CHAPTER II *CRYSTAL STRUCTURE*

2.1 Crystal lattices

2.1.1 Historical references

The first systematic theory of crystal structure is attributed to René-Just Haüy (1783). His ideas arose from the observation that many crystals naturally cleave along well-defined planes when fractured, a property now known as **cleavage**. The specific planes along which crystals split are called **cleavage planes**. Haüy investigated calcite ($CaCO_3$), which consistently cleaves along three distinct planes forming dihedral angles of 105°5′. From this, he noted that calcite crystals break into smaller parallelepipeds with the same characteristic angles, called **rhombohedra**. A rhombohedron is a special type of parallelepiped in which all dihedral angles are equal and each face is a rhombus.

Extending the atomic hypothesis to crystalline matter, Haüy proposed that this process of cleavage could not continue indefinitely. Instead, he suggested there must be a smallest repeating unit—an **elementary rhombohedron**—which he named the *molécule intégrante*. In modern crystallography, this concept corresponds to what is now known as the **primitive unit cell**.

A crystal comprises a group of identical unit cells that stack perfectly with no gaps. In such an

$$\vec{t} = m_1\overrightarrow{a_1} + m_2\overrightarrow{a_2} + m_3\overrightarrow{a_3} \tag{2.1}$$

arrangement, each unit cell is deduced from another by a translation of the form:

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, groups of atoms, or molecules) did not fill all the available space. Assuming the crystal pattern's symmetry was that of a polyhedron and utilizing 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 ($0.5Å < \lambda < 2Å$) was interpreted by Von Laue, admitting that a crystal was formed by a crystal pattern repeated in space by translation $m_1\overrightarrow{a_1} + m_2\overrightarrow{a_2} + m_3\overrightarrow{a_3}$.

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 three-dimensional 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 formed by these three vectors constitutes 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 **vertices of the unit cells** are called **nodes** of the lattice.

At the eight vertices 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:

$$\overrightarrow{OJ} = j_1\vec{a_1} + j_2\vec{a_2} + j_3\vec{a_3} \qquad (2.2)$$

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

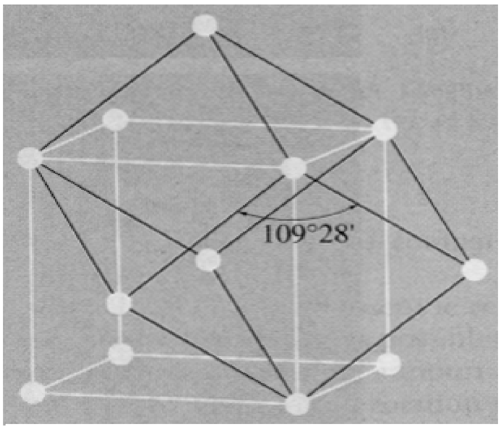


***Figure 2-1**: Representation of a primitive cell and the multiple conventional cell of a centered cubic structure*

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:

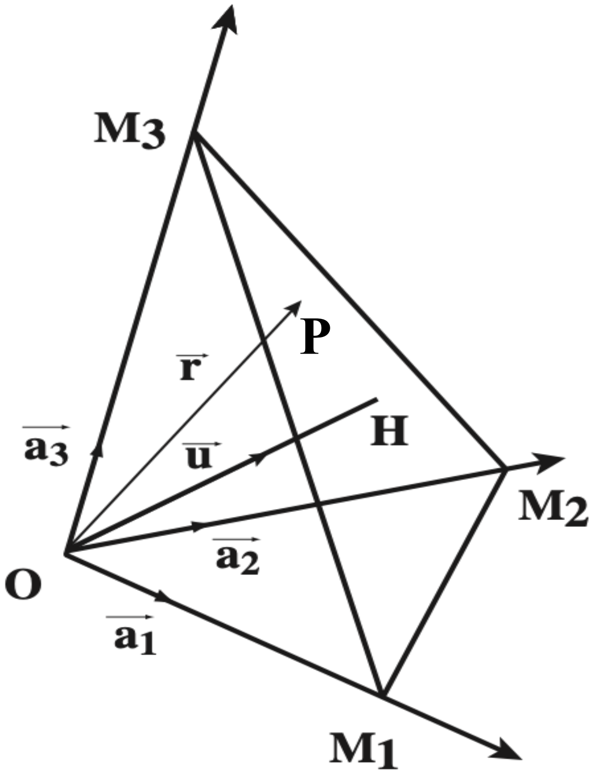
$$\overrightarrow{OM} = m_1\vec{a_1} + m_2\vec{a_2} + m_3\vec{a_3} \qquad (2.3)$$

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

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

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

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 $\vec{a}_1,\vec{a}_2,\vec{a}_3$ so that:

$$\overrightarrow{OM_1} = n_1\overrightarrow{a_1}$$
$$\overrightarrow{OM_2} = n_2\overrightarrow{a_2}$$
$$\overrightarrow{OM_3} = n_3\overrightarrow{a_3}$$

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

$$\overrightarrow{M_1M_2} = n_2\overrightarrow{a_2} - n_1\overrightarrow{a_1}$$
$$\overrightarrow{M_2M_3} = n_3\overrightarrow{a_3} - n_2\overrightarrow{a_2}$$

$$\overrightarrow{M_1M_3} = n_3\overrightarrow{a_3} - n_1\overrightarrow{a_1}$$

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 OH_n and let *P* be any point in the plane located at $\overrightarrow{OP} = \vec{r}$ so that:

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

$$\vec{r}\cdot\vec{u} = OH_n \tag{2.6}$$

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

where $$OH_n = x(\vec{u}\cdot\vec{a}_1) + y(\vec{u}\cdot\vec{a}_2) + z(\vec{u}\cdot\vec{a}_3) \tag{2.7}$$

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

$$\vec{u}\cdot\vec{a}_1=\frac{OH_n}{n_1} \qquad \vec{u}\cdot\vec{a}_2=\frac{OH_n}{n_2} \qquad \vec{u}\cdot\vec{a}_3=\frac{OH_n}{n_3} \tag{2.8}$$

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:

$$n_1=nn_1' \qquad n_2=nn_2' \qquad n_3=nn_3' \tag{2.9}$$

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 with center O (the origin of the lattice) and a ratio of 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:

$$\overrightarrow{OM_1'}=n_1'\vec{a_1} \qquad \overrightarrow{OM_2'}=n_2'\vec{a_2} \qquad \overrightarrow{OM_3'}=n_3'\vec{a_3}$$

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

$$n_2'n_3'x+n_1'n_3'y+n_1'n_2'z=n_1'n_2'n_3' \tag{2.10}$$

If we call:

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

The equation can be written in the form:

h, ***k***, ***l*** are called Miller indices of the lattice plane, which intercepts the axis in $n_1'\vec{a_1}, n_2'\vec{a_2}, n_3'\vec{a_3}$.

$$hx+ky+lz=n_1'n_2'n_3'=hn_1'=kn_2'=\ln_3' \tag{2.11}$$

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 the Miller indices of the plane cutting the three axes $\vec{a_1}, \vec{a_2}, \vec{a_3}$ 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 $n_1'=1,\quad n_2'=2,\quad n_3'=3$ 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*

$$\vec{u} = (n_2'\overrightarrow{a_2} - n_1'\overrightarrow{a_1}) \times (n_3'\overrightarrow{a_3} - n_1'\overrightarrow{a_1})$$

$$\begin{aligned}\vec{u} &= n_2'n_3'(\overrightarrow{a_2} \times \overrightarrow{a_3}) + n_1'n_3'(\overrightarrow{a_3} \times \overrightarrow{a_1}) + n_1'n_2'(\overrightarrow{a_1} \times \overrightarrow{a_2}) = \\ &= h(\overrightarrow{a_2} \times \overrightarrow{a_3}) + k(\overrightarrow{a_3} \times \overrightarrow{a_1}) + l(\overrightarrow{a_1} \times \overrightarrow{a_2})\end{aligned} \tag{2.12}$$

Defining:

$$\overrightarrow{a_1}^{\star} = \overrightarrow{a_2} \times \overrightarrow{a_3} \qquad \overrightarrow{a_2}^{\star} = \overrightarrow{a_3} \times \overrightarrow{a_1} \qquad \overrightarrow{a_3}^{\star} = \overrightarrow{a_1} \times \overrightarrow{a_2} \tag{2.13}$$

We note that the indices *h,k, and l* represent the components of the normal to the plane in the coordinate system $\overrightarrow{a_1}^{\star}$, $\overrightarrow{a_2}^{\star}$, $\overrightarrow{a_3}^{\star}$. The nodes corresponding to the vectors $\overrightarrow{a_i}^{\star}$ define a new lattice of points: the **reciprocal lattice**. The distances in $\mathring{A}^{-1}$ of the reciprocal lattice vectors correspond to the inverse of the distance between the crystal lattice planes:

$$\left\|\vec{r}_{hkl}^{\,\star}\right\| = \frac{1}{d_{hkl}} \tag{2.14}$$

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 $\overrightarrow{a_i}^{\star}$ in such a way that:

$\overrightarrow{a_i} \cdot \overrightarrow{a_i} = 1$ so that the normal definition is $\overrightarrow{a_1}^{\star} = \dfrac{\overrightarrow{a_2} \times \overrightarrow{a_3}}{\overrightarrow{a_1}(\overrightarrow{a_2} \times \overrightarrow{a_3})}$ (2.15)

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

$$\overrightarrow{a_i} \cdot \overrightarrow{a_j}^{\star} = \delta_{ij} \tag{2.16}$$

The product $V = \overrightarrow{a_1}(\overrightarrow{a_2} \times \overrightarrow{a_3})$ 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

$$\overrightarrow{a_1}^{\star} \times \overrightarrow{b_2}^{\star} = \frac{\vec{c}}{V} \tag{2.17}$$

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

Example

Consider two planes:

$h_1x+k_1y+l_1z=0$ and $h_2x+k_2y+l_2z=0$

A line belonging to the two planes is given by a vector in the direct base $(\overrightarrow{a_1},\ \overrightarrow{a_2},\ \overrightarrow{a_3})$:

$$(k_1l_2-k_2l_1)\overrightarrow{a_1}+(l_1h_2-l_2h_1)\overrightarrow{a_2}+(h_1k_2-h_2k_1)\overrightarrow{a_3}$$

whereas, given two vectors of the direct lattice:

$x\overrightarrow{a_1}+y\overrightarrow{a_2}+z\overrightarrow{a_3}$ and $x'\overrightarrow{a_1}+y'\overrightarrow{a_2}+z'\overrightarrow{a_3}$

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

$$(yz'-y'z)\overrightarrow{a_1}^{\star}+(x'z-xz')\overrightarrow{a_2}^{\star}+(xy'-yx')\overrightarrow{a_3}^{\star}$$

We can demonstrate, using a non-orthonormal basis such as one of a non-symmetric 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:

$$(x\overrightarrow{a_1}+y\overrightarrow{a_2}+z\overrightarrow{a_3})\cdot(x'\overrightarrow{a_1}+y'\overrightarrow{a_2}+z'\overrightarrow{a_3})=\begin{bmatrix} x & y & z \end{bmatrix}\begin{bmatrix} a_1^2 & \overrightarrow{a_1}\cdot\overrightarrow{a_2} & \overrightarrow{a_1}\cdot\overrightarrow{a_3} \\ \overrightarrow{a_1}\cdot\overrightarrow{a_2} & a_2^2 & \overrightarrow{a_2}\cdot\overrightarrow{a_3} \\ \overrightarrow{a_1}\cdot\overrightarrow{a_3} & \overrightarrow{a_2}\cdot\overrightarrow{a_3} & a_3^2 \end{bmatrix}\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}=\overrightarrow{u_T}M\vec{u} \tag{2.18}$$

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:

$$(x\overrightarrow{a_1}^{\star}+y\overrightarrow{a_2}^{\star}+z\overrightarrow{a_3}^{\star})\cdot(x'\overrightarrow{a_1}^{\star}+y'\overrightarrow{a_2}^{\star}+z'\overrightarrow{a_3}^{\star})=\begin{bmatrix} h & k & l \end{bmatrix}\begin{bmatrix} (a_1^{\star})^2 & \overrightarrow{a_1}^{\star}\cdot\overrightarrow{a_2}^{\star} & \overrightarrow{a_1}^{\star}\cdot\overrightarrow{a_3}^{\star} \\ \overrightarrow{a_1}^{\star}\cdot\overrightarrow{a_2}^{\star} & (a_2^{\star})^2 & \overrightarrow{a_2}^{\star}\cdot\overrightarrow{a_3}^{\star} \\ \overrightarrow{a_1}^{\star}\cdot\overrightarrow{a_3}^{\star} & \overrightarrow{a_2}^{\star}\cdot\overrightarrow{a_3}^{\star} & (a_3^{\star})^2 \end{bmatrix}\begin{bmatrix} h' \\ k' \\ l' \end{bmatrix}=\overrightarrow{h_T}M^{\star}\vec{h} \tag{2.19}$$

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

2.1.5 Crystal systems

Let's consider only rotational symmetries and exclude the others. Crystals can be classified into **seven crystal systems** based on the type and number of axes of rotation they possess. 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 , $\alpha=\angle(\vec{b},\vec{c})$, $\beta=\angle(\vec{c},\vec{a}),\gamma=\angle(\vec{a},\vec{b})$.

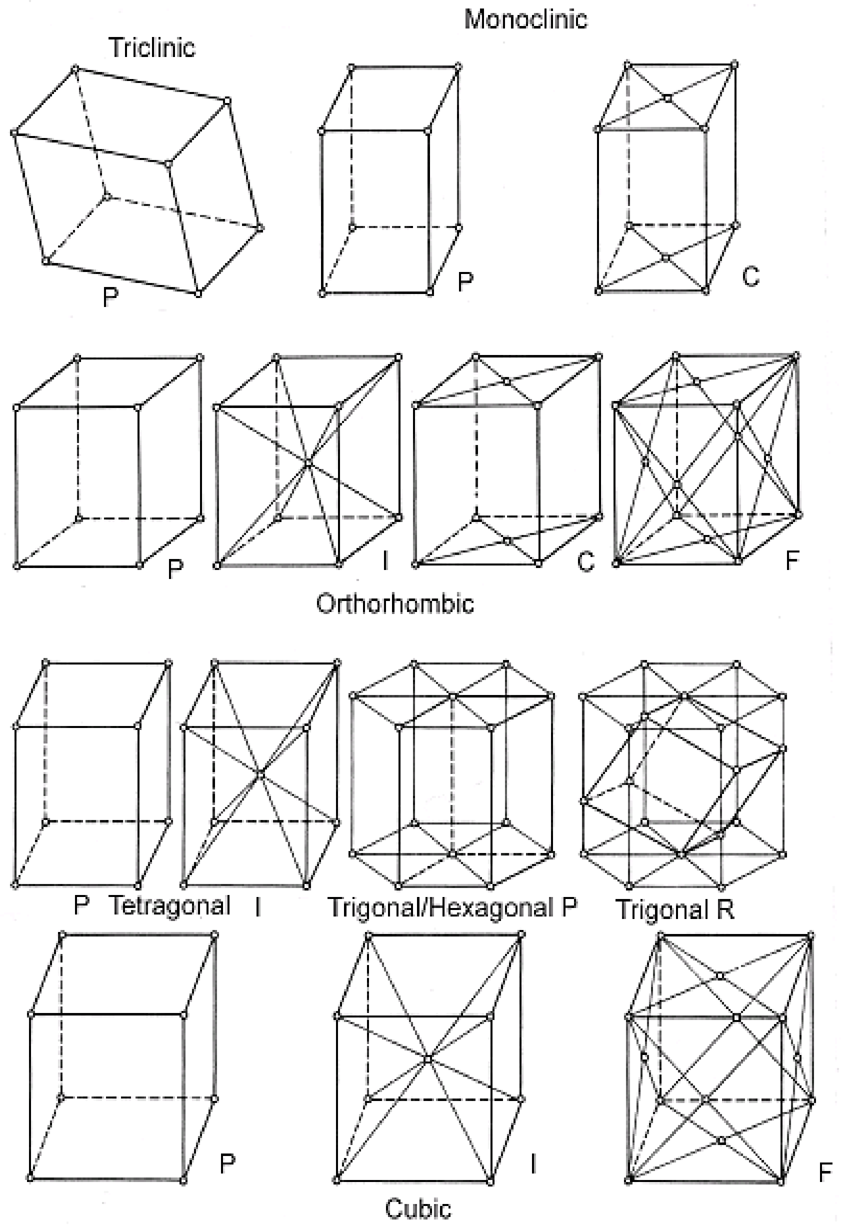


Figure 2-3: *The 14 Bravais lattices*

2.2 Compact structures

Suppose we statistically observe which structures are the most common for the periodic table of elements. Due to the nature of metallic bonding, metals generally crystallize with structures that 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)** (see Figure 2-4), hexagonal close-packed **(HCP)**, or **cubic-centered (CC)**. The tendency to form highly symmetric crystal structures is related to metallic bonding. On the one hand, this type of bonding is weak (lower melting points, lower strength, etc.). However, on the other hand, the atoms have a high probability of forming the maximum number of bonds. When bonding is isotropic, it implies the formation of highly symmetric crystal structures.

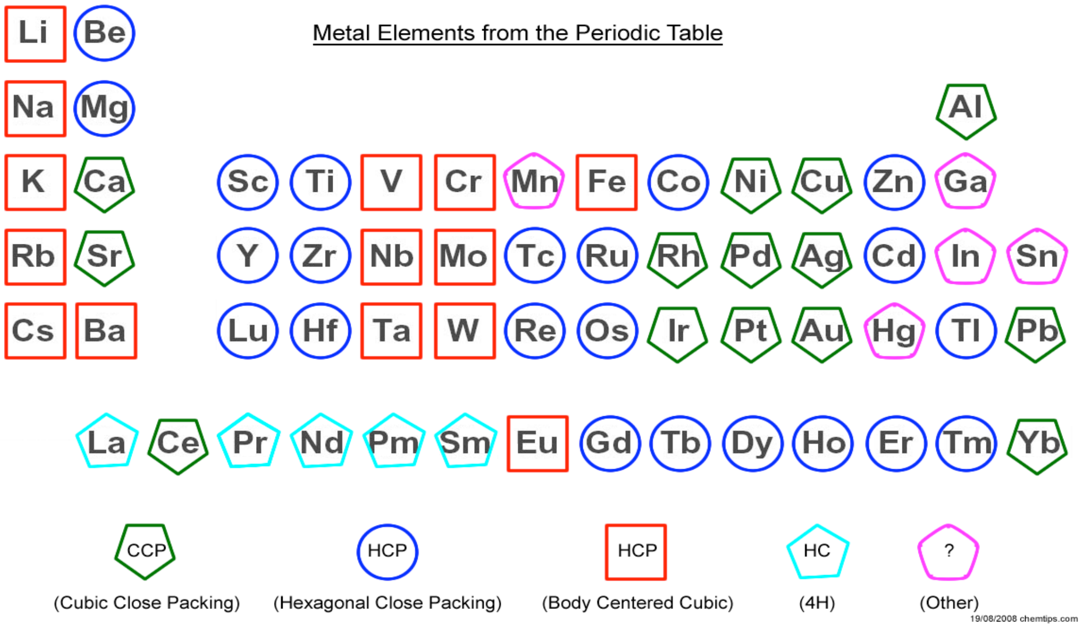


Figure 2-4: *Crystal structures of metals in the periodic table*

There are two ways of compactly stacking layers of spheres (Figure 2-5). The third layer can be placed either directly above the first, resulting in an **ABA stacking sequence**, or above the holes left in the first layer, providing an **ABC sequence**. The first case corresponds to the **hexagonal close-packed (HCP)** structure, while the second produces the **face-centered cubic (FCC)** structure, which achieves the highest possible packing density.

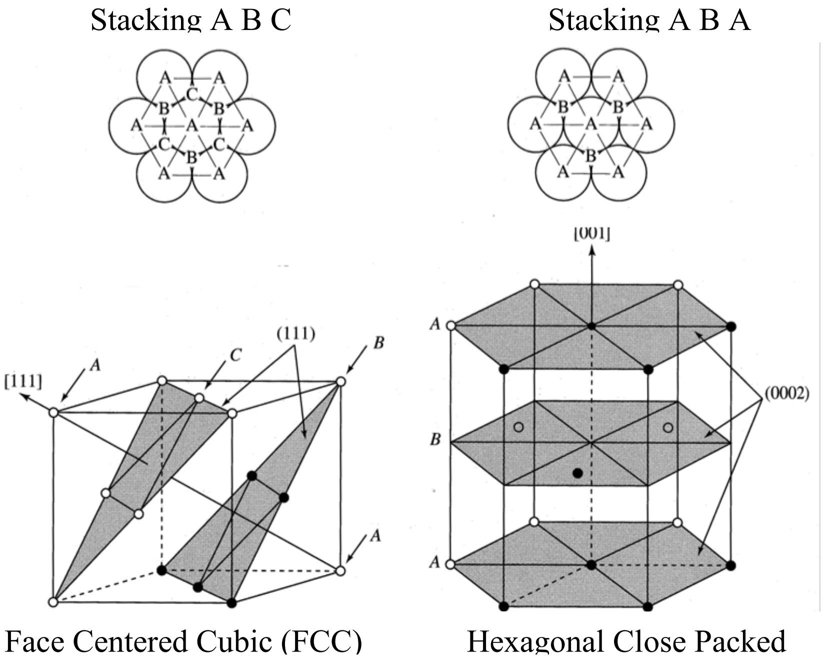


Figure 2-5: *Close packing in FCC and HCP structures*

The **body-centered cubic (BCC)** structure, on the other hand, is not close-packed. Nevertheless, in many metallic crystals, the distances to second-nearest neighbors are comparable to those of nearest neighbors. Thus, the atom at the center of the cell can coordinate with its eight nearest neighbors at the cube corners and with the six second-nearest neighbors at the face centers, giving a total coordination number of 14. This feature helps to explain the stability of BCC metals such as iron, chromium, and tungsten, despite their lower packing efficiency compared to FCC and HCP structures. It is also interesting to note that even in compact structures, the arrangement of spheres leaves empty regions at characteristic positions. These are known as **interstitial sites** and are defined by the symmetry of the surrounding atoms, often forming polyhedral geometries (Figure 2-6). The presence of such sites is essential for understanding the crystallography of many binary compounds. A diatomic crystal can consist of one element forming a high-symmetry lattice while the other occupies the interstitial sites. For instance, in sodium chloride, chlorine atoms form an FCC lattice and sodium ions occupy the octahedral sites (Figure 2-7). In zinc blende (ZnS), sulfur forms the FCC lattice and zinc atoms fill the tetrahedral sites (Figure 2-8).

The systematic study of these structures during the first half of the 20th century led to the development of general principles connecting ionic size, coordination, and crystal stability. Linus Pauling's rules, formulated in the 1920s and 1930s, provided a rational framework that remains central to understanding why certain compounds adopt specific structures based on atomic radii and coordination requirements. In the next section, the origin of these crystal structures will be discussed in more detail, with particular attention to the role of coordination geometry and ionic size ratios.

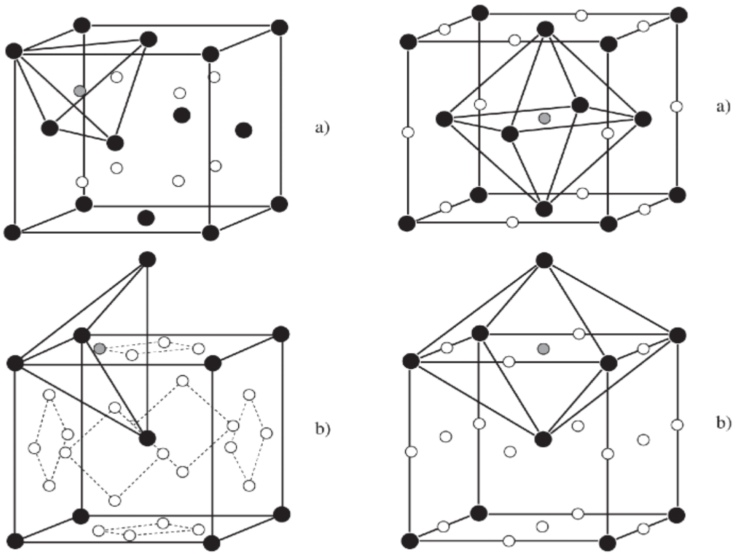


Figure 2-6: *Tetrahedral interstitial sites (left) and octahedral sites (right) in FCC structures (a) and CC (b).*

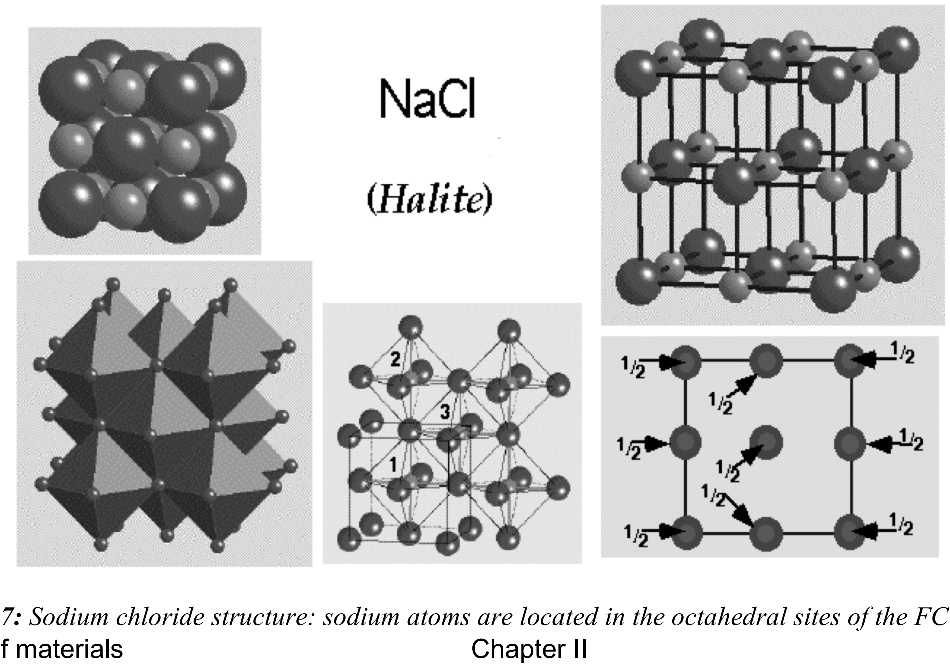


Figure 2-7: *Sodium chloride structure: sodium atoms are located in the octahedral sites of the FCC lattice of chlorine*

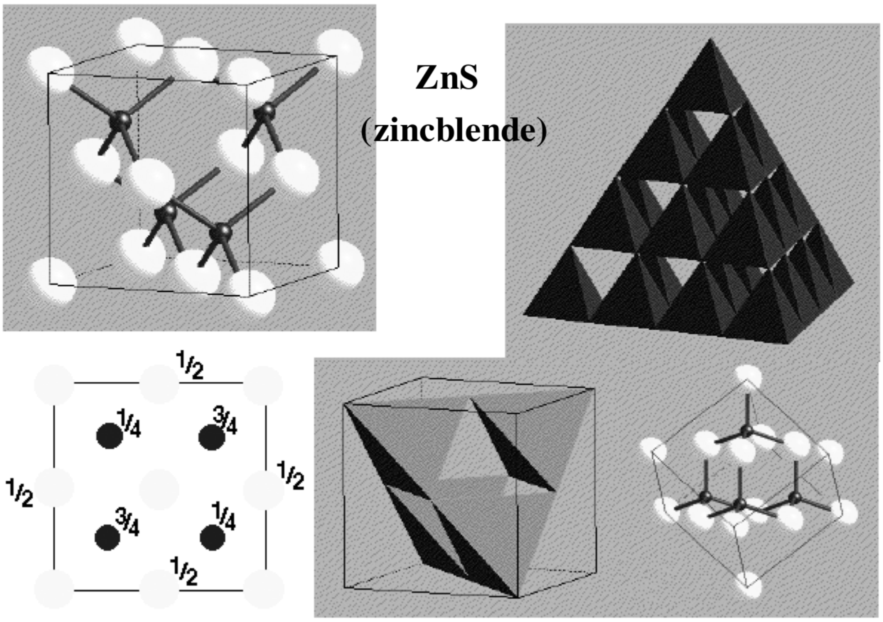


Figure 2-8: *Zinc sulfide structure: zinc atoms are located in the tetrahedral sites of the FCC lattice of sulfur*

As point of histotrical reference, these stacking principles were first formulated in the 19th century through geometric reasoning, but their atomic reality was only demonstrated in the early 20th century, when W. H. Bragg and W. L. Bragg used X-ray diffraction to reveal the periodic arrangement of atoms in crystals. Their solution of the NaCl structure in 1913 (Figure 2-7) stands as a milestone in crystallography. Their experimental breakthrough came with the formulation of **Bragg's law**:

$$n\lambda = 2dsin\theta \tag{2.20}$$

which relates the X-ray wavelength λ, the spacing between lattice planes d, the diffraction angle θ, and the integer order of reflection n. This deceptively simple relation provided the foundation for interpreting diffraction patterns and connecting them directly to the internal geometry of crystals.

In a typical **X-ray diffraction (XRD)** experiment, a monochromatic X-ray beam is directed onto a crystalline sample. The Bragg reflections generated at specific angles are recorded by a detector, producing a diffraction pattern that serves as a fingerprint of the crystal structure. The most common laboratory arrangement is the **Bragg–Brentano geometry**, in which the X-ray source and detector move symmetrically around the sample while the sample remains fixed at the center. In this configuration, the incident and diffracted beams always satisfy the Bragg condition for some lattice planes, allowing accurate measurement of diffraction peaks. In the **powder diffraction method**, the sample is ground into a fine powder containing many randomly oriented crystallites. Because all orientations are represented, diffraction peaks corresponding to all possible lattice planes appear. The resulting pattern consists of sharp peaks at specific angles that can be indexed to determine lattice parameters, phase composition, and crystallite size. Powder diffraction is therefore the standard for routine materials characterization (Figure 2-9). In **single-crystal diffraction**, a single oriented crystal is mounted in the X-

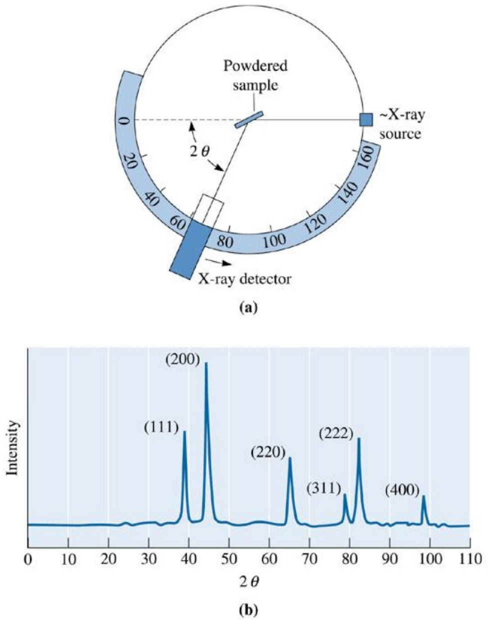


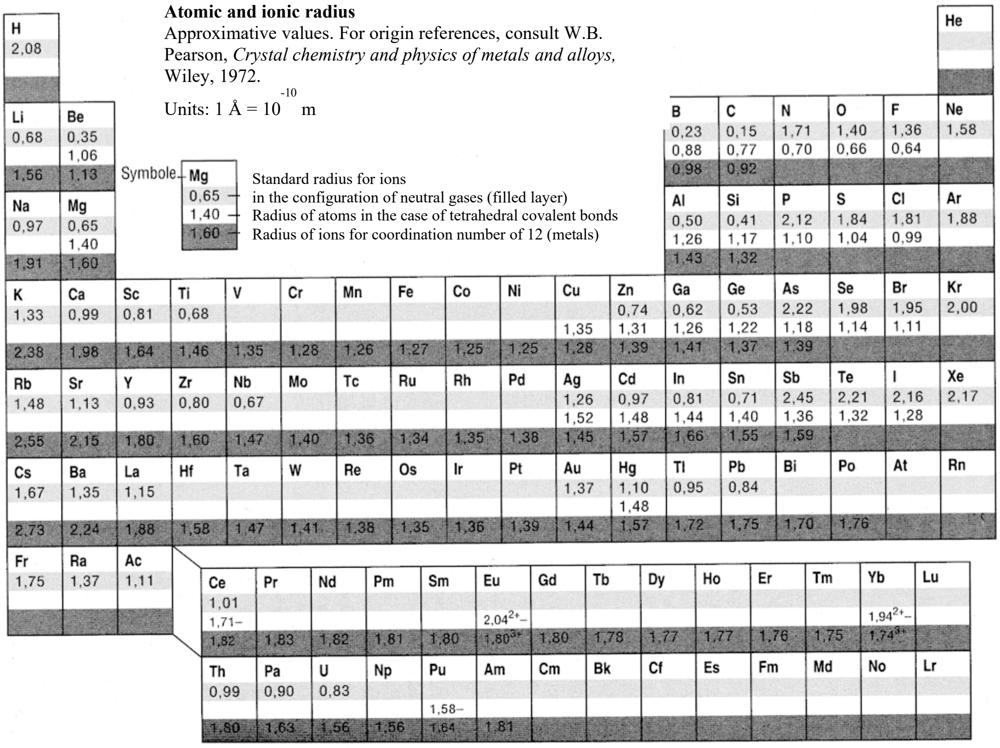
Figure 2-9 a: Schematic of powder XRD in Bragg–Brentano geometry, showing the X-ray source, powdered sample, and moving detector, b: producing 2-D plot of diffraction with twic Bragg angle, 2θ.

ray beam and systematically rotated. By collecting the diffracted intensities from different orientations, it is possible to reconstruct the three-dimensional distribution of atoms within the unit cell. Modern XRD instruments employ a variety of detectors, from traditional scintillation counters to two-dimensional CCD and pixel array detectors, which can capture entire diffraction rings in real time. The recorded data are analyzed with crystallographic software, applying symmetry constraints and structural refinement methods to obtain accurate atomic positions.

2.3 Coordination number

The structure of a crystal can be related to its chemical composition. We have discussed how the study of the chemical bond enables the determination of the equilibrium position of atoms in molecules. Can we state that the distance observed between two atoms can be split up into a contribution from atom A and another from atom B? Strictly speaking, we cannot. We have shown how bonding within solids leads to a superposition and hybridization of atomic orbitals, displacing the electrons, which are not confined in a rigid sphere. The atomic radii in a crystal are then related to the type of bonds. Table II-1 shows that the atomic radius of bonded atoms is often larger than that of neutral atoms.

***Table II-1:** Atomic radii and bonds*



Atomic and ionic radius
Approximative values. For origin references, consult W.B. Pearson, *Crystal chemistry and physics of metals and alloys,* Wiley, 1972.
Units: 1 Å = 10^{-10} m

Symbole – Mg
0,65 – Standard radius for ions in the configuration of neutral gases (filled layer)
1,40 – Radius of atoms in the case of tetrahedral covalent bonds
1,60 – Radius of ions for coordination number of 12 (metals)

H	2,08		
He			
Li	0,68		1,56
Be	0,35	1,06	1,13
B	0,23	0,88	0,98
C	0,15	0,77	0,92
N	1,71	0,70	
O	1,40	0,66	
F	1,36	0,64	
Ne	1,58		
Na	0,97		1,91
Mg	0,65	1,40	1,60
Al	0,50	1,26	1,43
Si	0,41	1,17	1,32
P	2,12	1,10	
S	1,84	1,04	
Cl	1,81	0,99	
Ar	1,88		
K	1,33		2,38
Ca	0,99		1,98
Sc	0,81		1,64
Ti	0,68		1,46
V			1,35
Cr			1,28
Mn			1,26
Fe			1,27
Co			1,25
Ni			1,25
Cu		1,35	1,28
Zn	0,74	1,31	1,39
Ga	0,62	1,26	1,41
Ge	0,53	1,22	1,37
As	2,22	1,18	1,39
Se	1,98	1,14	
Br	1,95	1,11	
Kr	2,00		
Rb	1,48		2,55
Sr	1,13		2,15
Y	0,93		1,80
Zr	0,80		1,60
Nb	0,67		1,47
Mo			1,40
Tc			1,36
Ru			1,34
Rh			1,35
Pd			1,38
Ag	1,26	1,52	1,45
Cd	0,97	1,48	1,57
In	0,81	1,44	1,66
Sn	0,71	1,40	1,55
Sb	2,45	1,36	1,59
Te	2,21	1,32	
I	2,16	1,28	
Xe	2,17		
Cs	1,67		2,73
Ba	1,35		2,24
La	1,15		1,88
Hf			1,58
Ta			1,47
W			1,41
Re			1,38
Os			1,35
Ir			1,36
Pt			1,39
Au	1,37		1,44
Hg	1,10	1,48	1,57
Tl	0,95		1,72
Pb	0,84		1,75
Bi			1,70
Po			1,76
At			
Rn			
Fr	1,75		
Ra	1,37		
Ac	1,11		
Ce	1,01	1,71–	1,82
Pr			1,83
Nd			1,82
Pm			1,81
Sm			1,80
Eu		$2,04^{2+}$–	$1,80^{3+}$
Gd			1,80
Tb			1,78
Dy			1,77
Ho			1,77
Er			1,76
Tm			1,75
Yb		$1,94^{2+}$–	$1,74^{3+}$
Lu			
Th	0,99		1,80
Pa	0,90		1,63
U	0,83		1,56
Np			1,56
Pu		1,58–	1,64
Am			1,81
Cm			
Bk			
Cf			
Es			
Fm			
Md			
No			
Lr			

If we can predict or measure the atomic radii of elements in a compound, we can deduce the crystal structure. It has been scientifically proven that atoms choose the most compact structure permitted by their radii. This radius determines the number of closest neighbors, i.e., the coordination number (figure 2-9).

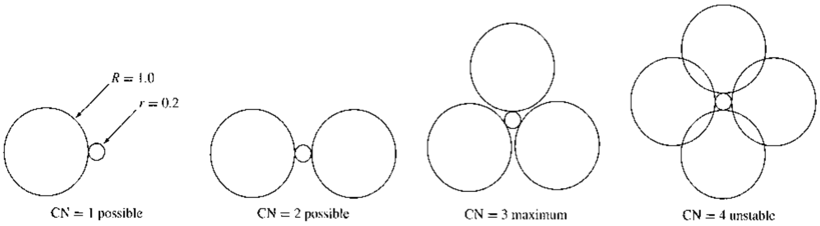
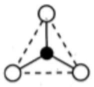
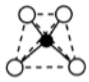
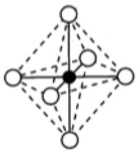
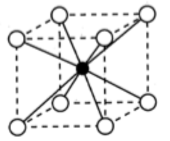
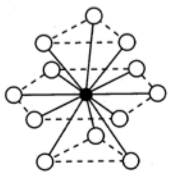
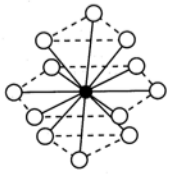


***Figure 2-9:** The maximum number of neighbors compatible with a radius ratio of 0.2 is 3*

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	 or^{a} 

We refer to this number as the coordination number. For example, in ionic materials, we can calculate the precise interatomic distance *D* between the closest neighbors from the simple formula (Table II-3):

$$D = R_a + R_b + \Delta_N \tag{2.20}$$

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 large coordination numbers*

N	Δ_N(Å)	*N*	Δ_N(Å)	*N*	Δ_N(Å)
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