

Crystal lattices are in principle build up of very small identical units. The smallest existing unit is called a *unit cell*. These small building blocks/unit cells can be compared to Lego® building blocks. They are the smallest building units and they can be built up to constitute at very large structure. We are going to see several of these unit cells in the description of the different crystal lattice structures in this section. We are mainly going to look at the four major types of structures:

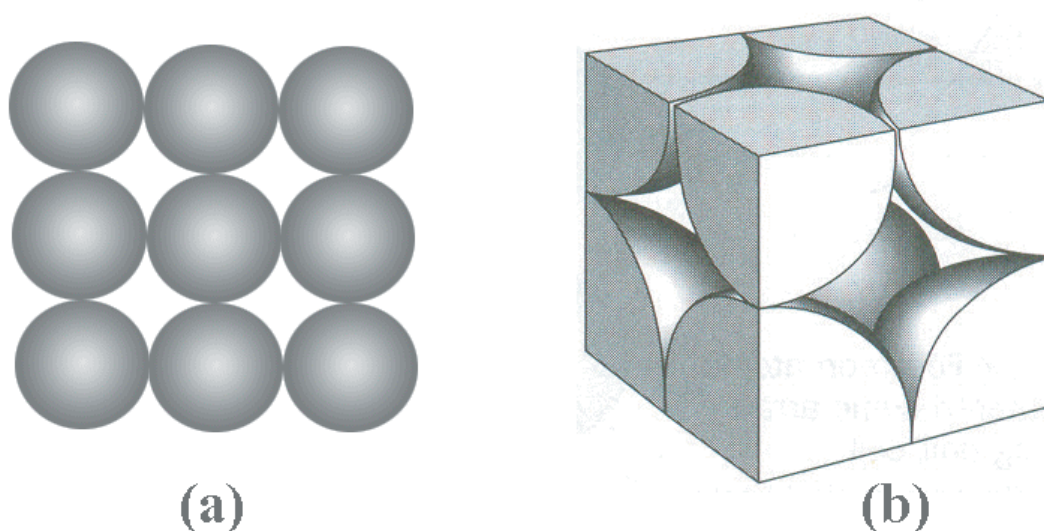
Simple cubic packing (sc)

Body-centered cubic packing (bcc)

Hexagonal closest packing (hcp)

Face-centered cubic packing (fcc)

The simplest lattice structure is the so-called *simple cubic packing* (sc). This structure consists of identical layers of atoms placed exactly above and below each other. The structure is sketched in Figure 2- 20.



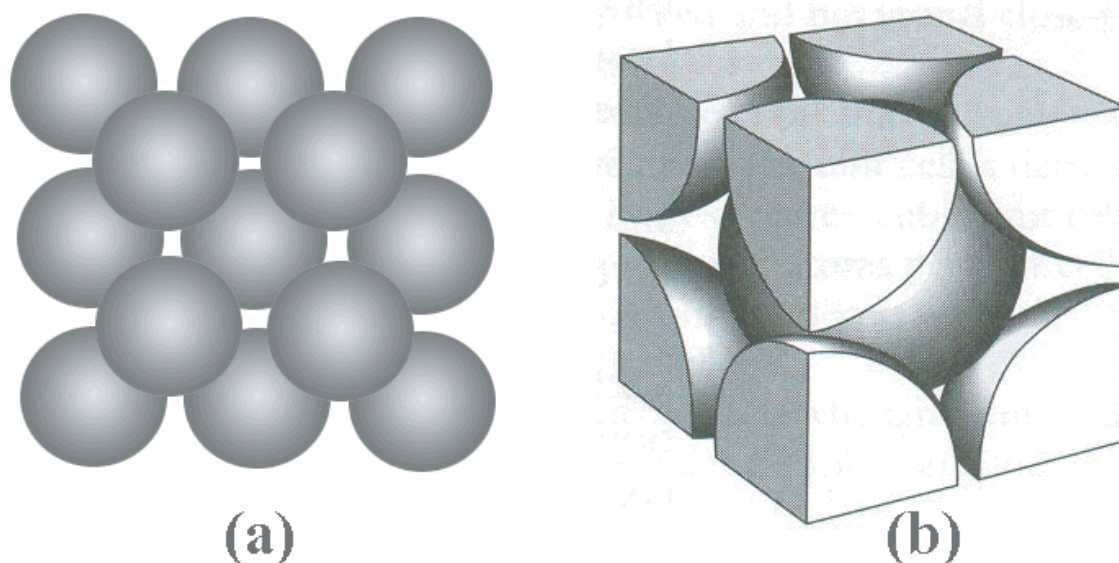
**Figure 2- 20: Simple cubic packing (sc)**

(a) One layer of the structure. (b) Unit cell. In the simple cubic packing every layer is placed exactly above and below each other. Thereby every atom touches six other atoms (four in the same layer, one above and one below). Thus the coordination number is 6.

Only the metal polonium (Po) has its atoms arranged in a simple cubic packing structure. In Figure 2- 20b it is seen that the unit cell in the sc-structure consists of 1 atom in total ( $8 \times 1/8$  part of an atom). From the unit cell it is further seen that the atoms touche along the edges of the unit cell. Thus the lengths of the edges of the unit cell equals 2 times the atomic radius ( $b = 2 \times r$ ). The length of the edges of the unit cell is denoted  $b$  and the atomic radius is denoted  $r$ . Each atom in the sc-structure thus touches 6 other atoms and therefore the so-called *coordination number* is 6.

The atoms in a metal can also be packed according the so-called *body-centered cubic* packing structure (bcc). In this structure identical layers of atoms are placed above and below each other so that every second layer is

exactly above and below each other. The atoms in one layer is placed above the holes in the below and above lying layer. This is sketched in Figure 2- 21a.

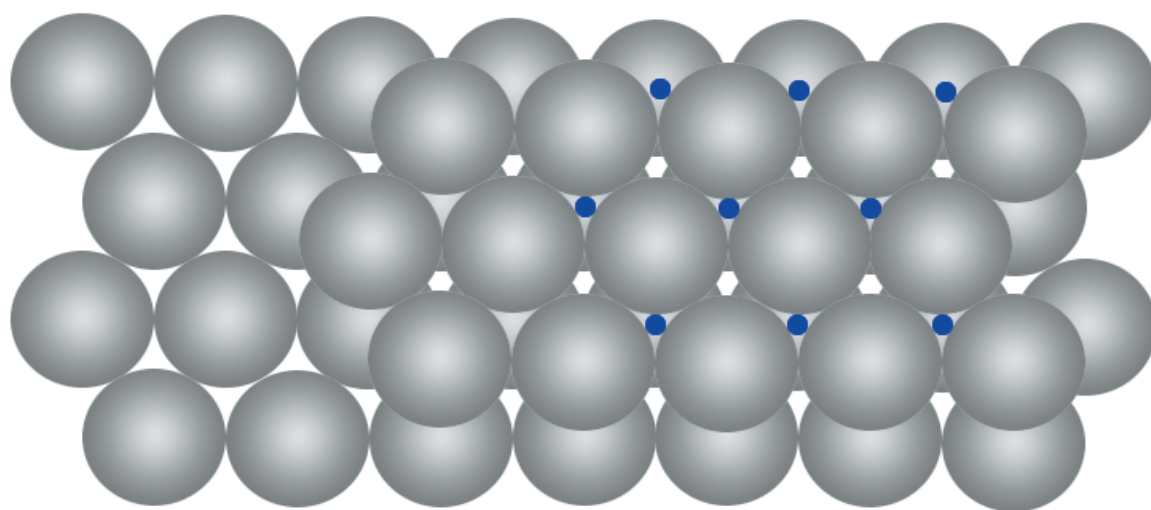


**Figure 2- 21: Body-centered cubic packing (bcc)**

(a) Two layers of the structure. (b) Unit cell. Every second layer is placed exactly above and below each other. Every atom touches eight other atoms (four in the layer below and four in the layer above). Thus the coordination number is 8.

In Figure 2- 21 it is seen that the atoms do not touch each other in the respective layers but they rather touch the atoms in the layer below and above. From the sketch of the unit cell it is seen that the atoms touch along the diagonal through the unit cell which gives rise to the name *body-centered* structure. Thus the length of the body-diagonal of the unit cell equals 4 times the atomic radius. By using the theorem of Pythagoras the length of the edge of the unit cell  $b$  is thus equal to:  $b = (4/3^{1/2}) \times r$ . The unit cell contains 1 whole atom plus 8 times  $1/8$  parts of atoms which correspond to 2 atoms in total in the unit cell. Each atom touches eight other atoms which give rise to a coordination number of 8 for this structure.

In stead of a square based arrangement of the atoms in each layer (as in the *sc* and *bcc* structures), the atoms can be arranged in a hexagonal manner. This means that each atom does not have four neighbours but rather six neighbours in a layer. That way the holes between the atoms in the layer will by far be smaller compared to the *sc* and *bcc* structures and overall the atoms will packed closer together. There are two different types of hexagonal structures. The first is the *hexagonal closest packed* structure (*hcp*) and the second is the *face-centred cubic* structure (*fcc*). The hexagonal closest packed structure (*hcp*) is sketched in Figure 2- 22. In this structure every second layer is placed exactly above and below each other.



**Figure 2- 22: Hexagonal closest packing (hcp)**

*Every second layer is placed exactly above and below each other. The centres of the atoms in the third layer are sketched with small blue dots. The third layer is placed exactly above the first layer. Every atom touches twelve other atoms (six in the same layer, three in the layer below and three in the layer above). Thus the coordination number is 12.*

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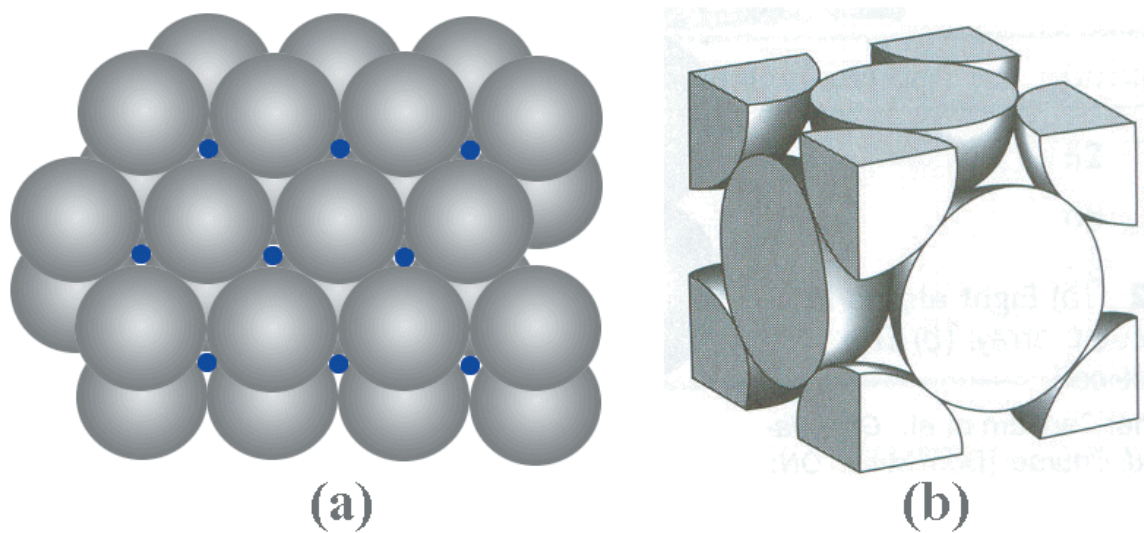


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Since each atom in the *hcp*-structure touches twelve other atoms (six in the same layer, three in the layer below and three in the layer above) the coordination number is 12. A unit cell for this structure can not be drawn as easily as for the other structures and thus only the layered structure is shown in Figure 2- 22. It is seen that it is only half of the “holes” in the layers that are covered by atoms in the layer above/below.

The other hexagonal packed structure is the so-called *face-centred cubic* structure (*fcc*). Here every third layer is placed above the holes in the first layer which means that every fourth layer is placed exactly above each other. The layered structure and the unit cell for the *fcc*-structure are sketched in Figure 2- 23.



**Figure 2- 23: Face-centered cubic packing (*fcc*)**



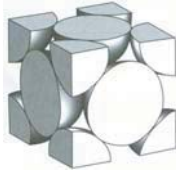
(a) The centre of the atoms in the third layer is placed above the holes in the first layer and the centres of the atoms in the third layer are sketched with small blue dots. (b) Unit cell. Every atom touches twelve other atoms (six in the same layer, three in the layer above and three in the layer below). Thus the coordination number is 12.

By comparing Figure 2- 22 and Figure 2- 23a it is seen that the difference between the *hcp*-structure and the *fcc*-structure lies in the placement of the third layer. As for the *hcp*-structure each atom in the *fcc*-structure touches twelve other atoms (six in the same layer, three in the layer below and three in the layer above). Thus the coordination number is 12. From the unit cell it is seen that the atoms touch each other along the diagonal of the “faces” of the unit cell. Thus the name of this structure is *face-centred* cubic structure, and the face-diagonal equals four times the atomic radius. By using the theorem of Pythagoras the length of the unit cell  $b$  can be calculated according to:  $b = (8^{1/2}) \times r$ . The unit cell contains six half atoms plus eight  $1/8$  parts of atoms which gives a total of 4 atoms pr. unit cell.

A survey of the four different structures is given in Table 2- 3.

**Table 2- 3: Crystal lattice structures**

The side length in the unit cell is denoted  $b$  and the radius of the atoms is denoted  $r$ . SC: simple cubic packing, BCC: Body-centered cubic packing, FCC: Face-centered cubic packing, HCP: Hexagonal closest packing.

Structure	Sketch	$b = f(r)$	Number of atoms in unit cell	Example
sc		$b = 2 \times r$	1	Polonium
bcc		$b = (4/3^{1/2}) \times r$	2	Niobium
fcc		$b = (8^{1/2}) \times r$	4	Osmium
hcp	*	-	-	Palladium

\*The unit cell for the hcp-structure is not given since it can not be sketched with the same methodology as for the other structures.

We are now able to determine the side length of a unit cell for different well known lattice structures from the atomic radius according to Table 2- 3. We also know the number of atoms in each unit cell and thus we can calculate the density of a metal from the way the atoms in the metal is packed and the atomic radius of the metal atoms. We are going to try this in the following example.



**Example 2- P:***Density of tungsten (W)*

The transition metal tungsten (W) assumes *bcc*-structure. The atomic radius of tungsten atoms is 1.37 Å ( $r = 1.37 \times 10^{-8} \text{ cm}$ ) and the molar mass of tungsten is  $M_w = 183.84 \text{ g/mole}$ . What is the density of tungsten metal?

We know that when we are dealing with *bcc*-structures each unit cell contains 2 atoms (see Table 2- 3 on page 84). The density of tungsten metal can thus be determined as follows:

$$\text{Density of tungsten} = \frac{\text{Mass of 2 W - atoms}}{\text{Volume of unit cell}}$$

The mass of 2 tungsten atoms can be calculated from the molar mass and Avogadro's number.

$$\text{Mass of 2 W - atom} = \frac{M_w}{N_A} \cdot 2 = \frac{183.84 \frac{\text{g}}{\text{mole}}}{6.022 \cdot 10^{23} \text{ mole}^{-1}} \cdot 2 = \underline{6.106 \cdot 10^{-22} \text{ g}}$$

The volume of the unit cell is determined from the atomic radius since we know the connection between the side length of the unit cell  $b$  and the atomic radius  $r$  according to Table 2- 3 on page 84.

$$\text{Volume of unit cell} = b^3 = \left[ \left( \frac{4}{3^{1/2}} \right) \cdot r \right]^3 = \left[ \left( \frac{4}{3^{1/2}} \right) \cdot 1.37 \cdot 10^{-8} \text{ cm} \right]^3 = \underline{3.167 \cdot 10^{-23} \text{ cm}^3}$$

The density of tungsten metal can now be calculated.

$$\text{Density of tungsten} = \frac{6.106 \cdot 10^{-22} \text{ g}}{3.167 \cdot 10^{-23} \text{ cm}^3} = \underline{\underline{19.28 \text{ g/cm}^3}}$$

The calculations can also go the other way. If the density of a metal and packing structure is known, the atomic radius can be calculated. We are going to try this in the following example.

**Example 2- Q:***Atomic radius for ruthenium (Ru)*

The transition metal ruthenium (Ru) has *fcc*-structure. The density of ruthenium metal is  $12.34 \text{ g/cm}^3$  and the molar mass is  $M_{\text{Ru}} = 101.07 \text{ g/mole}$ . What is the atomic radius of ruthenium atoms?

We know that when we are dealing with *fcc*-structure each unit cell contains 4 atoms according to Table 2-3 on page 84. The volume of the unit cell can thus be determined as follows:

$$\text{Volume of unit cell} = \frac{\text{Mass of 4 Ru-atoms}}{\text{Density of Ruthenium}}$$

The mass of 4 ruthenium atoms is calculated from the molar mass and the Avogadro's number.

$$\text{Mass of 4 Ru-atoms} = \frac{M_{\text{Ru}}}{N_A} \cdot 4 = \frac{101.07 \frac{\text{g}}{\text{mole}}}{6.022 \cdot 10^{23} \text{ mole}^{-1}} \cdot 4 = \underline{6.713 \cdot 10^{-22} \text{ g}}$$

The volume of the unit cell is calculated.

$$\text{Volume of unit cell} = \frac{6.713 \cdot 10^{-22} \text{ g}}{12.37 \text{ g/cm}^3} = \underline{5.427 \cdot 10^{-23} \text{ cm}^3}$$

The volume of the unit cell equals the side length of unit cell raised to the power of three (Volume =  $b^3$ ). Since we know the association between the side length  $b$  of the unit cell and the atomic radius  $r$  according to Table 2-3 on page 84, the atomic radius of ruthenium can now be calculated.

$$\begin{aligned} \text{Volume of unit cell} = b^3 &= \left[ \left( 8^{1/2} \right) \cdot r \right]^3 \Leftrightarrow \\ r &= \frac{(\text{Volume of unit cell})^{1/3}}{8^{1/2}} = \frac{(5.427 \cdot 10^{-23} \text{ cm}^3)^{1/3}}{8^{1/2}} = 1.34 \cdot 10^{-8} \text{ cm} = \underline{1.34 \text{ \AA}} \end{aligned}$$

Now we have been looking at metallic bonds and how metal atoms arrange in crystal lattice structures. In the following section we are going to look at the ionic bonds and compounds.

## 2.4 Ionic bonds

The transition from pure covalent bonds over polar covalent bonds to ionic bonds is fluent as described in the section 2.1.1 *Bond types*. In this section we are going to look at bonds with ionic character. We are also

going to look at how ionic compounds often are arranged in crystal lattices similar to the metallic structures described in the section 2.3.2 *Lattice structures*.

### 2.4.1 Ionic character

When the electronegativity between two atoms is zero (two identical atoms) you have a pure covalent bond while the bond is polar covalent if there is a difference in electronegativity between the atoms. When this difference in electronegativity reaches a certain level, at which the bond electrons in practice are totally placed around the most electronegative atom, the bond is categorized as ionic since we no longer have a bond electron pair but rather some electrostatic interactions between a cation and an anion. For chemical bonds you can talk about how much ionic character the bond exhibits. The ionic character can be calculated based on electron charge and bond distance which we will not go further into in this book. A relative connection between the degree of ionic character and difference in electronegativity between the atoms is sketched in Figure 2- 24.

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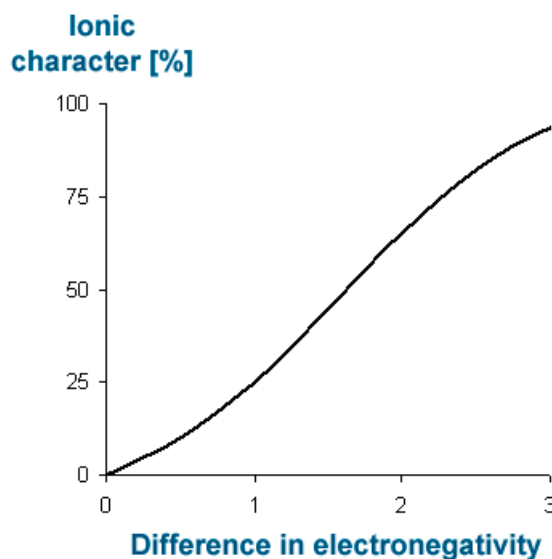
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**Figure 2- 24: Ionic character**

*Connection between the ionic character of a bond and the difference in electronegativity between the two atoms in a bond.*

A pure covalent bond (an H-H bond for example) exhibits 0 % ionic character while a polar covalent bond like hydrogen fluoride (H-F) exhibits 42 % ionic character. Bonds in sodium chloride (NaCl) are normally considered as ionic. These sodium chloride bonds exhibit 72 % ionic character. This emphasizes that the transition between covalent bonds over polar covalent bonds to ionic bonds is very fluent. No bonds actually exhibit 100 % ionic character since the bond electrons always will be located around the less electronegative atom at least for just a very little percentage of the time.

The strength of an ionic bond depends on the size of the ions. The smaller an ion is, the smaller is the surface area. This means that the charge of the ion only has to be distributed throughout a smaller area and the *charge density* thus increases when the ionic radius decreases. When the charge density is larger, the ionic bonds increase in strength. Therefore a LiF bond is stronger than a LiI bond since the radius of fluoride is smaller than the radius of iodide and thus the charge density of fluoride is larger than for iodide. This means that fluoride will be stronger bonded to the lithium ion than iodide.

#### 2.4.2 Lattice structures for ionic compounds

We saw in the section 2.3.2 *Lattice structures* that metal atoms are arranged in different crystal lattice structures. The same is the case for many solid ionic compounds. The anions are often much larger than the cations so these anions often constitute the lattice structure and the cations are then located in the “holes” in the lattice structure. As for the metal atoms we assume that the ions are hard spheres that can be packed together so that they just touch each other. The ratio between the radius of the cations and the anion determines which lattice structure the ionic compound adopts. This ratio is called the  $r_+/r_-$  *ratio*. In Table 2- 4 you can see which structure the ionic compounds adopt at the different  $r_+/r_-$  ratios. Of course there are some

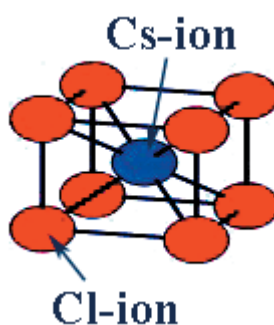
exceptions which you can find information about in more detailed educational textbooks. The coordination number tells how many anions each cation touches in the lattice structure.

**Table 2- 4: Structures for ionic compounds**

*The structure of an ionic compound depends on the  $r_+/r_-$  ratio. The coordination number tells how many anions each cation touches.*

$r_+ / r_-$ ratio	Coordination number	Name of structure	Example
0.732 – 0.999	8	Cubic	CsCl
0.414 – 0.732	6	Octahedral	NaCl
0.225 – 0.414	4	Tetrahedral	ZnS

When the  $r_+/r_-$  ratio is between 0.732 and 0.999 the structure is cubic. In this case the cations and anions are not that different in size and the structure corresponds to the simple cubic structure (sc) that we heard about for metals (section 2.3.2 *Lattice structures*). Anions and cations will be placed in a simple cubic structure so that each cation will be surrounded by eight anions and vice versa. A unit cell for such a structure is shown in Figure 2- 25.

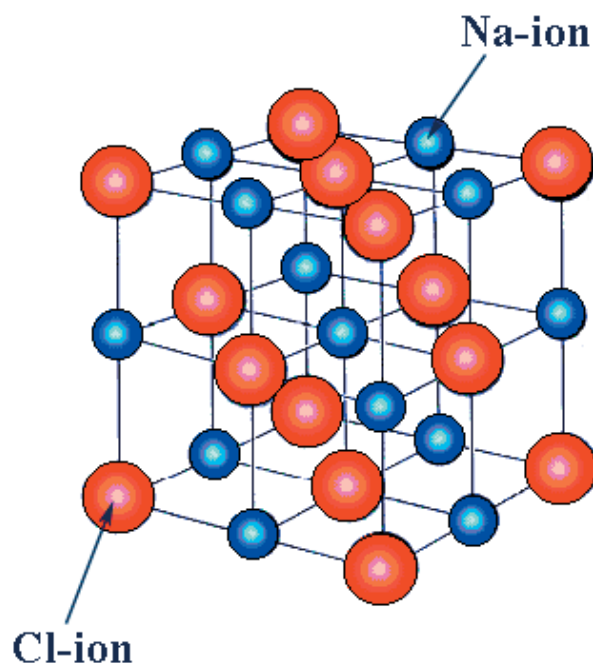


**Figure 2- 25: Cubic structure for an ionic compound**

*Unit cell for a cubic structure for an ionic compound with a  $r_+/r_-$  ratio in the interval 0.732 – 0.999. Each cation touches eight anions and each anion touches eight cations. Cesium chloride (CsCl) is an example of an ionic compound with cubic structure.*

In Figure 2- 25 it is sketched that in the unit cell the ions touch along the diagonal through the unit cell. This means that the diagonal has a length that corresponds to  $2 \times \text{radius of anion} + 2 \times \text{radius of cation}$ . Such a structure is seen for cesium chloride.

When the  $r_+/r_-$  ratio is between 0.414 and 0.732 the structure is octahedral. This means that the cations are placed in the octahedral holes in the anionic lattice. This structure is called *sodium chloride structure* because the very well known common salt has this structure. The sodium chloride structure for a unit cell is sketched in Figure 2- 26.



**Figure 2- 26: Octahedral structure for an ionic compound**

*Octahedral structure for an ionic compound with a  $r_+/r_-$  ratio in the interval 0.414 – 0.732. The cations are placed in the octahedral holes in the anion lattice. Thus each cation touches six anions. This structure is often called sodium chloride structure since the very well known "common salt" has this structure.*

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