

Lecture 5

ON CHEMICAL BONDING

Part 2: Applying bonding theories to metallic and ionic materials. Structures of metals and simple ionic compounds

General review

This lecture continues exploring the structures and bonding and focuses on the solid state. We shall look at the bonds found in ionic compounds, metallic elements and intermetallic compounds. Then the focus shifts to non-bonding interactions, i.e. forces that among other important functions, keep molecules together in the crystals. The text follows the outline from previous lecture: we shall look at the structures first, prior to describing the actual bonding.

Between the discovery of electrons and protons and mostly work of G.W. Lewis in early 20th century, the ionic bond was the only bond the chemists embraced. In this timeframe, electron-sharing as a concept was dismissed as impossible: how can electrons be shared when they have the same charge and hence repel each other? Lewis tried to resolve this paradox by introducing his cubic model of the atom with electrons found at the corners of the cube, well-separated negative charges. The “octet rule” has its origin in this atomic model: eight corners of a cube can accommodate an octet of electrons, when each corner has an electron the bonding ability of an atom is exhausted. Lewis did not dismiss ionic bond, but believed that it is one of three possibilities. His dot structures found its use in complete electron transfer mechanism often illustrated using sodium chloride as an example:



Both ions have the octet in their outer shells and are held together by electrostatic forces.

The origins of metallic bond theory can be traced to the early 1900s when Paul Drude in Germany and Hendrik Lorentz in the Netherlands developed electron gas bonding model. The development of molecular



orbital theory paved the road to the band theory of metallic bonding, which is today the theory of choice when describing not only metals but also other infinite solid-state structures such as diamond. The band theory is successful in explaining many properties of metals (electrical and thermal conductivities, luster, mailability etc.). The metallic bond, however, remains somewhat of a gray area in chemistry: some chemists find the metallic bond to be simply an extension of molecular orbital theory and the extra label is not needed. And, since it is applied to the elements and compounds with zero or small difference in electronegativity, it can be simply considered covalent bond.¹ In this text, we shall follow the lead of majority of texts and articles and employ “metallic bond” as a separate term.

5.1 Solid State Structures

When internal structure is considered, the solid materials come in two types: crystalline and amorphous. The crystalline materials are characterized by long-range order. The amorphous materials do not have a long-range order.² Examples of amorphous solids are amorphous carbon and precious stone opal (a form of hydrated silicon dioxide). Figure 5.1 shows parts of structures of three crystalline materials: iron, sodium nitrite (NaNO_2) and SF_4 . These illustrate quite well what we have learned so far and what is now ahead of us. The structure of iron was used as an example of metallic radius determination while here it shows a typical structure of metallic element with metallic bonding between the atoms. The anion in sodium nitrite, our example for deducing correct Lewis structures, has covalently bonded N and O atoms. It is ionic bond, however, that holds Na^+ and NO_2^- in this ordered structure. And finally, the structure and geometry of SF_4 molecule received quite a bit of attention in our last lecture, but now we have to look at forces that keep SF_4

¹ Same parts of this discussion can be found in Anderson, W.P., Burdett, J.K., Czech, P.T. *J. Am. Chem. Soc.* **1994**, 116(19), 8808-8809 (DOI: [10.1021/ja00098a050](https://doi.org/10.1021/ja00098a050)); Allen, L.C., Capitani, J.F. *J. Am. Chem. Soc.* **1994**, 116(19), 8810 (DOI: [10.1021/ja00098a051](https://doi.org/10.1021/ja00098a051)); Schön, *Angew. Chem. Int. Ed.* **1995**, 34(10), 1081-83 (DOI: [10.1002/anie.199510811](https://doi.org/10.1002/anie.199510811)); Allen, L.C., Burdett, J.K. *Angew. Chem. Int. Ed.* **1995**, 34(18), 2003 (DOI: [10.1002/anie.199520031](https://doi.org/10.1002/anie.199520031)) and Gilman, J.J. *J. Chem. Educ.* **1999**, 76(10), 1330-1331 (DOI: [10.1021/ed076p1330](https://doi.org/10.1021/ed076p1330)).

² Words ‘crystalline’ and amorphous’ are both of Greek origin. *Krustallos* is Greek for *ice* or *rock crystal* (transparent, colourless form of mineral quartz, SiO_2). *Amorphous* is derived from Greek *a*, meaning *without* or *lacking*, more generally a prefix indicating absence of a quality) and *morphe* meaning *form* or *shape*.



molecules together in SF_4 crystals. The last two examples also show the importance of understanding of all bonding and non-bonding types for inorganic chemist: finding more than one bond type and/or non-bonding force in one compound is almost a rule rather than an exception.

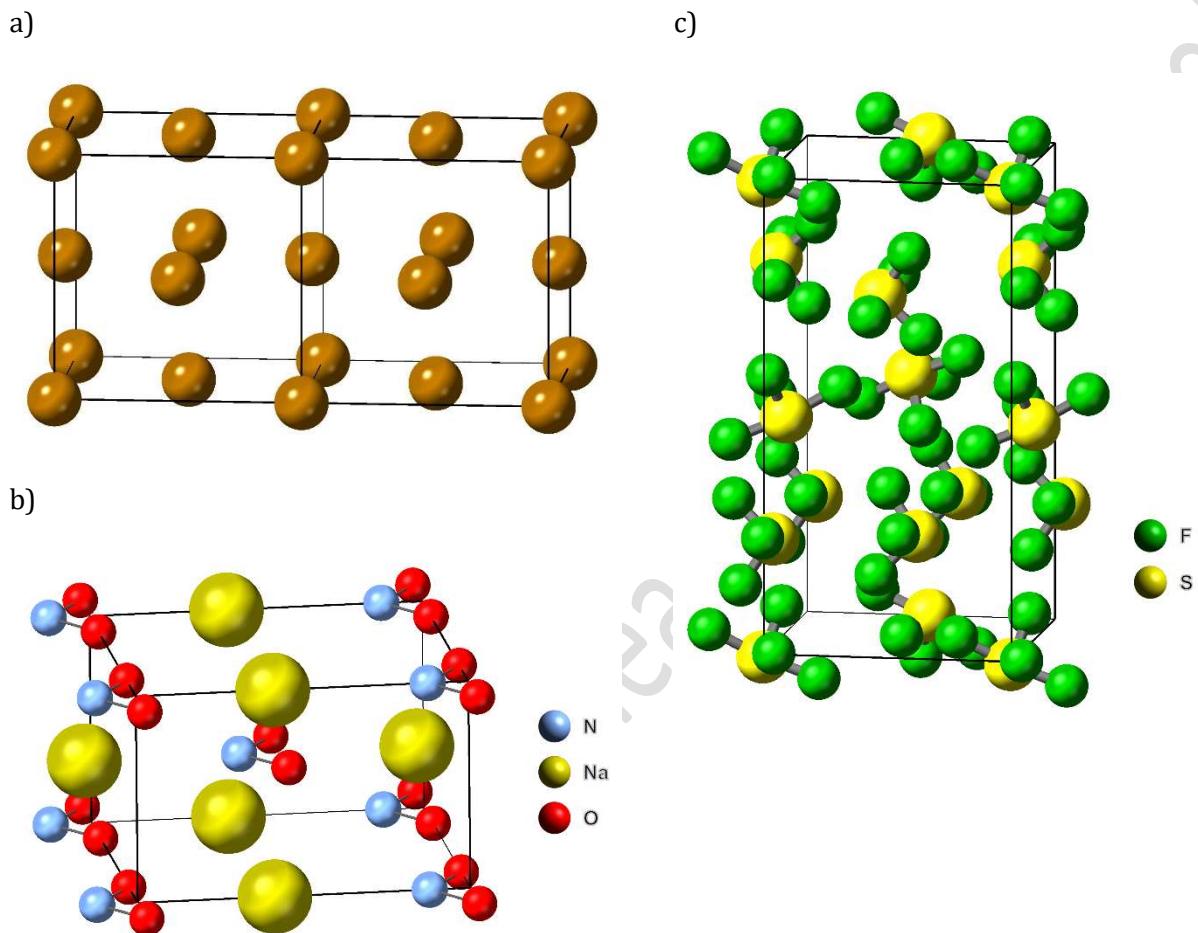


Figure 5.1 Ordered solid-state (crystal) structures of a) iron, b) sodium nitrite (NaNO_2) and c) sulfur tetrafluoride (SF_4)

5.1.1 The Unit Cell and Crystal Systems

To describe the structure of a crystalline material all we need to know is its unit cell: the smallest part of the crystal structure that contains all chemical and structural information of the material. In very simple terms, unit cells can be understood as 'bricks' of a crystal. Just as a wall is built by laying bricks of (more-or-

less) identical size in two dimensions (horizontally and vertically) so can a crystal be built by 'laying down' unit cells in three dimensions.

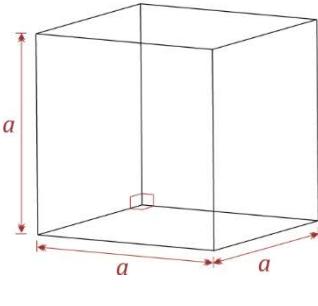
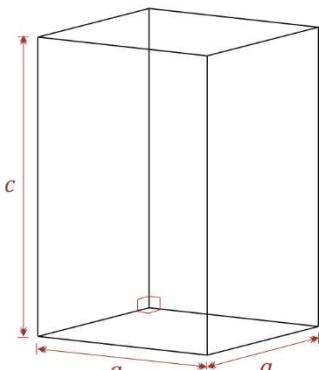
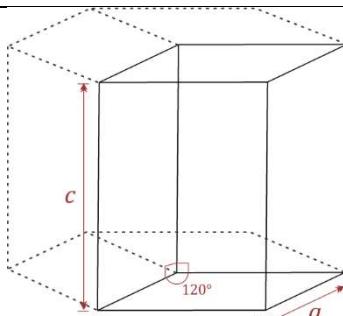
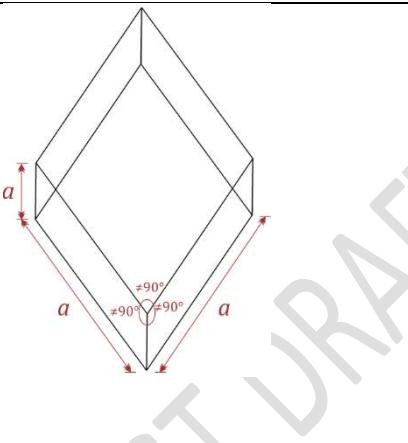
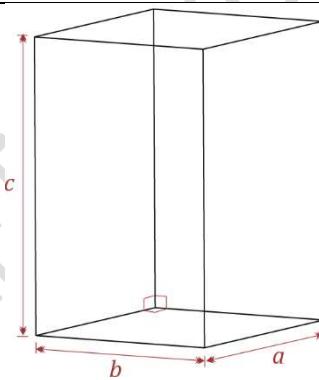
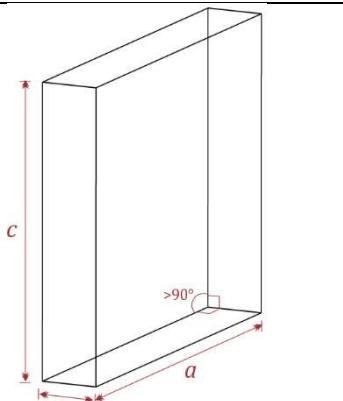
Unit cells can be classified into seven crystal systems based on unit cell parameters: three dimensions (length of unit cell edges) a , b and c ³ and three angles between them, α , β , and γ (Table 5.1). Angle α is formed by directions b and c , β by a and c while γ by a and b . If all three edges of the unit cell are identical and three angles are 90° , then the unit cell is a cube and the system is cubic (sometimes called isometric) system. Thus, it is enough to know parameter a to describe the cubic unit cell, it. The unit cell belonging to the tetragonal system is a square prism (i.e. a stretched or compressed cube) that is defined by two identical directions a (defining a square) and height c which is different than a . All three angles are still at 90° . The rhombic prism is the shape of the unit cell in hexagonal system. Rhombic prism has a base of equal lengths, a , but the γ angle between them is 120° . The height of the prism, c , is different than a and is perpendicular to the base (i.e. $\beta = 90^\circ$). The unit cell of rhombohedral system again has all dimensions the same (we only need to know a), but the angle between the unit cell edges are not 90° (i.e. $\alpha \neq 90^\circ$). If our prismatic unit cell has three different edges (or directions), a , b and c , but all angles are at 90° , the unit cell belongs to the orthorhombic system. The monoclinic unit cell is based on the orthorhombic one, but the angle γ is greater than 90° . Finally, triclinic unit cell has all three directions different and all angles different from 90° (we say that all unit cell parameters in triclinic system are unique). The systems and their corresponding unit cells are summarized in Table 5.1. The table also gives the equations used to calculate the volume of unit cells. Volume is a derived unit cell parameter, it depends on the six unit cell parameters described above, and is frequently used to calculate the density of crystalline material as shall be illustrated later on.

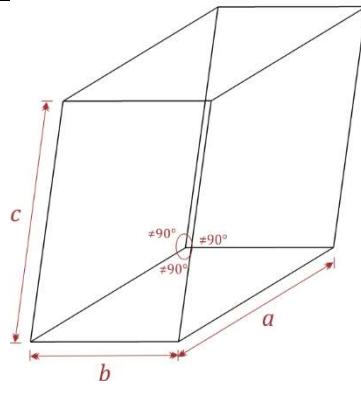
Table 5.1 The seven crystal systems

| Cubic | Tetragonal | Hexagonal |
|-------|------------|-----------|
|-------|------------|-----------|

³ In the pure crystallography language, a , b and c are vectors. The intensity of the three vectors (that equals the length of the unit cell) tell us the distance at which the next unit cell is located, and their direction tell us where to look.



| | | |
|---|---|---|
| $a = b = c (= a)$, $\alpha = \beta = \gamma = 90^\circ$ | $a = b (= a) \neq c$ $\alpha = \beta = \gamma = 90^\circ$ | $a = b (= a) \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$ |
|  |  |  |
| $V = a^3$ | $V = a^2c$ | $V = \frac{\sqrt{3}}{2}a^2c$ |
| Rhombohedral | Orthorhombic | Monoclinic |
| $a = b = c (= a)$, $\alpha = \beta = \gamma \neq 90^\circ$ | $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ | $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta > 90^\circ$ |
|  |  |  |
| $V = a^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$ | $V = abc$ | $V = abc \sin \beta$ |
| Triclinic | | |
| | $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ | |



$$V = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

The directions a , b and c are also conveniently used as coordinate system to describe the locations of atoms inside the unit cell. The convention is to place the origin of this coordinate system (i.e. its zero) in the far bottom left corner. (Table 5.1 does not follow this convention for clarity reasons. However, the convention will be followed from now on.) The atomic positions are then conveniently reported as fractions of unit cell lengths. We'll practice this once we start describing some representative structures.

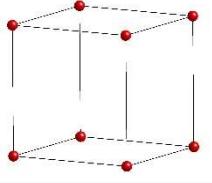
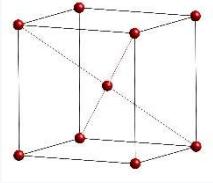
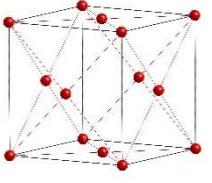
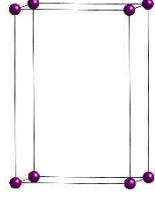
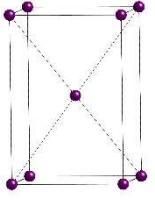
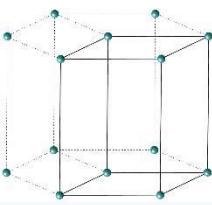
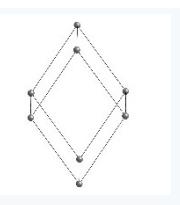
Example 5.1 Unit cells and crystal systems

The unit cell of mineral calcite (CaCO_3) has the following parameters: $a = 637 \text{ pm}$, $\alpha = 46^\circ$. To which crystal system does calcite's unit cell belong? Calculate the unit cell volume.

Crystal structures, even very complex ones can be reduced to lattices which are three dimensional arrays of points—lattice points. The structural elements (atoms, ions, molecules) are held together at or around lattice points. This means that it is not a necessity that a chemical species occupies the lattice point. There are only 14 distinctive lattices, called Bravais lattices after French physicist Auguste Bravais who published

their description in 1850.⁴ The Bravais lattices are obtained by combining the crystal systems with possible centering types (locations of lattice points within the unit cell). A primitive lattice (symbol P) has points only at the corners of the unit cell.⁵ If there is a point at the center of two parallel faces, then the lattice is base-centered (symbol C). Lattice with points at the corners of the unit cell and at the center of the cell is called body centered (symbol I). And finally, face-centered lattice (symbol F) has lattice points at each corner and at the center of every face. The distribution of Bravais lattices among crystal systems is shown in Table 5.2. You will note that all systems have a primitive lattice, and that other lattice types are not very common. The reason is that we can find a simple, smaller unit cell for any other potential lattice. Example 5.2 illustrates this point.

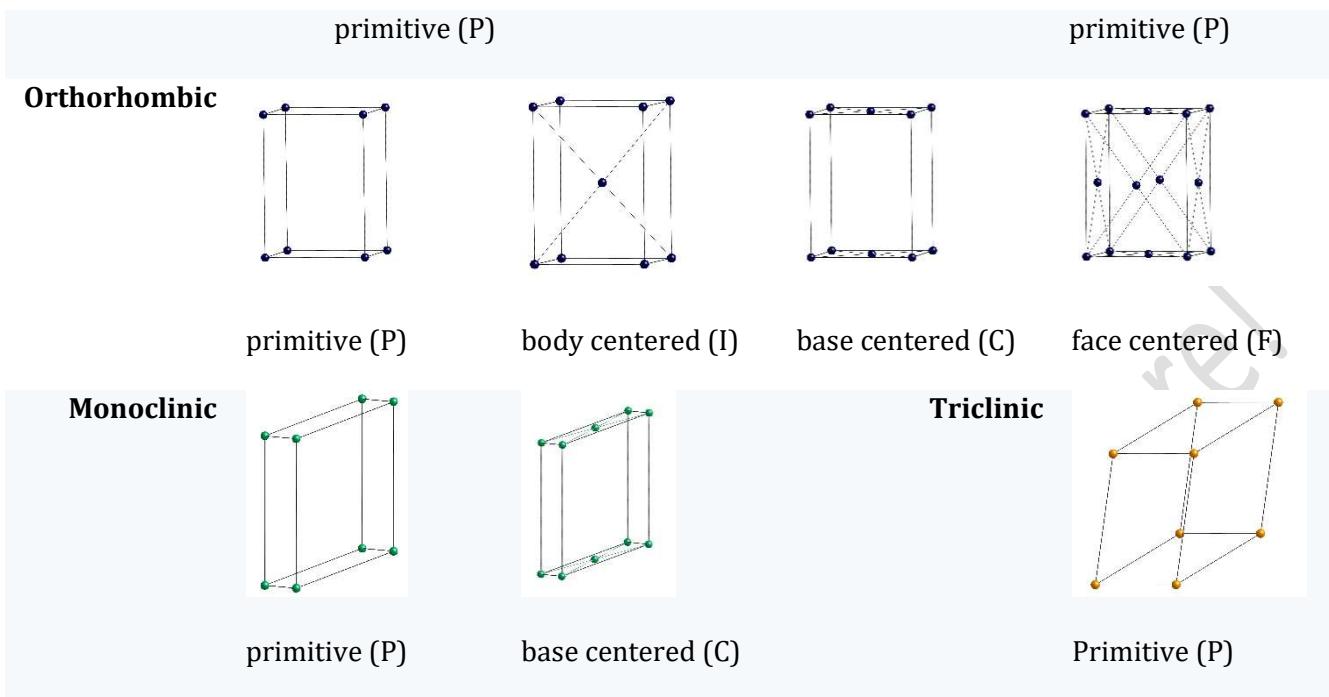
Table 5.2 The distribution of Bravais lattices among crystal systems

| Cubic | | |
|---|---|--|
| primitive (P) | body-centered (I) | face centered (F) |
|  |  |  |
| Tetragonal | | |
|  |  | |
| primitive (P) | body centered (I) | |
| Hexagonal | | |
|  | Rhombohedral | |
| |  | |

⁴ The first description

⁵ In some texts the primitive lattice is called simple lattice.





(Insert Example 5.2)

(Insert a note on crystal morphology)

5.1.2 Structures of metals and alloys

An easy way to describe the structures of metals is to treat the atoms as hard spheres and consider the ways in which they can fill the space. In general, the atoms are going to pack so that the maximum occupancy of space is achieved. Structures that achieve the maximum occupancy are called close-packed structures. Structures that do not achieve the maximum occupancy are called non-close-packed structures. Although less common, non-close-packed structures are still found for some metals. Both are important as a starting point for description of more complex, ionic structures that lie ahead.

Imagine a two-dimensional layer of tennis balls (substituting for the metal atoms), packed as tightly as possible to (for example) cover a bottom of a carton box. A part of that layer is shown in Figure 5.2a). Notice that the packing is based on the hexagonal pattern. Even this tight packing does not cover completely the bottom of the box: some of it is visible where three spheres touch and form a trigonal hole. In the close-packed structures, the spheres of the next layer are going to settle exactly above the holes. We now have

two different layers, A and B, in side our box (Figure 5.2, middle). Layer B is also based on hexagonal pattern and has trigonal holes. This time, however, there are two types of holes: those located above the spheres of layer A and those located above the holes in layer A. The spheres making up the next layer can settle in either type of holes. If the third layer fills the holes above atoms of layer A, the result is a layer identical to the first one, i.e. another layer A (Figure 5.2, top right). This process continues giving an ABABAB... sequence of layers. If the third layer atoms lie above holes of layer A, a new layer results, layer C (Figure 5.2, bottom right). Continuing this process results in ABCABC... sequence of layers.

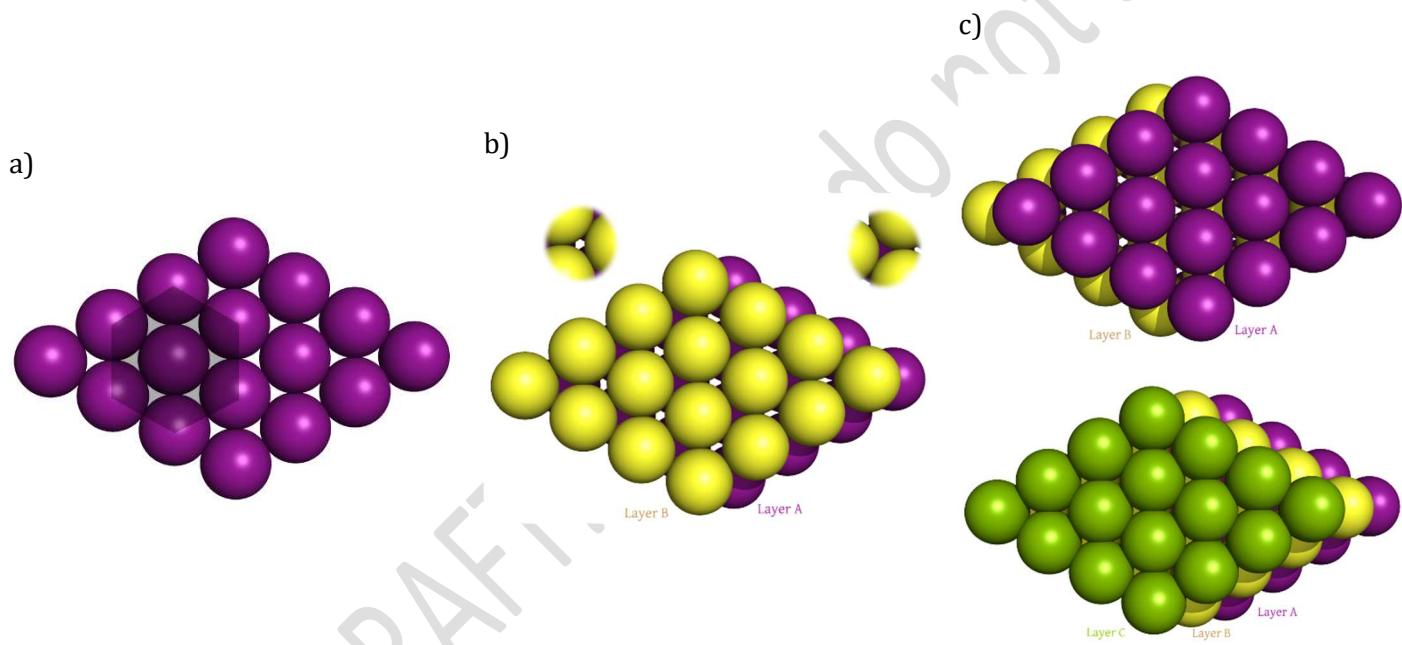


Figure 5.2 Layers of hexagonal close-packing: a) bottom layer, shaded region emphasizes the hexagonal pattern; b) second layer, Layer B, with two different holes (inserts)—above hole in Layer A and above an atom of Layer A; c) *top*, the atoms of the third layer situated above the atoms of the first layer give another layer A; *bottom*, the atoms of the third layer situated above holes in layer A give a new layer C.

The first scenario produces hexagonal close-packed (hcp) structure because it belongs to the hexagonal crystal system with a primitive unit cell. While not clearly evident from Figure 5.2, this unit cell can be easily

derived if we first describe the hcp structure in terms of two interpenetrating hexagonal lattices. Connecting four atoms in contact from two A layers we obtain one primitive hexagonal unit cell for one hexagonal lattice. If we do the same for atoms in layer B, we have a primitive hexagonal unit cell of the second hexagonal lattice. Both are shown in Figure 5.3. The actual primitive hexagonal unit cell is shown in Figure 5.4. Two atoms, one from each layer, reside in side the unit cell and not on the actual lattice points.

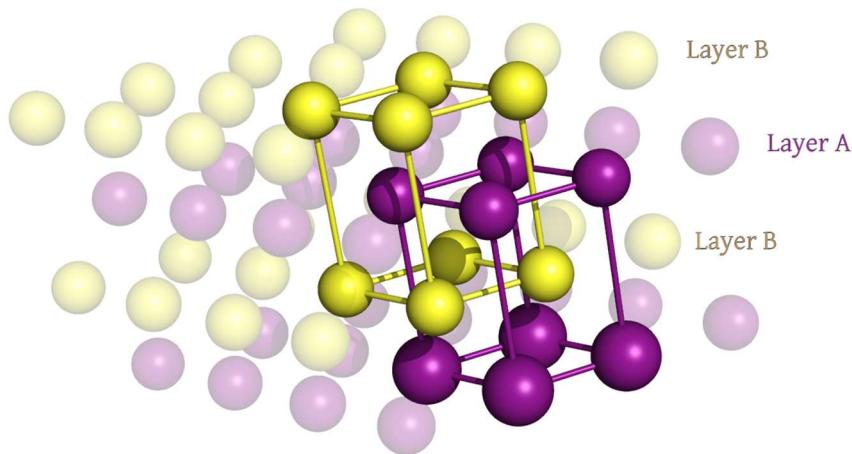


Figure 5.3 Two interpenetrating hexagonal lattices make up the hcp structure.

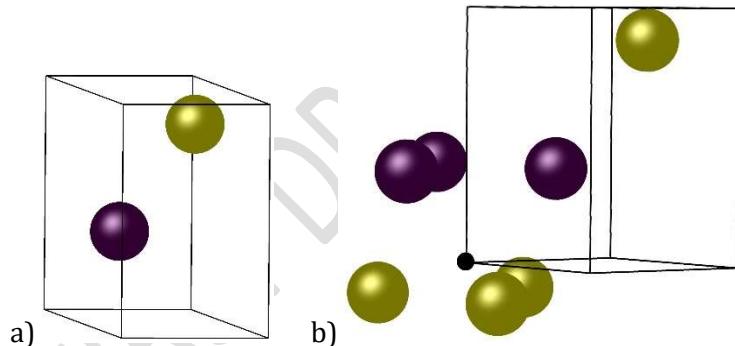


Figure 5.4 The primitive hexagonal unit cell of the hcp structure: (a) The unit cell outline and the two atoms inside the unit cell, (b) three atoms from layer A and three atoms of layer B centered round one lattice point (small, dark circle on the cell corner).

The ABC sequence of layers gives cubic close-packed (ccp) structure with cubic unit cell (Figure 5.5). The structure has a face centered cubic lattice, and in this case atom positions lie on the lattice points. In this case, it is not straightforward to decide on number of atoms that unit cell contains. To calculate the number of atoms in one unit cell we can follow the following general rules:

- Atom in side unit cell completely belong to that unit cell and contribute one atom;
- Atoms on the face of a unit cell contribute one-half of an atom to one unit cell;
- Atoms on the edges of a unit cell contribute one quarter to one unit cell, and
- Atoms on the corners of a unit cell contribute one eighth to the unit cell.

The rules can be obtained when we consider how many unit cells meet at certain locations. For example, two unit cells share a common face; thus, an atom on the face belongs equally to two unit cells and contribute one half to each cell. Following these steps, for the ccp unit cell we have:

$$\frac{1}{8} \times 8 \text{ (for eight cube corners)} + \frac{1}{2} \times 6 \text{ (for six cube faces)} = 4 \text{ atoms.}$$

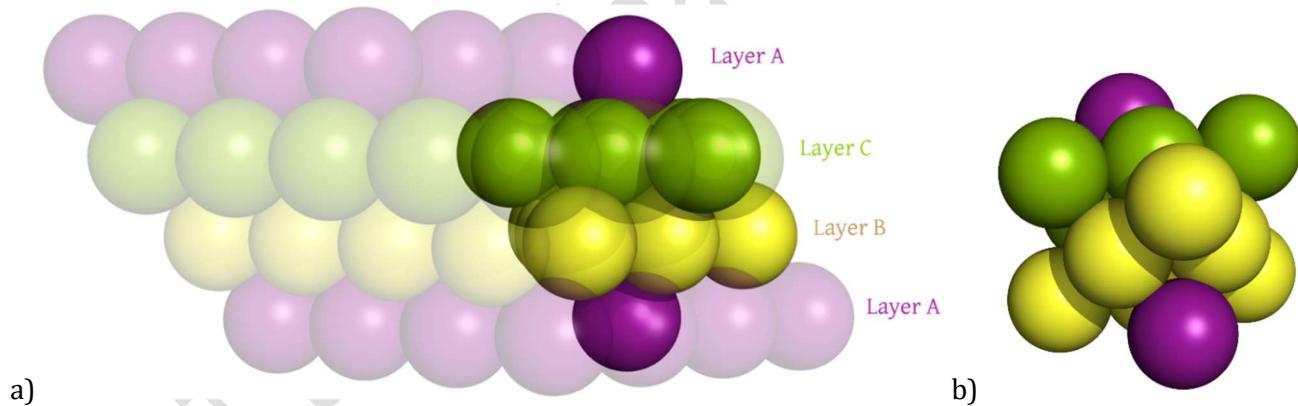


Figure 5.5 The unit cell of the cubic close-packing: (a) location of the unit cell in the structure, (b) isolated unit cell (compare with the cubic F lattice of Table 5.1). Notice that in (a) the unit cell is placed along the space diagonal of the cube.

Another important feature used to describe the structures is coordination number. For metallic structures, the coordination number is the number of closest neighbors. Both hcp and ccp structures have coordination

number 12, Figure 5.6. Both have six atoms in one plane surrounding the central atom and three above and below the plane. The difference between the two is the orientation of the three atoms in the parallel planes: in ccp structure the atoms are staggered while in hcp they are eclipsed.

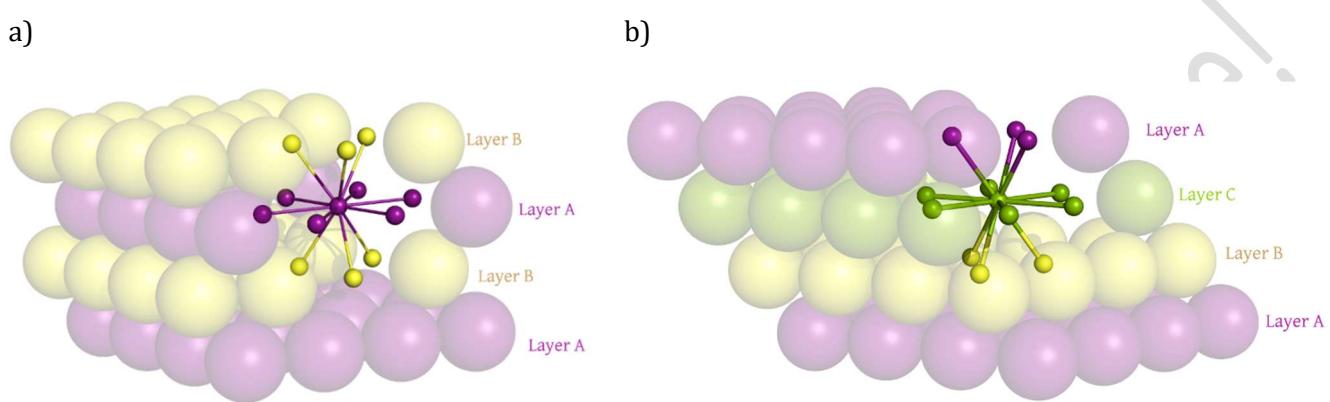


Figure 5.6 Coordination numbers in a) hcp and b) ccp structures. The two triangles of hcp structure, formed from atoms (yellow) in Layer B, are eclipsed; the triangles formed from atoms in Layer A (purple) and Layer B (yellow) of ccp structure are staggered.

In addition to close-packed structures, there are two important non-close-packed structures, i.e. structures that have lower economy of space than hcp and ccp. These are based on layers comprising of square pattern of spheres, Figure 5.7a). We can easily show that this pattern results in more empty space between the spheres (Example 5.3). The next layer is going to be placed above the holes of the first one (Figure 5.7b) followed with a layer identical to the first one (Figure 5.7c). The result is body-centered cubic structure based on volume centered cubic lattice. Figure 5.7d) shows five layers of bcc structure with one unit cell emphasized in Figure 5.7e). The atoms in the unit cell are located on the lattice points.

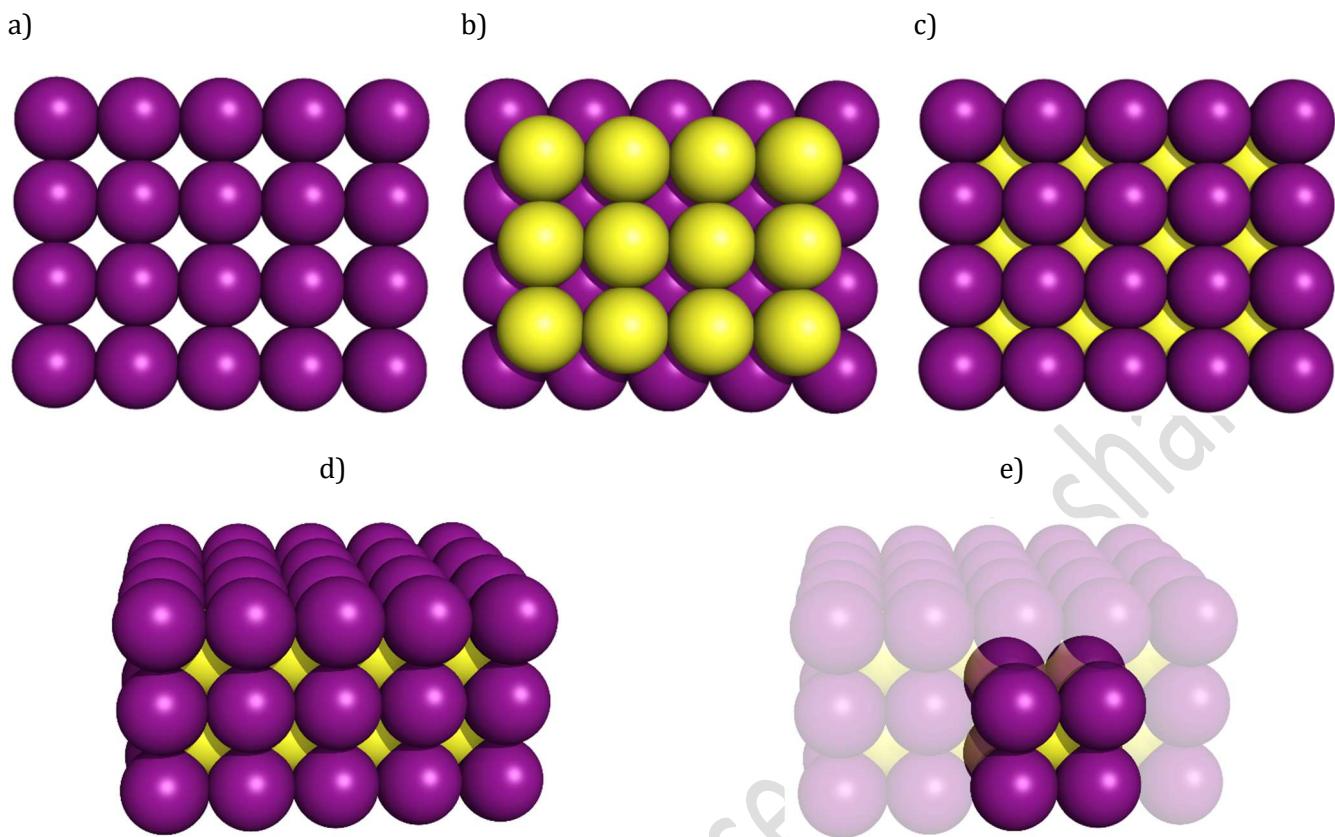


Figure 5.7 The layers based on cubic pattern of spheres: a) one layer only; b) second layer occupying the holes in the first layer; c) the third layer is identical to the first; d) five layers in side view and e) unit cell

A structure with even lower economy of space is based only on one layer of spheres in the cubic pattern, with spheres on top of each other. The result is a very hollow structure called simple cubic (sc) structure based on primitive cubic lattice. Figure 5.8 shows layers of this structure and one unit cell within the layers. The atoms are, again, located on the lattice points.

a) b)

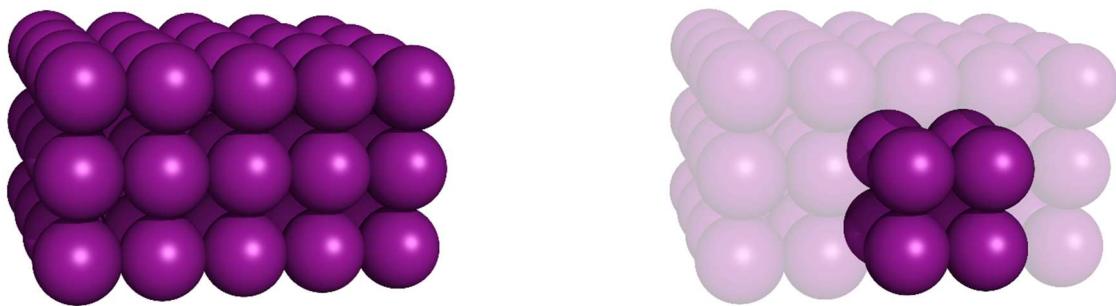


Figure 5.8 a) Simple cubic packing and b) its unit cell.

The unit cell content (number of atoms per unit cell) for each can be calculated easily:

For bcc structure:

$$\frac{1}{8} \times 8 \text{ (for eight cube corners)} + 1 \text{ (for the atom in the center of the unit cell)} = 2$$

For sc structure:

$$\frac{1}{8} \times 8 \text{ (for eight cube corners)} = 1$$

The coordination numbers are eight and six for bcc and sc structures respectively (Figure 5.9)

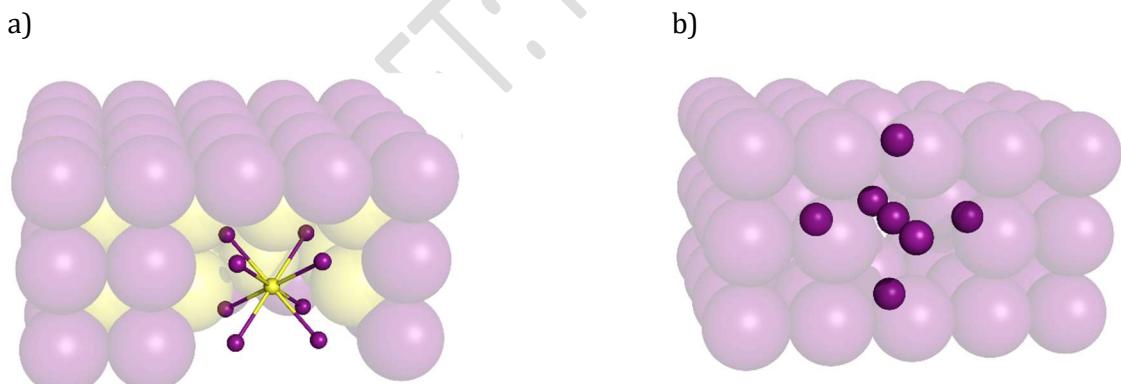


Figure 5.9 Coordination in a) bcc and b) sc structures.

Even the close-packed structures of spheres cannot completely fill the space with spheres—there are always holes left behind. The close-packed structures have two types of holes: tetrahedral and octahedral.

Both types are found between the layers. Tetrahedral holes are formed when four atoms meet: three are in one layer forming a triangle and the fourth is located in the layer above (or below) that triangle. Figure 5.10 shows two tetrahedral holes for each hcp and ccp structures. Octahedral holes are also formed by six atoms: two triangles defined by three atoms in two parallel layers. Note that the triangles point in opposite directions. Figure 5.11 highlights two octahedral holes found in hcp and ccp structures.

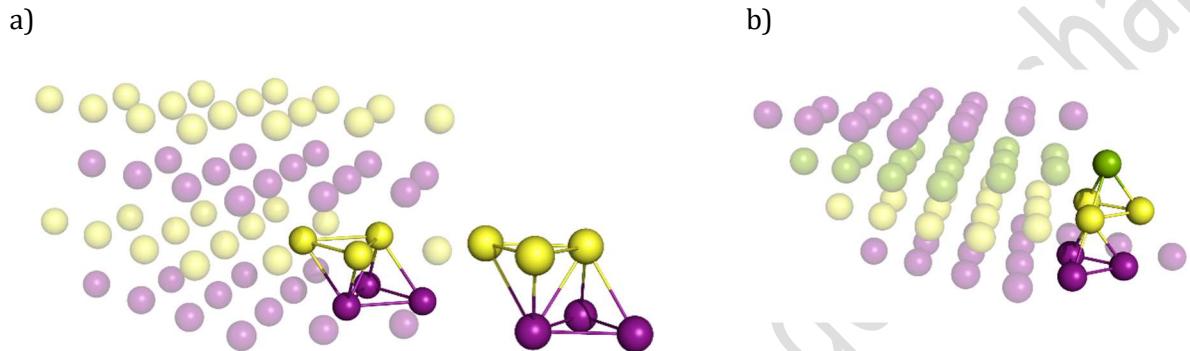


Figure 5.10 Two tetrahedral holes in a) hcp structure and b) ccp structure.

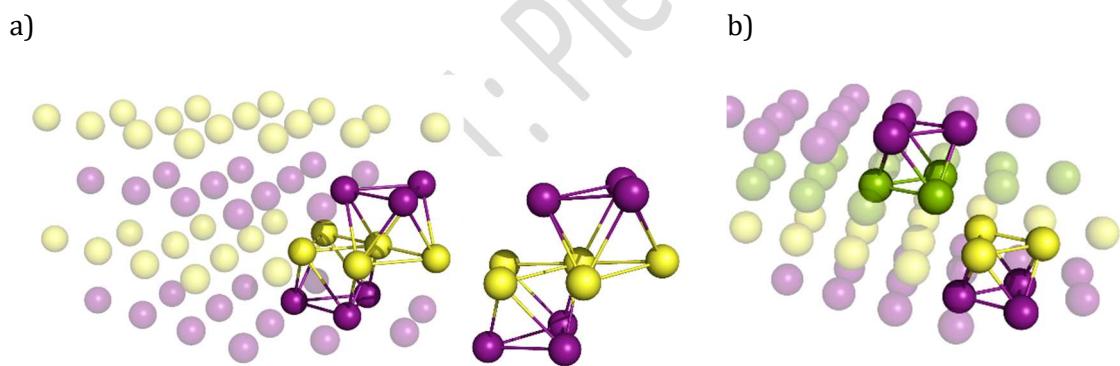


Figure 5.11 Two octahedral holes in a) hcp structure and b) ccp structure

The bcc structure has octahedral holes only. These are distributed equally across the layers (Figure 5.12a).

The simple cubic structure has only cubic holes (Figure 5.12b).



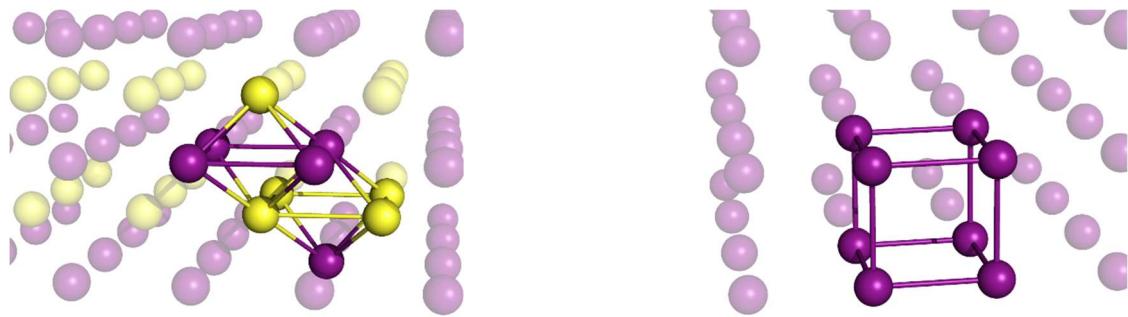


Figure 5.12 a) Octahedral holes in bcp structure and b) cubic holes in primitive cubic structure.

In theory other layering patterns are possible, for example..... But the four described are the most common and majority of metals adopt them. For example, at ambient conditions, all group 1 metals have bcc structure, while those of group 2 have hcp (except beryllium). Polonium is one of the rare examples of simple cubic structure—having the lowest packing efficiency of the four, the simple cubic structure is not frequently encountered.

The solid-state structures are systematized according to the “prototypes” or simply “type.” Compounds whose structures are determined first (historically) are commonly chosen as prototypes. Thus, the prototypical structure for bcc is W, for ccp is Cu, for hcp is Mg and for sc is Po. Saying that sodium has W-type structure is another way of identifying its structure as bcc. Although it might look redundant to use prototypes as structural descriptors (since we already use hcp, bcc, etc.), they simplify the conversation (as we’ll see later).

The structures of a material can change with temperature and pressure; change in either can cause the atoms to re-arrange in order to adjust to new conditions. All structures of an element under different conditions are called allotropes and the phenomenon of structural change is allotropy.⁶ Allotropes have

⁶ The word *allotropy* comes from two Greek words: *allos* meaning *other* and *tropos* meaning *form*.

different properties (hardness, ductility etc) because of structural differences. The best-known example of allotropy is the allotropic forms of carbon: graphite and diamond.

Atoms in metallic structures can be easily rearranged with change in temperature and/or pressure and allotropy in metals is rather common. For example, under atmospheric pressure and below 910°C iron has bcc structure, which changes to ccp above 910°. To differentiate between the allotropes, Greek letters are added as prefix starting with α for the structure stable at standard conditions. Thus, bcc iron is α Fe while higher temperature allotrope is γ Fe. The intermediary form, β Fe, has the same structure as α Fe but has different magnetic properties. The difference in magnetic properties (the change takes place at 771°C) was initially thought to be due to the difference in structures. Since this is not the case, β Fe is now considered redundant.

Understanding the structural changes of metals as a function of temperature and pressure as well as resulting change in properties is one of the tasks of *metallurgy*.

Several metals have unique structures, structures that cannot be derived from packing of the spheres. Most notably, there is liquid mercury (in a sense mercury for the metals is what penguins are for birds: mercury is not a solid and penguins cannot fly). Other important examples are manganese, gallium, bismuth and uranium. Manganese structure at standard conditions is commonly given as bcc (see for example Wikipedia page for this element). The situation is, however, more complicated to the extent that manganese is its own structural prototype called α Mn. The structure is based on body centered cubic lattice with a large unit cell containing 58 Mn atoms, Figure 5.13a (recall that the unit cell of a bcc structure contains only two atoms). There are four unique Mn atoms with varied coordination numbers: two have coordination number 16, one has 13 and one has 12 (Figure 5.13b). When heated to 710°C, manganese changes its structure to another unique one based on primitive cubic lattice with 20 atoms in the unit cell, β Mn (Figure 5.14). This structure is also its own prototype. Only above 1080°C Mn adopts ccp structure (Cu type), γ Mn. If heating is continued, the structure changes to bcc lattice (W type), δ Mn.

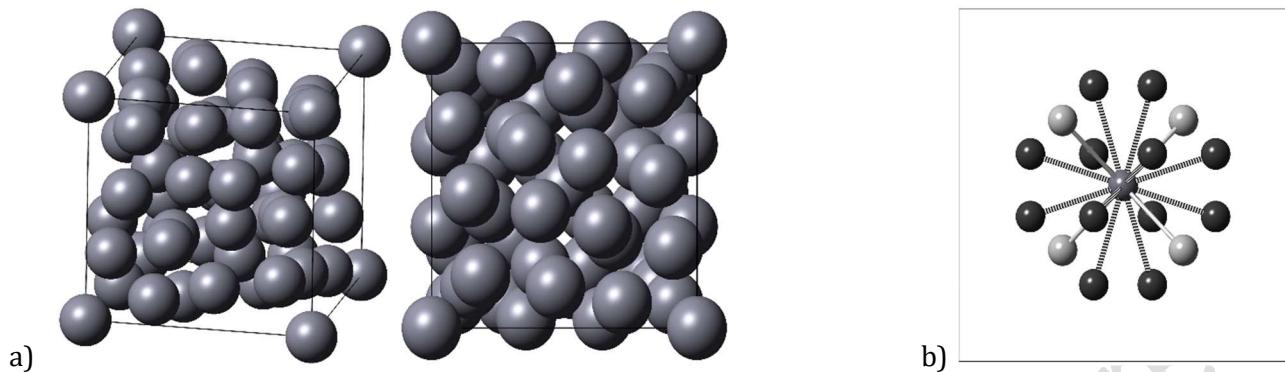


Figure 5.13 The unit cell of and coordination in α Mn: (a) full unit cell in a side view (left) and front view (right) and (b) coordination environment around one of four unique Mn atoms; the central atom has coordination 4+12 with four Mn atoms (light spheres, solid lines) at 285 pm distance and 12 Mn atoms (dark spheres, dashed lines) at 275 pm distance, the solid border is outline of the unit cell.

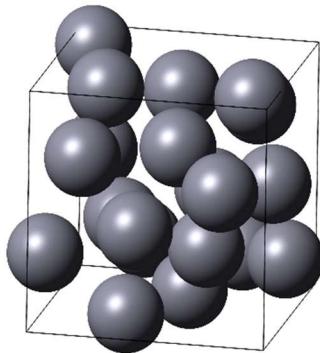


Figure 5.14 The unit cell of β Mn

Unfortunately, there is no equivalent of VSEPR theory that would help us predict the structure of a metal. We do not even have a satisfactory explanation for the unique structures some metals have. Why manganese, located in the middle of d block and surrounded by close-packed structures, would adopt the distinctive structure is still poorly understood.

5.1.3 Atomic radii of metals revisited

The atomic radii of metals (metallic radii) depend on the environment in which atom resides. For example, in hcp structures each atom is surrounded by 12 neighbors and it is going to appear larger than when surrounded by, for example, eight neighbors only in bcc structure. Since allotropy is frequent for metals and all four basic packings of spheres described above are represented (plus there are several unique ones), we need a 'standard' environment in order to compare the metallic radii on equal grounds. Victor Goldschmidt, the father of geochemistry, proposed coordination number 12 as a standard and introduced corrections that convert metallic radii calculated from less closely packed structures into radii the atoms would have if they had coordination number 12. The relative radius value in coordination 12 is taken as 1, and the corrections are then applied as fractions (Table 5.3)

Table 5.3 Goldschmidt's correction for metallic radii

| Coordination number | Relative radius |
|---------------------|-----------------|
| 12 | 1 |
| 8 | 0.97 |
| 6 | 0.96 |
| 4 | 0.88 |

(Example 5.4)

We do not have Goldschmidt correction for some unique structures as those mentioned above; due to the uniqueness there are insufficient data to derive reliable corrections. For example, the metallic radius of Mn is calculated from the α Mn structure and, since Mn atoms on average have coordination number greater than 12, manganese's atomic radius is greater than expected from the periodic trends based on standardized values—hence the 'blip' at Mn in Figures 3.4 and 3.5 in Section 3.4.

5.1.3 Alloys and Intermetallic Compounds



Alloys are mixtures of two or more metals. They belong to much larger group of mixtures called solid solutions, solid state materials composed of two or more components neither of which have to be metals. Just as is the case with “regular” solutions, solid solutions are composed of solvent, present in a larger amount, and a solute. For example, bronze is an alloy usually composed of about 88% copper and about 12% tin; thus, we can say that bronze is a solid solution of tin (solute) in copper (solvent).⁷

(Insert note on solid solutions)

There are two broad types of solid solutions: (1) substitutional solid solutions where the atoms of the solute replace (substitute) the atoms in the solvent’s lattice, and (2) interstitial solid solutions where atoms of the solvent fill the holes in the lattice of the solvent.⁸ The Hume-Rothery⁹ rules can help us determine if the solid solution is going to be substitutional or interstitial:

- I. The atomic radii of solvent and solute should not differ by more than 15%. In general, the closer the atomic radii are, the better solubility tends to be. Greater difference results in significant limitations in solubility. The difference can be calculated using Equation 5.x:

$$\text{difference (\%)} = \left(\frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \right) \times 100\% \quad (5.1)$$

For the interstitial solid solution, the atomic radius of the solute should be less than 59% of the solvent’s atomic radius.

- II. The solute and solvent should have similar electronegativities. If the electronegativity difference is too great, the two are likely going to react and form an intermetallic compound.
- III. The structures of solute and solvent should be the same—a solute that crystalizes with hcp structure, for example, is more likely to dissolve in a solvent with the same structure.

⁷ Bronze can contain other metals as well (such as nickel and zinc) but copper and tin are basic constituents.

⁸ The solvent is commonly called the host as well and ‘solvent lattice’ is ‘host lattice.’

⁹ William Hume-Rothery (1899-1968) was famous British metallurgist, the founder of the Department of Metallurgy at University of Oxford whose work focused on the intersection between metallurgy and chemistry, notably the structures and properties of alloys.



IV. The solubility is increasing if the solute atoms have the same or higher number of valence electrons.

Of these four rules, the first is the most influential one. Increase in the difference over 15% severely impedes the formation of substitutional solid solutions simply because the solute atoms do not fit in the solvent lattice. If the first rule is satisfied, then an analysis of the following three can give us a good indication on how likely the formation of solution is. Regardless how well two metals conform to the Hume-Rothery rules, complete solubility of one metal in another is rather uncommon.

Substitutional solid solutions can be ordered or disordered depending on how the atoms of the solute are distributed within the solvent's lattice. Disordered solid solutions have random distribution of solute atoms within the solvent's lattice. In ordered solid solutions, the solute atoms occupy fixed, well-defined positions within the lattice. Disordered solid solutions are more common than ordered ones, the most common reason being high temperatures required for the formation of these solutions. High temperatures expand the solvent's lattice and increase the mobility of both solute and solvent atoms resulting in significant disorder in the final structures. Examples of ordered solid solutions are Au-Cu alloys Au_3Cu , AuCu and AuCu_3 (Figure 5.14).

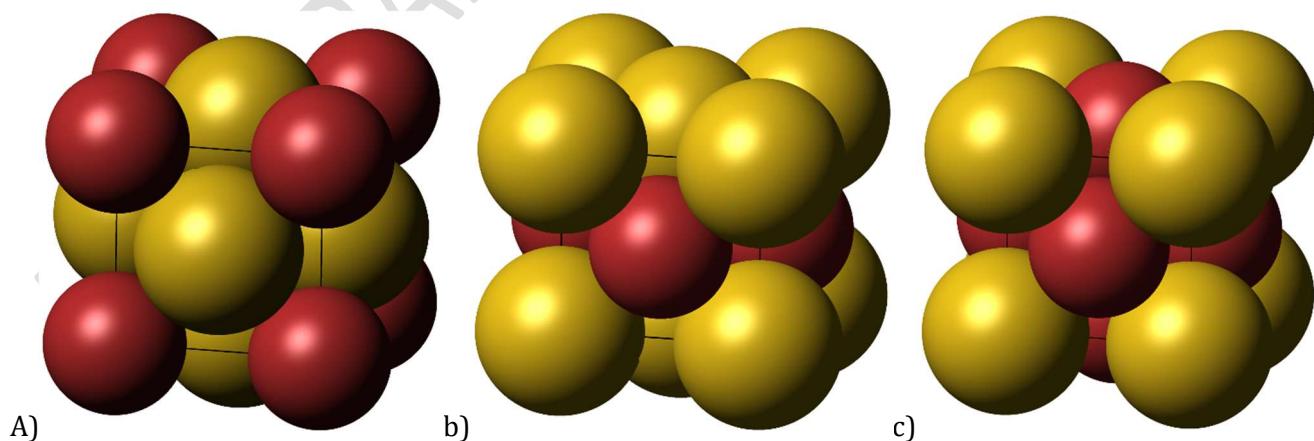


Figure 5.14 The unit cells of (a) Au_3Cu , (b) AuCu and (c) AuCu_3 . Although it is not obvious from figure (b), AuCu crystalizes tetragonal with c axis just slightly shorter than a (367 pm vs. 396 pm). The other two are

cubic. All structures are based on primitive lattices. As the amount of Au in the unit cell increases so are the unit cell dimensions: (a) $a = 409$ pm; (b) $a = 396$ pm, $c = 367$ pm and (c) $a = 374$.

Only a few elements have small enough atoms to form interstitial solid solutions with metals by filling the holes in the metal structure. These elements are H, B, C and N. Although O and F are even smaller, they are also very reactive—rather than filling the holes, O and F would react forming compounds oxides and fluorides. Best known interstitial solid solution is carbon dissolved in iron which forms basis of steel. All listed elements, except hydrogen, improve the strength of iron (and metals in general). Hydrogen, on the other hand, with its small atomic radius and only one electron makes the materials more brittle.

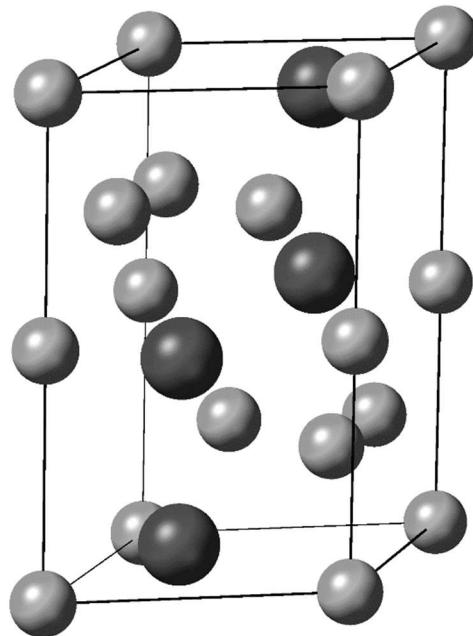
As mentioned previously, the complete solubility is very uncommon. In the case of solid solutions, the solubility is also affected by temperature, but for different reasons than liquid solutions. When heated, metals can change its structure, convert from one allotrope to another. This change can result in two compounds having the same structure and conforming to the third Hume-Rothery rule. Even the interstitial solid solutions show temperature dependence. Looking again at iron and carbon, α Fe with its bcc structure can dissolve only a little bit over 0.02% of carbon by weight. But γ Fe with ccp lattice dissolves 2% of carbon by weight, a hundred times more.

Intermetallic compounds are chemically similar to alloys. They are composed of two or more metals and can contain small amounts of non-metallic elements. Structurally, however, intermetallic compounds are different from those of pure metals they are composed of. The different structures give these compounds unique properties. The difference between substitutional solid solutions and intermetallic compound is rather blurred. Thus, AuCu with its tetragonal structure can be considered an intermetallic compound as well as alloy. Most intermetallic compounds, however, contain a main group metal and a transition metal. Such is MgZn₂ with structure shown in Figure 5.15. The structure is hexagonal (just as are both Mg and Zn), however it cannot be described in terms of simple sphere packings. Notice also very unusual coordination



around Mg in the structure. It is not uncommon to encounter intermetallic compounds with very complex structures, and large unit cells but details are not necessary at this point.

a)



b)

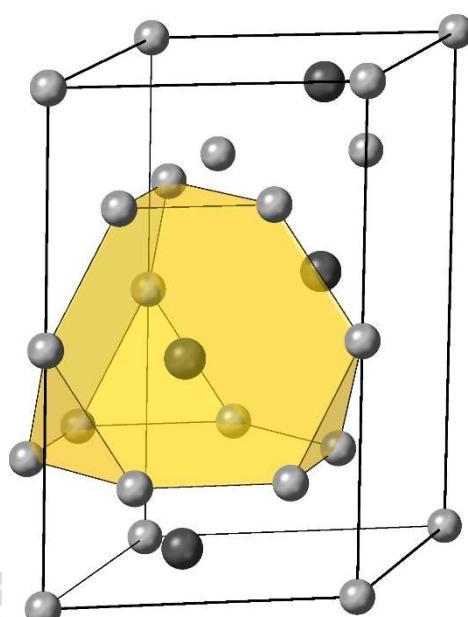


Figure 5.15 Structure of MgZn₂: a) the hexagonal unit cell (larger, darker spheres are Mg; smaller, lighter are Zn) and b) the coordination around Mg.

One final note. The noble gases (Group 18 elements) do not form molecules among themselves (as we have seen in the previous lecture). Their solid state structures are also composed of the atoms and all have face-centered cubic lattice.

5.2 The Band Electronic structure of solids

Of the two major bonding theories covered in the previous lecture, the molecular orbital theory serves as the basis for the band theory. Our previous 'scuffle' with the MO theory focused on isolated molecules. Materials such as metals have a lattice structure (more on these later) and any chunk of metal—small or

large—can be considered as one molecule. How many atoms this ‘molecule’ has depends on the size of piece of solid we have; but keeping in mind the orders of magnitude (sizes of atoms vs. dimensions of a piece of metal) we can assume that the number of atoms is very large. For example, the lightest metal, lithium, has a density of 0.534 g cm^{-3} (this is not a mistake, lithium is indeed lighter than water). Thus, a lithium cube with volume 1 cm^3 weighs 0.534 g and has $\frac{0.534 \text{ g}}{6.941 \text{ g mol}^{-1}} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 4.63 \times 10^{22}$ atoms. In this cube, Li 2s valence orbitals, all 4.63×10^{22} of them, combine to form delocalized molecular orbitals that extend through the whole volume.

This type of interaction between the atomic orbitals is certainly not easy to visualize, but commonly used starting point is an infinite (or very long) linear array of metallic atoms, in our case Li atoms. We can build this array starting with Li_2 molecule (Figure 5.16a) and forming a familiar set of two MOs, one bonding and one antibonding. Li_3 would have three MOs: a bonding, a non-bonding and an antibonding. The linear Li_4 molecule has four MOs and so on (Figure 5.16b).

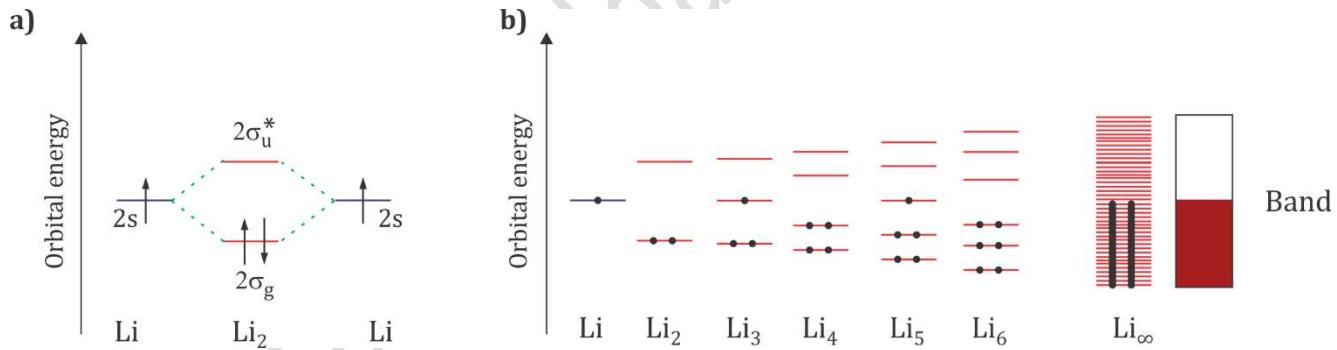


Figure 5.16 a) simplified MO diagram for Li_2 , b) a band forms from a large number of lithium's 2s atomic orbitals.

As we add more Li atoms, the number of MOs is increasing, but their energy span remains limited. Consequently, the energy difference between the sequential MOs is decreasing. If we were to make an array of 10^{22} Li atoms, the successive MOs are going to be so closely packed that they will form a band (the infinity limit in Figure 5.16b). The bottom half of the band shown in Figure 5.16b contains bonding molecular

orbitals, the top half antibonding molecular orbitals. The bands are delocalized over whole structure of the metal and, since the energy difference between the MOs making up the band is negligible, the electrons can move freely within a band and the structure. Only the bottom, predominantly bonding, part of the band in Figure 1.15b) is filled with the electrons, because lithium atoms have only one valence electron—compare with MO diagram in Figure 1.15a), only half of MOs are filled with electrons. The number, energies and shapes of the bands as well as the number of electrons populating the bands determine the properties of metals.

(NOTE) To get some sense of energy separation between the individual MOs forming a band, consider these values:

- the energy difference between 2s and 2p atomic orbitals in Li atom is 1.85 eV,
- the energy difference between 2σ and $2\sigma^*$ is 1.13 eV,
- the energy difference between two consecutive MOs inside a band formed from 10^{23} Li atoms is about 10^{-23} eV.

The total energy span of a band (also called width of a band) depends in part on the strength of interaction between atomic orbitals. This is schematically shown on Figure 5.17 for sodium atoms. The x axis represents the distance between Na atoms. At the far right, we have atoms completely separated and the energies show are essentially energies of atomic orbitals (at this distance there is no interaction between the atoms). As we move from right to left along the x axis, the distance between the atoms decreases, the orbitals start to overlap, and the bands begin to form. As we move further left, we reach equilibrium distance separating sodium atoms in the structure (368 pm). If we try to further decrease the distance, the system's energy is going to rise because the internuclear repulsion starts to dominate the energy.



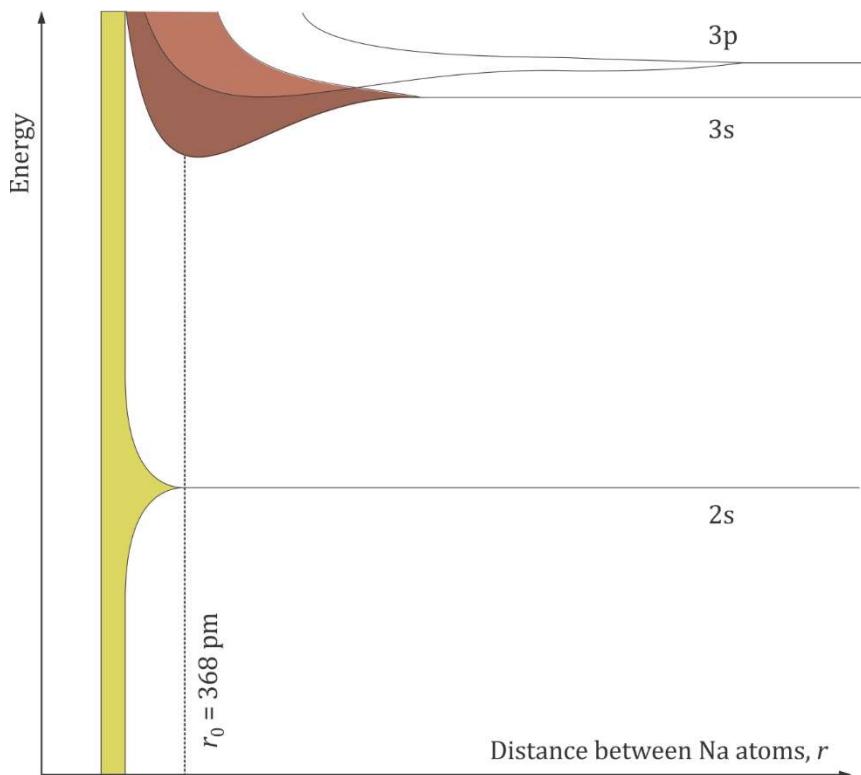


Figure 5.17 Band width and overlap as a function of distance for Na atoms

Figure 5.17 illustrates three other important points. First, the core electrons do not give bands to any significant extent at equilibrium intermetallic distances and thus they do not contribute to metallic bonding either. Second, all valence orbitals form bands at the equilibrium distance. Depending on the original atomic orbitals the bands can be s bands, p bands, d bands etc. And finally, the bands from different atomic orbitals can overlap. When this happens, the electrons are no longer confined to a band formed from their original atomic orbitals. When there is no overlap, an energy band gap exists between the bands. There are no MOs within band gaps and consequently electrons cannot be found inside the gap (just as they cannot be found “in between” atomic orbitals). The band overlap and band gap play an important role in describing bonding as well as physical properties of the solids. For example, recall from Lecture 4 that Be_2 molecule was deemed unstable because four electrons from two Be atoms fill both bonding $2\sigma_g$ and antibonding $2\sigma_u^*$. We can expect that the s band in beryllium is filled with no net bonding. The same reasoning applies to all metals of Group 2, with their electronic configuration ns^2 would produce a filled s band. However, the energy

difference between 2s and 2p orbitals in Be is about 2.73 eV which allows for significant overlap between filled s band and empty p band. This relatively small difference in energy results in significant overlap between s and p band at interatomic distances (the Be-Be distance is about 225 pm in Mg-type structure). Therefore, electrons occupying the top, the most antibonding part of s band have access to the bottom, most bonding part of the p band and can easily be excited to move within p band. For d block metals the most extensive overlap is between $(n - 1)d$ band and ns band. It is not uncommon for these metals that the d band lies completely within the s band. Figure 5.18 illustrates the band overlap and band gap. The extent of overlap and the width of a band gap depend on initial orbital energies, interatomic distance and the structure.

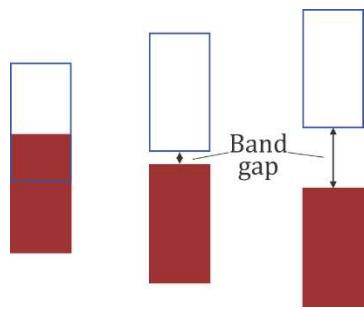


Figure 5.18 Band overlap and band gap

A good measure of metallic bond strength comes from enthalpies of atomization, $\Delta_a H$. The enthalpy of atomization is a change in enthalpy that accompanies formation of atoms in a gaseous phase. In the case of metallic elements, conversion from solid to atomic gas involves only breaking of metallic bond:



(NOTE) In other cases, the process might be more complex. For example, in case of solid sulfur composed of S_8 molecules, $\Delta_a H$ includes not only breaking of S-S bonds but also change in enthalpy that follows breaking of the interaction between individual S_8 molecules in solid sulfur. If we start from S_8 molecule in the gas phase, however, then $\Delta_a H$ would depend on the strength of S-S bonds in the molecule.

The enthalpy of atomization for the metals of periods 4-6 are shown in Figure 5.19. The values correlate quite well with the number of electrons found in the atoms. Thus, the values increase from left to right and for Period 5 and 6 they hit maximum for elements of groups 6 (Mo and W) and 7 (Tc and Re). These elements have four and five electrons in $(n - 1)d$ subshell and one or two electrons in ns subshell. Taking into account significant $(n - 1)d$, ns and np band overlaps, these electronic configurations result in filled bonding MO levels within the bands. The significant outliers are Cr and Mn. Both elements have significant exchange energy which favors single occupancy of orbitals (as opposed to electron paring, recall unique electronic configuration for Cr!). A rather unique structure of Mn also contributes to the weakening of the Mn atomization enthalpy. As we move to the right along a period, the number of electrons per atom is increasing and anti-bonding band regions are slowly filled and $\Delta_a H$ decreases.

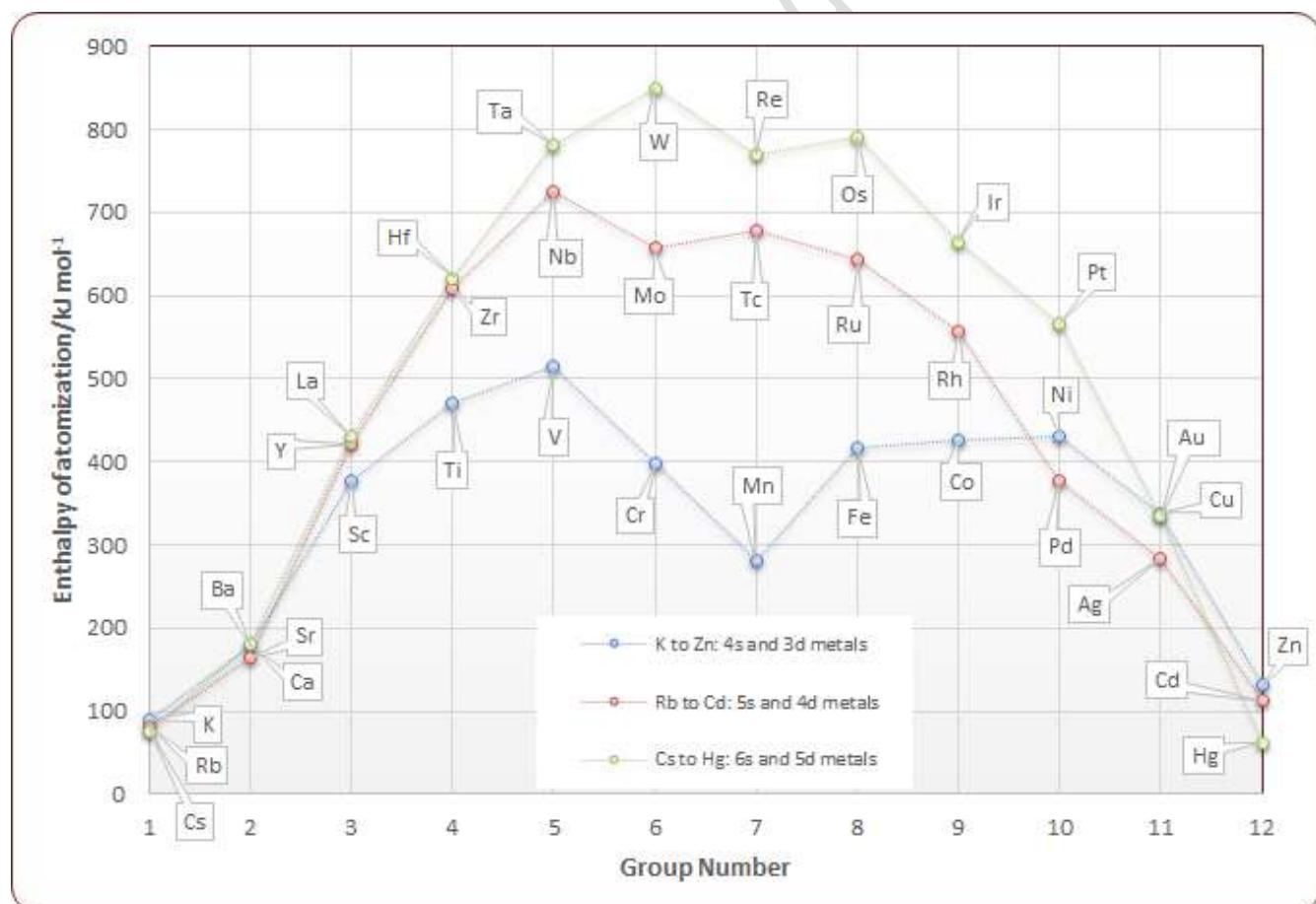


Figure 5.19 Enthalpies of atomization for selected metals in periods 4-6.

5.2.1 Applying the Band Theory: Physical Properties of Metals

Many physical properties of metals can be explained using even this very simple description of band theory combined with our discussion on structures. Metals are known for their thermal and electrical conductivity, ductility, high luster (on freshly cut surfaces) as well as a uniformity of color (all are silvery-white except cesium and gold, which are yellow and copper which is red). Thermal conductivity is the ability of a material to transfer heat from the heat source in contact. Thus, if a piece of material with a good thermal conductivity is heated on one end, the other end will soon reach the same temperature. Reverse applies: if the material had a low thermal conductivity, it would take longer for the other end to reach the same temperature. The ability of material to conduct heat is expressed as coefficient of thermal conductivity, or simply thermal conductivity, λ :¹⁰

$$\lambda = \frac{q}{A} \frac{dx}{dT} \quad (5.2)$$

In Equation 4.1, where q is the power applied to one end of material, A area of the material and dT/dx is the temperature gradient, can be applied to any solid material. The unit for λ is $\text{W m}^{-1} \text{K}^{-1}$. Materials with higher values of λ have better thermal conductivity.

In general, the heat in a solid material is carried by lattice waves, or phonons. A phonon can be defined as a quantum of crystal wave energy, similarly what photon is to light, and an increase in heat increases the number of phonons. Phonons are also responsible for transmission of sound in solids: phonons of with a long wavelength transmit the sound. In metals, however, the mobile electrons further increase the thermal conductivity. The contribution of electrons is significant because they move faster than phonons through the structure as evidenced by the values of thermal conductivities: the λ values for metals are one to two orders of magnitude (10^1 to 10^2) greater than that for non-metallic solids (for example, Al $237 \text{ W m}^{-1} \text{K}^{-1}$ vs. Al₂O₃ $30 \text{ W m}^{-1} \text{K}^{-1}$ at 300 K).

¹⁰ Some texts use k or κ as a symbol for thermal conductivity.



(Insert example 5.1)

Thermal conductivity is dependent on temperature (Figure 5.20). Initially the increase in temperature results in an increase in thermal conductivity until a maximum is reached. After the maximum, further increase in temperature decreases the thermal conductivity. The maximum, which occurs at the Debye temperature, is characteristic of each metal. The explanation for this behavior is above what is required for our text. At this point it is enough to give one reason: after the Debye temperature, further increase in T results in more phonon collisions causing a decrease in thermal conductivity.

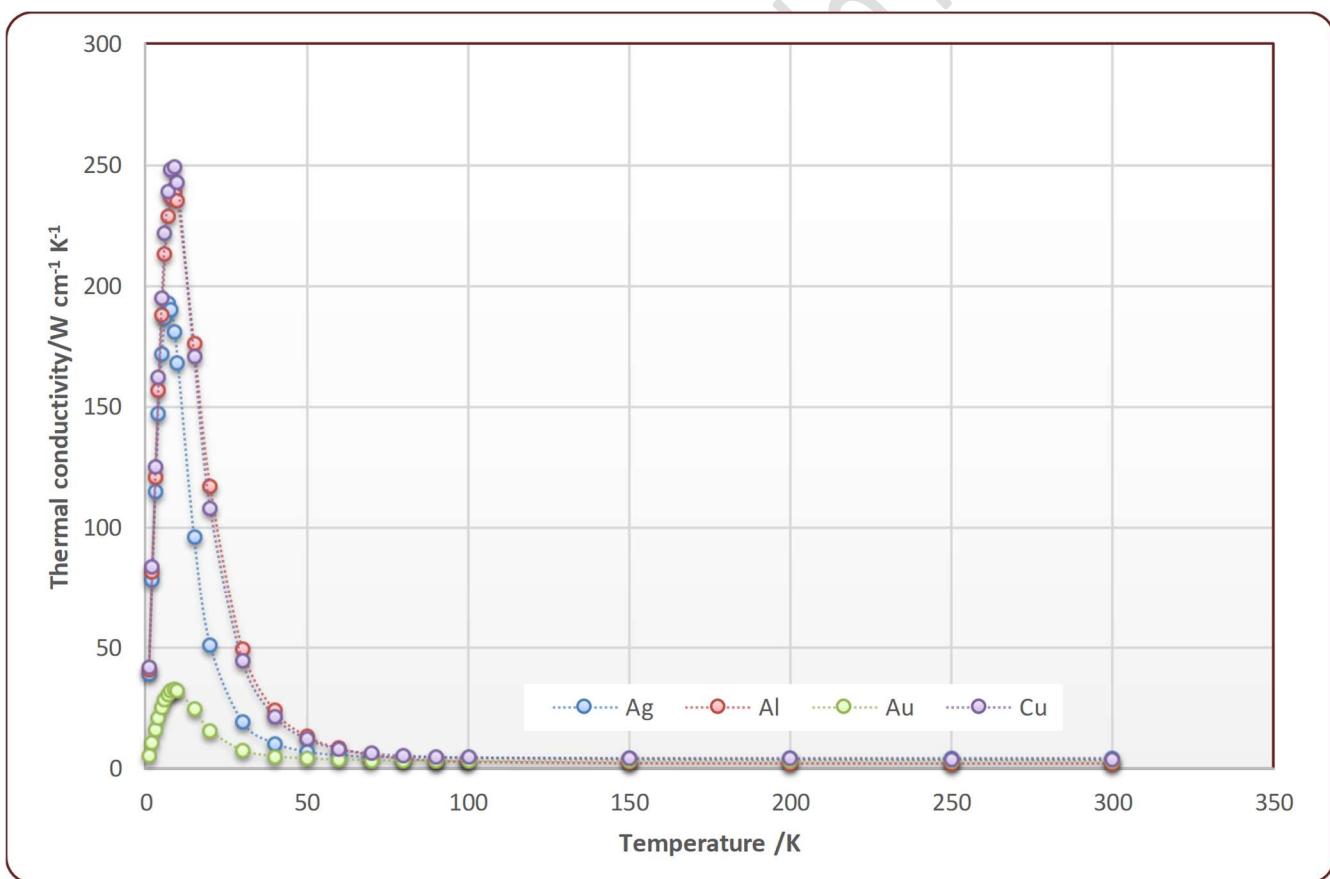


Figure 5.20 Thermal conductivity as a function of temperature. Data from "Thermal Conductivity Of Metals And Semiconductors As A Function Of Temperature." Section 12-29 in CRC Handbook of Chemistry and Physics, 98th ed. (2018), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

Another way to force otherwise randomly moving electrons to move in one direction is to apply a potential difference at two ends. The potential difference is going to drive the electrons to flow towards more positive side of the potential difference. Every material, however, has some resistance to the electron flow as its essential property. This resistance, R , is related to the length, L , and the area, A , of the material to which the potential difference is applied:

$$R = \rho \left(\frac{L}{A} \right) \quad (5.3)$$

The constant ρ , with units $\Omega \text{ m}$ (ohm meter), is called resistivity and is a characteristic of the material and is a function of temperature. Related to resistivity, and frequently used, is the electrical conductivity (or just conductivity), σ , of the material. The conductivity is reciprocal of resistivity: $\sigma = \rho^{-1}$ and has units $\Omega^{-1} \text{ m}^{-1}$. Metals have typically high conductivity values ($\sigma > 10^4 \Omega^{-1} \text{ m}^{-1}$) because they either have incompletely filled bands (as was the case with Li) or overlapping filled and empty band (beryllium). In both cases there are empty MOs inside bands to allow free movement of electrons. As the band gap is increased, the conductivity value decreases, and we move from semimetals, through semiconductors to insulators. Semimetals have a very small overlap between two bands and have conductivity in lower range of that for metals. Semiconductors have conductivity in the range $10^{-3} \Omega^{-1} \text{ m}^{-1} < \sigma < 10^4 \Omega^{-1} \text{ m}^{-1}$. Insulators, with their large band gaps have conductivities below $10^{-3} \Omega^{-1} \text{ m}^{-1}$.

Besides the difference in band structure, metals and semiconductors have one more very important and defining difference: the dependence of their resistivity values as a function of temperature. The resistivity of metals is increasing with the increase in temperature (Figure 5.21, left vertical axis for Cu, Ag and Au). The increase is almost linear except at very low temperatures (see the insert in Figure 5.21). The explanation for this behaviour is a relatively simple one. As the temperature increases so is the mobility of atoms. Atoms moving energetically around their equilibrium positions disrupt the overall structure and consequently the evenness of bands. This unevenness disrupts electrons ability to move smoothly through the solid. The resistivity of semiconductors, on the other hand is exponentially decreasing with an increase in temperature (Figure 5.21, right vertical axis for Si). In this case the increase in temperature increases the



number of electrons that can jump over the band gap separating the valence and conduction bands. This increase in number of mobile electrons results in a decrease in resistivity.

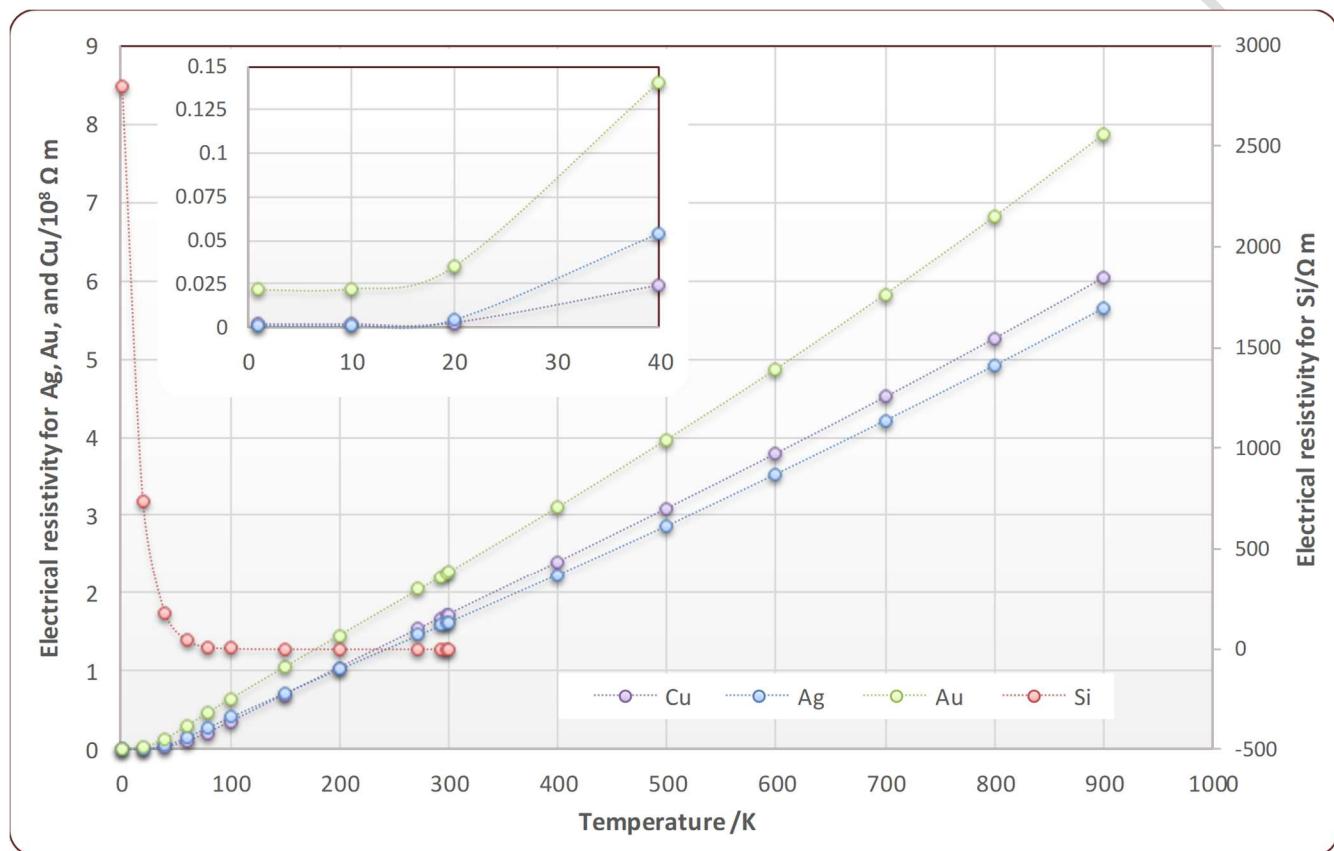


Figure 5.21 The resistivity of metals (Cu, Ag, Au; left vertical scale) and semiconductor Si (right vertical scale) as a function of temperature. Data for Cu, Ag and Au from “Electrical Resistivity of Metals.” Section 12-09 in CRC Handbook of Chemistry and Physics, 98th ed. (2018), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL. The data points for Si have been calculated using the resistivity temperature coefficient -0.075 and $\rho_0 = 3 \times 10^3 \Omega \text{ m}$. Note the different orders of magnitude for the two vertical axes: the resistivity values for the metals should be multiplied by 10^{-8} , the silicon values by 10^1 .

Since the resistivity (and its reciprocal value, conductivity) depends on temperature, relying on a range of resistivity values to define conductors, semiconductors and insulators is not a very good practice. A better way is to define these classes based on the band gap width (besides the definition of conductors and semiconductors based on the effect of temperature on resistivity as described above). Thus, conductors have a band gap of 0 eV, semiconductors $0 < \text{eV} < 4 \text{ eV}$ and insulators $> 4 \text{ eV}$.

Compounds can also be good conductors or behave as semiconductors. The band theory can be used to explain their conductivity as well. As a matter of fact, only eight elements have semiconductor properties, all other semiconductors are compounds. Frequent binary semiconductor compounds (binary compounds are composed of two elements) contain elements of Group 14 (example SiC), Groups 13 + 15 (such as GaAs) and Groups 12 + 16 (CdSe). Notice that the compounds of Groups 13-15 and 12-16 have the same average number of valence electrons as Group 14 elements: three electrons for Ga and five for As averages to four valence electrons.

A compound's ability to carry electricity can change with change in structure. For example, at temperatures below 340 K, VO_2 crystalizes monoclinic and behaves as a semiconductor. Above 340 K, VO_2 crystalizes tetragonal and is a conductor (oxides with high values of conductivity, in the range found for metals, are called metallic oxides). Band theory can be applied to explain the conducting property of materials as VO_2 as well. This example also illustrates that the band structure depends on the crystal structure.

5.3 Ionic Structures and Bonding

5.3.1 Simple Ionic Structures

Simple ionic structures can be described following similar principles used for structures of metals because simple ions (such as Na^+ and Cl^- , or monoatomic ions) can be taken as spheres. This allows us to illustrate the ionic structures as packing of spheres. We are starting with simple binary ionic structures composed of one type of monoatomic cation and monoatomic anion. This composition can be generalized if we use A as



general symbol for a cation and X as a symbol for an anion. We are using A and X as symbols, two letters far removed in the alphabet to indicate significant difference in electronegativity (and hence location in the periodic table) between the two elements. This allows us to give general formulas for more complex compounds. For example, AX is used as a general formula for NaCl, CsCl and ZnS. If the compound is tertiary such as MgAl₂O₄, then we use AB₂X₄ general formula where A and B (in our example Mg²⁺ and Al³⁺, respectively) indicate elements close in electronegativities. Similarly, AcOF (actinium oxide fluoride) would be generalized as AXY compound where X and Y stand for O and F.

Our starting point, then, are binary ionic compounds with general formulas AX, A₂X and AX₂. We'll describe their prototypical structures and have a look at how these can be used to describe structures in which A and X are not necessarily monoatomic ions. Then we'll move to somewhat more complex cases of AB₂X and ABX₃ tertiary compounds and their prototypes.

AX structural prototypes

There are four prototypical structures for binary compounds with general formula AX: halite (NaCl), caesium chloride (CsCl), sphalerite and wurtzite (both ZnS). They all, except CsCl, have names of minerals with the same formula. Sphalerite and wurtzite, with the same composition, are example of polymorphs—compounds with the same formula but different crystal structures. The sphalerite prototype is more frequently encountered than wurtzite which is formed at higher temperatures.

(NOTE) Polymorphism, although similar, should not be confused with previously mentioned allotropy which is a property of elements. Both are distinct from isomers, isolated molecules with the same chemical composition but different connectivity or orientation of atoms in space.

The unit cell of sodium chloride is shown in Figure 5.22. The cell is cubic with a face centered lattice.



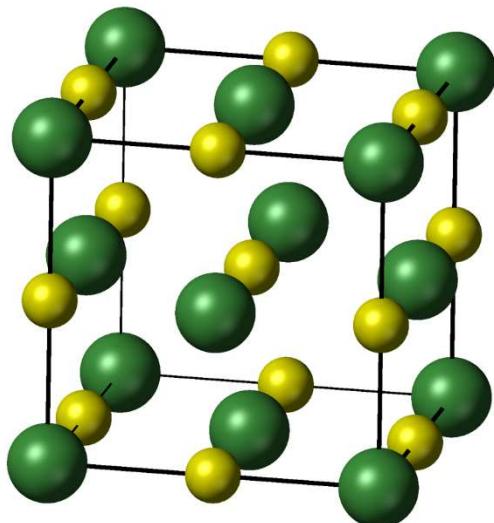


Figure 5.22 Sodium chloride unit cell: Na^+ yellow spheres, Cl^- green spheres. This coloring scheme is used in every figure showing NaCl structure. The thick lines are unit cell edges, not bonds.

Since anions are usually larger than cations, the ionic structures can be described as packing of anions as spheres with cations occupying the holes in this packing. For sodium chloride structure, the chlorides pack in CCP structure. Figure 5.23 shows the NaCl unit cell with sodium cations removed to emphasize the anion packing (compare with Figure 5.5(b)) and the the face centered lattice. As we have seen, despite being very high in space economy, the close-packed structures still have empty spaces defined by tetrahedral and octahedral holes (see Figures 5.10 and 5.11). Figure 5.24 shows locations of two (out of eight) tetrahedral holes and the central octahedral hole. In sodium chloride structure, all octahedral holes in Cl^- lattice are occupied with Na^+ cations while tetrahedral holes remain empty. This results in coordination number six for sodium cations and octahedral coordination geometry (Figure 5.25). If we repeat the unit cell once along horizontal direction and then transalte these two unit cells in vertical direction, we get four unit cells and a better emphasise on the coordination environments. Figure 5.26(a) shows the coordination of several Na^+ cations, while Figure 5.26(b) illustrates the coordination of chlorides. Notice that both ions have the same coordination environment—coordination number six with octahedral coordination geomtry. This is in short-hand notation written as (6, 6) coordination where the first nuber in brackets is the coordination number of the cation and the second number the coordination number of the anion.

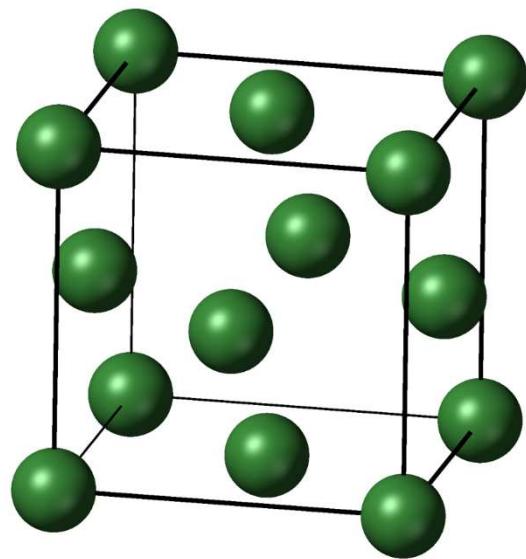


Figure 5.23 NaCl unit cell with Na^+ cations removed to emphasize face centered arrangement of Cl^- anions

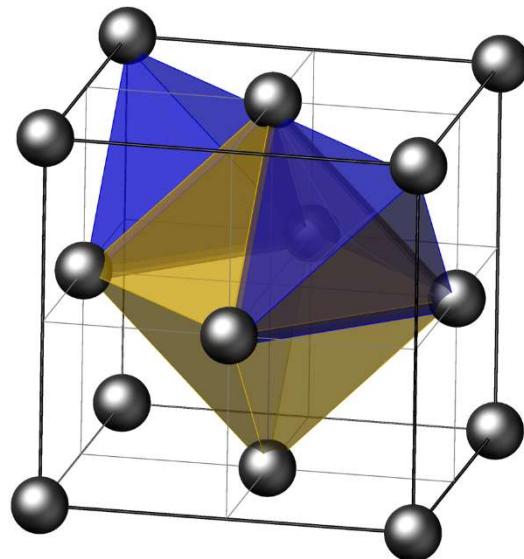


Figure 5.24 General face centered cubic unit cell showing the location of two tetrahedral and one octahedral hole. The thinner gray lines divide the unit cell into eight smaller cubes, each has a tetrahedral hole in the center.

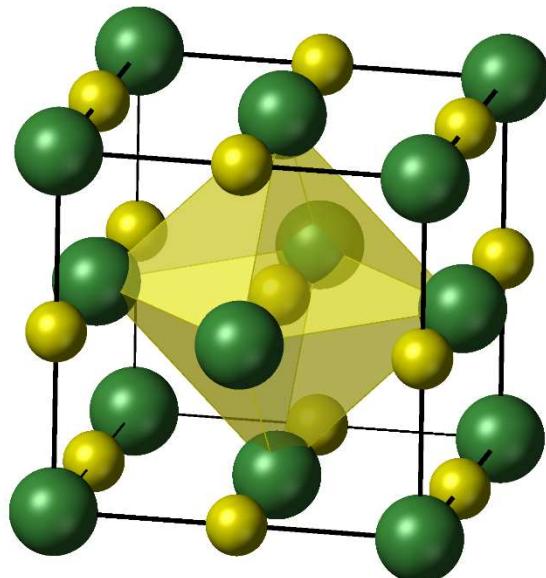


Figure 5.25 Coordination of central Na^+ cation in NaCl unit cell

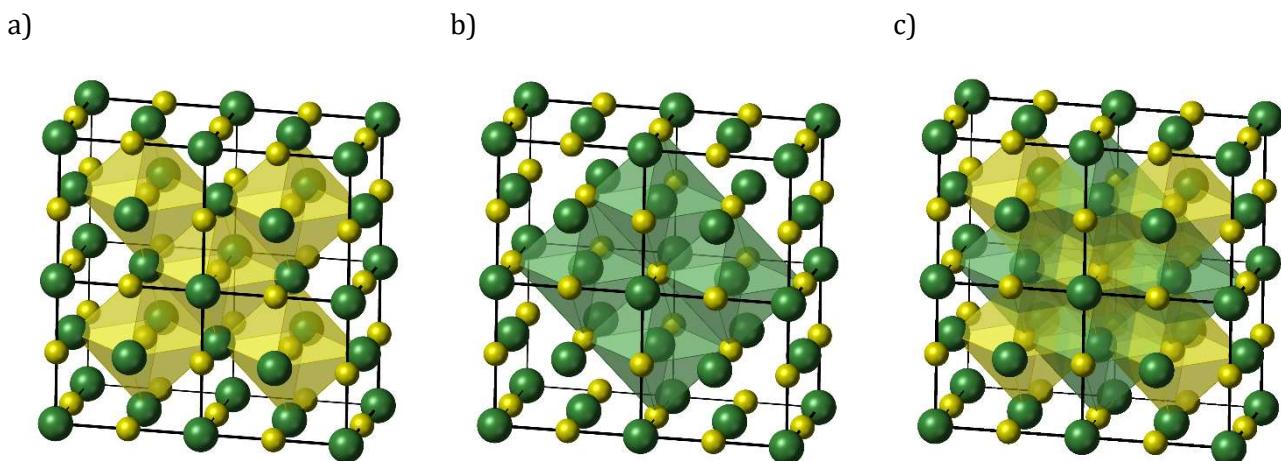
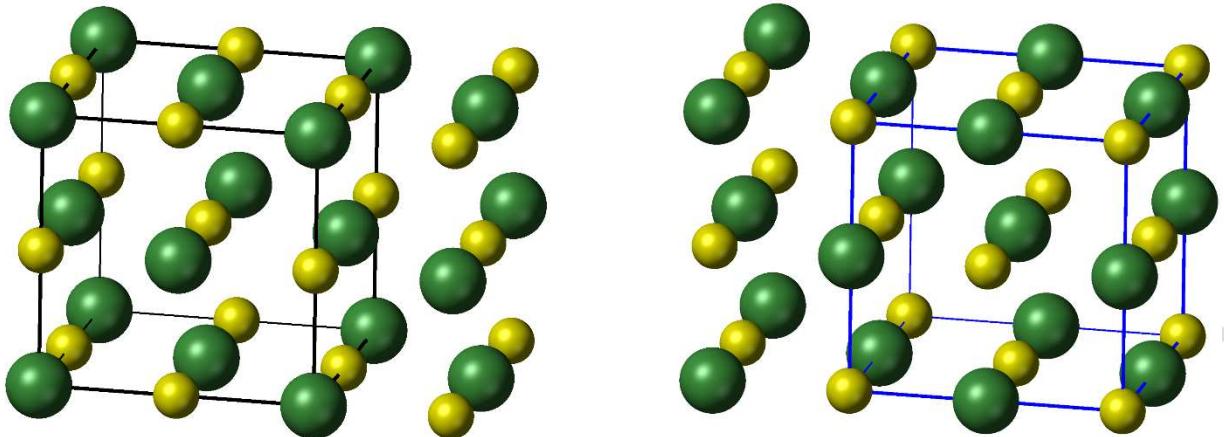


Figure 5.26 The coordination environments of a) sodium cations, b) chloride ions and c) both Na^+ and Cl^- in NaCl structure.

As a summary we can give the following description of the sodium chloride structure as cubic close packing of chloride ions with sodium cations occupying all octahedral holes. The unit cell is cubic, within face centered lattice. Coordination of cation and anion is (6, 6).

(NOTE) It is possible to choose a slightly different unit cell for sodium chloride, one that has sodium cations at the corners of the unit cell. This is illustrated in the figure below. Note that nothing fundamental about the structure has changed: the coordination environments are the same, but the structure could now be described as cubic close packing of sodium cations with chloride ions occupying all octahedral holes. It is, however, more appropriate to use smaller ions as hole-filers and consequently, use larger ions to determine the packing as described above. There are, however cases when this convention cannot be followed. Once we encounter these cases, the appropriate explanations will be given.



Our original NaCl unit cell (left) and an alternate unit cell with cube defined by Na^+ ions (right)

We frequently need to have a more mathematical (geometrical) description of location of atoms and/or ions in the unit cells. To do this we need a coordinate system to lock the atom/ion positions within the unit cell. By convention the origin of the coordinate system is taken to be the bottom far left corner of the unit cell. The unit cell edges (or directions) are then convenient axes of the system. As another convention, the vertical unit cell direction would coincide with z -axis, horizontal one with y -axis and the one perpendicular to the plane of the paper with x -axis of typical three-dimensional Cartesian system. The positions are then expressed as fractional coordinates (x, y, z) . As an example, we'll analyse the NaCl unit cell. There is a chloride ion located at the origin of the coordinate system. This ion has $(0, 0, 0)$ fractional coordinates. Now we can move along one of the three identical edges of the unit cell, for example, the vertical one. We see that there is a sodium cation in the middle, at the half length, of the unit cell edge. This sodium cation has fractional coordinates $(0, 0, \frac{1}{2})$. Moving along the same direction we find another chloride ion with coordinates $(0, 0, 1)$. The chloride ion in the middle of the back face has coordinates $(0, \frac{1}{2}, \frac{1}{2})$ and the sodium cation in the middle of the cube has $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Figure 5.27)

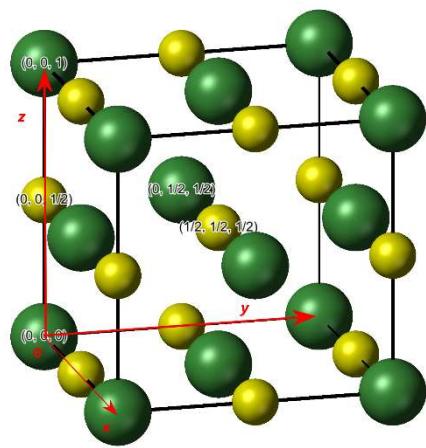


Figure 5.27 Determining the fractional (x, y, z) coordinates of ions in NaCl unit cell. The red arrows are the x, y and z axes of a coordinate system.

(NOTE Another convention in crystallography involves a proper orientation of the unit cell. The unit cell is oriented in such a way that b crystallographic direction is horizontal, direction c is vertical and a is perpendicular to the plane of paper. This convention will be followed for all non-cubic unit cells. For cubic unit cell this convention makes no difference since all three directions of the cube are identical.)

The unit cell of CsCl structure is shown on Figure 5.28. It might be tempting, albeit incorrect, to describe the CsCl lattice as body-centered cubic one. The body centered lattice and packing have identical species on cube corners and in the middle of the cube. This is not the case for CsCl structure—chloride ions occupy the corners while caesium cation the middle of the cubic unit cell. Thus, the CsCl prototype is based on simple cubic packing of Cl^- anions with every cubic hole occupied by Cs^+ cations. This results in (8, 8) coordination environment (Figure 5.29). The increase from (6, 6) found in sodium chloride to (8, 8) is due to the greater radius of Cs^+ cation which allows for increased number of anions in an immediate neighborhood.

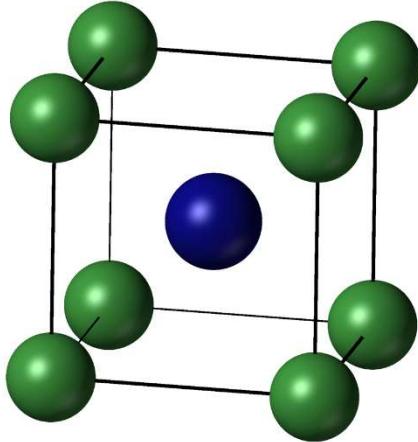


Figure 5.28 CsCl unit cell. Chloride anions are green while Cs⁺ cations is blue sphere. This coloring scheme is used in every figure showing CsCl structure. The thick lines are unit cell edges, not bonds.

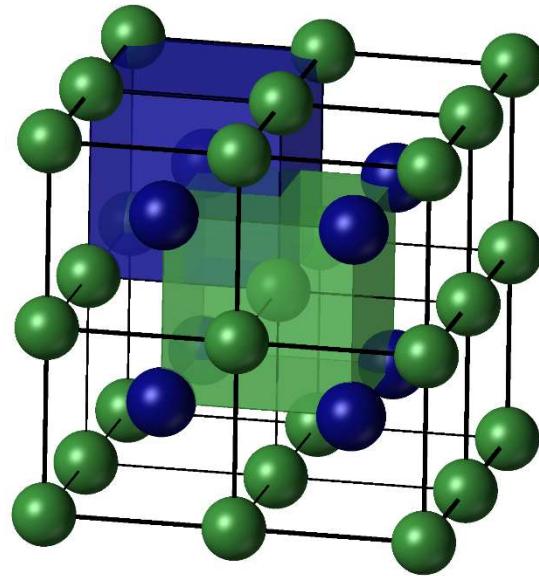


Figure 5.29 The coordination environment of Cl⁻ anions (green) and Cs⁺ cations (blue). Both ions are in (8,8) coordination.

(Insert Example 5.6 – Fractional coordinates of CsCl structure)

Sphalerite ZnS polymorph is cubic as well (Figure 5.30a). The structure is again based on the cubic close packing of anions, this time sulfide anions. Zinc cations are occupying every second tetrahedral hole in this packing. The thinner solid lines inside sphalerite unit cell of Figure 5.30 divide the cell into eight smaller cubes, incenter of each is a tetrahedral hole. The fractional coordinates of two Zn²⁺ cations are shown in Figure 5.30b. The coordinates are determined using the same convention guidelines as described above.

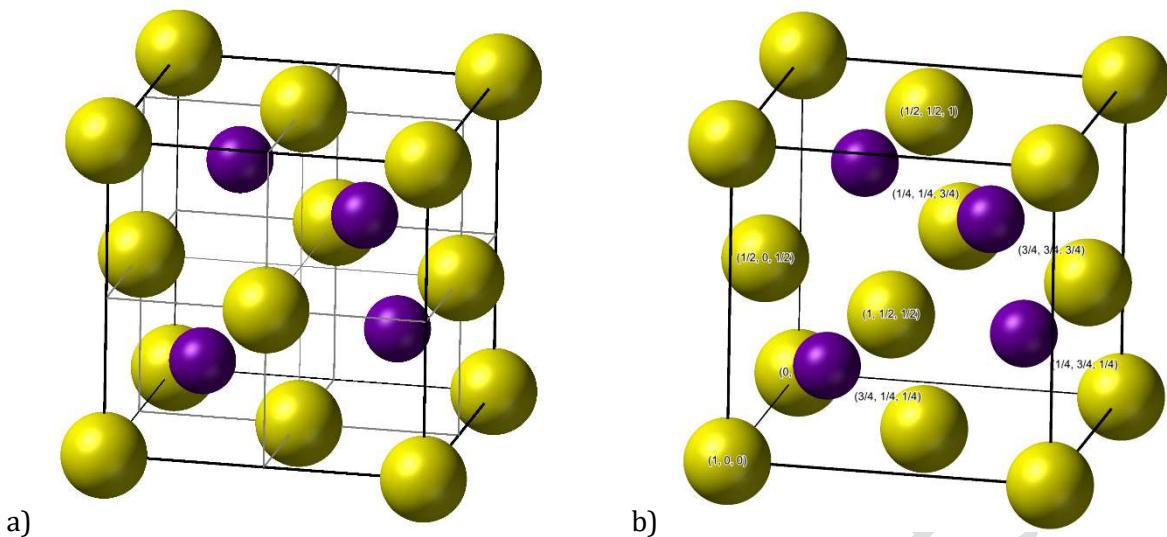


Figure 5.30 Unit cell of ZnS sphalerite polymorph: a) locations of ions in the unit cell, b) fractional coordinates of selected ions. Sulfide anions are yellow, zinc cations are dark purple. This coloring scheme is used in every figure showing ZnS structure. The solid lines are unit cell edges, not bonds.

Since Zn^{2+} cations reside in tetrahedral holes, the coordination number of Zn^{2+} is four with tetrahedral geometry around it (Figure 5.31a). The sulfide anions have the same coordination environment (Figure 5.31b). This gives (4, 4) coordination environment in sphalerite structure.

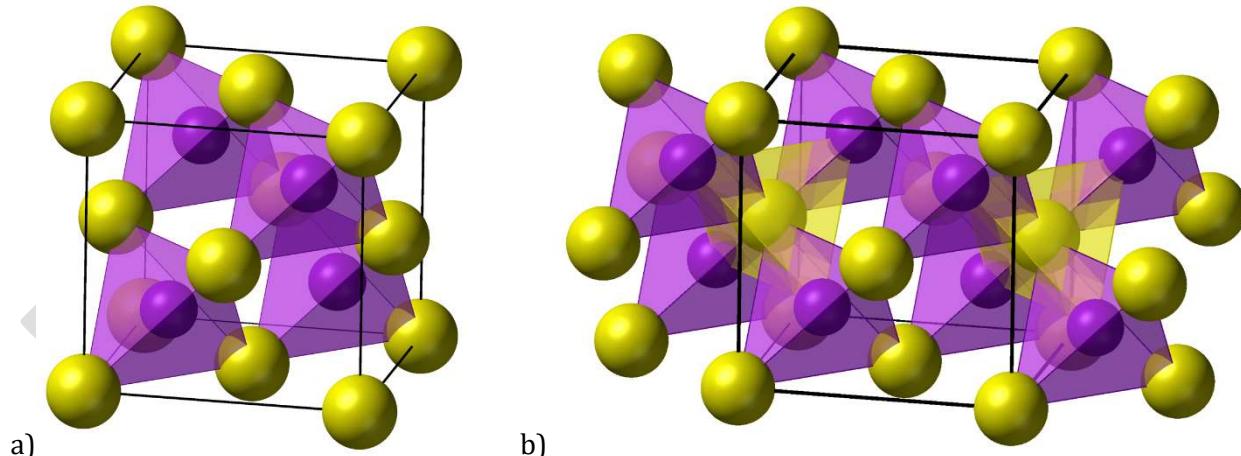


Figure 5.31 Coordination environments in ZnS sphalerite polymorph: a) for Zn^{2+} within one unit cell and b) for Zn^{2+} and two S^{2-} (on the centre of side cube faces) with extended structure

The wurtzite ZnS polymorph is hexagonal. Figure 5.32(a) shows part of wurtzite structure with the unit cell outlined. The structure can be described as consisting of two intermeshed hexagonal close packed structures: one formed by S^{2-} anions and the other by Zn^{2+} cations (Figure 5.32b)). The actual content of the unit cell is shown in Figure 5.33 together with fractional coordinates for both the cation and the anion. The intermeshing of two hexagonal close packings is also evident here.

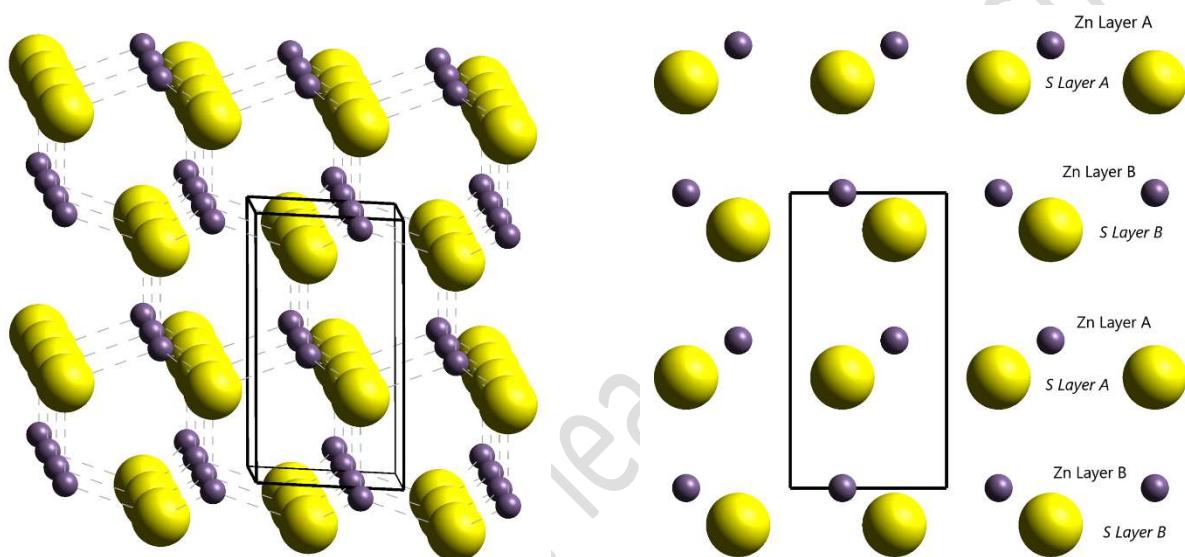
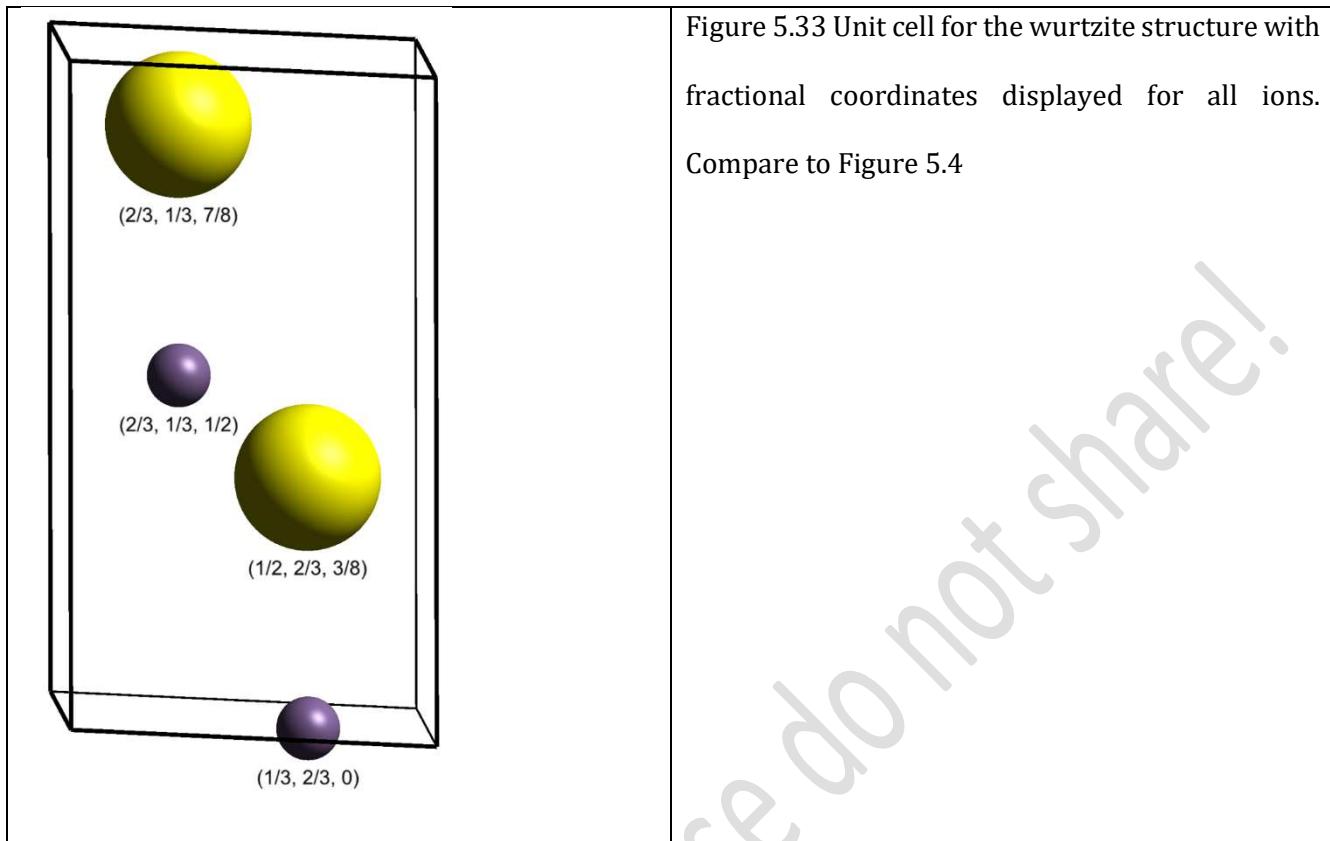


Figure 5.32 The structure of wurtzite ZnS polymorph: a) layered structure with unit cell outlined and b) view along a axis, parallel to hexagonal close packing of the ions, ABAB... layering of ions is clearly visible.



AX₂ and A₂X structural prototypes

AX₂ composition has two important structural prototypes: fluorite (CaF₂) and rutile (TiO₂), both common minerals. The antifluorite prototype is important for A₂X composition.

The fluorite structure is cubic (Figure 5.34). The structure can be described as cubic close packing of cations with every tetrahedral hole occupied by fluoride anions. This description departs from our previous convention in a sense that we use cations, not anions, to determine the packing of the spheres. This departure is justified since fluoride is a very small anion and the structure is more conveniently described in terms of cation packing. The coordination environment for F⁻ ions is determined by the type of hole they occupy: tetrahedral coordination geometry and coordination number four. The coordination number for Ca²⁺ is eight and geometry is cubic (Figure 5.35). Thus, the fluorite structure has (8, 4) coordination which is consistent with the cation : anion stoichiometry of 1 : 2. Higher coordination of Ca²⁺ is necessary to balance the charge.

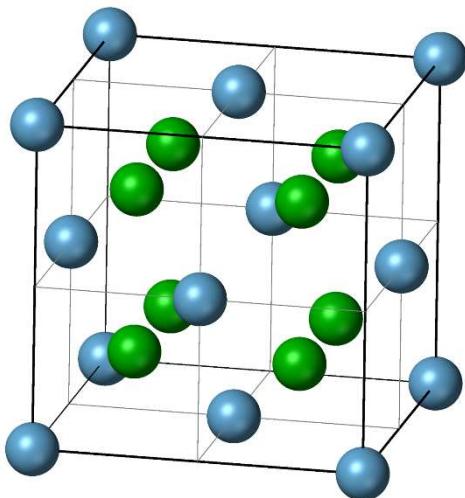


Figure 5.34 The unit cell of fluorite prototype. Calcium cations are green-blue, fluoride anions are green. This coloring scheme is used in every figure showing CaF_2 structure. The solid lines are unit cell edges, not bonds. Compare with the sphalerite unit cell in Figure 5.30.

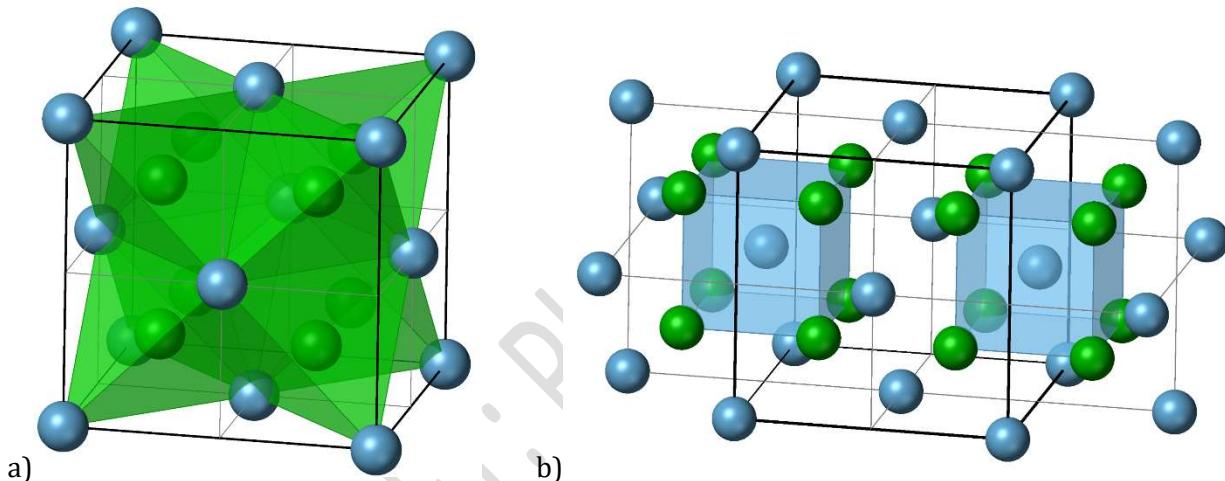


Figure 5.35 The coordination environments in fluorite structure: a) tetrahedral coordination of fluoride anion, and b) cubic coordination of Ca^{2+} cation

If the locations of cations and anions in the fluorite structure are reversed—cations are placed in the tetrahedral holes of anion's CCP array, we obtain antifluorite structure. These structures have large anions and smaller cations (thus we can again use anions to build up the appropriate close packing of the spheres), as is found in Li_2O (Figure 5.36). The antifluorite structure has (4, 8) coordination—again inverse form fluorite.

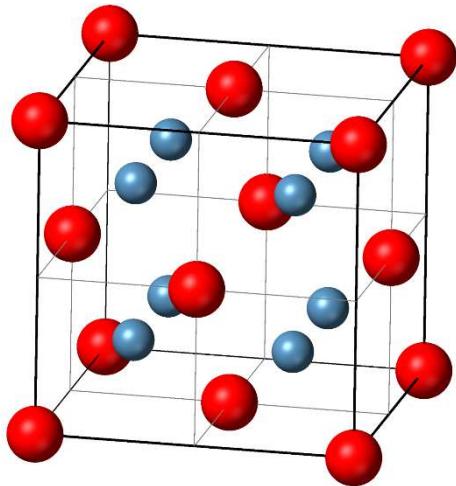


Figure 5.36 Lithium oxide, Li_2O , has antifluorite structure in which anions and cations have exchanged locations found in the fluorite structure. Oxide anions (red spheres) are now forming ccp array with Li^+ cations filling all tetrahedral holes.

The rutile structure is tetragonal (Figure 5.37). The cations in rutile prototype are surrounded by six oxide anions but this time, unlike NaCl structure, the six anions are not equidistant from the cation: four of the six are closer than the remaining two (Figure 5.38a)). In this case, and similar ones, the coordination number is usually given as $4 + 2$ to emphasize the difference in distances. Consequently, the coordination geometry is not an ideal octahedral but rather tetragonal bipyramidal (Figure 5.38b). These differences can be expected for tetragonal structures that are either stretched or compressed in comparison to cubic ones (compare NaCl and TiO_2 prototypes). Oxide anions are surrounded by three titanium cations in trigonal planar geometry (Figure 5.38b)). Thus, the rutile structure has $(4 + 2, 3)$ coordination.

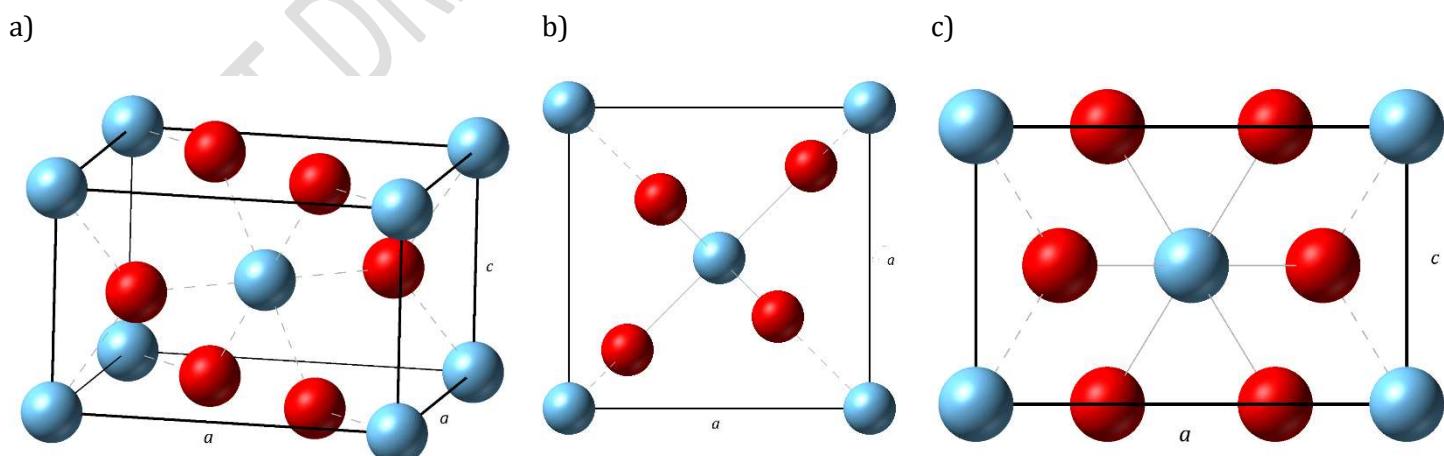


Figure 5.37 The unit cell of rutile prototype. This unit cell belongs to tetragonal crystal system with c axis shorter than a . a) Unit cell with oxide anions red and Ti^{4+} cations light blue, b) the same cell viewed along c direction showing the two equivalent a directions, and c) view along one of the a directions emphasizing shorter c unit cell edge. This coloring scheme is used in every figure showing TiO_2 structure. The solid lines are unit cell edges, not bonds.

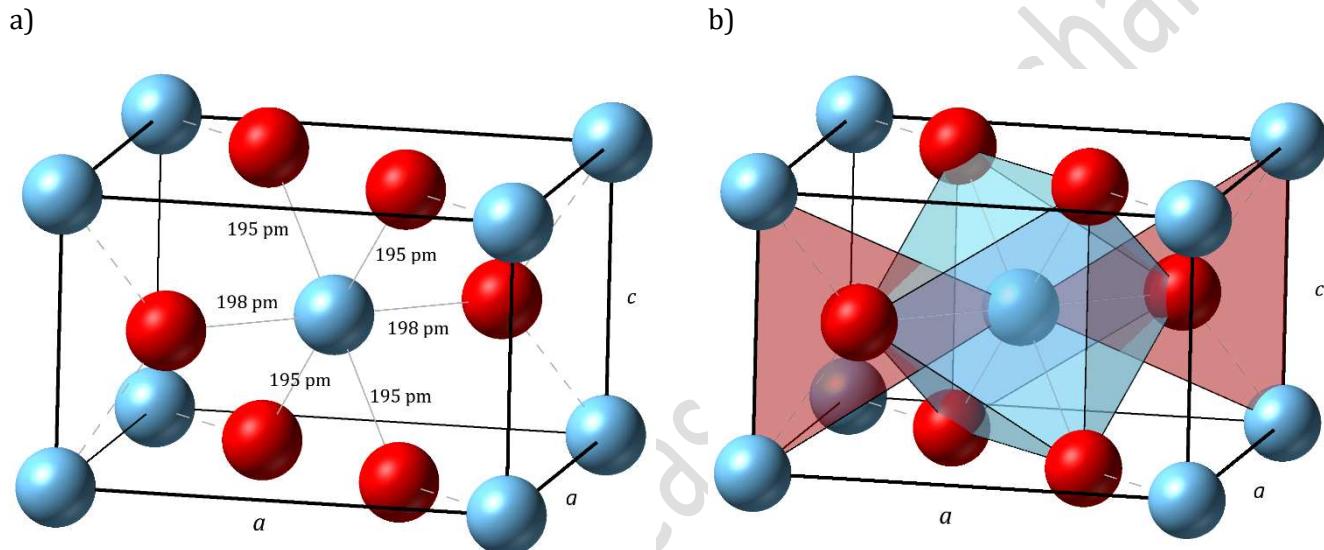


Figure 5.38 The coordination environments of rutile structure: a) the distances between the Ti^{4+} cations and six O^{2-} anions are not identical—two are slightly longer than other four resulting in 4 + 2 coordination for Ti^{4+} , and b) coordination of both cation and anion in rutile structure gives (4 + 2, 3) coordination.

These six prototypes are the most common ones for simple binary compounds. There are more prototypical structures, of course, but they occur less frequently and will be covered as needed.

5.3.2 Two important ternary structures: perovskite and spinel

Ternary compounds contain three elements in their composition. Perovskite is calcium titanium oxide, CaTiO_3 , while spinel is magnesium aluminum oxide, MgAl_2O_4 . Both are important, naturally occurring oxides

and their structures are prototypical for many compounds with general formulae ABX_3 and AB_2X_4 , respectively. Cation A is larger and has lower charge than B cation for both groups.

Perovskite structure is common when $X = O$ or F . The cation B is smaller and has higher charge than the cation A, but the sum of charges has to equal 6+ (for $X = O$) or 3+ (for $X = F$). The idealized, cubic perovskite unit cell is shown in Figure 5.39a). In reality, ABX_3 compounds deviate from cubic structure (perovskite itself is actually orthorhombic) since various allowed combinations of A^{a+} and B^{b+} for a given X dictate the packing of the structure. Although this deviation from ideal presents a bit of a problem when describing the structure, it does result in important and interesting physical properties—many compounds with this structure (or the structure derived from it) are superconductors or have unusual magnetic and optical properties. The corners of the unit cell are defined by positions of B^{b+} cation, in $CaTiO_3$ that is Ti^{4+} . The X^{x-} anions are located in the middle of every cube edge (O^{2-} in perovskite) and the large A^{a+} are found in the middle of the unit cell (Ca^{2+} in $CaTiO_3$). A different ideal perovskite unit cell can be used (Figure 5.39b)) with A^{a+} cations at the corners or unit cell and X^{x-} anions in the middle of every unit cell face. This results in a close packing of A^{a+} and X^{x-} arranged so that each A^{a+} is surrounded by twelve anions. The B^{b+} cations occupy octahedral holes defined by anions only.

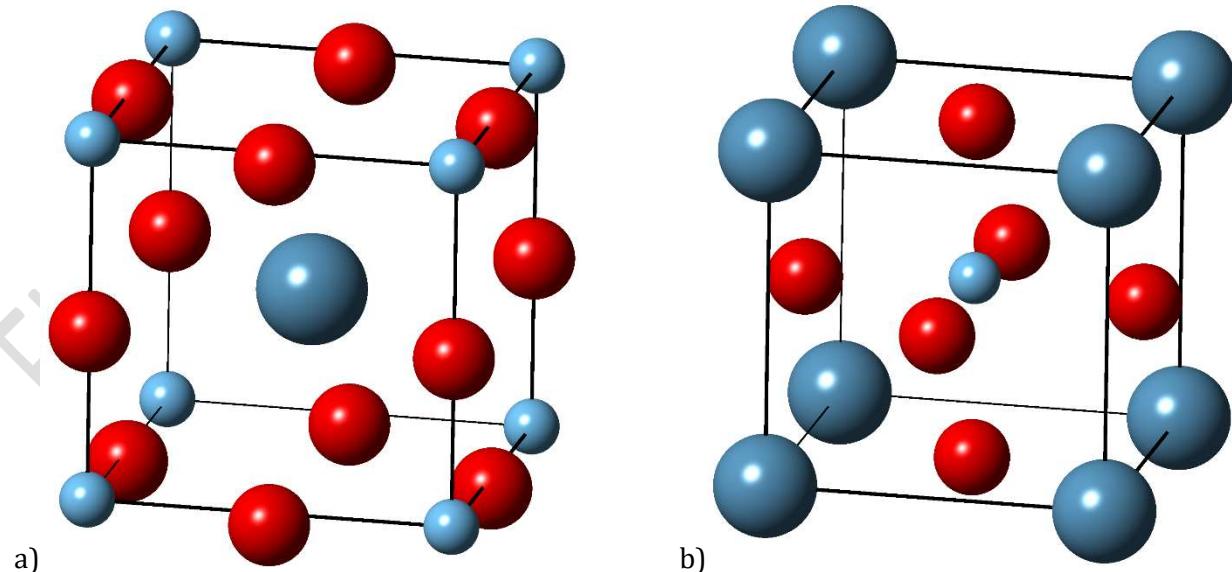


Figure 5.39 Unit cell of perovskite (CaTiO_3) prototype structure: a) conventional idealized cubic unit cell defined by smaller B^{b+} ($= \text{Ti}^{4+}$) cations (smaller light blue spheres), and b) alternative, also idealized unit cell defined by larger A^{a+} ($= \text{Ca}^{2+}$) cations at the corners; notice the similarity with face centered cubic unit cell. X^{x-} ions ($= \text{O}^{2-}$) are red spheres.

As is already evident from Figure 5.39b), the B^{b+} cation is surrounded by six X^{x-} anions in an octahedral fashion. Figure 5.40a) emphasizes this using the conventional perovskite unit cell. The A^{a+} cation is surrounded by 12 X^{x-} anions and is resting in a centre of a cuboctahedron (Figure 5.40b)).

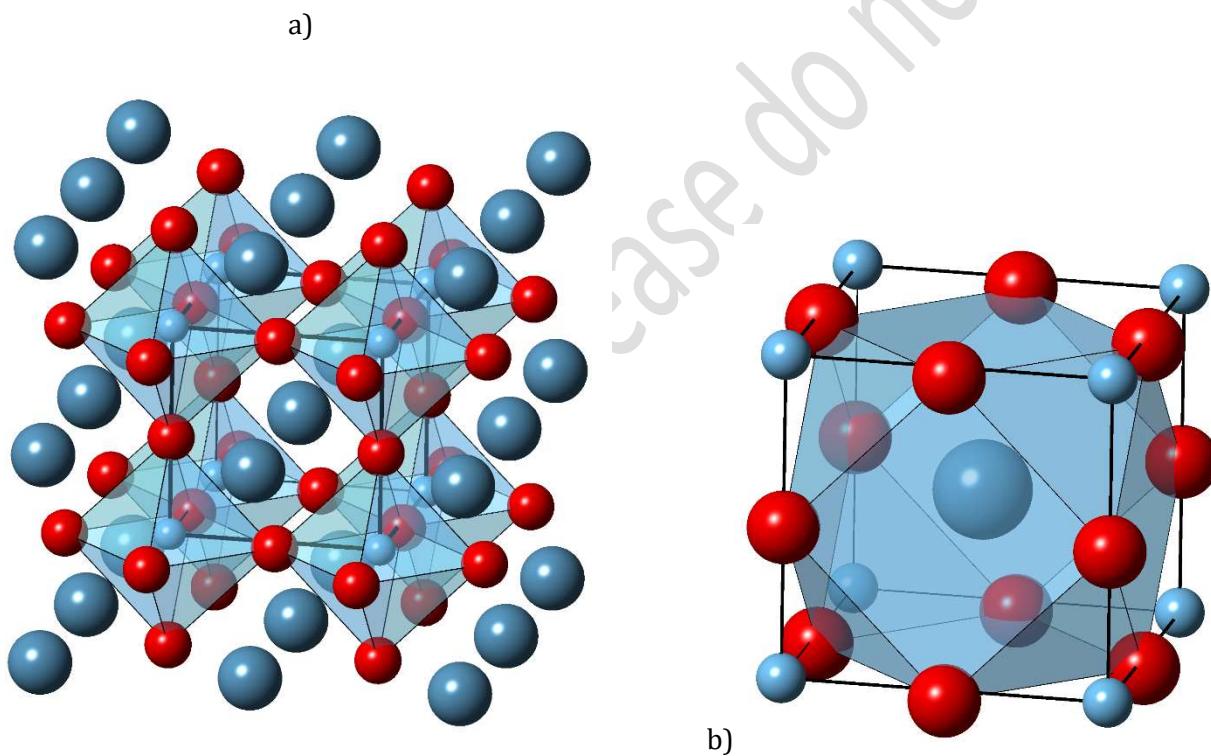


Figure 5.40 The cation coordination environments in perovskite structure: a) for B^{b+} cation and b) for A^{a+} cation.

Figure 5.40a) shows an alternative way of describing this structure using cation's coordination environment. Notice that the BX_6 octahedra are connected through X anions and form their own lattice of

corner-sharing octahedra. Since the centres of octahedra define a cube (Figure 5.40a)), the structure can be described as a primitive cubic lattice of corner-sharing BX_6 octahedra with every cubic hole occupied by A^{2+} cations. The approach to describing structures using coordination polyhedrons is very common for more complex cases since it simplifies the process.

Our next prototype structure—as mentioned above—is the spinel structure, based on mineral MgAl_2O_4 . Spinel's unit cell is cubic and rather large—its edge length is 809 pm, almost twice than for MgO (420 pm) and contains eight Mg^{2+} , 16 Al^{3+} and 32 oxide anions (Figure 5.41). It is somewhat challenging to see that the oxide anions (or X^{x-} in general case) form a cubic close-packed array even with cations removed (Figure 5.42a). Figure 5.42b) shows the same unit cell but emphasizes the packing of anions with an equivalent of an CCP unit cell marked (compare with Figure 5.x).

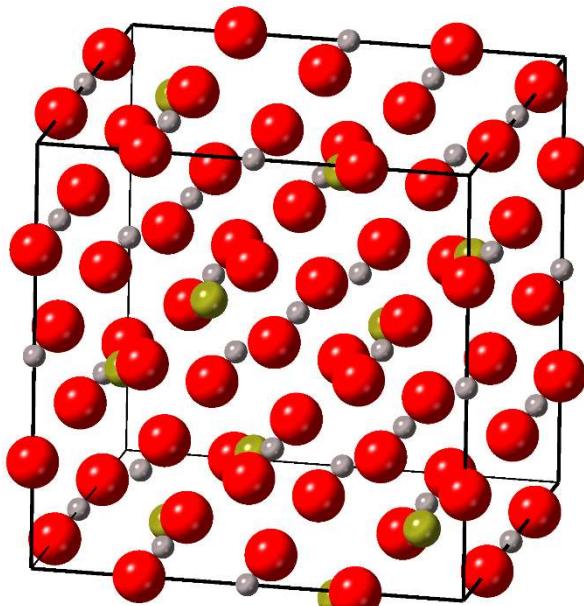


Figure 5.41 The spinel (MgAl_2O_4) unit cell.

Magnesium cations (A cations) are dark yellow-green, aluminum cations (B cations) are gray and oxygen anions (X) are red. This coloring scheme is used in every figure showing MgAl_2O_4 structure. The solid lines are unit cell edges, not bonds.

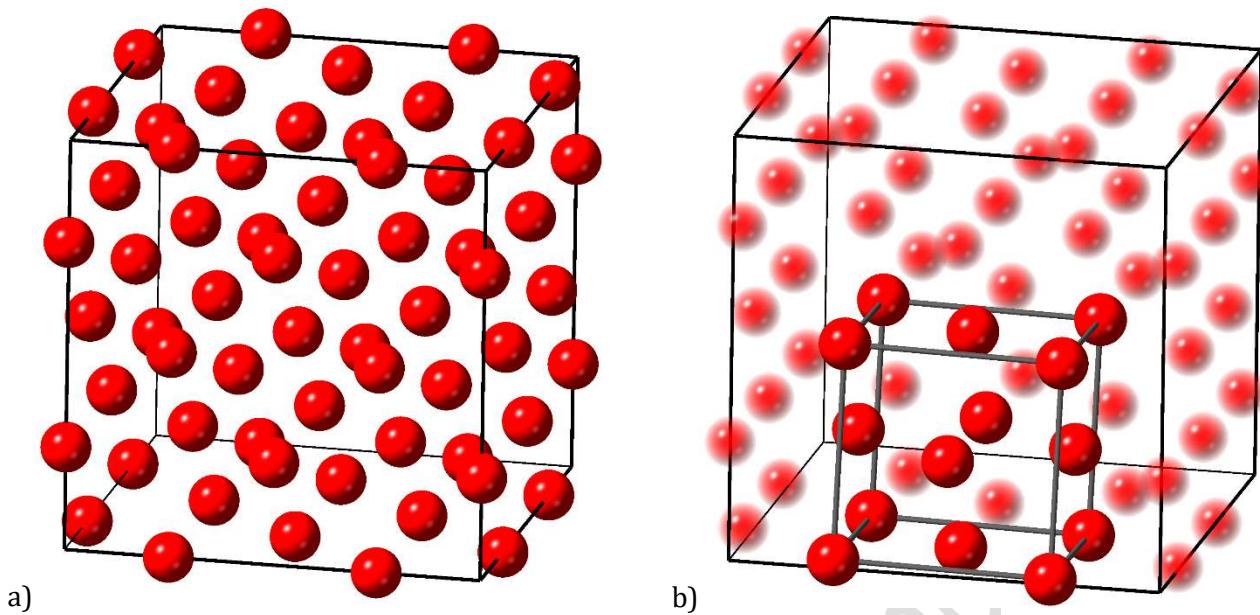


Figure 5.42 The packing of oxide anions (X anions) in the spinel structure: a) unit cell with only anions shown and b) the same view as a) but with an outline of ccp unit cell equivalent emphasizing the cubic close-packing of anions in the structure.

The A cations (Mg^{2+}) are occupying $\frac{1}{8}$ of the tetrahedral holes (Figure 5.43a)) and B cations (Al^{3+}) $\frac{1}{2}$ of octahedral holes (Figure 5.43b)). Notice that the BO_6 octahedra share edges but AO_4 tetrahedra are isolated from each other (Figure 5.43c)).

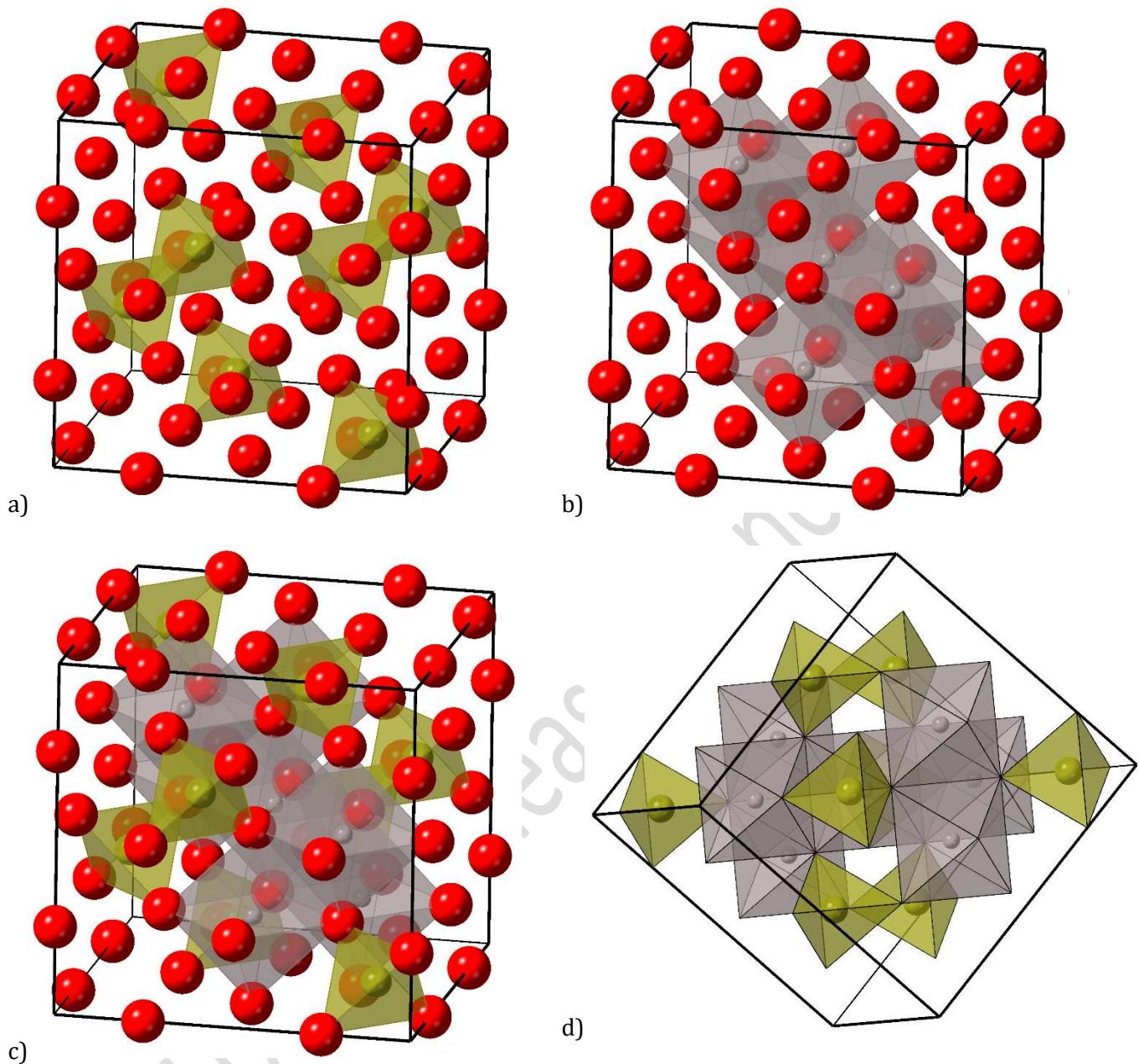


Figure 5.43 The coordination environments for actions in the spinel structure: a) Mg²⁺ (A cation) tetrahedral coordination, b) Al³⁺ (B cation) octahedral coordination, c) both cations together and d) with anions removed and unit cell rotated.

There is also an inverse spinel structure in which cation B is found in both tetrahedral and octahedral holes.

The general formula is then usually written as B[AB]X₄ to emphasize two coordination environments for cation B.

5.3.2 Predicting the structure of binary ionic compounds: The radius ratio rule.

We have seen that the coordination numbers of cations in NaCl and CsCl structures are six and eight, respectively. The reason for this difference lies in the difference in ionic radii for Na^+ and Cs^+ : the larger Cs^+ can surround it self with more anions than smaller Na^+ . This difference in coordination environments produced different structures for the two prototypes. We would observe similar changes if we modify the anion. Thus, caesium fluoride, CsF, has NaCl structure with (6, 6) coordination. In this case, smaller fluoride anion can surround itself with fewer Cs^+ cations in comparison to larger Cl^- .

This quick analysis shows that the structure adopted by binary compounds depend on relative radii of cations and anions that make up the solid. Indeed, the radius ratio, defined as $\gamma = r_{\text{small}}/r_{\text{large}}$ can be used to suggest the likely structure of a ionic solid. The r_{small} is simply the smaller of the two radii, generally (but not always) the radius of the cation. To see how the radius ratio is used, we'll first consider the radius of a small ion (usually a cation) that just fits into a tetrahedral hole formed by four larger ions (usually anions).

(Insert Example 5.7)

Following a similar procedure, we can find that 0.414 is the minimum radius ratio required to fill an octahedral hole. Thus, as long as the radius ratio remains between 0.225 and 0.414 the coordination is going to remain four. Once the ratio becomes 0.414 there is sufficient space around the smaller ion to add two more ions of the opposite sign and the coordination becomes six.

Note that the radius ratio rule relates the γ value to the coordination environments. Now we can extrapolate and look for the prototypical structures that have a coordination environment required by the γ value. For example, tetrahedral coordination environment is found in ZnS polymorphs for AX compounds and in fluorite and antifluorite for AX_2 and A_2X compounds respectively. Table 5.x summarizes the ranges of γ values for various coordination and their associated prototypical structures.

Table 5.x Radius ratios and their corresponding coordination environments and prototypical structures.

| γ | Coordination number | Coordination geometry | Prototypical structure for general formula | |
|-------------|---------------------|-----------------------|--|------------------|
| | | | AX | AX ₂ |
| 0.150–0.225 | 3 | Trigonal planar | — | — |
| 0.225–0.414 | 4 | Tetrahedral | ZnS | Antifluorite |
| 0.414–0.732 | 6 | Octahedral | NaCl | TiO ₂ |
| 0.732–1 | 8 | Cubic | CsCl | Fluorite |
| 1 | 12 | Varies | Found in metallic structures | |

(Insert Example 5.7)

There are a few points worth mentioning in regard to the data in Table 5.x. There are no structures that have coordination number 3. Its values are here given for completeness. This γ range, however, is important for the discussion of other structures (to be encountered later). Further, we cannot use the γ values to differentiate between sphalerite and wurtzite structure since both have (4, 4) coordination—the table has just “ZnS” under AX composition for this γ range.

At this point we need to re-visit our discussion of ionic radii from Section 3.X. If we were to measure the radius for Cl⁻ using structural data for NaCl and CsCl we would discover that the radius obtained from CsCl structure is longer than that from NaCl structure. This discrepancy is due to the differences in coordination environment of Cl⁻ anion. In CsCl structure, chloride anion is surrounded by eight Cs⁺ cations and resides in a cubic hole, a hole that is bigger than the octahedral hole of NaCl structure. Hence, the measured radius is going to be greater for CsCl structure. The tables listing ionic radii are going to have different values for each ion depending on coordination. For example, the radius of Cs⁺ is 167 pm for coordination six but 174 pm for coordination 8. Considering that vast majority of ions (except a few of the smallest ones) can have coordination number 6, we use the radii for this coordination number when we need to compare/discuss the trends in radii.



The radius ratio rule predicts the structure of a binary compound correctly in about $\frac{2}{3}$ of the cases.¹¹ Interestingly, it fails to correctly predict the structure for ZnS. Thus, if we find the ratio $r(\text{Zn}^{2+})/r(\text{S}^{2-})$ using Zn²⁺ and S²⁻ radii for coordination number 4 we obtain $(74 \text{ pm})/(170 \text{ pm}) = 0.435$, and using radii for coordination number 6 we have $(88 \text{ pm})/(170 \text{ pm}) = 0.518$. Both values would indicate coordination 6 and NaCl structure rather than actual ZnS structure with (4, 4) coordination. The reason behind the discrepancy between the predicted and observed structure is bonding. Structures that have higher covalent character do not follow the radius ratio rule. Covalent bonding results in directionality of bonds forcing different structures from those expected based on simple packing of the spheres. As the covalent character increases, the structures become layered and polymeric as we'll see soon.

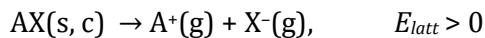
5.4 The Ionic Bond and Lattice Energies

The ions in the lattice are held together through electrostatic force manifested through a uniform electric field around each ion. This results in a non-directional interaction between the ions. Therefore, cations are surrounded uniformly by anions (and vice versa) in the ionic crystal as we have seen from the discussion of the structures. The description of the basic structural prototypes also revealed that the number of anions around any given cation depends on their relative sizes and charges. One of the consequence of non-directionality of this bond type is that the distances between a cation and the anions surrounding it are the same. For example, as we have seen in NaCl structure, each Na⁺ is surrounded by six Cl⁻ with all six distances equal to about 280 pm (Figure 5.44). The same can be said for Cl⁻ anions: each is surrounded by six Na⁺ at 280 pm distance. The cation-anion separation is equilibrium distance of minimum energy, a point where the attractive force is balanced with repulsive force. The attractive force gets stronger as the distance is reduced, and the energy of the system decreases. As the two approach each other, the electron clouds and the nuclei get closer together triggering a short-range repulsion between electron clouds and two nuclei. Somewhere, there is a point where the two are in balance and the energy is minimized. This minimum in

¹¹ Insert the ref



energy is called lattice energy, and is defined as energy required to dissociate one mole of crystalline solid into gaseous ions of which it is composed:



(NOTE: Every crystalline solid, ionic or molecular, has its lattice energy defined similarly. For example, solid sulfur, composed of S_8 molecules has its lattice energy: $S_8(s) \rightarrow S_8(g)$. However, our focus at the moment is on ionic bond and ionic lattices, and we'll leave the discussion of others for a bit later.)

Defined as above, the lattice energy is positive—dissociation of the lattice requires breaking of the ionic bond, which in turn requires energy. The magnitude of E_{latt} is one of the most important factors instability of crystalline lattice. Thus, we'll have a closer look at both attractive and repulsive forces governing its magnitude and the ways how to calculate it.

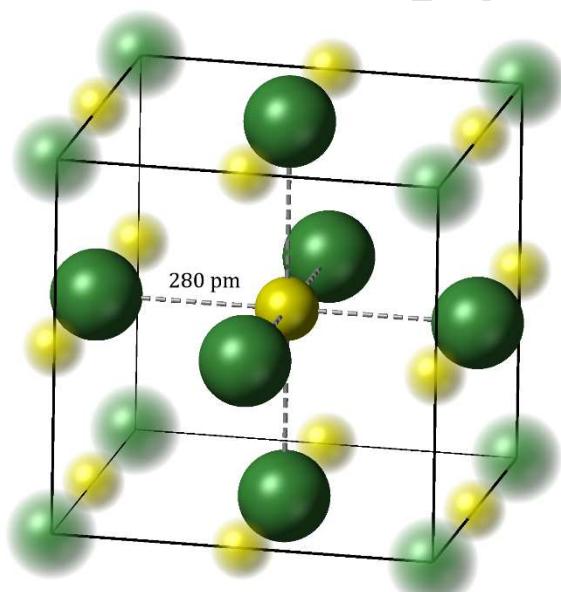


Figure 5.44 The sodium cations (yellow) are surrounded by six chloride anions (green) in the NaCl structure. The anions are equidistant from the central cation. The dotted lines are not bonds, rather visual aids.

The Coulombic potential is our starting point to evaluate the attractive forces between two ions in the lattice:

$$E_{Coul} = -\frac{z_+ \times z_- \times e^2}{4\pi\epsilon_0 d} \quad (5.x)$$

where: $z_{+/-}$ are charges on ions, e is elementary charge (1.6022×10^{-19} C), ϵ_0 is vacuum permittivity (8.854×10^{-12} F m $^{-1}$) and d is the distance between the ions. The potential is negative since the force between the two ions of opposite charge is attractive one.

Equation 5.x needs to be modified in order to be more representative of actual crystal structures. For example, to account for six first Cl $^-$ neighbors surrounding an Na $^+$ cation, Equation 5.x must be multiplied by 6:

$$E_{Coul,1} = -\frac{6 \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d}. \quad (5.x)$$

Further, each Na $^+$ cation is surrounded by 12 other Na $^+$ cations at the distance $d\sqrt{2}$ (Figure 5.45). The repulsion is given by:

$$E_{Coul,2} = \frac{12 \times z_+ \times z_+ \times e^2}{\sqrt{2} \times 4\pi\epsilon_0 d}. \quad (5.x)$$

$$X = d\sqrt{2}$$



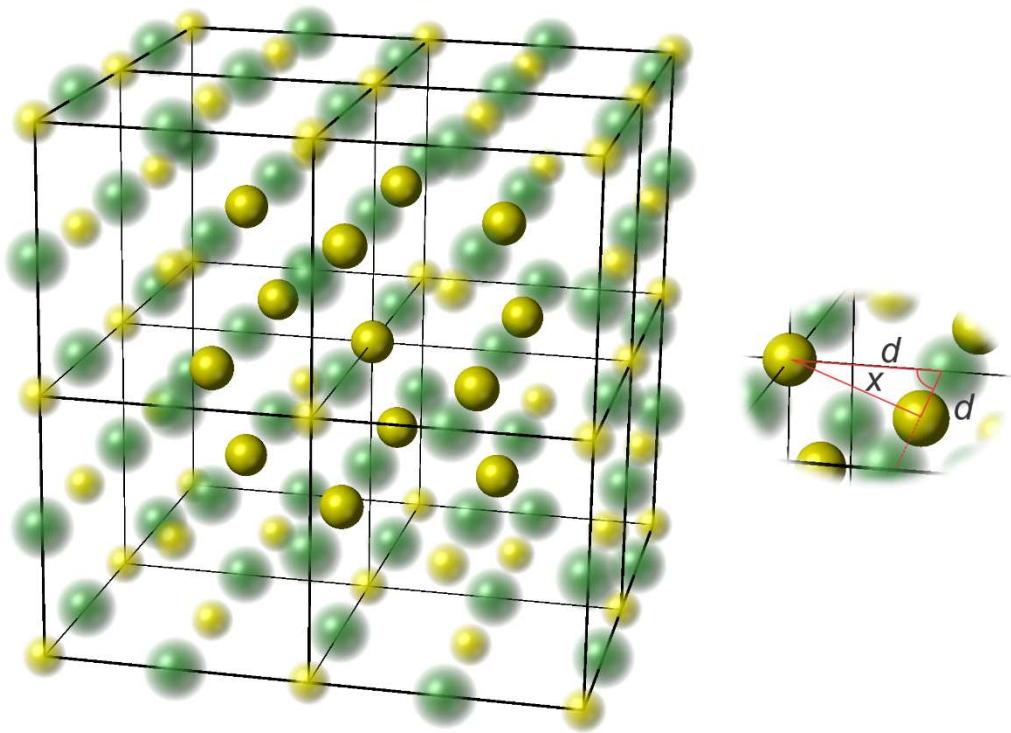


Figure 5.45 The closest 12 Na^+ cations. Insert shows calculation, x is the distance between the central Na^+ and its Na^+ cations.

Note that the sign is now positive since the interaction is repulsive. If we go further, we encounter another eight Cl^- ions at distance ___ from Na^+ cation (Figure 5.46). The interaction between Na^+ and the third neighbors is given by:

$$E_{\text{Coul},3} = -\frac{8 \times z_+ \times z_- \times e^2}{\sqrt{3} \times 4\pi\epsilon_0 d} \cdot (5 \cdot x)$$

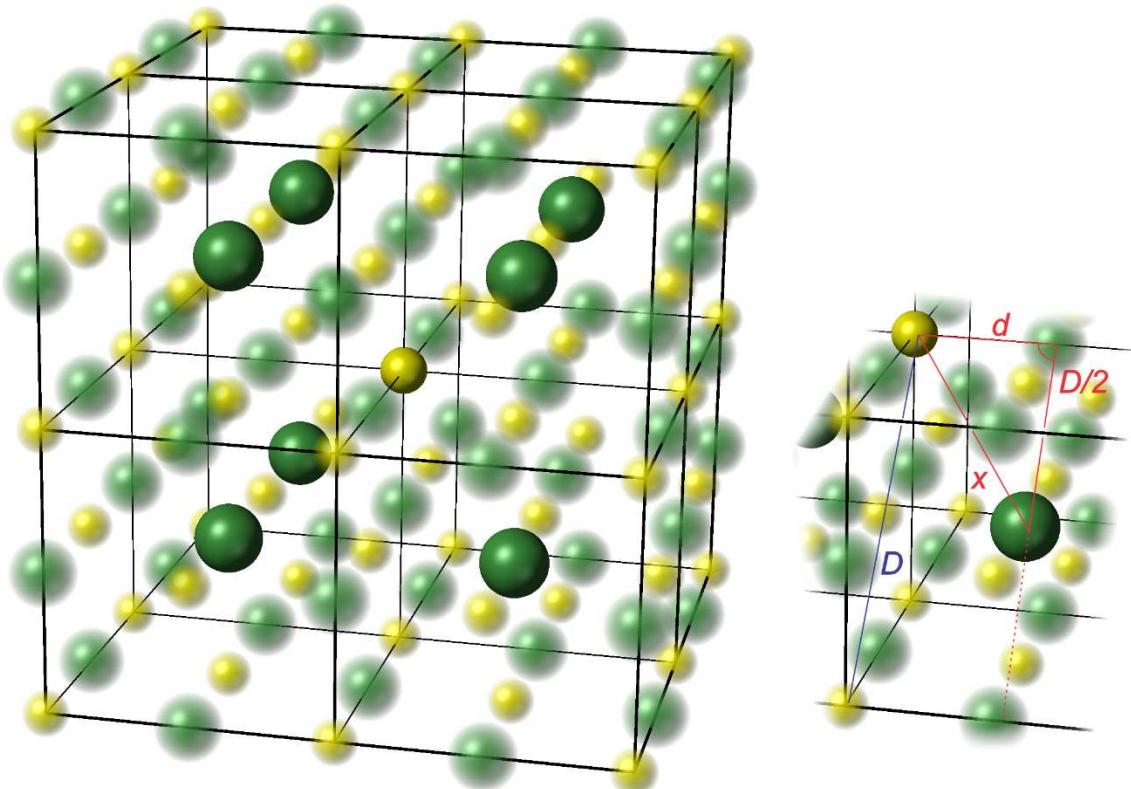


Figure 5.46 The eight Cl^- third neighbors for our Na^+ . The insert shows how to calculate the distance x . The blue line, D , is face diagonal of the cubic unit cell.

This process can be continued, and we could look at the fourth, fifth etc. neighborhoods of Na^+ cation. The final electrostatic potential experienced by an Na^+ cation is then given by the sum of all derived individual potentials:

$$E_{\text{Coul},\text{Na}^+} = -\frac{6 \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d} + \frac{12 \times z_+ \times z_- \times e^2}{\sqrt{2} \times 4\pi\epsilon_0 d} - \frac{8 \times z_+ \times z_- \times e^2}{\sqrt{3} \times 4\pi\epsilon_0 d} \dots$$

$$= -\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \dots\right) \frac{z_+ \times z_- \times e^2}{4\pi\epsilon_0 d}. \quad (5.x)$$

The expression in brackets is an infinite series that can be derived for any prototype structure described previously. The series elements become progressively less and less important since the neighbors are further and further away. The values of the series for all AX , AX_2 , and A_2X have been evaluated by the German physicist Erwin Madelung in 1918. Thus, to fully evaluate the electrostatic interactions within a ionic crystal

we must multiply Equation 5.x by appropriate value of the Madelung constant (A) and by Avogadro's constant to level all values to one mole of the substance. Thus, we obtain:

$$E_{Coul} = -\frac{A \times N_A \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d} \cdot (5.x)$$

The values of Madelung constant are given in Table 5.x

Table 5.x The values of Madelung constant for prototype structures. *

| Prototype | NaCl | CsCl | ZnS | | CaF ₂ | TiO ₂ |
|-----------|---------|---------|------------|----------|------------------|------------------|
| | | | Sphalerite | Wurtzite | | |
| A | 1.74756 | 1.76267 | 1.63806 | 1.64132 | 2.51939 | 2.408 |

* Data from "The Madelung constant and crystal lattice energy." In CRC Handbook of Chemistry and Physics, 98th Ed. (2018), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL. The value of Madelung constant has been determined for many other prototype structures.

The short-range repulsive interaction can be estimated using Equation 5.x:

$$E_{Rep} = \frac{B}{d^n} \cdot (5.x)$$

In this equation B is a constant that accounts for the strength of the repulsion, d is distance and n is the Born exponent, calculated from compressibility experiments (higher values of n indicate greater compressibility of a compound under pressure). The exponent n depends on the electronic structure of the ions, with values ranging from 5 to 12 (Table 5.x).

Table 5.x Values of the Born exponent, n .

| | | | | | |
|-------------------------|------|------|-----------------------|-----------------------|-----------------------|
| Electronic conf. of ion | [He] | [Ne] | [Ar], Cu ⁺ | [Kr], Ag ⁺ | [Xe], Au ⁺ |
|-------------------------|------|------|-----------------------|-----------------------|-----------------------|



| | | | | | |
|---|---|---|---|----|----|
| n | 5 | 7 | 9 | 10 | 12 |
|---|---|---|---|----|----|

We shall see how to use these values shortly but for now notice that the repulsive term plays an important role only at very small values of d , when d^n denominator is small. Now, we can obtain an expression for the total energy of a crystal:

$$E = E_{Coul} + E_{Rep} = -\frac{A \times N_A \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d} + \frac{B}{d^n}. \quad (5.x)$$

The crystals are stable when the value of E is at its minimum. To find the distance d_0 at which the E value is minimal we have to find the first derivative of Equation 5.x with respect to d and make it equal to 0:

$$\frac{dE}{dd} = 0 = \frac{A \times N_A \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d_0^2} - \frac{nB}{d_0^{n+1}}. \quad (5.x)$$

From this equation we can find B as a function of d_0 :

$$B = \frac{A \times N_A \times z_+ \times z_- \times e^2}{4\pi\epsilon_0} \times \frac{d_0^{n+1}}{n}. \quad (5.x)$$

Substituting Equation 5.x into 5.x gives us the Born—Landé equation, published first in 1918, used to calculate the lattice energy:

$$E_{latt} = -\frac{A \times N_A \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d_0} \left(1 - \frac{1}{n}\right). \quad (5.x)$$

Born and Mayer provided a better approximation of the repulsion term and derived the Born—Mayer form of the Equation 5.x:

$$E_{latt} = -\frac{A \times N_A \times z_+ \times z_- \times e^2}{4\pi\epsilon_0 d_0} \left(1 - \frac{\rho}{d_0}\right). \quad (5.x)$$

The constant ρ in the above equation takes into the consideration the compressibility of the material. Generally, the value $\rho = 34.5$ pm gives satisfactory results in many cases.

From equations 5.x and 5.x we can draw two important conclusions: (i) the higher the charges on the cation and anion, the more stable the structure is (its energy is more negative) and (ii) the shorter the equilibrium distance between the cation and anion in the structure, the more stable the structure is. These are two



important points that we'll use over and again in our discussion of reactivity, so it is necessary to keep them in mind.

To use Equations 5.x and 5.x, however, we need to know the structure our ionic compound; otherwise we do not know d_0 and cannot decide on an appropriate value of the Madelung constant. The Kapustinskii's equation, derived from the Born—Mayer equation in 1956, allows us to calculate the approximate lattice energies for ionic compounds of unknown structure. Kapustinskii approximated d_0 with the sum of cation and anion ionic radii ($d_0 = r_+ + r_-$). Then he noticed that the value of Madelung constant for each structure roughly equals the number of ions in the formula unit multiplied by 0.88. All other values in Equations 5.x and 5.x are constants and can be combined with 0.88 to give one, new constant. Without going into mathematical derivation steps, this analysis leads to the Kapustinskii equation:

$$E_{latt} = 12100 \frac{\text{kJ pm}}{\text{mol}} \times \frac{v \times |z_+| \times |z_-|}{r_+ + r_-} \times \left(1 - \frac{34.5 \text{ pm}}{r_+ + r_-}\right). (5.x)$$

In this equation v is the sum of ions in the formula unit (for example, $v = 2$ for NaCl and $v = 3$ for CaF₂—one Ca²⁺ and two F⁻) while the cation and anion radii are taken for coordination number six. This can be even further simplified to:

If E_{latt} is known, the Kapustinskii equation can also be used to calculate the unknown ionic radii—another helpful feature of this equation. The values obtained using this route are called “thermochemical radii.” This approach is particularly useful for complex anions such as CO₃²⁻ that cannot be taken as spheres. Table 5.x lists some useful thermochemical radii.

(Insert Table 5.x)

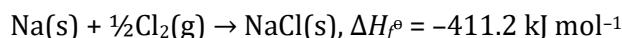
It is rather challenging to directly determine the lattice enthalpies (energies). Most lattice enthalpies are determined using Born-Haber-Fajans cycles based on Hess' law. One way to formulate the law is to state that the enthalpy change of a chemical reaction is independent of a pathway taken—it does not matter if a



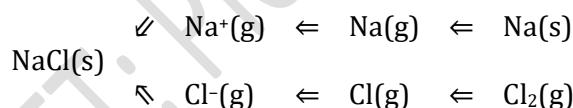
reaction takes place in one step or many as long as we start from the same reactant and end with the same product. The overall enthalpy change is given by:

$$\Delta H_{reaction} = \sum \Delta H_{products} - \sum \Delta H_{reactants}. \quad (5.x)$$

We are going calculate the lattice enthalpy of sodium chloride using the Hess' law and the Born–Haber cycle. As a starting point, the one step reaction, we are going to take the direct formation of solid, crystalline NaCl from the elements in their standard states. Recall from introductory courses that the enthalpy change for this reaction equals the standard enthalpy of formation for NaCl:



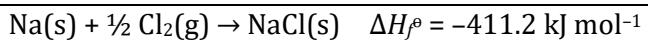
Now, we have to think which steps can lead from Na(s) and Cl₂(g) to NaCl(s). To decide on the steps involved, we can resort to the retro-synthesis: starting from the products and going towards the reactants. Thus, since sodium chloride is a ionic solid, we need ions Na⁺ and Cl⁻ and they need to be in the gas phase as dictated by the definition of the lattice enthalpy. To make these ions we need atoms Na and Cl in the gas phase. To make the atoms, we need to sublime Na(s) and break Cl—Cl bonds. The result of the retro-synthesis can be summarized schematically as follows:



We have now several steps that lead from sodium and chlorine to sodium chloride. All we have to do is write the chemical equations for each and associate proper energy changes. The scheme, red from left to right, gives the following:

| | | |
|--|--|---|
| Step 1: Atomization of Na(s) | $\text{Na(s)} \rightarrow \text{Na(g)}$ | $\Delta H_{a^\circ} = +89 \text{ kJ mol}^{-1}$ |
| Step 2: Ionization of Na(g) | $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$ | $I_1 = +496 \text{ kJ mol}^{-1}$ |
| Step 3: Breaking of Cl—Cl bond | $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$ | $\frac{1}{2} \text{BDE} = \frac{1}{2} 243 \text{ kJ mol}^{-1} = +121.5 \text{ kJ mol}^{-1}$ |
| Step 4: Formation of Cl ⁻ (g) | $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$ | $EA = -348.6 \text{ kJ mol}^{-1}$ |
| Step 5: Formation of NaCl(s) | $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(s)}$ | $\Delta H_{latt^\circ} = X$ |

Total



The equations listed above are the Born–Haber cycle for NaCl(s). The sum the above reactions gives our one step synthesis from the elements. Then according to the Hess' law, the sum of energies related to each step must equal the energy of the one-step reaction—the start and end are the same for both. Thus:

$$\Delta H_a^\circ + I_1 + \frac{1}{2}BDE + EA + \Delta H_{latt}^\circ = \Delta H_f^\circ$$

$$89 \text{ kJ mol}^{-1} + 496 \text{ kJ mol}^{-1} + 121.5 \text{ kJ mol}^{-1} - 348.6 \text{ kJ mol}^{-1} - X = -411.2 \text{ kJ mol}^{-1}.$$

From here we obtain the lattice enthalpy for NaCl:

$$X = \Delta H_{latt}^\circ = 769.1 \text{ kJ mol}^{-1}.$$

The lattice enthalpies obtained using the Hess' law and the Born–Haber cycle are considered experimental values since they are based on experimentally determined enthalpy changes for each individual step of the cycle.

A schematic way of representing the Born–Haber cycle for NaCl is shown in Figure 5.47. From the figure it becomes clear why do refer to the Born–Haber approach as a “cycle.” Note that the reaction steps that are endothermic (need energy) have their arrows pointing up; while those that are exothermic (release energy) have arrows pointing down. Another point is of importance: the order of “steps” is not important, as long as all necessary ones are accounted for. To illustrate this point, Figure 5.47 has different order of reactions in comparison to our tabular breakdown above.

To properly complete the Born–Haber cycle we must clearly indicate the state of each chemical species involved (i.e. (s), (g) or (l)) otherwise the thermodynamic values used might be incorrect or ill-defined.



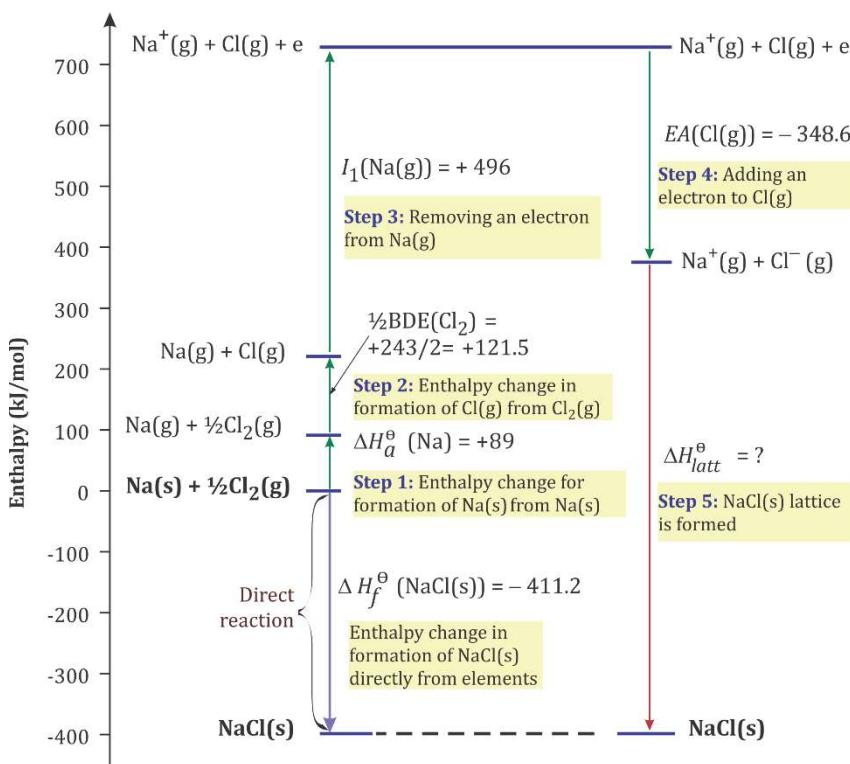


Figure 5.47 The Born–Haber cycle for NaCl(s) . Notice the direction of the red arrow for formation of NaCl(s) from the ions in the gas phase: it points down indicating an exothermic process because it follows the cycle direction (counterclockwise). This direction is opposite from the definition of lattice enthalpy, which we have to bear in mind when determining the sign of the calculated value. All values are in kJ mol^{-1} .

Many physical and chemical properties of ionic compounds can be explained using the material covered above. For example, ionic compounds typically have high melting and boiling points due to high lattice energies. Although they are composed of charged particles, ionic solids are not conductors since all ions are surrounded uniformly by ions of the opposite charge. The exception to this behavior is found in so-called solid electrolytes—ionic solids that can conduct electricity.

5.5 The “Gray Areas”: Around covalent–ionic boundary.

Discussion so far concentrated on the compounds where the bonding is predominantly ionic and all prototypical structures discussed so far are derived from almost purely ionic compounds (very electropositive cations and very electronegative anions)—see Figure 5.48. As we have seen during the discussion of van Arkel–Ketelaar triangle, the transition from one type of bonding (for example, covalent to

ionic) is not sharp, but gradual. The borderlines shown in Figure 4.x are based on detailed analysis of many compounds but are still artificial. Increasing covalent bonding character introduces more directionality in bonding and some consequences of this we have seen with ZnS—the radius ratio rules do not predict the correct structure for ZnS.

Commonly mentioned prototype structures of AX_2 compounds with higher degree of covalent bonding are $CdCl_2$ and CdI_2 . The two structures are similar, so we'll have a quick look at CdI_2 structure.

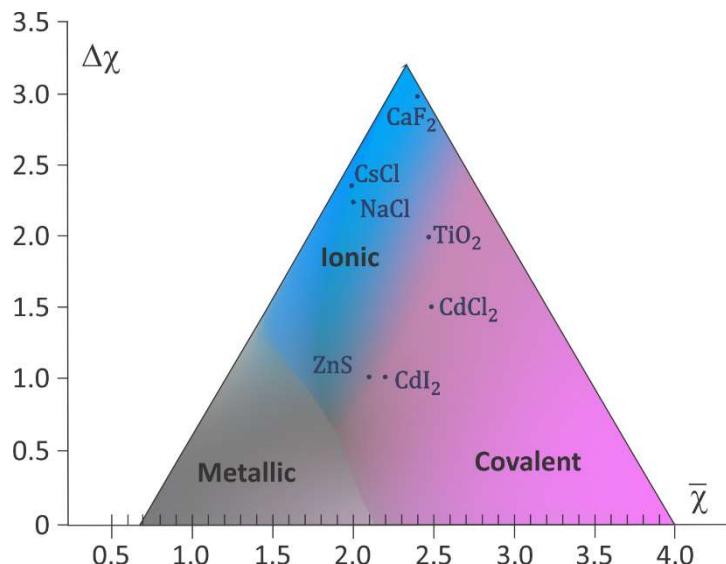


Figure 5.48 The van Arkel-Ketelaar triangle showing the locations of the prototype structures covered in the text. Notice the location of ZnS.

The CdI_2 structure is a layered (Figure 5.49) with I^- ions forming an hcp array while Cd^{2+} ions occupy octahedral holes in alternate layers. The result is a sheet-like structure composed of layering $[CdX_2]_\infty$ sheets. Much weaker bonding exists between the two sheets than within a sheet. No cations are required between I^- — Cd — I^- sheets due to polarization of the bonds: the negative charge of the anions is pulled inwards to Cd^{2+} . The structure of $CdCl_2$ differs in the location of anions— Cl^- ions form a ccp array—while Cd^{2+} still occupy octahedral holes of alternative layers.

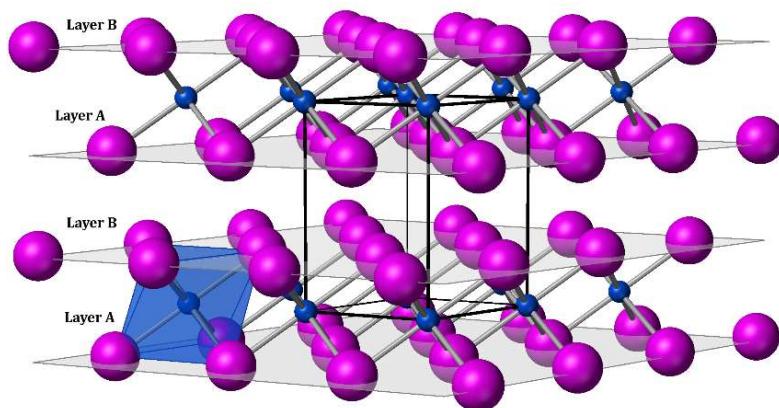


Figure 5.49 The structure of CdI_2 .

Purple spheres are I^- ions while smaller, blue spheres are Cd^{2+} ions.

The hexagonal unit cell is outlined in solid black lines. This time the bonding $\text{Cd}—\text{I}$ interactions are indicated with gray cylinders. The octahedral coordination environment around Cd^{2+} ions is emphasized bottom left.

The difference in structure is reflected in physical properties as well. Weaker bonding between the sheets significantly lower the melting and boiling points evident from the data in Table 5.x for CdF_2 (antifluorite structure), CdCl_2 and CdI_2 .

Table 5.x Melting and boiling points for CdF_2 , CdCl_2 and CdI_2 . Data from “Physical Constants of Inorganic Compounds.” In CRC Handbook of Chemistry and Physics, 98th Edition (2018), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

| Compound | CdF_2 | CdCl_2 | CdI_2 |
|---------------|----------------|-----------------|----------------|
| Melting point | 1075 | 568 | 388 |
| Boiling point | 1750 | 964 | 744 |

The radius ratio rule correctly predicts the coordination geometry of Cd^{2+} cations for both CdCl_2 and CdI_2 but the structure is not of TiO_2 -type as the coordination and general formula AX_2 would suggest. The question is, now, what kind of forces keep the sheets, chains and molecules inside a crystal?

5.6 Intermolecular forces



Both metallic bond and ionic bond result in solid materials composed of infinite lattices of atoms or ions at normal conditions. Many other substances composed of discrete molecules are also solids; for example, already mentioned solid S₈, ice and iodine.

In solids such as these the molecules, sheets and/or chains are held together through intermolecular forces. Intermolecular forces are much weaker and generally decrease in strength rapidly with the increase in the distance. They are also considered non-bonding interactions since their breaking leads to a physical, rather than chemical change. For example, boiling water is enough to break intermolecular forces and change the state from liquid to vapor (physical change) but vapor is still chemically H₂O. In order of decreasing attraction, these interactions are: hydrogen bond, ion-dipole, dipole-dipole and van der Waals forces.

The hydrogen bond is formed between a hydrogen atom bonded to a more electronegative atom and another electronegative atom of the same or different molecule. The “other electronegative atom” to which H is bonded is most commonly N, O or F but S and P. The first three are the most electronegative element and H—E bond (E = F, O, or N) is very polar covalent bond, H^{δ+}—E^{δ-}. This partially positive H atom and the electronegative E atom constitute a donor component of the hydrogen bond. The general notation for the donor side is D—H. The acceptor side is also an electronegative element or an anion with one or more lone electron pairs and partial negative charge. It is denoted simply as A. Thus, the general form of hydrogen bond is represented as D—H…A where the three dots represent the hydrogen bond.

The strength of hydrogen bond depends on the partial charges on both H atom on the donor side and acceptor atom but generally lies within 4 — 50 kJ mol⁻¹ range for neutral molecules (such as H₂O). The greater the difference in electronegativity between hydrogen and other elements, the stronger the hydrogen bond is. Thus, the strongest hydrogen bond is found in anion HF₂⁻ where HF molecule is hydrogen donor while fluoride anion is the bond acceptor. In the anion the hydrogen is “flanked” by an atom of the most electronegative element, fluorine, and its anion. The bond is so strong that the hydrogen atom is found mid-way between two F atoms. The molecular orbital theory suggests that in this case a molecular orbital is formed spanning over all three nuclei. The anion is linear and explains the solubility of metal fluorides in liquid HF. It can be isolated in combination with many cations.



The anion HF_2^- is an extreme example of hydrogen bonding. In general, in the hydrogen bonded system, D—H bond is retained but is longer than in non-hydrogen bonded. For example, in liquid HF we find polymer-like chains and rings in which HF molecules are held through hydrogen bonding. In these structures, the H—F bond length is around 95 pm, slightly longer than 92 pm in free, gaseous HF, while the H—F—F angle is about 120° (Figure 5.50).

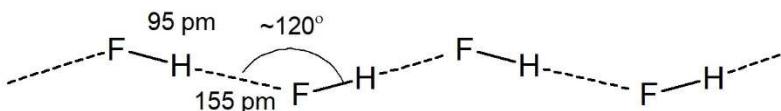


Figure 5.50 The chain structure found in solid and liquid HF.

The hydrogen bond is rather universal, since it should be considered whenever there are polar bonds involving H atoms. This bond is very important in structural chemistry of not only solid and liquid materials but also biologically active molecules. Consequently, we shall encounter this bond very frequently and discuss other details of its nature and importance.

Pure ion-dipole interactions, not very common in solid structural chemistry, are forces acting between free ions and molecules with permanent dipole. Most common example is the interaction of the Group 1 cations and water molecules (Figure 5.51). The positive charge of the cation orients the negative side of polar water molecules toward itself. A similar behaviour would be exhibited by chloride anions in water, the only difference would be the orientation of water molecules, now “facing” the ion with their positive end—hydrogen atoms. The force acting between the two bonding partners can be estimated using the following equation:

$$E = -\frac{z \times \mu \times e}{4\pi \times \epsilon_0 \times d^2}. \quad (5.x)$$

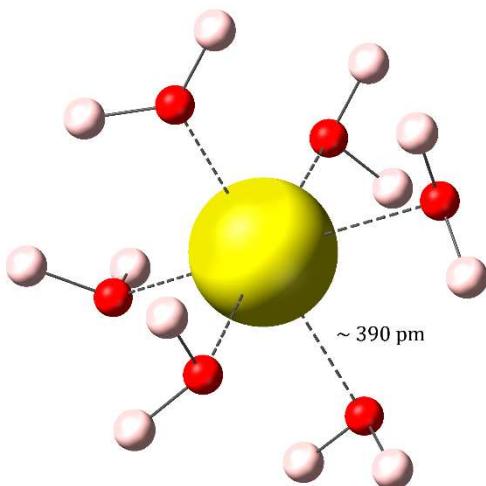


Figure 5.51 Ion – permanent dipole interaction between Na^+ cation (yellow) and water molecules (O atoms red, H atoms gray-pink). The $\text{Na}^+—\text{O}$ distance is indicated.

In the above equation, z is the ion charge, μ is the dipole moment and the rest is as in Equation 5.x. Notice that the strength of this interaction is inversely proportional to the square of the distance (d) between the cation (or in a general case, an ion) and the centre of the dipole. The dipoles are relatively weakly bonded ($10 - 40 \text{ kJ mol}^{-1}$) and can be easily displaced from the ion's environment. Thus, the water molecules in the bulk of the solvent can easily and rapidly displace the bonded ones through collisions. Many main group, monoatomic cations and anions would interact with dipoles as described above for Na^+ and Cl^- in water. The transition metal cations, however, with their high charge densities would pull the dipole such as water or ammonia so strongly that the lone electron pair would form a new bond with the cation, called coordination bond. In this case a coordination compound is formed and the collision with other dipole molecules does not result in rapid and easy displacement.

The ion – dipole interactions are important in biology. For example, the potassium channel, a protein found in cell membranes, moves K^+ into the cell through ion – dipole interactions between K^+ and $\text{C} = \text{O}$ bonds from the peptide linkages,

The dipole – dipole force acts between two or more permanent dipoles. Just as the ionic charge forced the dipole to orient their opposing charge, so two dipoles can orient each other so that their opposite charges face each other. The force of the permanent dipole – dipole interaction is given by:

$$E = -\frac{2\mu_1 \times \mu_2}{4\pi \times \epsilon_0 \times d^3} \quad (5.x)$$

where μ_1 and μ_2 are dipole moments of two molecules, and d is the distance from the centres of two dipoles. This type of interaction is, for example, is found in solid SO_2 . This bent molecule possesses a permanent dipole with oxygen atoms on the negative end. In the solid structure these are oriented towards sulfur atoms that bear a partial positive charge (Figure 5.52). The distance between O atoms and S atoms in neighboring molecules is much shorter than the distance between two ends of dipoles with partial charges of the same sign.

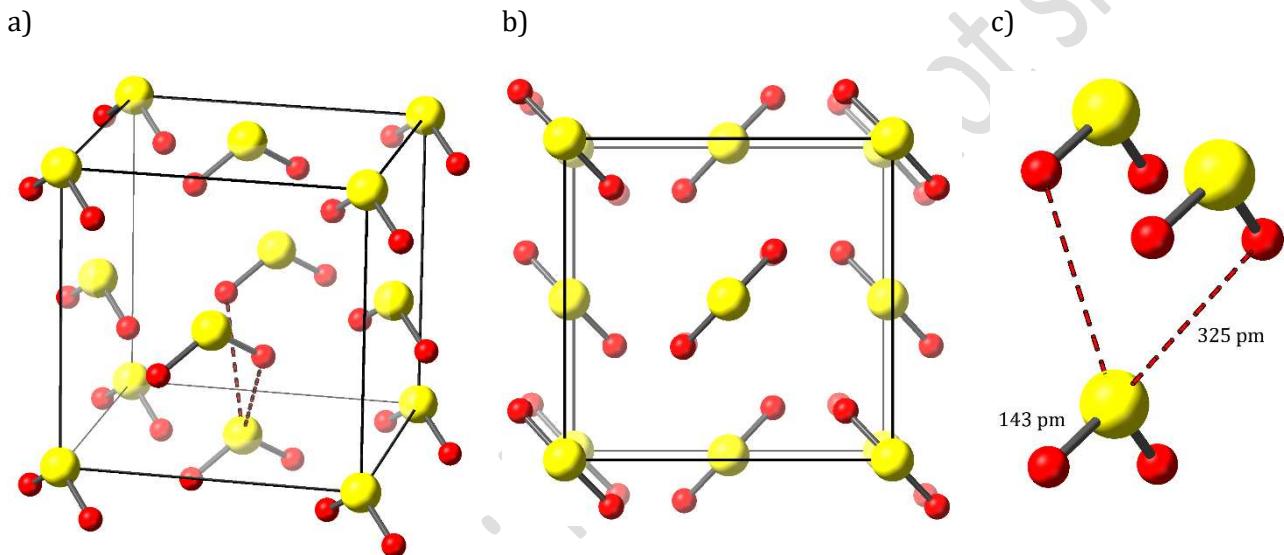


Figure 5.52 The structure of $\text{SO}_2(s)$ (S atoms yellow, O atoms red): a) the unit cell, the two dashed lines indicate two weak permanent dipole – permanent dipole $\text{S}^{\delta+}$ — $\text{O}^{\delta-}$ interactions; each S atom is surrounded by four O atoms, two covalently bound and two at greater distance with dipole – dipole interactions; b) view along one of the cube directions showing layering of SO_2 molecules under the influence of dipole – dipole interactions and c) a detail from part a) showing distances between sulfur and oxygen atoms.

The same interaction is visible in other physical properties. For example, the boiling point of NF_3 ($\mu = 0.23$) is higher than the boiling point of CF_4 ($\mu = 0$): -130°C vs. -160°C . This is despite the fact that CF_4 has greater molecular weight than NF_3 .

The van der Waals forces is a group name for three different interactions in which at least one partner has no permanent dipole: ion– induced dipole, dipole – induced dipole and induced dipole–induced dipole (or London dispersion force). The ion – induced dipole interaction generally plays a minor role since other interaction usually predominate—its magnitude is about $1 - 3 \text{ kJ mol}^{-1}$. This type of interaction results in cases when molecules without a dipole moment ($\mu = 0$) find themselves within the electrostatic field of an ion. Under the influence of this field the neutral molecule obtains a dipole moment because its electronic cloud is distorted. For example, a cation is going to pull the molecule's electrons resulting in build-up of negative charge on one side of the molecule, the side facing the ion. Consequently, the molecule becomes polarized and has small, but measurable dipole moment. Permanent dipole can also induce a dipole in a otherwise non-polar molecule. The mechanism is similar as in the case of ion – induce dipole interaction. This type of attractive force can be found acting between, for example, noble gas atoms and polar molecules such as water. It is very weak ($\sim 0.05 - 2 \text{ kJ mol}^{-1}$). Equations 5.x and 5.x define the magnitude of the interaction for ion – induced dipole and dipole – induced dipole, respectively. In these equations α is polarizability of the neutral species (tells us how easy it is to induce a dipole), and μ is the dipole moment of permanent dipole. The other quantities are as defined before.

$$E = -\frac{Z^2 \times \alpha \times e^2}{2d^4} \quad (5.x)$$

$$E = -\frac{\mu^2 \times \alpha}{r^6} \quad (5.x)$$

Notice that the strength of the attraction rapidly declines with increase in d .

The instantaneous dipole – induced dipole interaction (also known as dispersion force or London force ¹²) acts between non-polar molecules. Every non-polar molecule is non-polar on average. The electrons, however, move around the molecule rapidly and, as a result of this movement, at any moment a part of the molecule can end up with higher concentration of negative charge resulting in a formation of a dipole. This

¹² Afer Fritz London, a German-American physicist and professor at Duke University, who identified the force and provided its first quantum mechanical description in 1930.



dipole is very short lived—on the order of 10^{-14} to 10^{-15} seconds—but it can induce a dipole in a neighboring non-polar molecule. This induction increases the life-span of instantaneous dipole and results in attractive force that is responsible for liquid and solid states of many compounds. It is commonly mentioned in the texts that this interaction increases with an increase in mass of the molecule. The mass itself has little role to play, however, with increase in mass there is usually increase in size and in number of electrons. Both promote the formation of instantaneous dipoles. For example, under normal conditions, Cl_2 is a gas, heavier and more polarizable Br_2 is a liquid and I_2 is a solid. The same is observed in noble gases: larger, heavier group members, with polarizable atoms have higher melting and boiling points.

It is not straightforward to determine which of the van der Waals forces are in action (or predominate) in a given structure. Thus, it is common and correct to say that van der Waals forces hold both I_2 molecules and sheets in the structure of CdI_2 together without being more specific. The van der Waals radius is used to determine the closest approach two non-bonded atoms can make in the structure. This radius is taken to be half a distance between two closest non-bonded atoms in the structure (Figure 5.53).

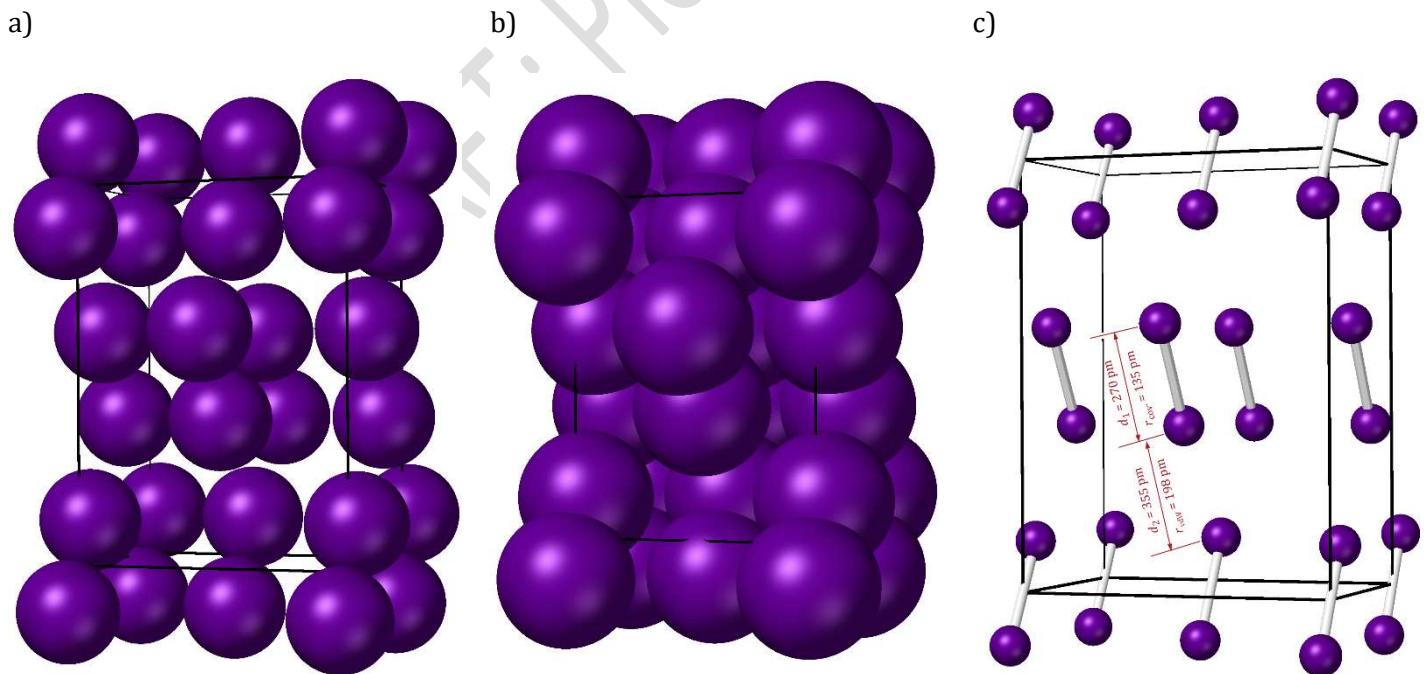


Figure 5.53 The orthorhombic unit cell of $I_2(s)$: a) the iodine atoms as spheres with covalent radius; b) the iodine atoms as spheres with van der Waals radius and c) the difference between to radii: bonding vs. non-bonding interactions in $I_2(s)$; notice that the van der Waals radius (r_{vdW}) is not exactly a half of the non-bonding distance because as with all other radii, the tabulated values are averages of a great number measurements.

In general, the most clear-cut case can be made for the presence of hydrogen bond even in the cases when the small hydrogen atom cannot be located—the presence of two electronegative atoms at close range, defined as less than the sum of their van der Waals radii, is good indication of hydrogen bond. Thus, if hydrogen bond is present between two non-bonded oxygen atoms or between non-bonded oxygen and nitrogen atoms their separation is shorter for about 20 – 30 pm in comparison to the sums of van der Waals radii.

5.7 A bonding epilogue

Example 5.1

(Find a compound, give the unit cell parameters, ask for a system and to calculate the volume)

FIRST DRAFT: Please do not share!

Example 5.2

Why is there C-centered lattice in orthorhombic system, but no A- or B-centered lattice? Monoclinic system does not have an I lattice. Why?

FIRST DRAFT: Please do not share!

Example 5.3

(Empty space in hexagonal and cubic pattern)

FIRST DRAFT: Please do not share!

Example 5.4

The distance between two iron atoms in α Fe is 258 pm. Calculate the metallic radius for Fe in α Fe structure and apply Goldschmidt correction to obtain a standardized value.

FIRST DRAFT: Please do not share!

Example 5.5

Thermal conductivity of Miracle Thaw (see “Properties of Materials” p. 153) and ?

FIRST DRAFT: Please do not share!

Example 5.6

(Fractional coordinates of CsCl structures)

Example 5.7

(Ideal, minimum radius for the tetrahedral hole)

Example 5.7

(using γ)