Chapter II. Crystallochemistry

II.1 Introduction

Crystallochemistry (or crystal chemistry) is the branch of chemistry that studies the complex relationships between the chemical composition of crystals and their structures, and how these relationships influence their properties. It focuses on how atoms, ions, or molecules arrange themselves in a crystalline lattice, including the types of chemical bonds involved, leading to an ordered, periodic structure.

In nature, matter exists in three physical states: solid, liquid, and gas. In each state, the molecules adopt a distinct arrangement, which determines the substance's macroscopic structure and properties.

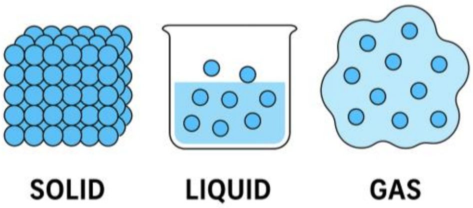


Figure II.1: The three state of matter.

Example: water in real life can be founded in 3 states:

Note:

In the fluid stat (liquid & gas): molecules deformable under the influence of very weak forces.

In the solid stat the shape is regular. Distorting it requires a significant force.

II.2 Categories of Solid

There are two main categories of solids: crystalline solids and amorphous solids.

a/ **Crystalline solids** are those in which the atoms, ions, or molecules that make up the solid exist in a regular, well-defined arrangement. The smallest repeating pattern of crystalline solids is known as the **unit cell**, and unit cells are like bricks in a wall—they are all identical and repeating.

b/ **Amorphous solids** do not have much order in their structures. Though their molecules are close together and have little freedom to move, they are not arranged in a regular order as are those in crystalline solids. Common examples of this type of solid are glass and plastics.

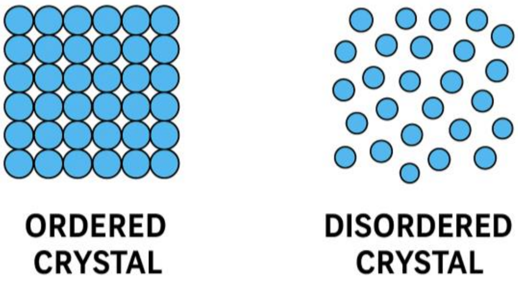


Figure II.2: Ordered and disordered crystal.

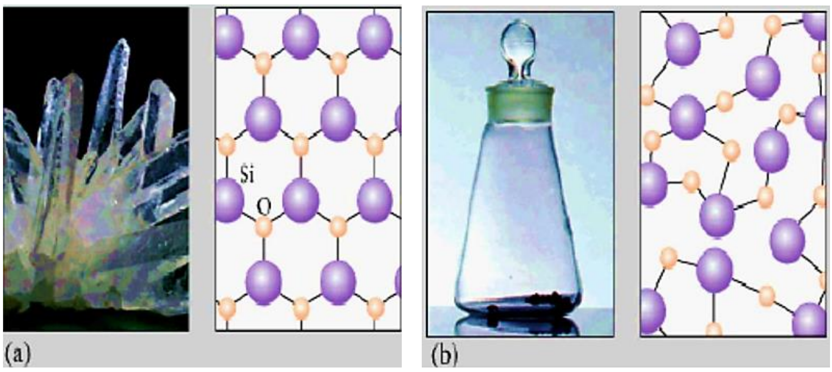


Figure II.3: a/crystalline solid '*Quartz*', b/amorphous solid '*Glass*'.

II.3 Crystalline solids

Crystalline solids are generally classified to four categories:

a/ Ionic solids: Made up of positive and negative ions and held together by *electrostatic attractions*. They're characterized by very high melting points and brittleness and are poor conductors in the solid state. An example of an ionic solid is table salt, NaCl.

b/ Molecular solids: Made up of atoms or molecules held together by *Van der Waals* forces, *dipole-dipole* forces, or *hydrogen bonds*. Characterized by low melting points and flexibility and are poor conductors. An example of a molecular solid is sucrose.

c/ Covalent-network: (also called atomic) solids—Made up of atoms connected by *covalent bonds*; the intermolecular forces are covalent bonds as well. Characterized as being very hard with very high melting points and being poor conductors. Examples of this type of solid are diamond and graphite, and the fullerenes.

d/ Metallic solids: Made up of metal atoms that are held together by *metallic bonds*. Characterized by high melting points, can range from soft and malleable to very hard, and are good conductors of electricity.

II.4 Identification of crystalline zone

To identify the crystalline phases in a solid, scientists use a technique called XRD (X-ray diffraction). It is based on the bending of X-rays in certain directions by crystals. An essential characteristic of crystals is their diffraction pattern, which can be captured on film or examined using an X-ray detector.

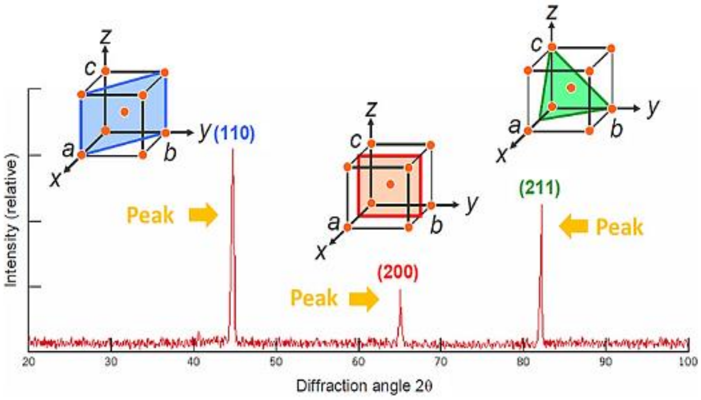


Figure II.4: Example of XRD pattern: it shows different peak with corresponding structures.

XRD allows to:

- ✓ Identifying the type of crystal, especially if the diffraction pattern is already present in a database.
- ✓ Locating the positions of atoms in the unit cell, essential for determining the crystal structure.
- ✓ Analysing the electron density in the crystal lattice.
- ✓ Recognizing the crystal symmetry and dimensions of the unit cell. The behaviour of crystals towards X-rays contrasts with the behaviour of non-crystalline solids (amorphous solids), liquids, or gases.

II.4.1 Crystal

In crystallochemistry, a crystal is defined as a solid material in which the atoms, ions, or molecules are arranged in a highly ordered and repeating three-dimensional pattern (the repetition along three reference directions), extending in all directions and the obtained crystal is called ***'' unit cell ''***.

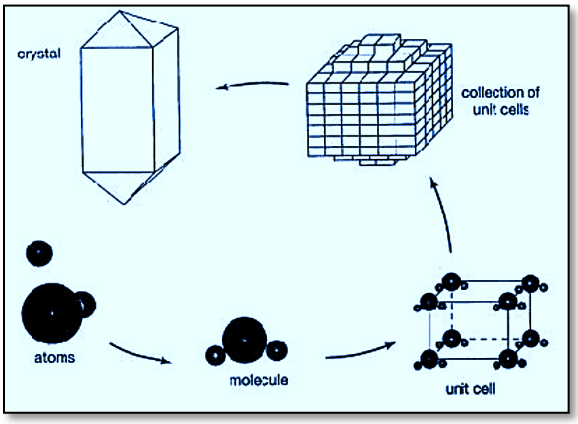
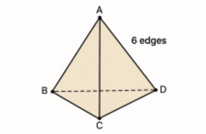


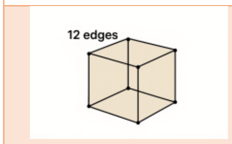
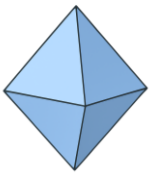
Figure II.5: Formation of crystal from atoms.

II.4.2 Polyhedron

A polyhedron (poly: many, hedron: face or base) is a three-dimensional geometric shape with flat faces and straight edges. The gemstones such as calcite and quartz are characterized by flat, regular surfaces intersecting at sharp angles, following an unusual symmetry. They display cubes, pyramids, or prisms, or more complex shapes with flat faces called polyhedra.

Table II.1 types of common polyhedron

Types of Polyhedrons					
Polyhedron	Name	Faces	Vertices (corners)	Edges (line segments joining the vertices)	Example
	Tetrahedra	4	4	4	**Eg.1** Ammonium ion (NH_4^+) Central atom N, surrounded by 4 atoms of H

					All four N-H bonds point to the corners of a regular tetrahedron. **Eg.2** Silicon tetrafluoride (SiF_4)
	Hexahedra	6	8	12	**Eg. 1** Sulfur hexafluoride (SF_6) Each F atom is located at one corner of an octahedron, giving 90° bond angles.
 	Octahedra	8	6	12	**Eg. 1** Metal Complex $[Co(NH_3)_6]^{3+}$ The cobalt ion is at the center, surrounded by 6 ammonia ligands. **Eg. 2** Fluorit CaF_2 each Ca^{2+} ion is surrounded by 8 F^- ions, and each F^- ion is surrounded by 4 Ca^{2+} ions.
	Dodecahedra	12	20	30	**Eg.1** Spinel ($MgAl_2O_4$) **Eg.2** Magnetite (Fe_3O_4)
	Icosahedron	20	12	30	**Eg.1** Boron carbide (B_4C) **Eg. 2** Aluminum-manganese (Al_6Mn)

II.4.3 Crystalline lattice

A crystal lattice is a three-dimensional arrangement of particles in a crystalline solid. It is a repetitive pattern that extends throughout the entire crystal. The particles in a crystal lattice can be atoms, ions or molecules.

Generally speaking, this arrangement or structure is described by:

- ✓ A crystal lattice defined by a set of nodes (arrangement of particles at specific points in space).
- ✓ An elementary pattern (generally, in metals and inert gases, the elementary pattern contains a single atom, but there are structures whose patterns contains over 1000 atoms).

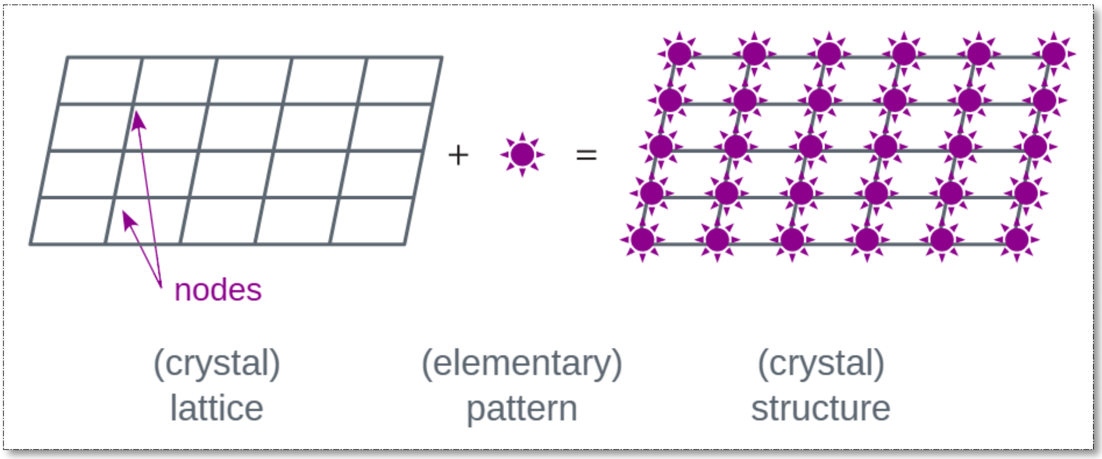


Figure II.6: Crystal lattice, elementary pattern (motif) and crystal structure.

II.4.4.1 Motif

The motif is the fundamental chemical component that forms the crystal: it is the atom, molecule, or ionic group that occupies the nodes of the crystal lattice, which repeats periodically in three spatial directions.

II.4.4.2 Crystallographic sites

Crystallographic sites are specific locations within a crystal lattice where atoms, ions, or molecules are situated. These sites play a crucial role in determining the structure and properties of the crystal. The arrangement of particles within these sites contributes to the overall symmetry and periodicity of the crystal lattice. The most common ones are tetrahedral sites, defined by 4 atoms, and octahedral sites, defined by 6 atoms.

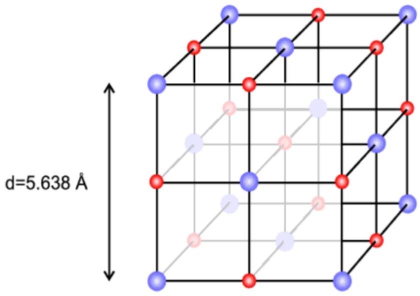
II.4.4.3 The coordination number

The coordination number (CN) is the number of nearest neighbor atoms or ions that surround a given atom or ion in a crystal structure. It tells you how many atoms are directly bonded (or in close contact) with a central atom.

Example 1: NaCl molecule:

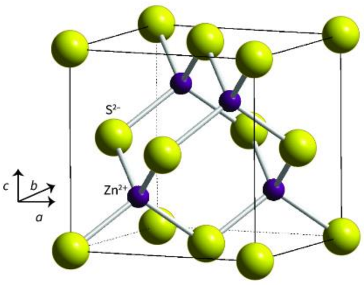
Each Na^+ is surrounded by 6 Cl^- → **CN = 6 (octahedral coordination)**

Each Cl^- is also surrounded by 6 Na^+ → **CN = 6**

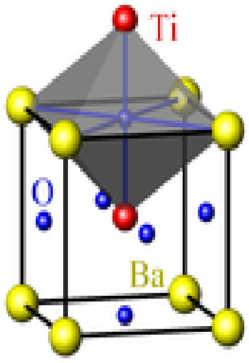


Example 2: (zinc blende or sphalerite):

Each Zn^{2+} is surrounded by 4 S^{2-} → **CN = 4 (tetrahedral coordination)**



Example 3: (Barium Titanate ($BaTiO3$)):



Each Titanium (Ti) is coordinated with 6 adjacent oxygen (O^-) ions, → **CN = 6.**

Barium (Ba) is coordinated with twelve adjacent oxygen (O^-) ions, → **CN = 12.**

Oxygen (O) is coordinated with two adjacent Ti ions and four Ba ions. → **CN = 2 + 4 = 6.**

II.4.4 Unit Cell

The unit cell is the parallelepiped defined by the three primitive vectors a, b and c (three periods along the three spatial directions in the space Ox, Oy, and Oz, respectively) also referred to as lattice parameters, and three angles α, β, and γ. Using this unit cell, we can completely fill the crystal space without leaving gaps.

Note that the angles between vectors a, b and c can be random. The position of a given vector in the lattice is given by the vector: $r = ua + vb + wc$ (with u, v, w as whole numbers), which generally represent a translation of the lattice.

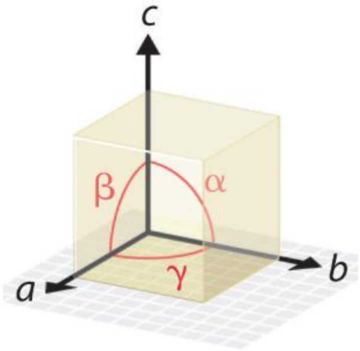


Figure II.7: a cell with primitive vector a, b and c and angles α, β and γ.

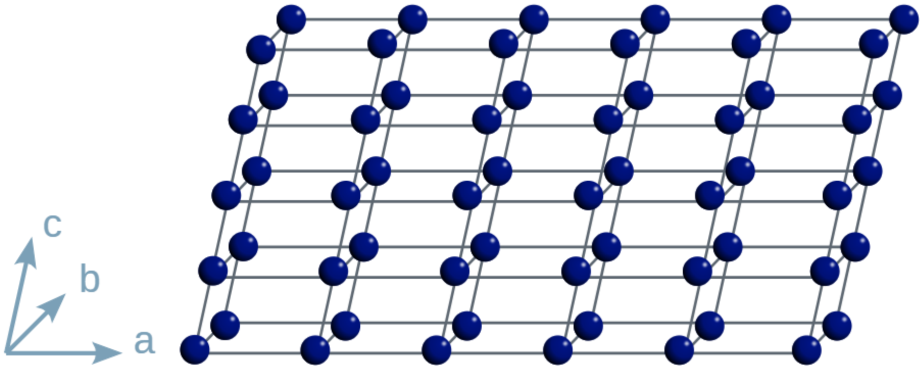


Figure II.8: Unit cell of a three-dimensional lattice defined by the 3 primitive vectors a, b and c.

Long before experimental crystal studies began, **Auguste Bravais (1848)** used theoretical and mathematical analysis to explore all possible structures with three-dimensional periodicity. He showed that only 14 distinct lattice types can exist, grouped into 7 crystal systems. These systems result from different possible combinations of the cell edge lengths (a, b, c) and the interaxial angles (α, β, γ).

In nature, there are only 7 fundamental forms with multiple facets (7 unit cells allowing for the infinite structural construction of crystals). (**Figure II.9**), which are represented as follow:

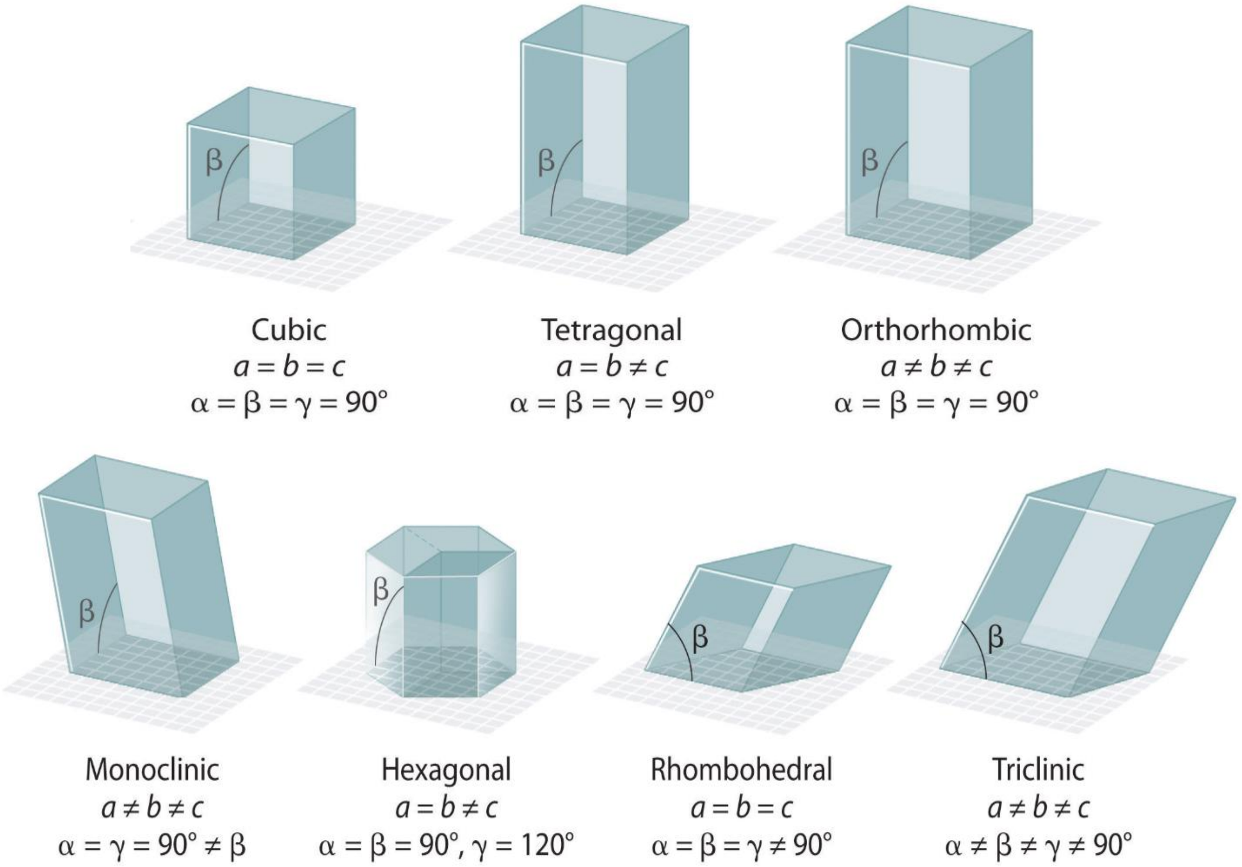


Figure II.9: The 7 types of unit cells.

II.5 Types of crystalline system

Each type of unit cell (crystalline system) has special Bravais system.

II.5.1 Cubic System

Divided into 3 types:

1/**Cubic Primitive (cP)**

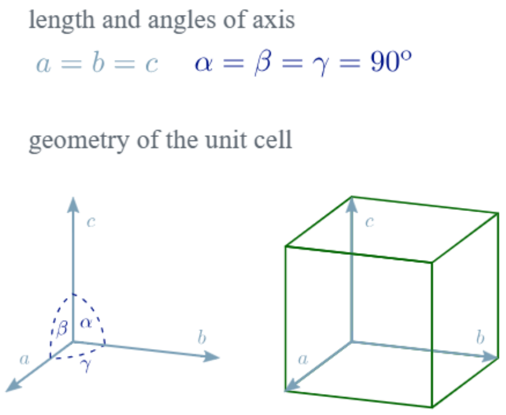
Number of lattice points per cell: 1
Diagram: only 8 corner atoms shared among 8 cubes.

2/ **Cubic Body-Centered (also called BCC)**

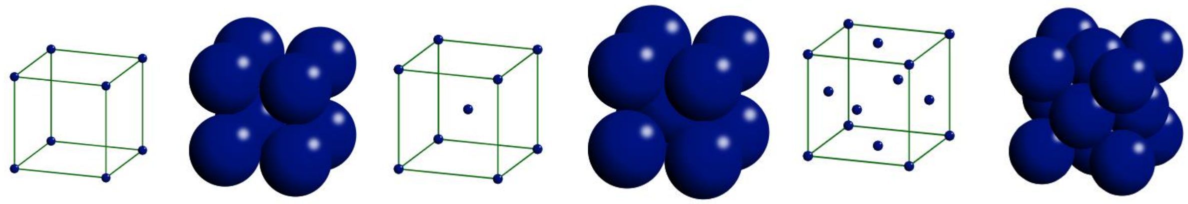
Or, cI (centred inside) Number of lattice points per cell: 2
One lattice point at each corner and one in the cube's center.

3/ **Cubic Face-Centered (also called FCC)**

Lattice points at each corner and at the center of each face.
Number of lattice points per cell: 4



Example: cP: Polonium (Po), cI: Iron (α-Fe), Chromium, Tungsten, cF: Copper (Cu), Aluminum (Al), Silver (Ag), Gold (Au)



II.5.2 Hexagonal System

Right prism with 6 equal rectangular side faces and two hexagonal bases with:

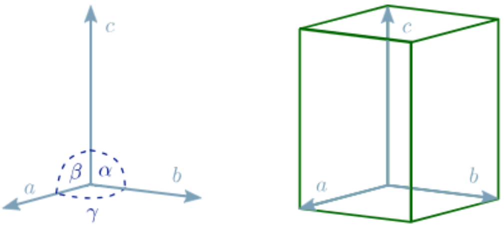
Symbolized by P → primitive lattice

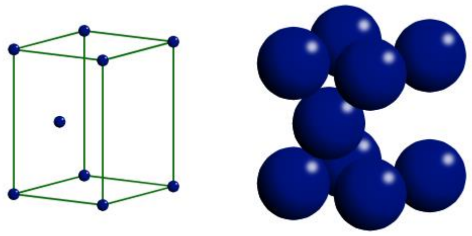
Example: Zinc (Zn), Magnesium (Mg)

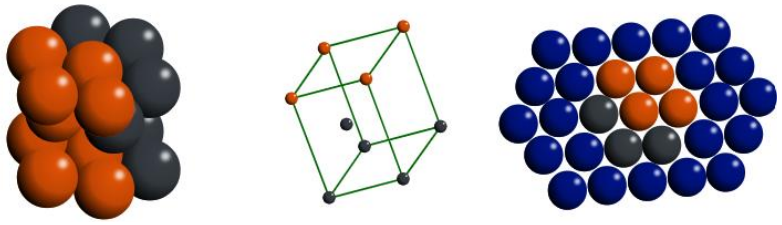
length and angles of axis

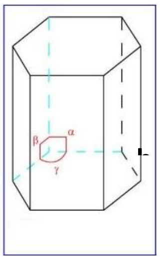
$a = b \neq c$ $\alpha = \beta = 90^o$ $\gamma = 120^o$

geometry of the unit cell









II.5.3 Orthorhombic system

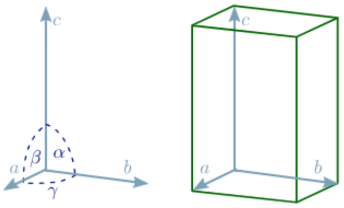
The unit cell is shaped like a rectangular box all angles are right angles (90°), but the edges have different lengths.

Example: Sulfur (S_8)

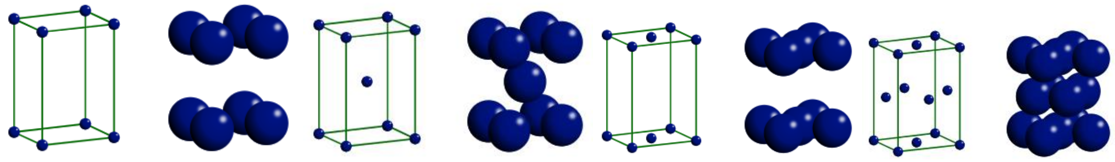
length and angles of axis

$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$

geometry of the unit cell



Symbol	***Name***	***Description***
oP	Primitive	Points only at the 8 corners
oI	Body-centered	One additional point in the center of the cell
oC	Base-centered (or end-centered)	Extra points in the center of two opposite faces
oF	Face-centered	Points at all corners and centers of all faces



II.5.4 Triclinic system

The triclinic system is the most general (and least symmetrical) crystal system.
All the edges and angles are unequal, and none of the angles are 90°.

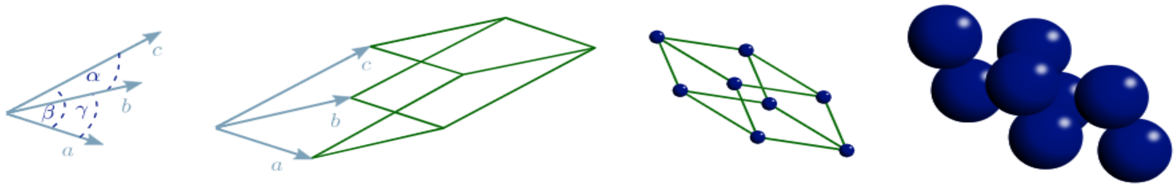
Symbolized by: tP → Triclinic Primitive

Example: Kyanite Al_2SiO_5

length and angles of axis

$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$

geometry of the unit cell



II.5.5 Monoclinic system

The monoclinic system is a crystal system where: The three edges have different lengths, and the two angles are 90°, but the third one is not.

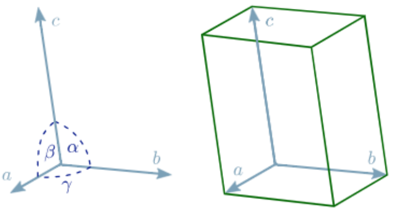
Example: Gypsum $CaSO_4 \cdot 2H_2O$

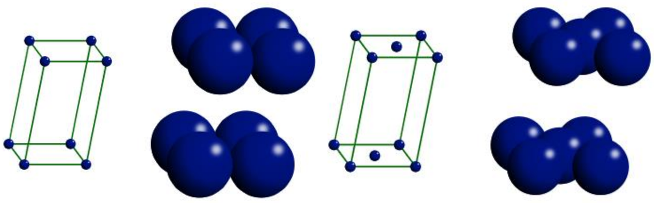
Symbol	*Name*	*Description*
mP	Primitive	Lattice points only at the corners
mC *(or* ***mI****)*	Base-centered (or end-centered)	Additional lattice points in the centers of two opposite faces

length and angles of axis

$a \neq b \neq c \quad \alpha = \gamma = 90^\circ \neq \beta$

geometry of the unit cell

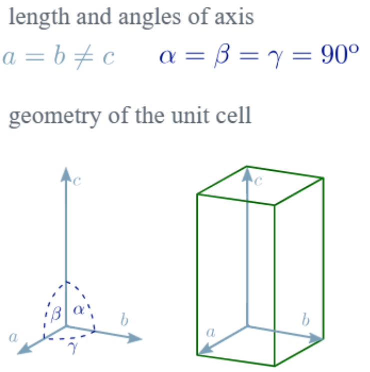




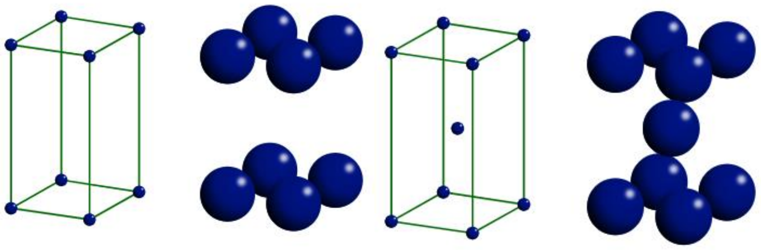
II.5.6 Tetragonal system

The tetragonal system looks like a stretched (or compressed) cube.
It has: Two equal horizontal edges (a = b), One different vertical edge (c ≠ a), All angles are right angles (90°)

Example: Zircon $ZrSiO_4$



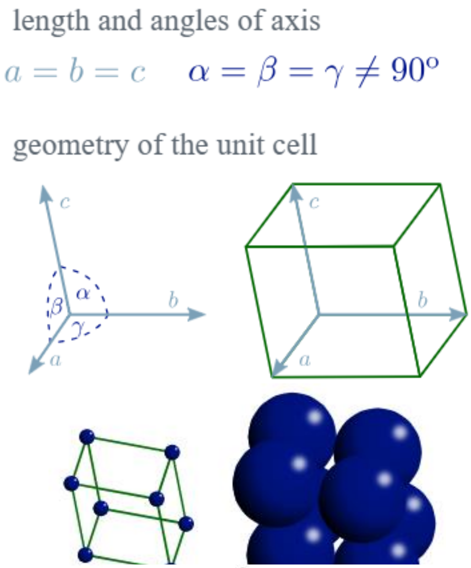
Symbol	Name	Description
tP	Primitive	Lattice points only at the 8 corners
tI	Body-centered	One extra lattice point in the center of the cube



II.5.7 Rhombohedral system

The rhombohedral system (also called the trigonal system) is a special case of the hexagonal family.
It can be thought of as a distorted cube where: All three edges are equal, All three angles are equal but not 90°.

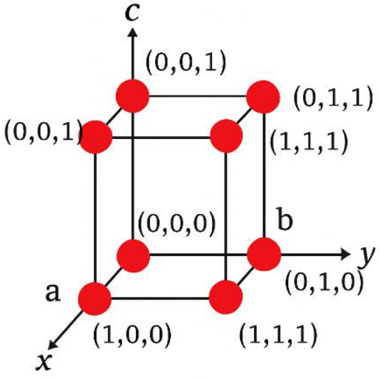
Example: Calcite $CaCO_3$



Symbol	Name	Description
R	Rhombohedral centered	Lattice points at corners + two along the body diagonal

II.6 Lattice parameter calculations (Computational crystallography)

In a simple cubic unit cell, the geometric coordinates for the atoms occupying the eight corners are: (0,0,0); (1,0,0); (0,1,0); (0,0,1); (1,1,0); (1,0,1); (0,1,1); (1,1,1).
The eight corners are equivalent because they are derived from each other through translations along a with respect to x, b with respect to y, and c with respect to z.



II.6.1 Directions in crystalline lattice

Crystal directions are all straight lines passing through two nodes in the lattice. Nodes are identified via their coordinates in the system defined by primitive vectors.

In a crystal lattice, every point represents an identical position in the crystal structure — it's a repeating 3D pattern. A vector in this lattice (often written as t) tells us how to move from one lattice point to another identical one, so this vector has two main properties:

- ✓ **Length** → how far apart the two lattice points are.
- ✓ **Direction** → the orientation of that line (which way you're moving in the crystal).

When we pick a translation vector t, we are choosing one of those repeating directions: it shows how the lattice repeats in space.
Now, according to international crystallographic conventions, the direction of a row (a line through the lattice) is represented mathematically by: $\mathbf{t} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$
where:

- **a, b, c** are the *lattice vectors* (the edges of the unit cell),
- **u, v, w** are integers (they tell how many times you move along each direction).

This means the direction in the crystal is defined by how many steps you take along **a, b,** and **c** — and this direction is usually expressed in ***Miller indices*** as [uvw].

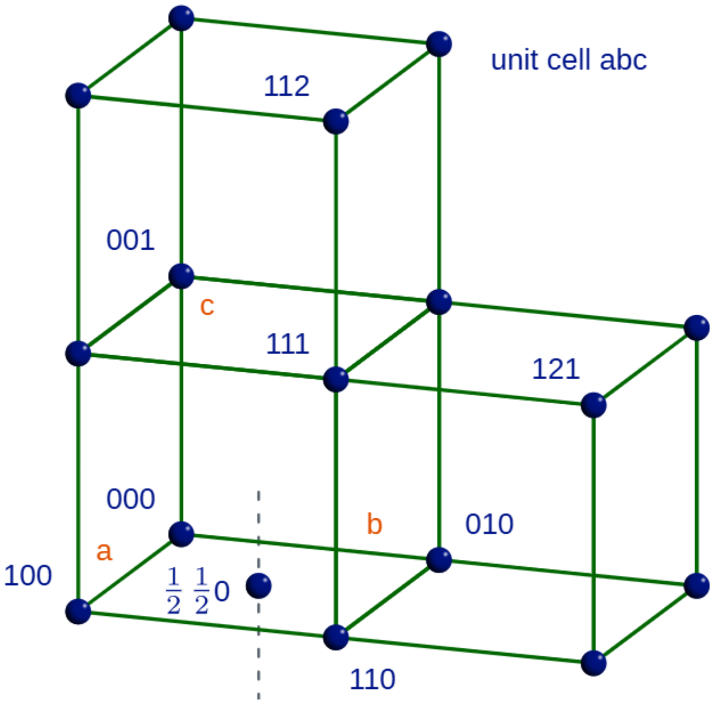


Figure II.10: Node coordinates in a lattice defined by primitive vectors.

Activity 01:

Represent the vector: (t=a+2b+0c), (t=1a+1b+0c)

Solution:

So, for example, the vector (t = a + 2b + 0c) corresponds to the [120] direction in the crystal.

Activity 02:

Form the following Miller indices, represent mathematically the following directions: [111], $[1\bar{1}2]$.

Solution :

t = 1a+1b+1c, t=1a-1b+2c

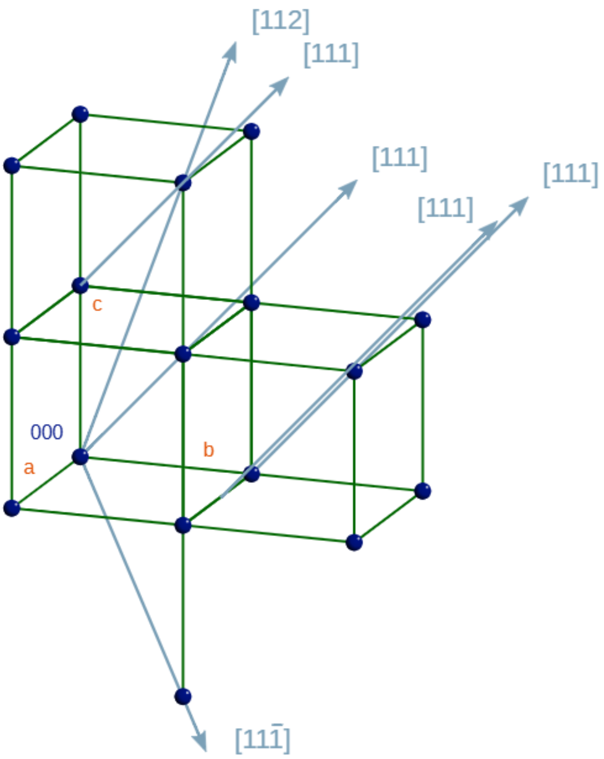
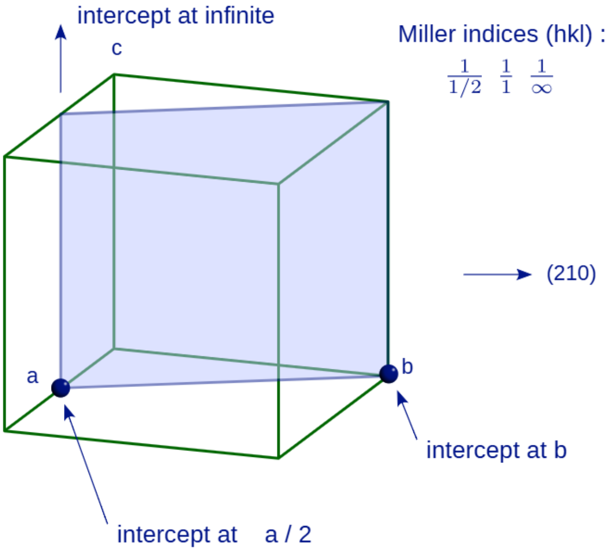


Figure II.11 : Crystal directions.

II.6.2 Crystal planes



Lattice nodes can be grouped into parallel and equidistant planes: this gives a family of crystal planes. If we consider two adjacent planes, one of which crosses the lattice origin; the second plane intersects axes a, b and c defining the crystalline unit cell as a/h, b/k and c/l.

Them numbers h, k and l positive or negative and prime to one another represent the **Miller indices** for the family of crystal planes under consideration. This is notated as (***h***, ***k***, ***l***) and the set of family of planes deduced from each other via symmetry operations constitutes a form of plane and is notated as {***h***, ***k***, ***l***}.

Activity & Solution:

Give the plane correspond to the following Miller indices: (010), (020), (111), (111)

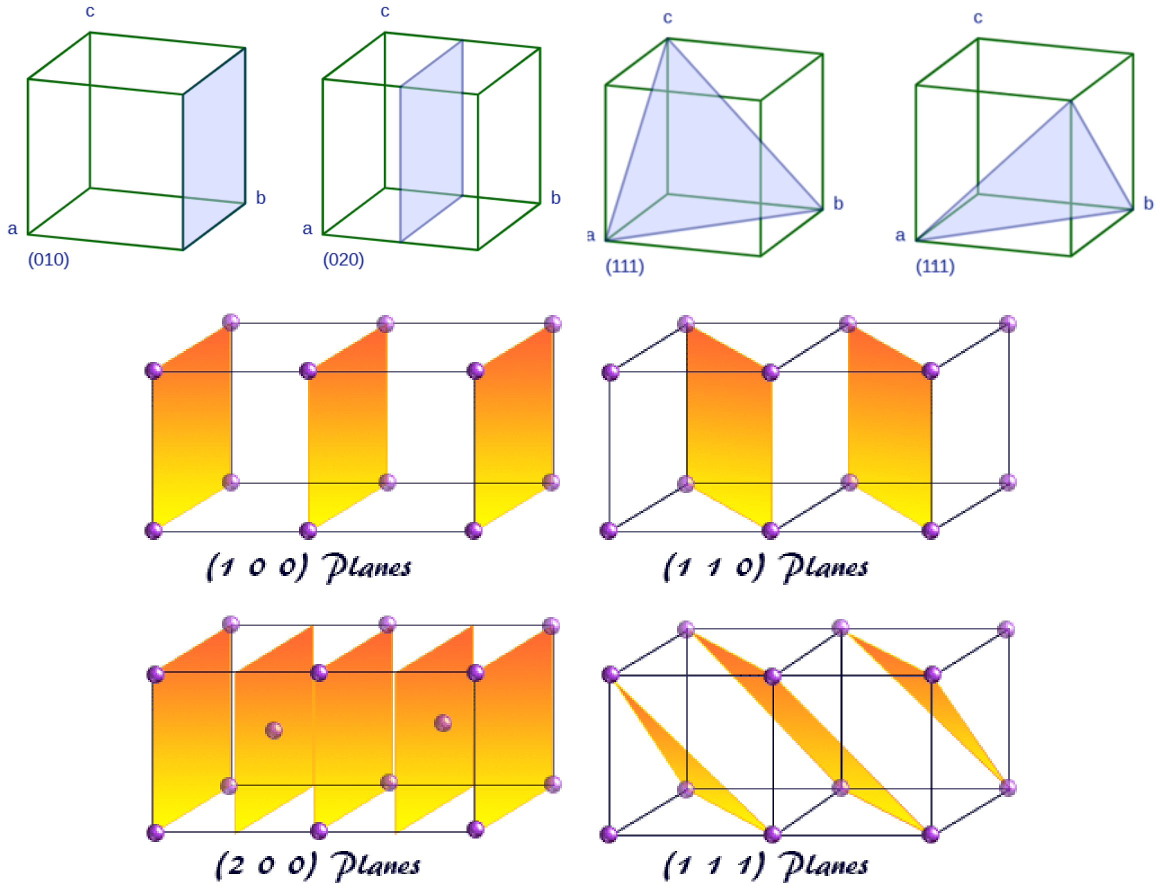


Figure II.12: Lattice planes in cubic crystal.

II.6.3 Difference between crystal direction and crystal planes

⇨ A crystal direction is a line that passes through lattice points (atoms) in the crystal.

- It shows how the structure repeats in a certain orientation.
- Mathematically, it's represented as [uvw] — square brackets.
- It's described by a vector like (t = ua + vb + wc).

⇨ A crystal plane is a flat surface cutting through the lattice points.

- It's represented by (hkl) — round brackets.
- The plane's orientation is defined by the reciprocals of the intercepts it makes with the *a*, *b*, and *c* axes.

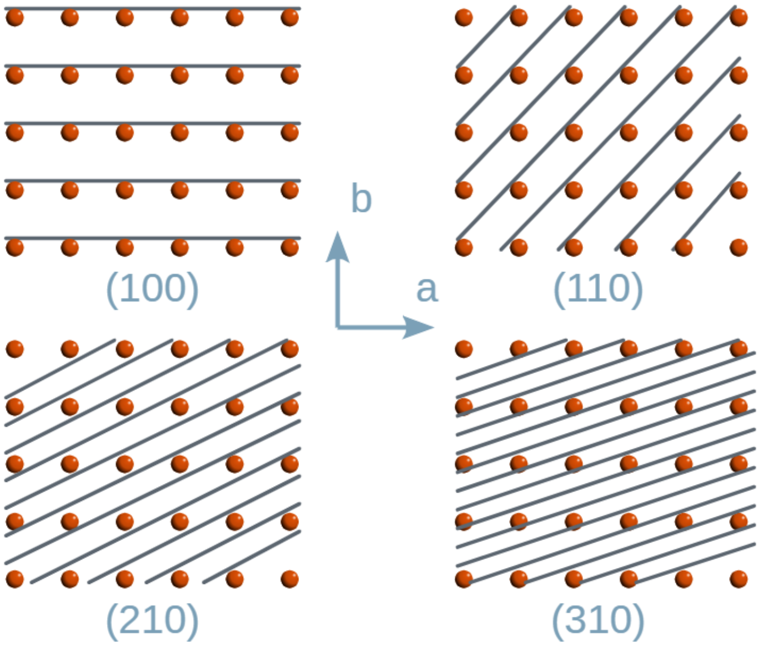


Figure II.13: Distance between crystal planes.

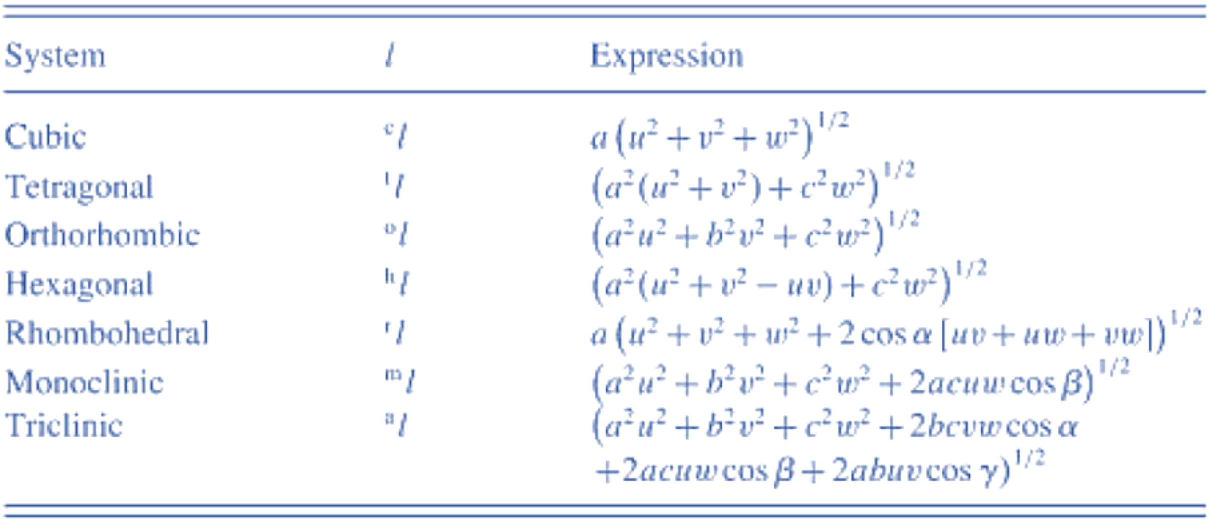
II.6.4. Distance between two points in crystalline lattice:

For two pints **P₁** (u_1,v_1,w_1) and **P₂** (u_2,v_2,w_2), the distance D between them is calculated using this following formula:

$$D^2=[(u_1-u_2)(v_1-v_2)(w_1-w_2)]\begin{bmatrix} a^2 & abcos\gamma & accos\beta \\ bacos\gamma & b^2 & bccos\alpha \\ cacos\beta & cbcos\alpha & c^2 \end{bmatrix}\begin{bmatrix} (u_1 & -u_2) \\ (v_1 & -v_2) \\ (w_1 & -w_2) \end{bmatrix}$$

$$\boldsymbol{D^2=(u_1-u_2)^2a^2+(v_1-v_2)^2b^2+(w_1-w_2)^2c^2+2(u_1-u_2)(v_1-v_2)abcos\gamma}$$
$$\boldsymbol{+2(u_1-u_2)(w_1-w_2)abcos\beta+(v_1-v_2)(w_1-w_2)abcos\alpha}$$

Table II.2 The expressions for the length of vector [uvw] in seven system

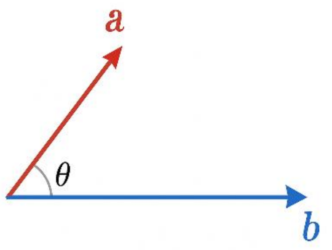


System	l	Expression
Cubic	${}^{c}l$	$a\left(u^2+v^2+w^2\right)^{1/2}$
Tetragonal	${}^{t}l$	$\left(a^2(u^2+v^2)+c^2w^2\right)^{1/2}$
Orthorhombic	${}^{o}l$	$\left(a^2u^2+b^2v^2+c^2w^2\right)^{1/2}$
Hexagonal	${}^{h}l$	$\left(a^2(u^2+v^2-uv)+c^2w^2\right)^{1/2}$
Rhombohedral	${}^{r}l$	$a\left(u^2+v^2+w^2+2\cos\alpha\,[uv+uw+vw]\right)^{1/2}$
Monoclinic	${}^{m}l$	$\left(a^2u^2+b^2v^2+c^2w^2+2acuw\cos\beta\right)^{1/2}$
Triclinic	${}^{a}l$	$\left(a^2u^2+b^2v^2+c^2w^2+2bcvw\cos\alpha\right.$ $\left.+2acuw\cos\beta+2abuv\cos\gamma\right)^{1/2}$

II.6.5 Angle between two vectors or planes in crystalline lattice

The vector dot-product, **a*b**, also known as the scalar product, is defined geometrically as the projection of the vector **a** onto the direction of **b** multiplied by the length of **b**: $\boldsymbol{a * b = |a||b|cos\theta}$

The angle between two direct space vectors is computed in a single operation, instead of using the three individual dot products described in the figure.



$$a \cdot b = |a|\ |b| \cos\theta$$

Consider a $[u_1v_1w_1]$ and b $[u_2v_2w_2]$ we have:

$$|a||b|cos\theta = \begin{pmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \end{pmatrix} \begin{bmatrix} a^2 & abcos\gamma & accos\beta \\ bacos\gamma & b^2 & bccos\alpha \\ cacos\beta & cbcos\alpha & c^2 \end{bmatrix} \begin{pmatrix} u_1 & u_2 \\ v_1 & v_2 \\ w_1 & w_2 \end{pmatrix}$$

The expressions for the cosine of the angle θ between two vectors in the seven crystal systems.

Table II.3 The expressions for the angle [θ] in seven system.

System	$l_1 \times l_2 \times \cos\theta$
Cubic	$a^2(u_1u_2 + v_1v_2 + w_1w_2)$
Tetragonal	$a^2(u_1u_2 + v_1v_2) + c^2w_1w_2$
Orthorhombic	$a^2u_1u_2 + b^2v_1v_2 + c^2w_1w_2$
Hexagonal	$a^2(u_1u_2 + v_1v_2 - \frac{1}{2}(u_1v_2 + v_1u_2)) + c^2w_1w_2$
Rhombohedral	$a^2(u_1u_2 + v_1v_2 + w_1w_2$ $+ \cos\alpha[u_1(v_2 + w_2) + v_1(u_2 + w_2) + w_1(u_2 + v_2)])$
Monoclinic	$a^2u_1u_2 + b^2v_1v_2 + c^2w_1w_2 + ac(w_1u_2 + u_1w_2)\cos\beta$
Triclinic	$a^2u_1u_2 + b^2v_1v_2 + c^2w_1w_2 + bc(v_1w_2 + v_2w_1)\cos\alpha$ $+ac(u_1w_2 + u_2w_1)\cos\beta + ab(u_1v_2 + u_2v_1)\cos\gamma$

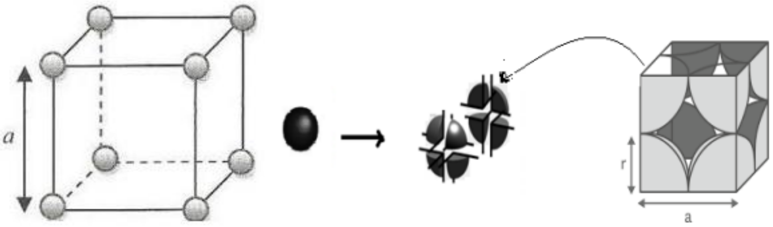
II.7 The crystal density

II.7.1 Multiplicity (z)

The multiplicity (z) represents how many motifs (or atoms, molecules, or groups) are contained inside one unit cell of a crystal. This tells us how many identical structural units (motifs) are repeated when the crystal extends in space.

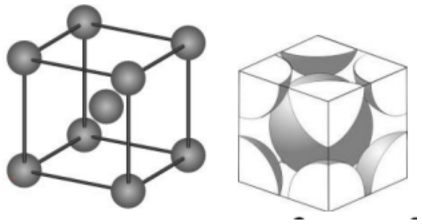
Case of cubic Primitive: atoms only at the 8 corners, each corner atom is shared by 8 neighboring cells, so only 1 atom per cell in total (z=1).

$$z = \frac{1}{8} \times 8 = 1$$



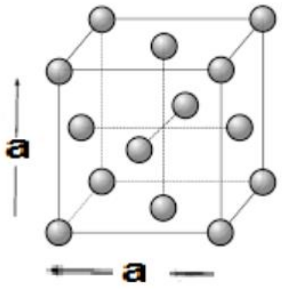
Case of Body Centered Cubic: atoms at the 8 corners, each corner atom is shared by 8 neighboring cells, and one atom in the center so 2 atom per cell in total (z=2).

$$z = \left(\frac{1}{8} \times 8\right) + 1 = 2$$



Case of Cubic Face Centered: atoms at the 8 corners, each corner atom is shared by 8 neighboring cells, and 1/2 atoms are in the faces of the cube so, 4 atoms per cell in total (z=4).

$$z = \left(\frac{1}{8} \times 8\right) + (\frac{1}{2} \times 6) = 4$$



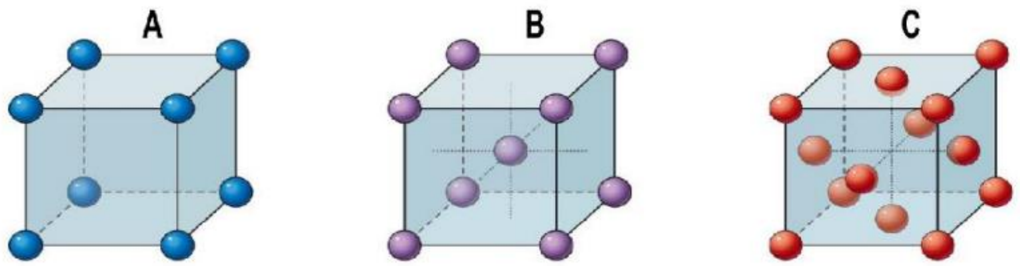


Figure II.14 Cubic unit cells (cP, cBC, cFC).

II.7.2 Compactness and/or packing density (C, τ)

The packing factor C is a dimensionless number that measures the actual occupancy rate of space by atoms or ions represented in the form of solid spheres. In other words, it is the ratio of the volume occupied by the entities (atoms, molecules, or ions) z belonging to the cell to the total volume of the cell.

$$C = \frac{volume\ occupied\ by\ the\ entities}{total\ volume\ of\ the\ cell} = \frac{z \times motif\ volume}{cell\ volume}$$

In crystallography, we assume that the components of the crystal (ions, atoms, molecules, etc.) are represented in the form of "rigid, non-deformable solid spheres." Therefore, the packing is:

$$C = \frac{\sum_i^z \frac{4}{3}\pi r_i^3}{(\vec{a} \times \vec{b}) \times \vec{C}}$$

In general, the packing density is expressed as a percentage.

$$\tau = C \times 100$$

II.7.3 The crystal density

As we know the density formula is:

$$\rho = \frac{mass}{volume}\ (g/cm^3)$$

for the crystalline cell we have:

$$\rho = \frac{mass\ of\ cell}{volume\ of\ cell} = \frac{z \times motif\ mass}{volume\ of\ cell} = \frac{z \times \mathcal{M}\ motif}{\mathcal{N}_{\mathcal{A}}\ V_{cell}}$$

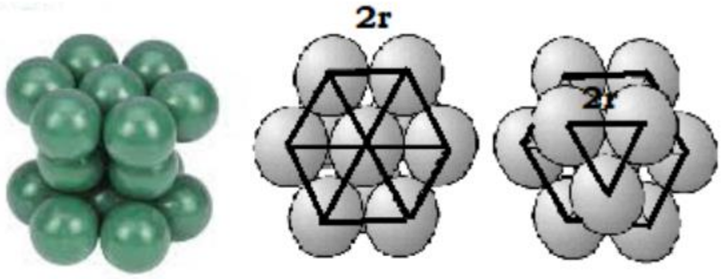
The density (**d**) is one of the important parameters in the study of crystal structure. It allows us to understand the optimal way to stack these spheres (atoms) or how to arrange them in a manner that maximizes the patterns in minimal space. It is calculated from the results of X-ray diffraction analysis. It can also be measured experimentally. Comparing these values confirms the crystal structure.

II.8 Examples of crystal structures

II.8.1 Metallic crystals

Most minerals have a densely packed or semi-densely packed crystalline structure of identical spheres. This results in three main structures: **cF**, **hCP** (Hexagonal Close Packing), and **cI** (Body-Centered Cubic).

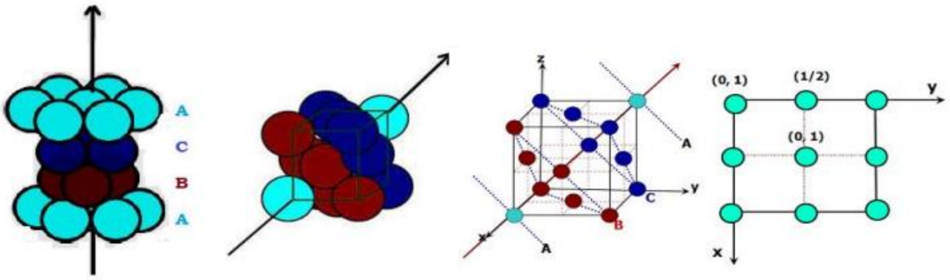
In the first level, each sphere is in contact with 6 neighbors and is placed in the center of a regular hexagon with a side length of r2, and the hexagon's vertices occupy the lattice points. These voids interlock with each other to occupy the smallest volume. If a second layer B of identical spheres is placed on the first layer A, each sphere in the upper layer B is positioned above 3 voids of the lower layer A while leaving 3 voids unoccupied.



The close packing of spheres gives rise to two types of structures: face-centered cubic) or hexagonal close-packed. These two types of close-packing structures differ in the number of consecutive layers. We have seen the stacking of two consecutive layers, A and B. A third layer, C, can be added to these two layers in two different ways.

a/ cF structure

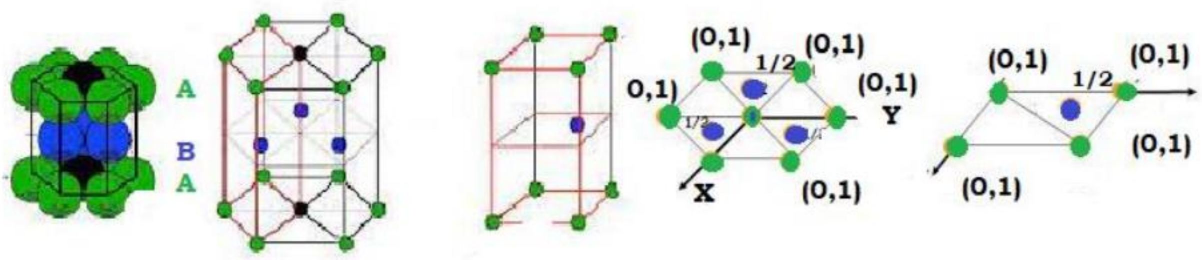
In cF (Face-Centered Cubic) structure, the C layer is such that the spheres forming it are placed in the voids of the B layer and drop vertically onto the remaining voids of the A layer.



The initial lattice (a = b = c and α = β = γ = 90) contains atoms at the eight corners of the cube and at the centers of the six faces. The geometric coordinates (XYZ) for these positions are: (000) (100) (010) (001) (110) (101) (011) (111) - (1/2 1/2 0) (1/2 0 1/2) (0 1/2 1/2) (1/2 /2 1) (1/2 1 1/2) (1 1/2 1/2).

b/ HcP structure

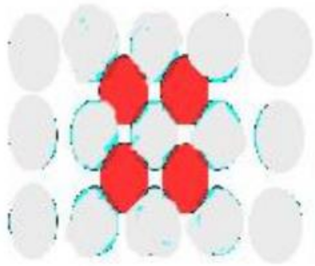
The HCP (Hexagonal Close-Packed) structure occupies the C layer positions in the voids of the B layer, dropping vertically above the spheres of the A layer.

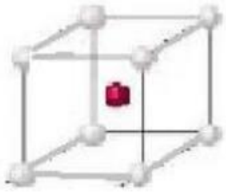


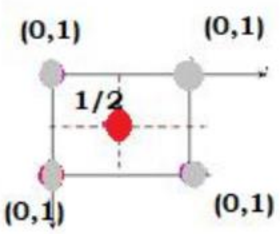
The initial cell describing the Hexagonal Close-Packed lattice (a = b ≠ c; α = β = 90° and γ = 120°) contains atoms at the eight corners and one atom in the center. The geometric coordinates (XYZ) for these atoms are: (000) (100) (010) (001) (110) (101) (011) (111) - (2/3 1/3 1/2) ou (1/3 2/3 1/2).

c/ cI structure

In the close-packing assembly cI (Body-Centered Cubic), spheres of the same layer are arranged in a manner where their centers form the vertices of a cube with an edge length of 'a'. The second layer is obtained by placing a sphere in each void space between the domains of the first layer.







The specified geometric coordinates (XYZ) for the atomic positions in Cell cI are: (000) (100) (010) (001) (110) (101) (011) (111) (1/2 1/2 1/2).