

CHAPTER II CRYSTAL STRUCTURE

2.1 Crystal lattices

2.1.1 Historical references

The first theory about the structure of crystals is attributed to Haüy (1783). This theory was based on the fact that some crystals split into certain planes when cracked open. We call this phenomenon cleavage. The plane along which the crystal splits is called the cleavage plane.

Haüy started from this observation to develop his theory: Calcite (CaCO_3) splits following only three cleavage planes forming dihedral angles of $105^\circ 5'$. That is, calcite breaks into small parallelepipeds with the same dihedral angles (with a difference of $\pm \pi$), called rhombohedrons. A rhombohedron is a regular parallelepiped: its dihedral angles are all the same, and its faces are rhombi. Following the hypothesis of atoms and applying it to crystals, Haüy stated that one could not proceed indefinitely splitting these rhombohedrons and that there was a limit to this process. He called this limit - or elementary rhombohedron - "*molécule intégrante*," called in modern crystallography as a **primitive cell**.

A crystal comprises a group of identical unit cells that stack perfectly with no gaps. In such an arrangement, each unit cell is deduced from another by a translation of the form:

$$\vec{t} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3 \quad (2.1)$$

where m_1, m_2 and m_3 are integer numbers. However, Haüy's theory did not thoroughly explain crystal symmetry. In 1845, Bravais completed it by supposing that the crystal pattern within the primitive cell (formed by one or more atoms or groups of atoms or molecules) did not fill all the available space. Assuming that the symmetry of the crystal pattern was the one of a polyhedron and using lattice symmetry, he could explain the symmetry of crystals.

In 1910, X-ray diffraction caused by crystals was discovered. The experiment by Friedreich and Knipping that indicated the electromagnetic nature of X-rays ($0.5\text{\AA} < \lambda < 2\text{\AA}$) was interpreted by Von Laue, admitting that a crystal was formed by a crystal pattern repeated in space by translation $m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$.

2.1.2 Description of a crystal lattice

According to this explanation, every crystal can be constructed by placing the same crystal pattern at the nodes of a tridimensional lattice:

Crystal structure = lattice + crystal pattern

First, we discuss the lattice that supports the structure of the crystal. This lattice is defined by three vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ called lattice vectors. The parallelepiped built with these three vectors forms the unit cell. The other cells are obtained by translating any form with integer numbers on the unit cell. In this way, a set of unit cells is obtained. The **vertexes of the unit cells** are called **nodes** of the lattice.

At the eight vertexes of a unit cell, there are eight nodes, and each of them belongs to eight distinct cells so that one node at a vertex of a unit cell counts for 1/8. If the unit cell used to describe the crystal contains only one node, this is the **primitive cell**. However, it is common to use **multiple cells** to make the symmetry more obvious; thus, n nodes are associated with one cell.

In this case, the crystal pattern defines the unit cell. Generally, the nature and the position of the atom centers inside the primitive cell are specified. For example, consider the center (J) of an atom (j) inside a cell. Its position is described by:

$$\vec{OJ} = j_1 \vec{a}_1 + j_2 \vec{a}_2 + j_3 \vec{a}_3 \quad (2.2)$$

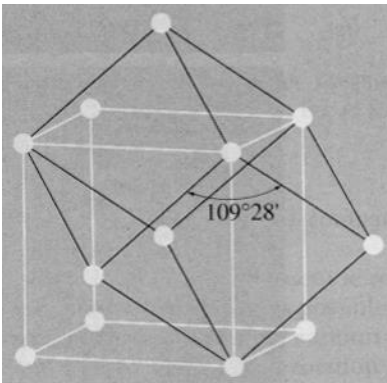


Figure 2-1: Representation of a primitive cell and the multiple conventional cell of a centered cubic structure

where j_1, j_2, j_3 are the numerical coordinates of the atom j . They are generally smaller than 1, and they cannot be equal to 1 in any case. Another atom (k) has its center in K, and its numerical coordinates are k_1, k_2, k_3 and so on.

Example:

In the conventional (multiple) cell cubic centered, the atomic sites are located at:

$$0, 0, 0 \text{ and } \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$

2.1.3 Direct lattice and reciprocal lattice

Having chosen an origin and a primitive cell, we can continue the description of crystals, introducing the node rows or **lattice rows**.

Joining the origin of the lattice with any node M, we have the vector:

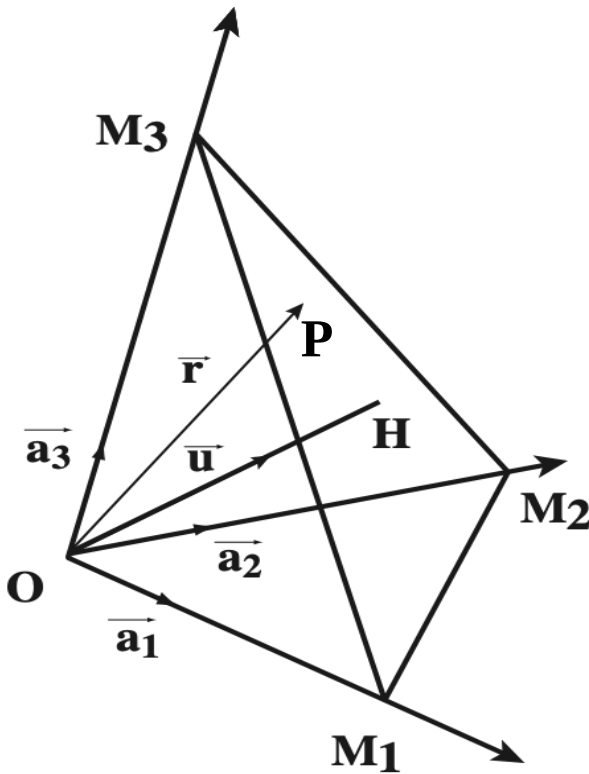
$$\vec{OM} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3 \quad (2.3)$$

With integer numbers m_1, m_2, m_3 . Let m be the greatest common divisor (gcd) of m_1, m_2, m_3 :

$$m_1 = m \cdot m_1' \quad m_2 = m \cdot m_2' \quad m_3 = m \cdot m_3'$$

so that
$$\overrightarrow{OM} = m(m_1' \overrightarrow{a_1} + m_2' \overrightarrow{a_2} + m_3' \overrightarrow{a_3}) = m \overrightarrow{OM'} \quad (2.4)$$

where M' is the closest node to the origin. The other nodes on this row are given by different values of $m = -2, -1, 0, 1, 2, 3$, etc. Nodes on this row are equidistant and form a one-dimensional lattice. It is a lattice row indicated by three numbers /brackets.



We use $[m_1', m_2', m_3']$ to indicate a particular crystallographic row.

We use $\langle m_1', m_2', m_3' \rangle$ to indicate the family of rows of the triplet m_1', m_2', m_3' .

Consider now the plane through the nodes M_1, M_2, M_3 situated on the three-axis $\overrightarrow{a_1}, \overrightarrow{a_2}, \overrightarrow{a_3}$ so that:

$$\begin{aligned} \overrightarrow{OM_1} &= n_1 \overrightarrow{a_1} \\ \overrightarrow{OM_2} &= n_2 \overrightarrow{a_2} \\ \overrightarrow{OM_3} &= n_3 \overrightarrow{a_3} \end{aligned}$$

This plane is the lattice plane containing the nodes M_1, M_2, M_3 and the vectors:

$$\begin{aligned} \overrightarrow{M_1 M_2} &= n_2 \overrightarrow{a_2} - n_1 \overrightarrow{a_1} \\ \overrightarrow{M_2 M_3} &= n_3 \overrightarrow{a_3} - n_2 \overrightarrow{a_2} \\ \overrightarrow{M_1 M_3} &= n_3 \overrightarrow{a_3} - n_1 \overrightarrow{a_1} \end{aligned}$$

Figure 2-2: Representation of a lattice plane

Every linear combination by an integer multiple of any two of these vectors is also a lattice plane through M_1, M_2, M_3 . For determining the equation of this plane, let the unit vector normal to the plane $\overrightarrow{OH_n}$ and let P any point in the plane be located at $\overrightarrow{OP} = \vec{r}$ so that:

$$\vec{r} = x \overrightarrow{a_1} + y \overrightarrow{a_2} + z \overrightarrow{a_3} \quad (2.5)$$

$$\vec{r} \cdot \vec{u} = OH_n \quad (2.6)$$

x, y , and z are the coordinates of point P . The equation of the plane is then:

$$\text{where} \quad OH_n = x(\vec{u} \cdot \vec{a_1}) + y(\vec{u} \cdot \vec{a_2}) + z(\vec{u} \cdot \vec{a_3}) \quad (2.7)$$

Writing that this plane passes through the points $M_1(n_1, 0, 0)$, $M_2(0, n_2, 0)$, $M_3(0, 0, n_3)$ we get:

$$\vec{u} \cdot \vec{a}_1 = \frac{OH_n}{n_1} \quad \vec{u} \cdot \vec{a}_2 = \frac{OH_n}{n_2} \quad \vec{u} \cdot \vec{a}_3 = \frac{OH_n}{n_3} \quad (2.8)$$

and the equation of the plane is then: $\frac{x}{n_1} + \frac{y}{n_2} + \frac{z}{n_3} = 1$

The numbers n_1, n_2, n_3 in general, are not prime numbers; let n be their gcd so that:

$$n_1 = nn_1' \quad n_2 = nn_2' \quad n_3 = nn_3' \quad (2.9)$$

Giving a plane with the equation: $\frac{x}{n_1'} + \frac{y}{n_2'} + \frac{z}{n_3'} = 1$

Thus, the plane is deduced from the previous one by a homothetic transformation of center O (the origin of the lattice) and ratio $1/n$. This plane is at a distance $OH = OH_n / n$ from the origin O and passes through the points M_1', M_2', M_3' respectively on the axes $\vec{a}_1, \vec{a}_2, \vec{a}_3$ so that:

$$\overrightarrow{OM_1'} = n_1' \vec{a}_1 \quad \overrightarrow{OM_2'} = n_2' \vec{a}_2 \quad \overrightarrow{OM_3'} = n_3' \vec{a}_3$$

The numbers n_i' are the relative prime numbers. The equation of the plane can be written as:

$$n_2' n_3' x + n_1' n_3' y + n_1' n_2' z = n_1' n_2' n_3' \quad (2.10)$$

If we call:

$$h = n_2' n_3' \quad k = n_3' n_1' \quad l = n_1' n_2'$$

The equation can be written in the form:

h, k, l are called Miller indices of the lattice plane, which intercepts the axis in $n_1' \vec{a}_1, n_2' \vec{a}_2, n_3' \vec{a}_3$.

$$hx + ky + lz = n_1' n_2' n_3' = hn_1' = kn_2' = ln_3' \quad (2.11)$$

With the relations $hn_1' = kn_2' = ln_3'$ the Miller indices, h, k, l are three relative prime numbers. As for crystallographic directions, a convention for the notation of Miller indices h, k, l exists:

The notation with parentheses (h, k, l) indicates the lattice plane defined by these indices while using the brackets $\{h, k, l\}$ defines the set of lattice planes corresponding to the triplet h, k, l for every permutation of it, e.g., for high-symmetry unit cells like cubic structures.

Example:

What are Miller indices of the plane cutting the three-axis $\vec{a}_1, \vec{a}_2, \vec{a}_3$ respectively in $\vec{a}_1, 2\vec{a}_2, 3\vec{a}_3$?
This plane has the equation:

$$x + \frac{y}{2} + \frac{z}{3} = 1$$

with $n_1' = 1, n_2' = 2, n_3' = 3$ and $n_1' n_2' n_3' = 6$ so that $h=6, k=3, l=2$.

Let us calculate now the normal to the plane $hx + ky + lz = 0$

$$\begin{aligned}\vec{u} &= (n_2 \vec{a}_2 - n_1 \vec{a}_1) \times (n_3 \vec{a}_3 - n_1 \vec{a}_1) \\ \vec{u} &= n_2 n_3 (\vec{a}_2 \times \vec{a}_3) + n_1 n_3 (\vec{a}_3 \times \vec{a}_1) + n_1 n_2 (\vec{a}_1 \times \vec{a}_2) = \\ &= h(\vec{a}_2 \times \vec{a}_3) + k(\vec{a}_3 \times \vec{a}_1) + l(\vec{a}_1 \times \vec{a}_2)\end{aligned}\quad (2.12)$$

$$\text{Defining: } \vec{a}_1^* = \vec{a}_2 \times \vec{a}_3 \quad \vec{a}_2^* = \vec{a}_3 \times \vec{a}_1 \quad \vec{a}_3^* = \vec{a}_1 \times \vec{a}_2 \quad (2.13)$$

We note that the indices h, k, l represent the components of the normal to the plane in the coordinate system $\vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^*$. The nodes corresponding to the vectors $\vec{a}_i^*$ define a new lattice of points: the **reciprocal lattice**. The distances in $\text{\AA}^{-1}$ of the reciprocal lattice vectors correspond to the inverse of the distance between the crystal lattice planes:

$$\|\vec{r}_{hkl}^*\| = \frac{1}{d_{hkl}} \quad (2.14)$$

Thus, for greater values of h, k , and l indices, planes are less dense and have smaller interplanar spacings.

2.1.4 Vector operations: dot product, cross product, metric

We prefer to normalize the vectors $\vec{a}_i^*$ in such a way that:

$$\vec{a}_i \cdot \vec{a}_i^* = 1 \quad \text{so that the normal definition is} \quad \vec{a}_1^* = \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad (2.15)$$

Following the previous definitions, we can write in a general way:

$$\vec{a}_i \cdot \vec{a}_j^* = \delta_{ij} \quad (2.16)$$

The product $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the parallelepiped constituted by the three vectors of the elementary base.

Using the formula, $\vec{a} \times \vec{b} \times \vec{c} = \vec{b}(\vec{a} \cdot \vec{c}) - \vec{c}(\vec{a} \cdot \vec{b})$ we can easily demonstrate that

$$\vec{a}_1^* \times \vec{b}_2^* = \frac{\vec{c}}{V} \quad (2.17)$$

Thus, in general, we can compute each component of the vector product using the well-known method of the symbolic determinant, keeping in mind that the numerical components are obtained in the reciprocal lattice.

Example

Consider two planes:

$$h_1x + k_1y + l_1z = 0 \quad \text{and} \quad h_2x + k_2y + l_2z = 0$$

A line belonging to the two planes is given by a vector in the direct base $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$:

$$(k_1l_2 - k_2l_1)\vec{a}_1 + (l_1h_2 - l_2h_1)\vec{a}_2 + (h_1k_2 - h_2k_1)\vec{a}_3$$

whereas, given two vectors of the direct lattice:

$$x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3 \quad \text{and} \quad x'\vec{a}_1 + y'\vec{a}_2 + z'\vec{a}_3$$

The normal to the plane containing these two vectors of the direct lattice is given by the vector:

$$(yz' - y'z)\vec{a}_1^* + (x'z - xz')\vec{a}_2^* + (xy' - yx')\vec{a}_3^*$$

We can show, using a non-orthonormal basis like one of a nonsymmetric crystal lattice, that the scalar product between two vectors is not given simply by the product of the components at the same index. Therefore, it is helpful to introduce the matrix notation:

$$(x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3) \cdot (x'\vec{a}_1 + y'\vec{a}_2 + z'\vec{a}_3) = \begin{bmatrix} x & y & z \end{bmatrix} \begin{bmatrix} a_1^2 & \vec{a}_1 \cdot \vec{a}_2 & \vec{a}_1 \cdot \vec{a}_3 \\ \vec{a}_1 \cdot \vec{a}_2 & a_2^2 & \vec{a}_2 \cdot \vec{a}_3 \\ \vec{a}_1 \cdot \vec{a}_3 & \vec{a}_2 \cdot \vec{a}_3 & a_3^2 \end{bmatrix} \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \vec{u}_T M \vec{u} \quad (2.18)$$

M is called a metric tensor; its determinant is the volume squared, V^2 . Similarly, we can define the dot product between vectors of the reciprocal lattice:

$$(x\vec{a}_1^* + y\vec{a}_2^* + z\vec{a}_3^*) \cdot (x'\vec{a}_1^* + y'\vec{a}_2^* + z'\vec{a}_3^*) = \begin{bmatrix} h & k & l \end{bmatrix} \begin{bmatrix} (a_1^*)^2 & \vec{a}_1^* \cdot \vec{a}_2^* & \vec{a}_1^* \cdot \vec{a}_3^* \\ \vec{a}_1^* \cdot \vec{a}_2^* & (a_2^*)^2 & \vec{a}_2^* \cdot \vec{a}_3^* \\ \vec{a}_1^* \cdot \vec{a}_3^* & \vec{a}_2^* \cdot \vec{a}_3^* & (a_3^*)^2 \end{bmatrix} \begin{bmatrix} h' \\ k' \\ l' \end{bmatrix} = \vec{h}_T M^* \vec{h} \quad (2.19)$$

We can show that $M^* = M^{-1}$.

2.1.5 Crystal systems

If we consider only rotational symmetries (excluding the others), crystals can be classified into **seven crystal systems** according to the type and the number of axis of rotation they have. These represent the minimum number of symmetries a crystal needs to belong to that particular system. The name of a specific system identifies the Bravais lattices (14), which are compatible with the point groups (32) that belong to the same crystal system.

The corresponding cells can be primitive, centered, face-centered, or body-centered.

In the conventional notation, we use $(\vec{a}, \vec{b}, \vec{c})$ for lattice vectors and $\alpha = \angle(\vec{b}, \vec{c})$, $\beta = \angle(\vec{c}, \vec{a})$, $\gamma = \angle(\vec{a}, \vec{b})$.

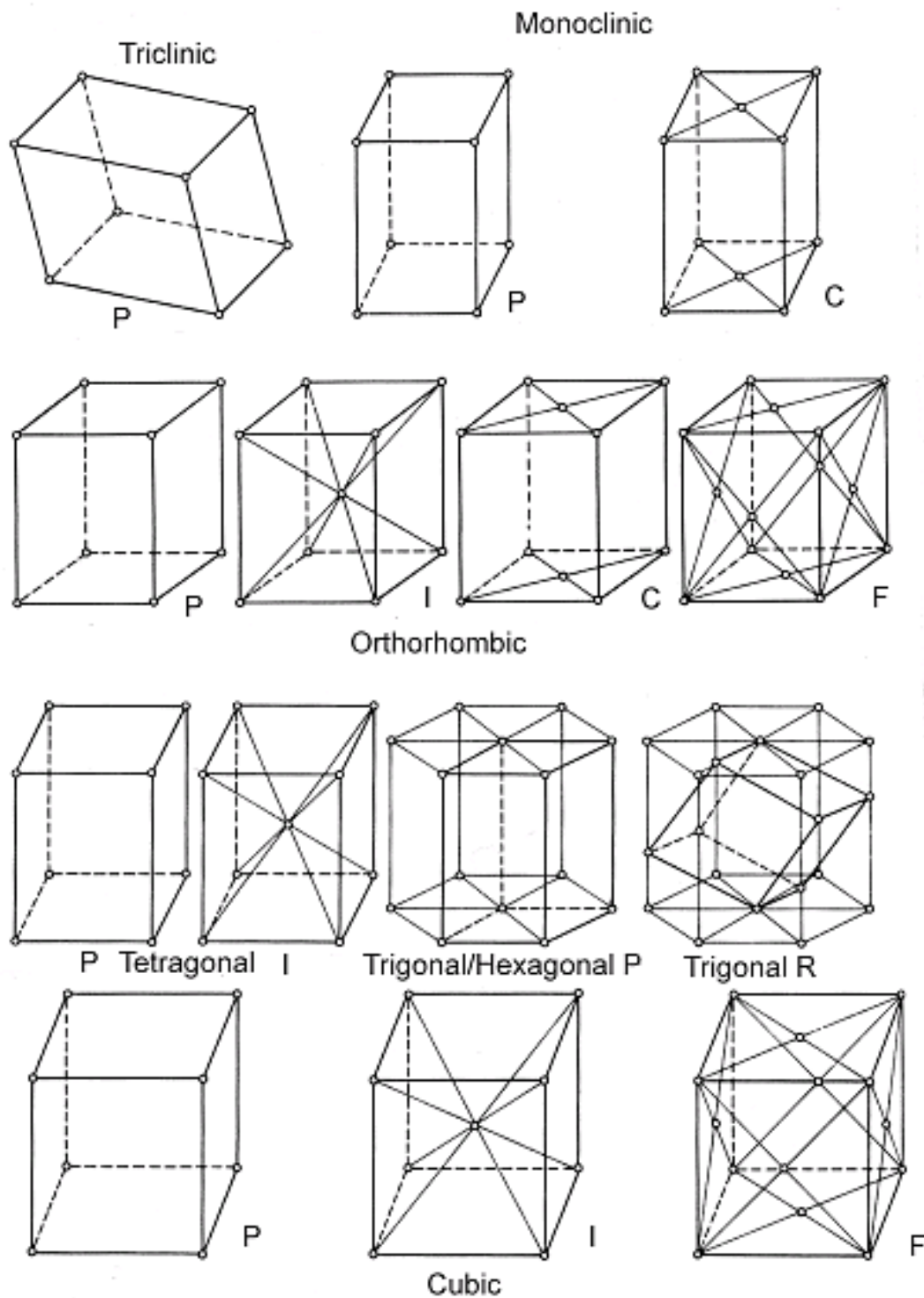


Figure 2-3: The 14 Bravais lattices

2.2 Compact structures

Suppose we statistically observe which structures are the most common for the periodic table of elements. In that case, we note that metals generally crystallize with structures, which enable each atom to have the highest possible number of bonds.

That is, metals tend to crystallize in the form of compact crystal structures such as face-centered cubic (FCC - figure 2-4), hexagonal close packing (HCP), or cubic-centered (CC). The tendency to form such highly symmetric crystal structures relates to metallic bonding. On the one hand, this type of bonding is weak (lower melting points, lower strength, etc.). But on the other hand, the atoms have a high probability of forming the highest possible number of bonds. When bonding is isotropic, it implies the formation of highly symmetric crystal structures.

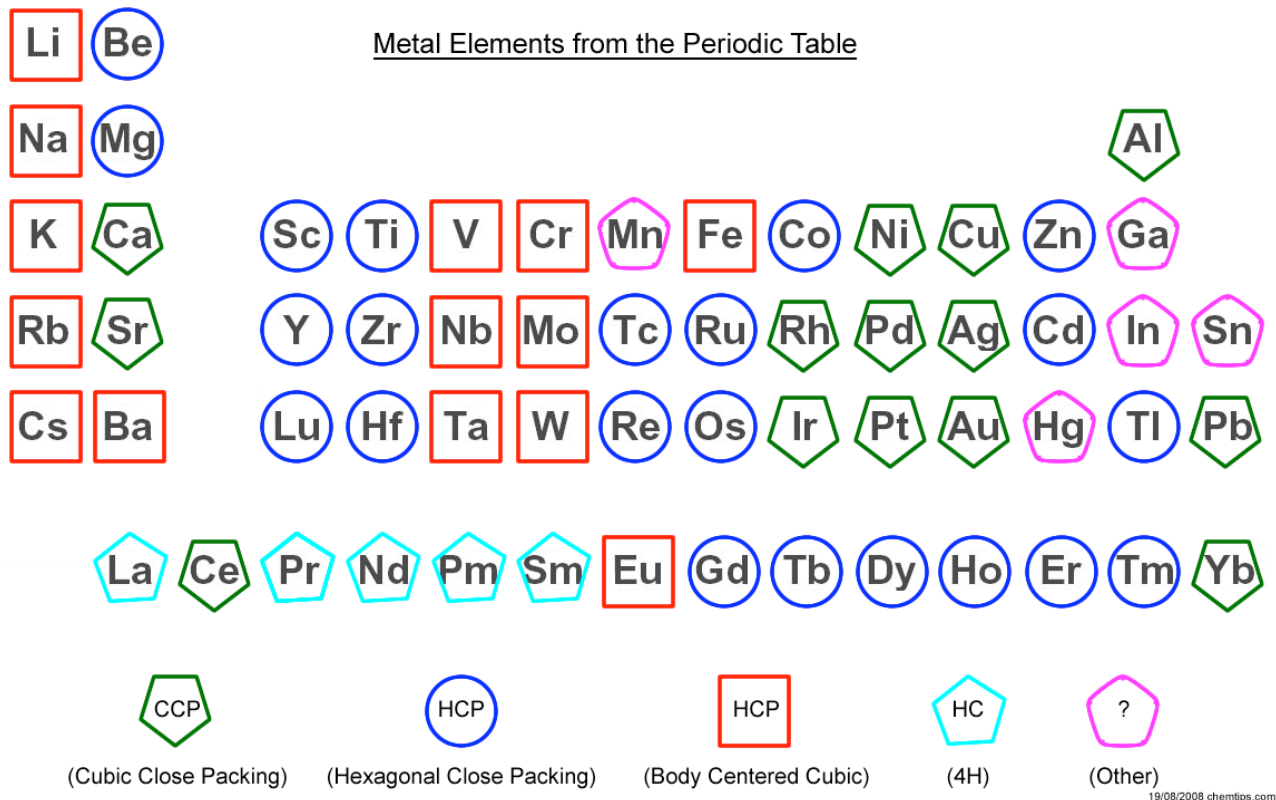


Figure 2-4: Crystal structures of metals in the periodic table

There are two ways of compactly stacking up layers of spheres (figure 2-5). The third layer can be either superposed to the first layer (ABA) arrangement or superposed to a hole in the first layer of the ABC arrangement. The first case corresponds to an HCP structure, and the second stacking arrangement is an FCC structure with the highest packing density. The cubic-centered structure is not compact, but the second closest neighbors (especially in metal compounds) are relatively comparable. Thus, an atom in the center of the cell can bind with its eight nearest neighbors and the six-second closest neighbors, giving a total of 14 bonds.

It is interesting to note how the arrangement of atomic spheres in compact structures leaves some empty spaces in particular locations. These are called interstitial sites. According to the symmetry in the position of the atoms surrounding an interstitial site, these sites are at specific locations on characteristic polyhedrons (figure 2-6).

The presence of interstitial sites helps to understand the crystallography of several crystals formed by diatomic molecules. A diatomic crystal can comprise an element A with a high symmetry lattice and an element B occupying the interstitial sites. For example, chlorine has an FCC arrangement in a NaCl crystal, and sodium sits on the octahedral sites (figure 2-7). In ZnS, sulfur is on an FCC lattice, whereas zinc is on the tetrahedral sites (figure 2-8). In the next section, the origin of the formation of these crystal structures based on their coordination and radii is presented.

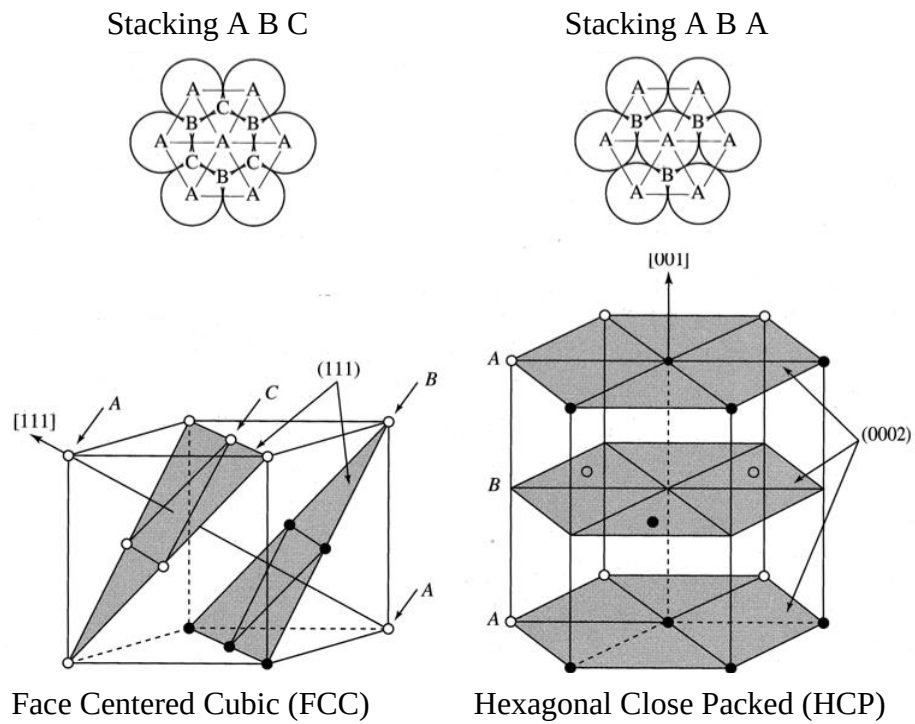


Figure 2-5: Close packing in FCC and HCP structures

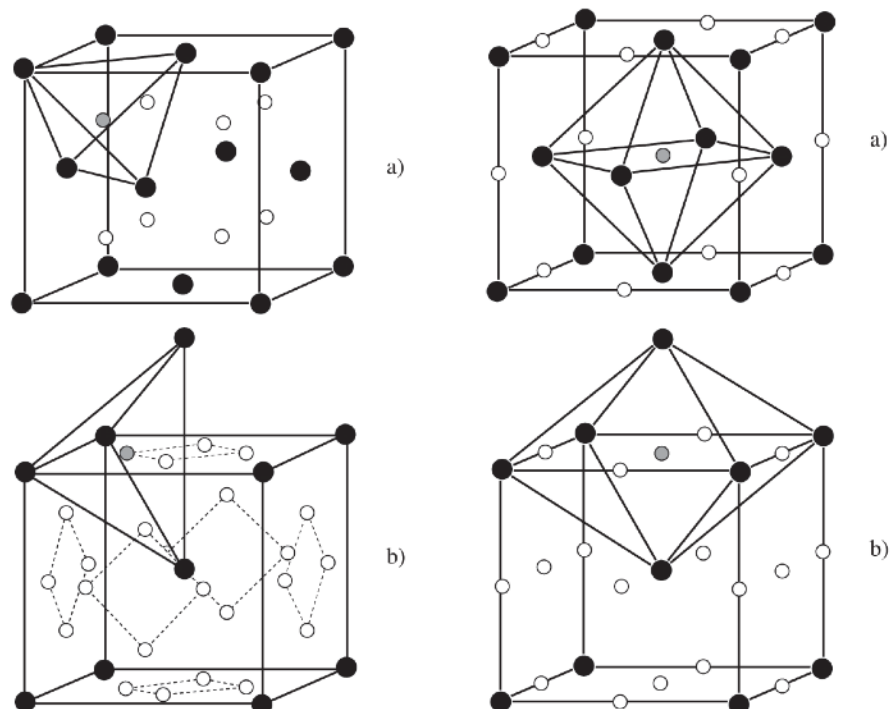


Figure 2-6: Tetrahedral interstitial sites (left) and octahedral sites (right) in FCC structures (a) and CC (b).

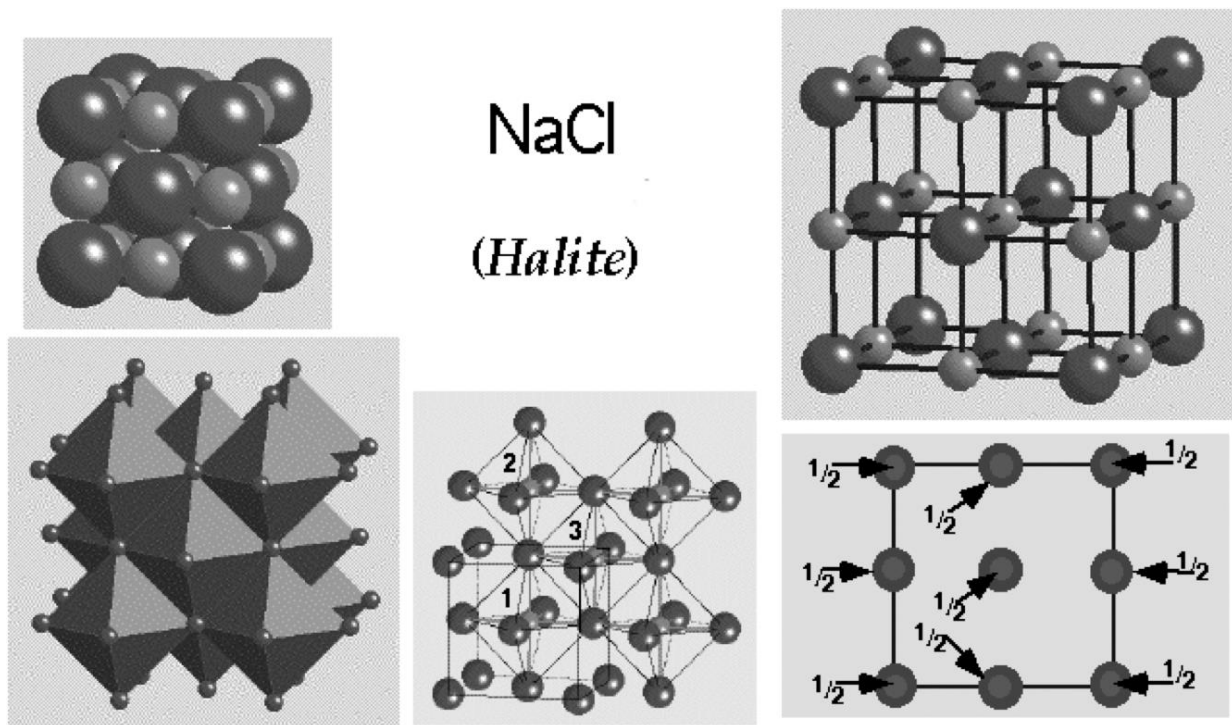


Figure 2-7: Sodium chloride structure: sodium atoms are located in the octahedral sites of the FCC lattice of chlorine

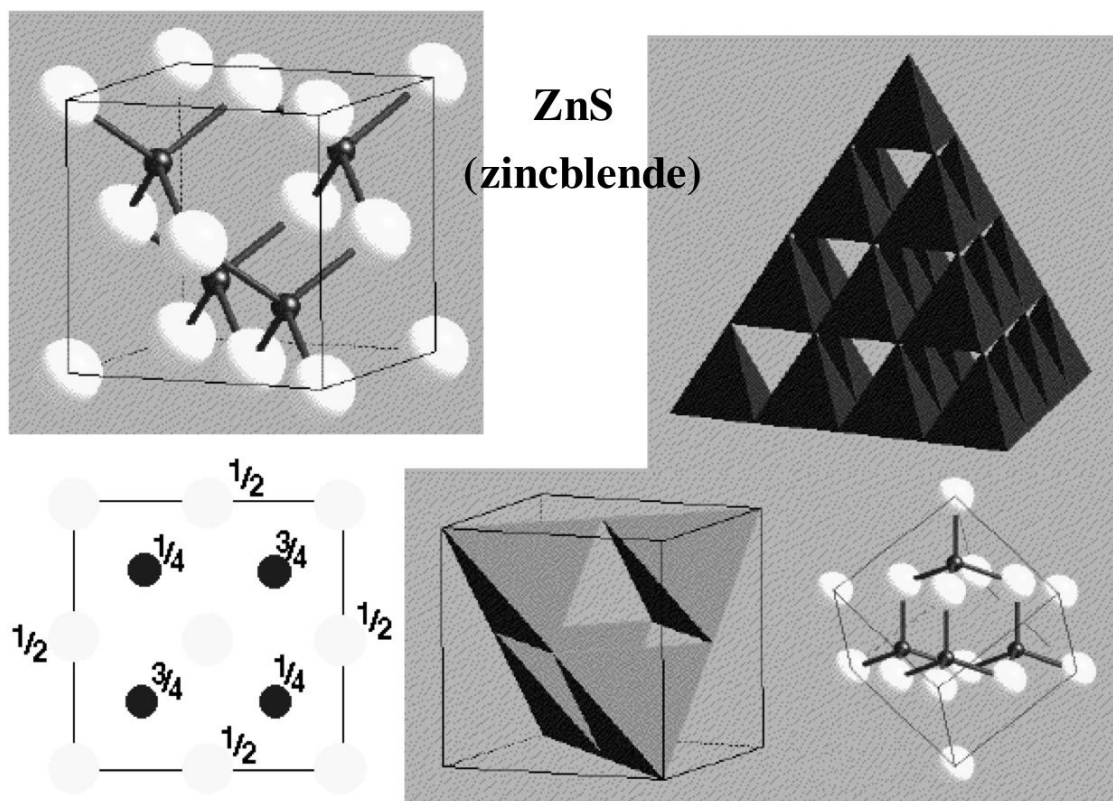
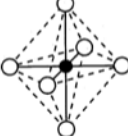
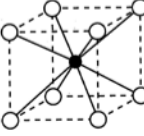
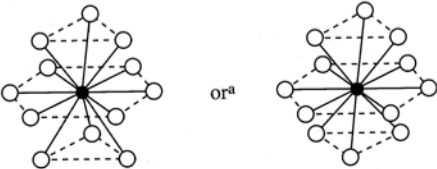


Figure 2-8: Zinc sulfide structure: zinc atoms are located in the tetrahedral sites of the FCC lattice of sulfur

Table II-2: Coordination number N as a function of atomic radiuses

N	radius ratio r/R	geometry
2	$0 < \frac{r}{R} < 0.155$	
3	$0.155 \leq \frac{r}{R} < 0.225$	
4	$0.225 \leq \frac{r}{R} < 0.414$	
6	$0.414 \leq \frac{r}{R} < 0.732$	
8	$0.732 \leq \frac{r}{R} < 1$	
12	1	

We call this number the coordination number. For example, in ionic materials, we can calculate the precise interatomic distance D between the closest neighbors from the simple formula (cf table II-3):

$$D = R_a + R_b + \Delta_N \quad (2.20)$$

The radii R_a and R_b are those of neutral atoms, and the correction Δ_N depends on the coordination number.

Table II-3: Corrections to interatomic distances in ionic crystals. The atomic radii in the crystal decrease for small coordination numbers and increase for big coordination numbers

N	$\Delta_N(\text{\AA})$	N	$\Delta_N(\text{\AA})$	N	$\Delta_N(\text{\AA})$
1	-0.50	5	-0.05	9	0.11
2	-0.31	6	0	10	0.14
3	-0.19	7	0.04	11	0.17
4	-0.11	8	0.08	12	0.19