction has a profound influence on the crystal structure of a compound. This is one of the major defects of the radius ratio method which neglects the van der Waals interaction and therefore predicts structure crossovers at *fixed* critical radius ratios. Now we see that the critical radius ratio varies as a function of the van der Waals interaction. The present two-dimensional picture of areas of stability of various structures is thus a natural generalisation of the one-dimensional radius ratio approach. The second point to be noted is the sensitivity of the results to the hardness parameter r_0/ρ. The radius ratio approach is obviously making an oversimplification by taking all ions to have infinite hardness.

Figures 2 and 3 show that the most common structure to be expected is the NaCl lattice. This is in agreement with observation. Further, these figures explain some interesting differences observed between monovalent and divalent AB crystals. Six out of 24 monovalent crystals occur in the CsCl structure while only 1 out 64 divalent crystals does so. This is explained by noting that the area of stability of the CsCl structure is much smaller for divalent crystals compared to monovalent crystals. Similarly, the area of stability of the ZnS structure is larger in figure 3 than in figure 2 explaining the larger number of ZnS structures observed among divalent crystals.

The effect of pressure on crystal structures is also qualitatively explained by figures 2 and 3. One expects the following changes as a function of increasing pressure.

(a) Since anions are more compressible than cations (Narayan 1979), the radius ratio $r_{+/-}$ will increase with pressure. Also, since r_0 decreases with pressure, c_{+-}/r_0^5 will increase. The net result of these two effects is that the points in figures 2 and 3 will move towards the upper right hand corner.

(b) The free energy will have a PV term of the form

$$PV = xPr_0^3, \tag{18}$$

where x is a structure dependent number. We see from table 2 that this term is smallest for the CsCl structure and hence it tends to stabilise the CsCl structure relative to the NaCl structure. Similarly, the stability of the ZnS structure is expected to decrease at high pressures. Hence the lines in figures 2 and 3 will open out *i.e.*, the CsCl area will increase while that of ZnS will decrease.

With the above background, we can now qualitatively understand the pressure transitions in the alkali halides. It is experimentally observed that RbCl, RbBr and RbI transform from the NaCl to the CsCl structure around 6 kbars pressure while

Table 2. Relative volumes per ion pair in common AB structures at the same nearest neighbour distance

Structure	x
CsCl	1·54
NaCl	2·00
ZnS	3·08

the corresponding potassium halides transform around 19 kbars. The sodium halides transform only at very high pressures. The explanation on the basis of figure 2 is obvious since the rubidium halides are nearest to the phase boundary followed by the potassium and sodium halides. The locations of the points in figure 2 further show that the chloride, bromide and iodide of a given cation would all transform at approximately the same pressure while the fluoride would be expected to behave quite differently. This is also in accord with experimental results.

Figure 3 suggests that, with the application of pressure, ThSe, BiTe and UTe may transform to the CsCl structure, while MgTe and MnTe may transform to the NaCl structure. We are not aware of any pressure studies on these systems, and strongly urge that these be carried out.

4. Structures of AB_2 crystals

When we consider AB_2 and more complicated structures, there are new interactions to be considered which do not occur in the simple AB structures. Here the ions often occur in low symmetry sites. Consequently, there will be crystal electric fields which would polarize the ions, leading to permanent dipoles on the ions. Thus, even the electrostatic energy of the crystal becomes more complicated and takes the form

$$W_{el}(r_0) = -\frac{\alpha Z^2 e^2}{r_0} - \tfrac{1}{2}[\alpha_+ E_+^2 + \alpha_- E_-^2], \tag{19}$$

where α_+ and α_- are the polarizabilities of the two ions and E_+ and E_- are the electric fields at their sites. Bertaut (1978) has shown that the dipole energy is quite significant and has suggested that it might be the main reason for the occurrence of many AB_2 halides in the layered $CdCl_2$ and CdI_2 structures. Figure 4 is a striking confirmation of this. Motivated by (19), we have plotted the AB_2 halides in a two-dimensional plot of the radius ratio $r_{+/-}$ versus the sum of the ionic polarizabilities $(\alpha_+ + \alpha_-)$. We note that the four structures CaF_2, $PbCl_2$, SnO_2 and CdI_2* are clearly separated into different areas of the plane. The lines are empirically drawn. Although we have plotted $(\alpha_+ + \alpha_-)$, it will be noticed that $E_+ = 0$ in the CaF_2, SnO_2 and CdI_2 structures and is non-zero only in the $PbCl_2$ structure. It might appear that α_- alone is the relevant quantity for the first three structures. However, it is significant that in the majority of these structures, α_+ is much smaller than α_- and it is only in the $PbCl_2$ structure compounds that both α_+ and α_- are large.

*We do not distinguish between the CdI_2 and $CdCl_2$ structures.

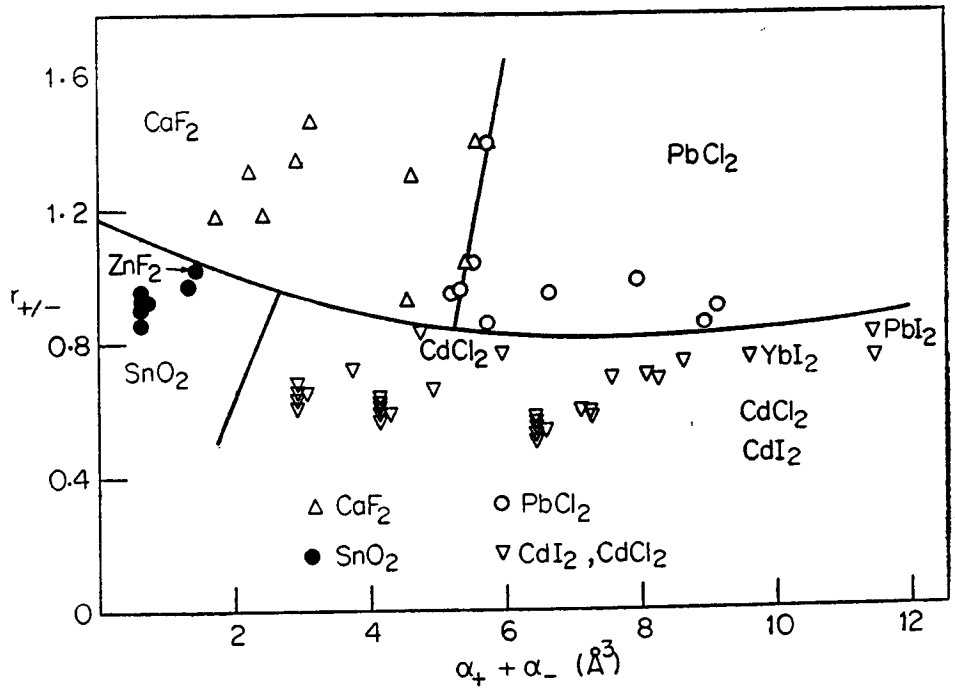

Figure 4. Areas of stability of the CaF_2, $PbCl_2$, SnO_2 and CdI_2 ($CdCl_2$) structures among $A^{2+}B_2^-$ halides. The separating lines have been drawn empirically.

It is easy to qualitatively understand the positions of the four structures in figure 4. The SnO_2 and CdI_2 structures are six coordinated *i.e.*, there are six nearest anions around each cation. The CaF_2 structure is eight coordinated and has a higher Madelung constant. The orthorhombic $PbCl_2$ structure is hard to describe in simple terms but can be said to have an effective coordination greater than six. Consequently, the CaF_2 and $PbCl_2$ structures occur at higher values of $r_{+/-}$ while the SnO_2 and CdI_2 structures occur at lower values. It should be noted that AB_2 structures do not have any symmetry between cations and anions and therefore there is no symmetry about $r_{+/-}=1$ as seen in figures 2 and 3. The right-left separation of structures in figure 4 is also understandable. In the CaF_2 structure, all ions occur in high symmetry points so that there is no dipole energy. On the other hand, in the $PbCl_2$ structure, all the ions develop dipoles. Hence, when the ionic polarizabilities are large, the dipole energy in this structure could compensate for the loss in the Madelung energy. Similarly, the CdI_2 structure has higher dipole energy than the SnO_2 structure (Bertaut 1978) but lower Madelung energy. Therefore, the SnO_2 structure occurs at low values of $(\alpha_+ + \alpha_-)$ and the CdI_2 structure at higher values.

In figure 4, ZnF_2 is seen to be close to the border between the SnO_2 and CaF_2 structures. This explains why this crystal transforms under pressure to the CaF_2 structure. $CdCl_2$, YbI_2 and PbI_2 are other good candidates for pressure studies. $CdCl_2$ would be particularly interesting since there is likely to be a three-way competition between the CdI_2, CaF_2 and $PbCl_2$ structures. It is hoped that a high pressure structural study of this compound will be taken up soon.

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