Some studies on the relative stabilities of the NaCl, CsCl and cubic ZnS structures in ionic crystals

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Abstract. The problem of the relative stability of ionic structures is still unsolved current semi-empirical theories wrongly predict the caesium halides to have the NaCl structure. We point out here that these theories also predict some of the other alkali halides to occur in cubic ZnS structure. To understand these discrepancies, we study the effect of various interactions (such as second neighbour repulsion, van der Waals interaction and differences in ionic compressibilities) on the relative stability of simple structures. The results throw into question the radius ratio approach. It is suggested that one could allow for the presence of three-body interactions by relaxing the requirement that the repulsion interaction should be strictly proportional to the number of neighbours. Such an approach might explain the relative stability of simple ionic structures.

Keywords. Ionic crystals; stability of structures; radius ratio; Börn theory.

1. Introduction

One of the outstanding problems in the theory of cohesion in ionic crystals is the question of the relative stability of even the simplest structures. Among the frequently studied alkali halides, the experimental observation is that all of them exist in the NaCl structure except CsCl, CsBr and CsI which take up the CsCl structure. Apart from some very detailed quantum mechanical calculations (e.g., Lombardi *et al* 1969; Cohen and Gordon 1975), no simple theory has made any significant progress in explaining the observed structures.

The earliest and simplest approach to the relative stability of ionic structures was based on the concept of radius ratio (see Evans 1964 for a discussion). This theory is basically qualitative and at best, only semi-quantitative. Although it has the advantage of simplicity, the very fundamental assumptions on which it is based may be questioned as will be shown in the present paper (§§ 2, 5.2). The approach is therefore not quite reliable.

Detailed theories of ionic crystals attempt to take into account the various known interactions present in these crystals. Since the attractive interactions are generally well understood, most theories concentrate on calculating the repulsive forces, the popular approach being semi-empirical. The pioneering studies were by Born (1923) who wrote the repulsion energy in a binary ionic crystal in the form B/r^n where r is the interionic spacing and B and n are parameters determined by fitting crystal data. This function was soon replaced by an exponential of the form $A \exp(-r/\rho)$ and has been further modified in many ways by later workers (Tosi 1964 gives a re-

view). All these theories have been quite successful in fitting the experimental lattice spacings and compressibilities of ionic crystals. But when the same potentials are used to calculate the free energies of competing structures to decide the stable structure, the results are often quite different from observation. In the alkali halides, there are two significant discrepancies (cf. table 1)

(i)   CsCl, CsBr and CsI are wrongly predicted to occur in the NaCl structure.

(ii) Some of the lithium and sodium halides are found to be more stable in the ZnS structure (this discrepancy is apparently being pointed out here for the first time).

There have been some suggestions such as van der Waals forces (May 1937, 1938; Jain *et al* 1976; Wallat and Holder 1978), multipolar deformation (de Wette 1959), etc., as to the important interaction determining the relative stability of structures, but none of them has been very convincing so far. Since there are a number of interactions and effects present in ionic crystals, the question is by no means straightforward. We attempt to clarify the issue in the present paper by presenting the results of a systematic study of the effect of various interactions on the relative stability of binary ionic structures. It is hoped that this will generate some new insight into and possibly a solution to the problem.

Table 1. Structures of the alkali halides predicted by the theory of Huggins and Mayer (1933). Wrong predictions are marked with crosses.

Crystal	Observed Structure	Structure predicted by Huggins and Mayer (1933)	
LiF	NaCl	ZnS	×
LiCl	NaCl	ZnS	×
LiBr	NaCl	NaCl	
LiI	NaCl	NaCl	
NaF	NaCl	ZnS	×
NaCl	NaCl	NaCl	
NaBr	NaCl	NaCl	
NaI	NaCl	NaCl	
KF	NaCl	NaCl	
KCl	NaCl	NaCl	
KBr	NaCl	NaCl	
KI	NaCl	NaCl	
RbF	NaCl	NaCl	
RbCl	NaCl	NaCl	
RbBr	NaCl	NaCl	
RbI	NaCl	NaCl	
CsF	NaCl	NaCl	
CsCl	CsCl	NaCl	×
CsBr	CsCl	NaCl	×
CsI	CsCl	NaCl	×

2. The radius ratio approach

The radius ratio approach to the relative stability of structures makes the following assumptions:

(i) Ions are hard spheres with fixed radii.

(ii) In the absence of contact between second nearest neighbours, the structure with the highest Madelung constant α occurs. In binary ionic crystals, this is the CsCl structure.

(iii) If the higher α structures have second neighbour contact, then the structure with the highest α among those not having such contact occurs. Thus, if CsCl is eliminated, NaCl structure occurs and if even this is not allowed, cubic ZnS structure occurs.

The presence or absence of second neighbour contact in a given structure is a geometrical question which evidently depends only on the radius of the constituent ions. Motivated by this, we use a plot of r_- (anion radius) against r_+ (cation radius) for the discussion in this paper. The twenty alkali halides have been marked on such a plot in figure 1a using the radii of Narayan and Ramaseshan (1976, 1977). On this figure, we can talk of regions of stability of the three simple structures CsCl, NaCl and ZnS. The experimental situation has been demarcated by the two lines. At large values of r_+, there is a region of stability of the CsCl structure; this region includes the crystals CsCl, CsBr and CsI. In the middle, there is the region of NaCl structures, which includes all the other alkali halides. Finally, at small values of r_+, we have introduced a region of stability for ZnS structure; this has been included on theoretical considerations, there being no experimental data here.

Using the experimental demarcations as reference, we have also shown in figure 1 the regions of stability predicted by the radius ratio approach. Here there is a problem because several estimates of ionic radii exist. Figure 1b corresponds to the classical ionic radii (Evans 1964) while figure 1c is obtained with the crystal radii of Shannon (1976). We may mention that the crystal radii are generally closer than the classical radii to actual ionic radii as obtained from x-ray electron density maps.

The results of the radius ratio approach are not very close to experiment, but they are rather good considering the qualitative nature of the argument. This is all the more surprising since, as we show in § 5, the underlying assumptions of the theory are quite questionable. One suspects the 'good' results of figure 1 to be a coincidence.

3. Predictions of current semi-empirical ionic theories

Taking the theory of Huggins and Mayer (1933), which is a typical semi-empirical theory of ionic crystals, we have calculated the predicted stable structure for the alkali halides. The results are shown in table 1.* We notice two kinds of discrepancies:

(i) The three crystals CsCl, CsBr and CsI are predicted to occur in the NaCl

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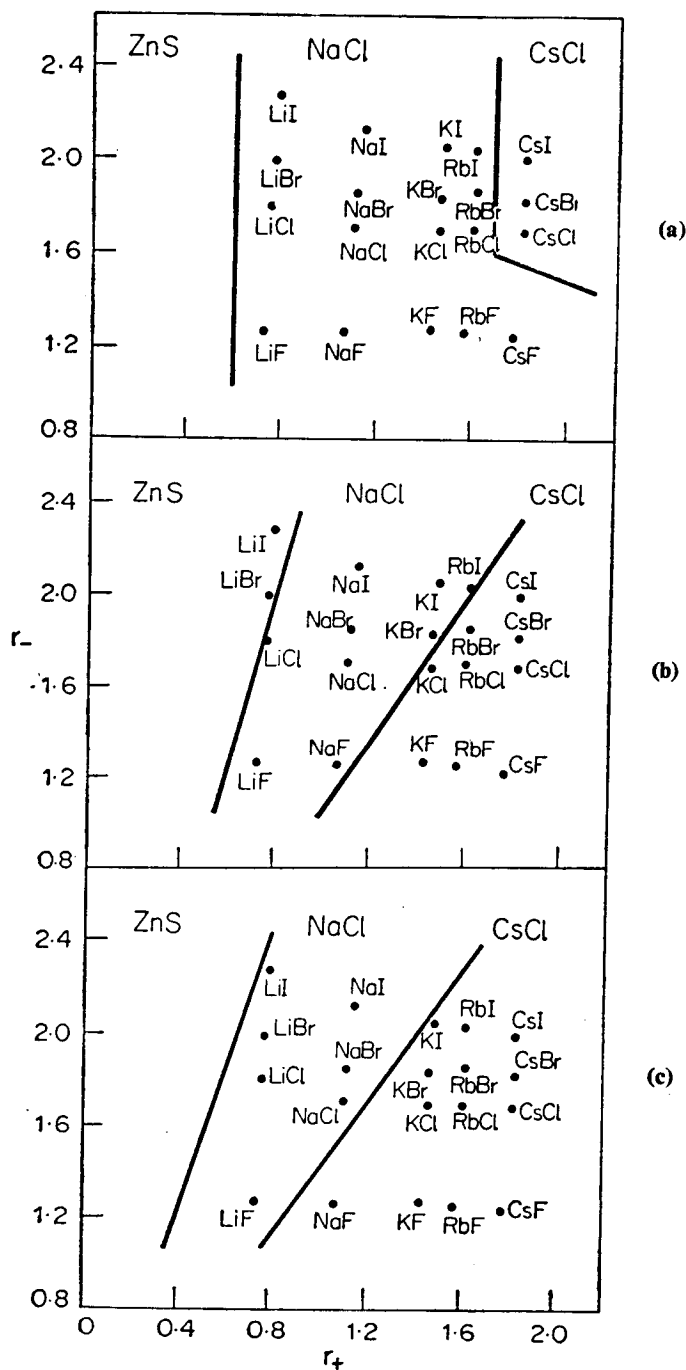*Other theories give similar results and so have not been included.

Figure 1. Regions of stability of CsCl, NaCl and cubic ZnS structures in the $r_+ - r_-$ plot of binary ionic crystals. (a) Experimental results. (b) Radius ratio approach using the classical ionic radii of Evans (1964). (c) Radius ratio approach using the crystal radii of Shannon (1976).

structure. This is a well-known problem and all attempts at resolving the question of relative stability of ionic structures have aimed at solving this, though without much success so far.

(ii) The three crystals LiF, LiCl and NaF are predicted to occur in the cubic ZnS structure. We have verified that this surprising and hitherto unrecognised defect is present in all other current theories of ionic crystals. The problem, it appears, is equally bad in divalent ion crystals; the predictions of the theory of Huggins and Sakamoto (1957), for instance, are shown in table 2. The surprising occurrence of the ZnS structure in ionic theories is explained in § 5.1(ii).

4. Effect of various interactions on the relative stability of structures

The few suggestions that have been made so far (such as increasing the van der Waals coefficients) have aimed at solving problem (i) above. Now that we recognise the presence of two discrepancies, at, so to say, opposite ends of the spectrum, the position becomes vastly more complicated and it is quite difficult to identify any single effect which could solve both problems. However, to make a beginning, we present here the effect of various prominent interactions on the relative stability of structures. The calculations and arguments are based on the compressible ion theory of ionic crystals (Narayan and Ramaseshan 1974, 1976, 1977; Narayan 1979).

Table 2. Structures of the alkaline earth chalcogenides predicted by the theory of Huggins and Sakamoto (1957). Wrong predictions are marked with crosses. No distinction is made here between cubic ZnS and hexagonal ZnO structures.

Crystal	Observed Structure	Structure predicted by Huggins and Sakamoto (1957)	
		$a = 2 \cdot 5 \text{Å}$	$a = 3 \cdot 0 \text{Å}$
BeO	ZnO	ZnS	ZnS
BeS	ZnS	ZnS	ZnS
BeSe	ZnS	ZnS	ZnS
BeTe	ZnS	ZnS	ZnS
MgO	NaCl	ZnS ×	ZnS ×
MgS	NaCl	ZnS ×	ZnS ×
MgSe	NaCl	ZnS ×	ZnS ×
MgTe	ZnO	ZnS	NaCl ×
CaO	NaCl	ZnS ×	ZnS ×
CaS	NaCl	ZnS ×	NaCl
CaSe	NaCl	NaCl	NaCl
CaTe	NaCl	NaCl	NaCl
SrO	NaCl	ZnS ×	NaCl
SrS	NaCl	NaCl	NaCl
SrSe	NaCl	NaCl	NaCl
SrTe	NaCl	NaCl	NaCl
BaO	NaCl	ZnS ×	NaCl
BaS	NaCl	NaCl	NaCl
BaSe	NaCl	NaCl	NaCl
BaTe	NaCl	NaCl	NaCl

To consider the effect of various interactions, we consider progressively more detailed pictures of ionic crystals, in each case delineating the regions of stability of the three simple structures in plots similar to those already discussed in figure 1.

(i) From the work of Narayan (1979), it is known that anions are much more compressible than cations. So, we initially assume the cations to be approximated by hard spheres of radius r_+. Also, as a crude first approximation, we consider the presence of only the Madelung energy among the attractive interactions and only first neighbour repulsion. These are the very minimum of features necessary to have a stable, compressible crystal. For this highly simplified model, calculations have been carried out for ionic crystals with the four anions F^-, Cl^-, Br^- and I^-, for cation radii r_+ ranging from 0 to 2 Å. The regions of stability so obtained are shown in figure 2b. Significantly, most of the area belongs to the NaCl structure with no region at all for the CsCl structure. Also, surprisingly, there is a small region of stability for the ZnS structure.

(ii) In the next set of calculations, the model of (i) above was improved by the inclusion of second neighbour repulsion. The results are shown in figure 2c. Now we see that CsCl has been pushed further away whereas ZnS has moved up, taking over all the lithium and one of the sodium halides.

(iii) In the next set of calculations, van der Waals interactions were also included. Using the known values of C and D for the alkali halides (Hajj 1966; Mayer 1933), values for hypothetical cations of intermediate radii were obtained by interpolation. The results (figure 2d) now show that the CsCl structure dramatically becomes competitive with NaCl for the larger cations, while the ZnS-NaCl boundary has hardly moved.

(iv) In the final set of calculations, the softness of the cations was also included so that this corresponds to the full theory, including all known effects. Here again, an interpolation was made for intermediate cations using the known univalent radii and compressibilities of the alkali ions (Narayan 1979). The results are shown in figure 2e. As mentioned earlier, in the full theory, the caesium crystals are more stable in the NaCl structure, though the heartening feature is that the boundary is not far away. However, the continuation of the ZnS region well within the range of the alkali halides is rather disturbing.

5. Discussion

5.1. *Results of figure* 2

The important results of the calculations depicted in figure 2 are:

(i) The CsCl structure occurs only when van der Waals interactions are considered and then too only when there are large, polarisable cations. The slightly larger value of α_{CsCl} compared to α_{NaCl} is inconsequential in deciding the relative stabilities of the two structures.

(ii) The lithium and some of the sodium halides are obtained in the ZnS structure. This result is hardly affected by the presence or absence of the van der Waals
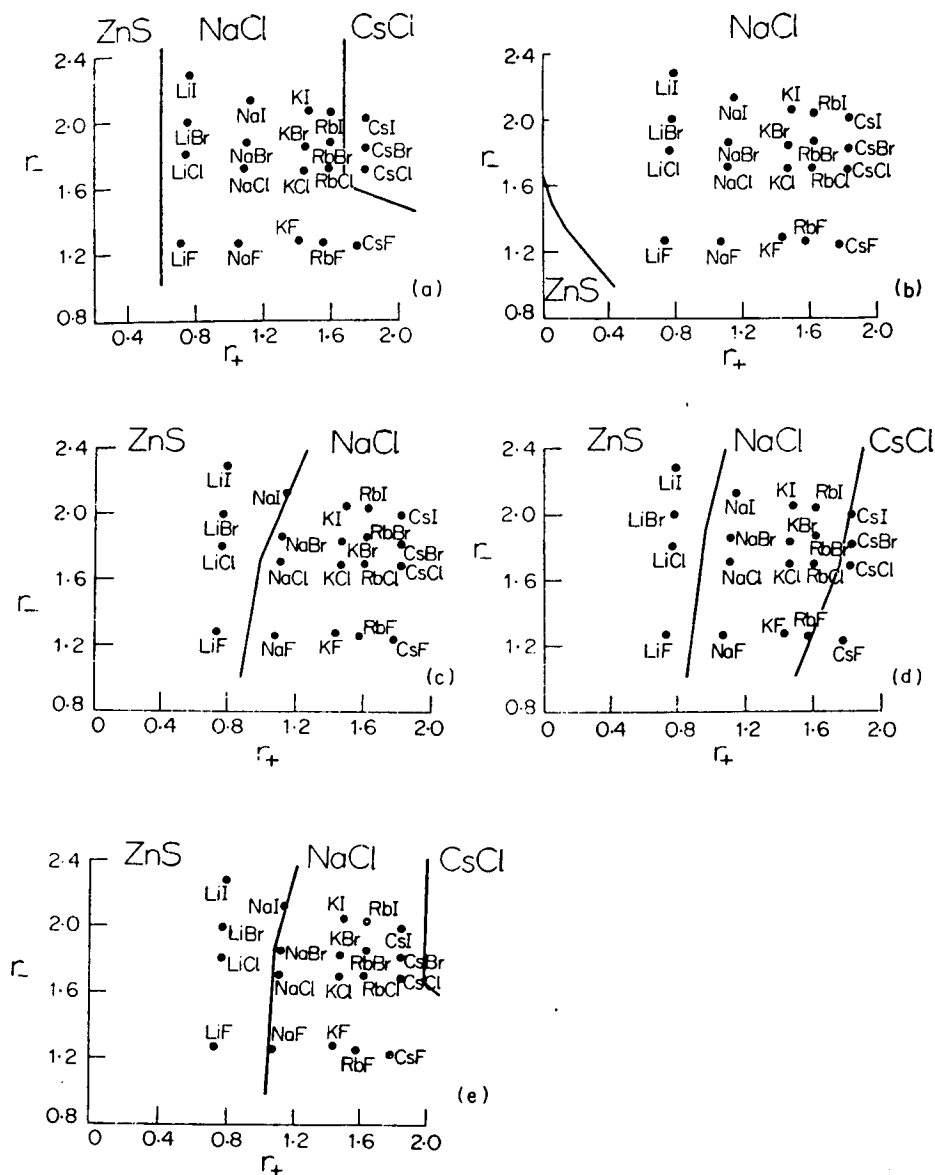
Figure 2. Regions of stability of CsCl, NaCl and cubic ZnS structures in the $r_+ - r_-$ plot of binary ionic crystals. (**a**) Experimental results. (**b**) Predictions with a highly simplified model having hard sphere cations and compressible anions and considering only Coulomb attraction and nearest neighbour repulsion. (**c**) Hard sphere cations and compressible anions; Coulomb attraction; nearest and next nearest neighbour repulsion. (**d**) Hard sphere cations and compressible anions; Coulomb and van der Waals attraction; nearest and next nearest neighbour repulsion. (**e**) Compressible cations and anions; Coulomb and van der Waals attraction; nearest and next nearest neighbour repulsion.

interactions. The occurrence of ZnS structure for some of the alkali halides needs some discussion. This fact has not earlier been mentioned anywhere in the literature. The general belief has been that the ZnS structure with its low value of α cannot occur in ionic crystals except in cases of abnormally large radius ratios. However, the low coordination number in ZnS actually causes a shift in equilibrium to smaller values of r, which in some cases can more than compensate the effect of smaller α. (Note: Madelung energy is $-\alpha\, e^2/r$). This can apparently stabilise the ZnS structure in many crystals (cf. tables 1 and 2).

(iii) Among the four sets of calculations discussed in § 4, the set (iii) is the closest to experiment, although set (iv) is the one which includes all the interactions.

5.2. *Implications for the radius ratio approach*

One of the definite results of the present calculations is that the radius ratio approach is thrown into doubt. In this approach, it is assumed that, in the absence of second neighbour repulsion, the CsCl structure would occur. On the other hand, the calculations of set (i) in § 4 where second neighbour repulsion is neglected show that CsCl does not occur at all. The reason is similar to that discussed in the previous paragraph *viz.*, that although $\alpha_{NaCl} < \alpha_{CsCl}$, r_{NaCl} is also $< r_{CsCl}$ and it turns out that in most cases $(\alpha\, e^2/r)_{NaCl} > (\alpha\, e^2/r)_{CsCl}$. Secondly, the radius ratio approach assumes hard sphere ions so that second neighbour repulsion arises only when the corresponding ions touch. On the other hand, in more realistic models, second neighbour repulsion occurs at all radius ratios *and is always higher in the CsCl structure*. Finally, our calculations show that the only interaction which favours the CsCl structure is the van der Waals interaction which is never considered at all in radius ratio calculations. Because of the above arguments, we believe that the radius ratio approach is not reliable and any correct results obtained from it are probably fortuitous.

5.3. *Implications for the problem of relative stability of structures*

(i) One of the popular approaches to the problem of the relative stability of structures is to attempt to increase the value of the van der Waals coefficients (e.g., May 1937, 1938; Jain *et al* 1976; Wallat and Holder 1978). Our studies indicate that this would stabilise the CsCl structure for larger cations. Since the NaCl-CsCl boundary is seen to be quite close to the crystals of interest (figure 2e), this would appear to be a promising line. However, it turns out that the value of C has to be increased almost three-fold, which is far-fetched. But, the bigger drawback to this approach is that the present calculations clearly indicate that the van der Waals interaction hardly affects the ZnS-NaCl boundary so that this method will not solve the problem of the occurrence of ZnS structures.

(ii) Set (iii) of § 4 seems closest to experiment. In this set of calculations, the cations are considered to be hard spheres. It is tempting to take this as a theory of ionic crystals in order to solve the problem of structural stability. However, the theoretical compressibilities of the crystals would then differ

considerably from the measured values, which is not acceptable. In fact, it was shown long ago by Hund (1925) that one can stabilise the CsCl structure by *reducing* the crystal compressibility.

(iii) We suggest here an alternate approach which is quite different from the main line of thought. A basic feature so far in all theories of ionic crystals is that the repulsion energy at a given interionic spacing is taken to be directly proportional to the number of neighbours. Thus, the nearest neighbour repulsion energies in CsCl, NaCl and ZnS structures at a constant value of r are taken to be in the ratios 8:6:4. We propose that this may not necessarily be so. Suppose the ratios are taken to be, say, 6:5:4. Obviously, this will shift the boundaries in figure 2e to the left; the important feature is that *both* boundaries (ZnS-NaCl as well as NaCl-CsCl) would move approximately to the same extent, which is a desirable objective. We point out that the above proposal is not as unreasonable as one might initially suppose. The presence of three-body forces will lead to similar effects. It is not without significance that the quantum mechanical theory of Lombardi *et al* (1969) requires the inclusion of three-body integrals to obtain reasonable results. We have incorporated the above suggestion in a physically attractive generalization of the compressible ion theory. The results, which are quite encouraging, are discussed in a forthcoming paper (Narayan and Ramaseshan 1979).

Acknowledgement

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