# E12 UNDERSTANDING CRYSTAL STRUCTURES

## 1 Introduction
In this experiment, the structures of many elements and compounds are rationalized using simple packing models. The pre-work revises and extends the material presented in the lecture course.

## 2 The Lattice Energy of Ionic Compounds
The compounds formed between elements of very different electronegativities are usually ionic in character. Ionic compounds are usually solids at room temperature, although ionic liquids also exist. They are held together in three-dimensional arrangements by the attractive forces between *every* pair of oppositely charged ions – not just by the interaction between neighbouring ions. The energy that is required to completely separate the ions is called the **lattice energy**.

The figures opposite show part of the structure of NaCl and the cubic unit cell which generates the whole lattice when repeated infinitely in all directions.

The distance between the ions is determined by the balance of the attractive force between cation and anion and the repulsive forces between both the core electrons of the ions and their nuclei.

The simplest model imagines that the ions are hard spheres with fixed radii. The ions touch but do not overlap. We first use this model to calculate the lattice energy and then show how the model is improved by including the compressibility of the ions.

If the charges on the cation and anion are $q_1$ and $q_2$, the attractive interaction between a pair is:

$$E_{\text{electrostatic}} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{q_1 q_2 e^2}{r}$$

where e is the charge on an electron, $\varepsilon_0$ is the permittivity of a vacuum and r is the distance between the centres of the ions.

**Figure 1**. The rocksalt structure.

In the sodium chloride structure, the $Na^+$ ion at the centre is surrounded by six $Cl^-$ at a distance r. The attractive potential energy is:

$$E_{\text{electrostatic}} = -6\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{q_1 q_2 e^2}{r} \tag{1}$$

The next nearest neighbours for the $Na^+$ ion are the twelve $Na^+$ ions on each edge of the unit cell, at a distance of $\sqrt{2}r$. This gives rise to a repulsive potential energy term:

$$E_{\text{electrostatic}} = +12\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{q_1 q_2 e^2}{\sqrt{2}r} \tag{2}$$
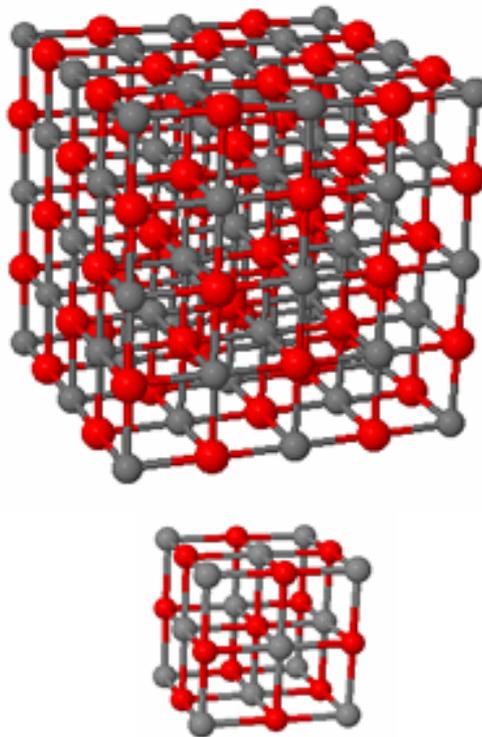
In the next shell, the $Na^+$ ion experiences an attractive potential energy with the eight $Cl^-$ ions at the corner of the unit cell, at a distance of $\sqrt{3}r$ :

$$E_{electrostatic} = -8\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{q_1 q_2 e^2}{\sqrt{3}r} \tag{3}$$

The net attractive energy between the $Na^+$ ion and all other ions in the crystal is given by the infinite (and slowly converging series):

$$E_{electrostatic} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{q_1 q_2 e^2}{r}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + ....\right) \tag{4}$$

This summation is repeated for every ion in the crystal (i.e. $2N_A$ ions per mole of NaCl). As this counts every interaction twice, it is then necessary to divide by two giving the total energy as:

$$\begin{aligned}
E_{electrostatic} &= -\frac{N_A q_1 q_2 e^2}{4\pi\varepsilon_0 r}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + ....\right) \\
&= -\frac{N_A q_1 q_2 e^2 A}{4\pi\varepsilon_0 r}
\end{aligned} \tag{5}$$

where the ***Madelung Constant***, A, is the numerical value of the infinite series summation. The Madelung constant depends *only* on the crystal structure *not* on the size or charge of the ions. Every compound with the rocksalt structure has the same Madelung constant. The table below lists the Madelung constant for a number of common structural types.

**Table 1.** The Madelung constant for common MX and $MX_2$ structures. The final column shows the Madelung constant divided by the number of ions in the chemical formula.

| Structural type | Coordination number | | Madelung constant, A | $\frac{A}{v}$ |
|---|---|---|---|---|
| | cation | anion | | |
| **1:1 MX** | | | | |
| Wurtzite | 4 | 4 | 1.63805 | 0.819 |
| Zinc Blende | 4 | 4 | 1.64132 | 0.821 |
| Rocksalt | 6 | 6 | 1.74756 | 0.874 |
| Caesium Chloride | 8 | 8 | 1.76267 | 0.881 |
| **1:2 $MX_2$** | | | | |
| Beta-quartz | 4 | 2 | 2.201 | 0.734 |
| Cadmium Chloride | 6 | 3 | 2.244 | 0.748 |
| Rutile | 6 | 3 | 2.408 | 0.803 |
| Fluorite | 8 | 4 | 2.51939 | 0.840 |

Note that, for a given stoichiometry, the Madelung constant and, hence, the lattice energy, increase with the coordination number:

**Solids adopt structures with higher coordination numbers to maximize the ionic bonding**

One curious feature of the expression in equation (5) is that the lattice energy has the largest magnitude when $r = 0$! The model does not implicitly include any repulsion between unlike charges. The hard sphere model instead imagines that the repulsion between ions with unlike charges is zero until they touch and is

then infinite. This turns out to be a poor approximation and equation (5) leads to lattice energies which are at least 10% greater than experimentally determined values.

A better treatment uses a repulsive force which is small at large separations but rises sharply when the ions come into contact. A possible function with this behaviour is $\dfrac{B}{r^n}$ where $n$ is large and both $n$ and $B$ are constants for each compound and can, in principle, be determined from measuring the compressibility of the crystal. The resulting lattice energy is the sum of the attractive term in equation (5) and this repulsive function:

$$E_{\text{electrostatic}} = -\frac{N_A q_1 q_2 e^2 A}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \tag{6}$$

At the equilibrium interatomic separation, $r_{eq}$, $E_{\text{electrostatic}}$ is minimized and $\dfrac{dE_{\text{electrostatic}}}{dr} = 0$. Differentiating equation (6) gives:

$$B = \frac{N_A q_1 q_2 e^2 A r_{eq}^2}{4\pi\varepsilon_0 n} \tag{7}$$

Substituting this into equation (6) gives the **Born-Landé equation**:

$$E_{\text{electrostatic}} = -\frac{N_A q_1 q_2 e^2 A}{4\pi\varepsilon_0 r_{eq}}\left(1 - \frac{1}{n}\right) \tag{8}$$

The $n$ value can be obtained from compressibility measurements and usually lies between 5 and 12. For ions with noble gas configurations, a reasonably accurate value for $n$ can be obtained by taking the weighted average of the empirical constants in the table below.

**Table 2.** Approximate compressibility factors, $n$, for ions.

| Noble gas configuration of ion | $n$ |
|:---:|:---:|
| He | 5 |
| Ne | 7 |
| Ar | 9 |
| Kr | 10 |
| Xe | 12 |

For example, $Na^+$ and $Mg^{2+}$ both have the same configuration as Ne and $Cl^-$ has the same configuration as Ar. The $n$ values for NaCl and $MgCl_2$ are thus:

$$\text{NaCl: } n = \frac{7+9}{2} = 8 \text{ and } MgCl_2\text{: } n = \frac{7 + (2\times 9)}{3} = 8.3$$

More recently, the repulsive part has been represented by the function $B\exp\left(-\dfrac{r}{\rho}\right)$ where $\rho$ is again determined from compressibility measurements and is typically $ca.$ 0.35.

Use of this function yields the **Born-Meyer equation**:

$$E_{\text{electrostatic}} = -\frac{N_A q_1 q_2 e^2 A}{4\pi\varepsilon_0 r_{\text{eq}}}\left(1 - \frac{\rho}{r_{\text{eq}}}\right) \tag{9}$$

The table below compares the experimental lattice energy for NaCl with that obtained using the hard-sphere model (equation (5)), the Born-Landé model (equation (8)) and the Born-Meyer model (equation (9)).

**Table 3.** Comparison of the experimental and calculated lattice energy for NaCl.

| Lattice Energy (kJ mol$^{-1}$) | | | | |
|---|---|---|---|---|
| **Experimental** | **Hard-Sphere** | **Born-Landé** | **Born-Meyer** | **Kapustinskii** |
| -772 | -858 | -762 | -752 | -753 |

The hard-sphere, Born-Landé and Born-Meyer equations unfortunately require knowledge of the Madelung constant and hence the crystal structure. They therefore cannot be used to predict stabilities of unknown compounds. The Born-Landé and Born-Meyer equations also require knowledge of the compressibility variables, $n$ and $\rho$ respectively.

Kapustinskii noticed that the Madelung constant divided by the number of ions in the chemical formula, v, is almost constant for many crystal structures. Table 1 includes the value of $\frac{A}{v}$ for various MX (v = 1), MX$_2$ (v = 3) and M$_2$X (v = 3) structures. It varies between 0.73 – 0.88. Kapustinskii also proposed using a universal value of $\rho$ = 0.345 and sums of tabulated values of cation ($r_+$) and anion ($r_-$ radii in place of the measured value of their separation in the structure. The result of these simplifications is, with all constants in SI units, the **Kapustinskii equation**:

$$E_{\text{electrostatic}} = -\frac{1.214\times10^5\, v q_1 q_2}{r_+ + r_-}\left(1 - \frac{0.345}{r_+ + r_-}\right) \tag{10}$$

As shown in Table 3, the Kapustinskii equation yields lattice energies which are very similar to those obtained using the more accurate equations. It has the distinct advantage that all it requires is knowledge of the chemical formula of the ionic compound.

**3 Which Crystal Structure Type Is Adopted?**
In this experiment, you will investigate the simple relationships between many different crystal structures. The question remains, however, which one will be adopted by any given compound? One simple factor is the stoichiometry of the compound – the ratio of the number of cations to anions is controlled by the need for the whole structure to be electrically neutral.

As noted above, for any given stoichiometry, the Madelung constant and hence the lattice energy increases with the coordination number of the cation and anion. This is the reason why higher coordination numbers are always favoured. However, as the coordination number around the cation increases, it becomes increasingly difficult to maintain cation-anion contact without the anions overlapping. This is the basis of the **radius ratio rules**. Details of the calculations are given in the appendix.

The table below lists the limiting radius ratio for different coordination numbers. If the relative size of the cation is smaller than the number indicated, the anions are no longer in contact with the cation and the structure is unstable. If the relative size of the cation is larger than the limiting value, the structure is stable as the anions do not touch. However, if the ratio exceeds the limiting value for a higher coordination number, the latter is adopted as it leads to a higher Madelung constant and lattice energy.

**Table 4.** Limiting radius ratios and common crystal structures for MX and MX$_2$ compounds.

| Cation Coordination Number | Limiting Radius Ratio $\left(r_+/r_-\right)$ | Possible Crystal Structures | |
| :---: | :---: | :---: | :---: |
| | | **MX** | **MX$_2$** |
| 3 | 0.150 | | |
| 4 | 0.225 | Zinc Blende, Wurtzite | Anti-Fluorite |
| 6 | 0.414 | Rocksalt, Nickel Arsenide | Rutile, Cadmium Chloride, Cadmium Iodide |
| 8 | 0.732 | Calcium Chloride | Calcium Fluoride |
| 12 | 1 | | |

## 4 Do The Radius Ratio Rules Work?

The figure below shows the actual structures adopted by the alkali metal halides – a set that must be considered the most ionic of all compounds. As can be seen, although the rules predict a spread of 4, 6, 8 and even 12-coordinate structures, all of the compounds except CsCl, CsBr and CsI actually adopt the rocksalt structure! The three exceptions have the CsCl structure. Clearly, the radius ratio rules should be used with extreme care.
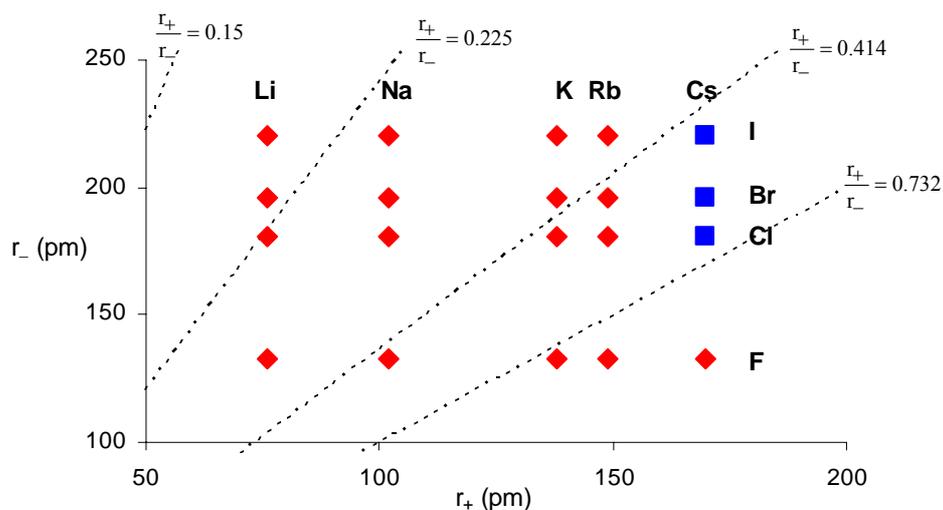


**Figure 2.** The relationship between the structures of the alkali metal halides (◆ NaCl and ■ CsCl) and ionic radii. The dotted lines showing the limiting radius ratios for 3, 4, 6 and 8 coordination.

**Limiting radius ratio for 8-coordination (caesium chloride structure)**

The figure opposite shows the CsCl structure in which the $Cs^+$ ion is surrounded by 8 $Cl^-$ ions.

To get as close to the cation as possible, the anions must touch along the edge of the cube. The side of the cube has a length, a, where:

$$a = 2r_-$$

Along the body diagonal, the $Cs^+$ is touching the two $Cl^-$ ions on either end so its length, d, is:

$$d = r_- + 2r_+ + r_- = 2r_+ + 2r_-$$

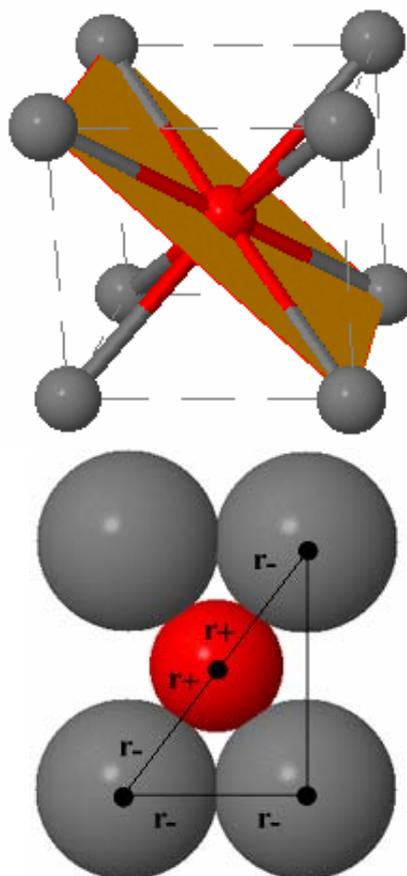Using Pythagoras' theorem, the length of the side and the body diagonal of a cube are related:

$$d^2 = a^2 + a^2 + a^2 = 3a^2 = 3 \times 4r_-^2 = 12r_-^2$$

$$d = 2\sqrt{3}\ r_-$$

So,

$$2r_- + 2r_+ = 2\sqrt{3}\ r_-$$

$$\frac{r_+}{r_-} = \sqrt{3} - 1 = 0.732$$

.

As long as the radius of the cation is *no smaller* than 73% that of the anion, the CsCl structure, with its high Madelung constant, is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch. If the cation is smaller than this, the cation and anion will not be in contact. A lower coordination number is then needed


**Limiting radius ratio for 6-coordination (sodium chloride structure)**

The figure opposite shows the NaCl structure in which the $Na^+$ ion is surrounded by 6 $Cl^-$ ions.

As shown overleaf, along the cube edge, the $Na^+$ is touching two $Cl^-$ ions so its length, a, is:

$$a = r_- + 2r_+ + r_- = 2r_+ + 2r_-$$

To get as close to the cation as possible, the anions must touch along the diagonal of a face of the cube. The diagonal has length, d, where:

$$d = r_- + 2r_- + r_- = 4r_-$$
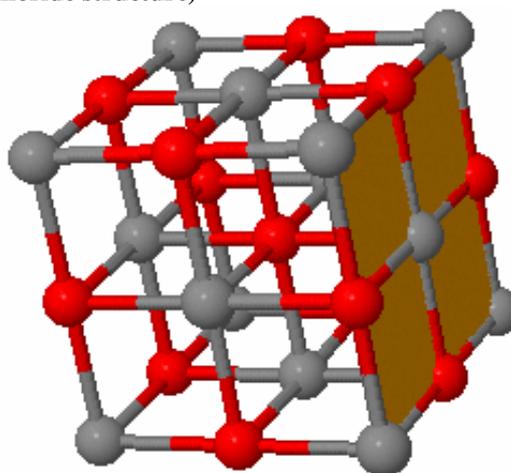
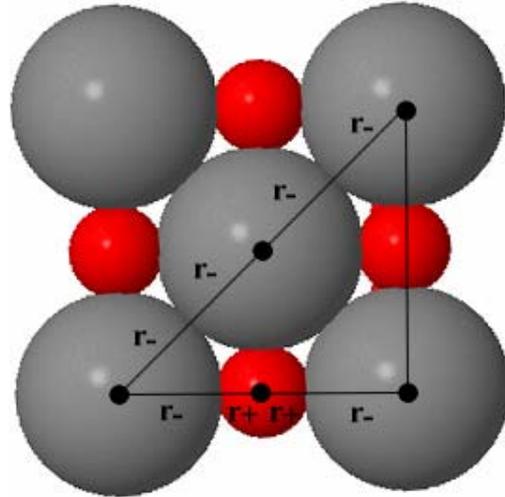Using Pythagoras' theorem, the length of the side and face diagonal of a cube are related:

$$d^2 = a^2 + a^2 = 2a^2$$

$$d = \sqrt{2}\, a$$

So,

$$4r_- = \sqrt{2}\,(2r_+ + 2r_-)$$

$$\frac{r_+}{r_-} = \sqrt{2} - 1 = 0.414$$



As long as the radius of the cation is *no smaller* than 41% that of the anion, the NaCl structure is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch but the CsCl structure is even more stable when the cation radius reaches 73% that of the anion.

If the cation radius is smaller than 41% that of the anion, the cation and anion will not be in contact. An even lower coordination number is then needed.

**Limiting radius ratio for 4-coordination (zinc blende structure)**
The figure opposite shows part of the ZnS structure in which the $Zn^{2+}$ ion is surrounded by 4 $S^{2-}$ ions.

The distance from the centre of the tetrahedron to the corner, d, is:

$$d = r_+ + r_-$$

To get as close to the cation as possible, the anions must touch along the edge of the tetrahedron. This distance, a, is

$$a = r_- + r_- = 2r_-$$

The tetrahedral angle, $\theta$, is 109.5° so
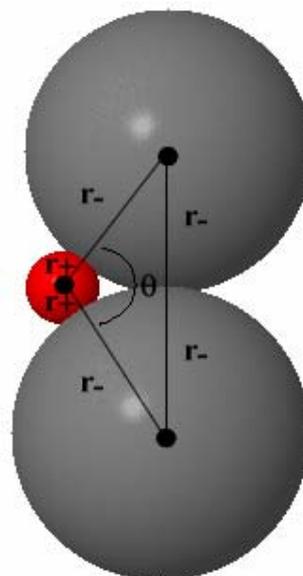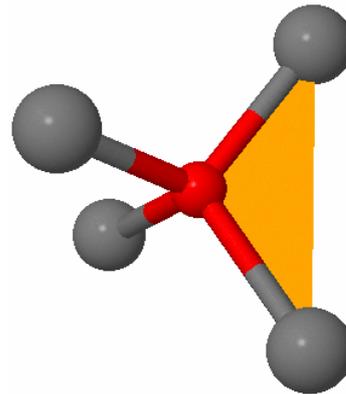
$$\sin\frac{\theta}{2} = \frac{r_+}{r_+ + r_-}$$

So,

$$\sin 54.7° = \frac{r_+}{r_+ + r_-}$$

$$\frac{r_+}{r_-} = 0.225$$

As long as the radius of the cation is *no smaller* than 23% that of the anion, the ZnS structure is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch but the NaCl structure is even more stable when the cation radius reaches 41% that of the anion.

If the cation radius is smaller than 23% that of the anion, the cation and anion will not be in contact. An even lower coordination number is then needed.