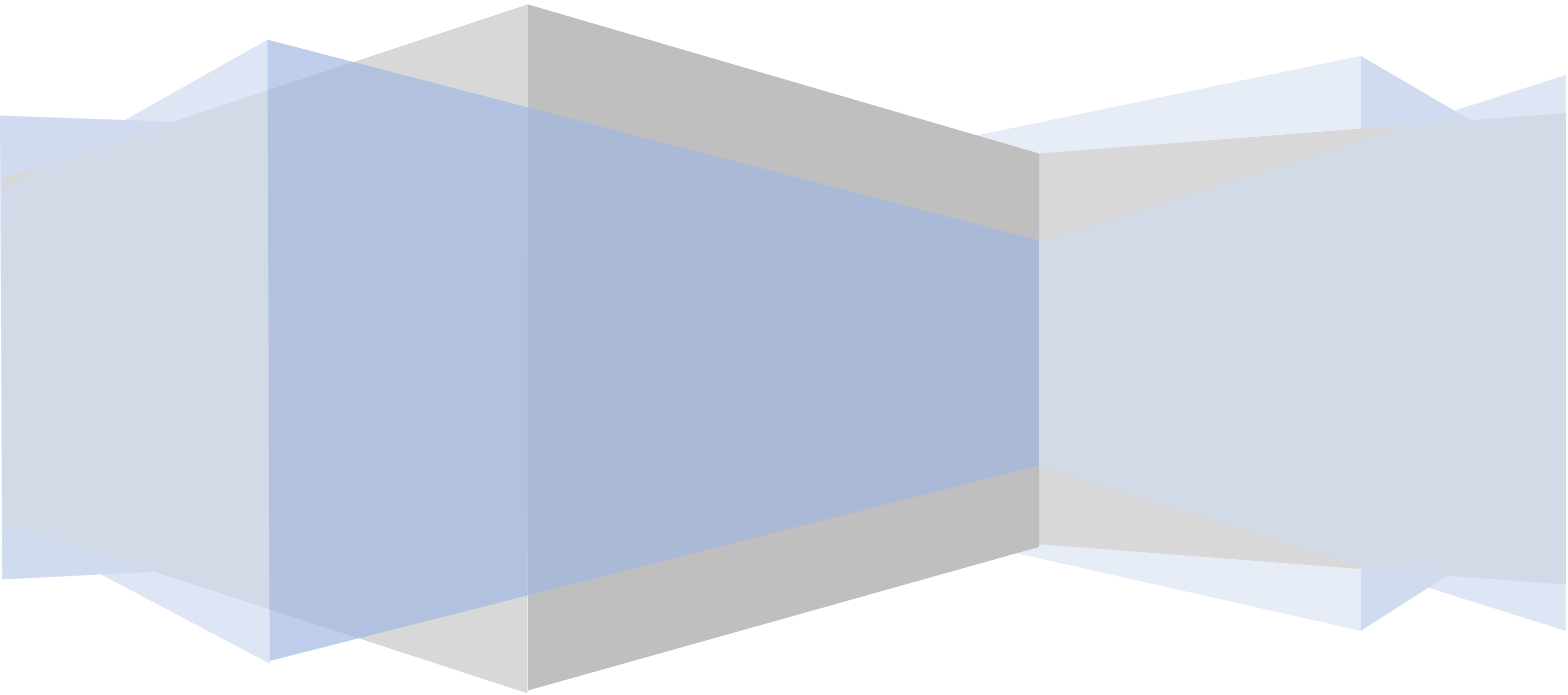
A. ELHAFIDH BOUSSOUF UNIVERSITY CENTER
SCIENCES & TECHNOLOGIE INSTITUTE
PROCESS ENGINEERING DEPARTEMENT

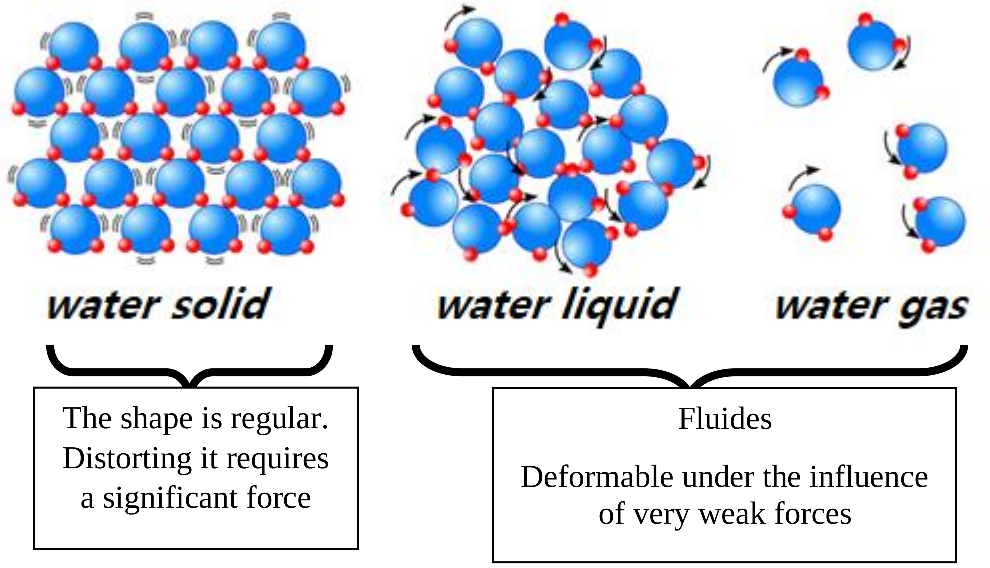
Mineral Chemistry



CHAPTER II : CRISTALLOCHEMISTRY

II.1.INTRODUCTION:

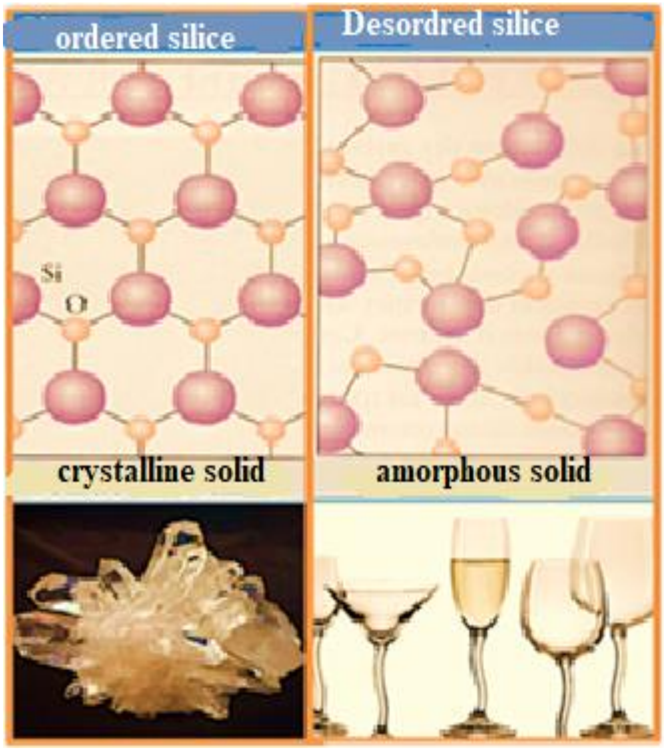
In nature, matter exists in three states: solid, liquid, and gaseous. The state in which matter exists is determined by the interaction between its particles



The shape is regular. Distorting it requires a significant force

Fluides

Deformable under the influence of very weak forces



Solid materials can exist in two different states:

- The disordered state characterized by an irregular structure; this is the state of non-crystalline systems, such as amorphous materials, for example, glasses.
- The ordered state characterized by a structured arrangement, corresponding to crystalline solid materials.

Crystalline solids are classified into three types:

- ***Covalent crystals***: If the difference in electronegativity is small, the crystals will be covalent like: non-metals, the simple substances as H_2, Di-halogens, noble gases.
- ***Metallic crystals***
- ***Ionic crystals***: If the difference in electronegativity is big, we have ionic crystals like NaCl

The physical properties vary depending on the nature of crystals:

A. Melting Point: Metallic crystals exhibit a relatively wide range of melting temperatures. In contrast, ionic crystals and covalent crystals have very high melting points.

	Metallic	Ionic	Covalent
He -272,2°C	Na 97.8°C	NaCl 801°C	C (diamant) < 3550°C
Cl_2 -101°C	Zn 419.6°C	CaO 2580°C	C (graphite) 3670°C
CO_2 -65,5°C	Cu 1083 °C	$CuCl_2$ 620°C	Si 1410
H_20 0°C	Fe 1535°C	ZnS 1020°C	SiO_2 (quartz) 1610°C

B. Electrical Conductivity: Metallic crystals are the best electrical conductors, followed by molten ionic crystals. Molecular and ionic crystals are insulators. Covalent crystals can be insulators (diamond) or semiconductors (Si, Ge), and one-dimensional conductors (graphite).

II .2.DIFINITIONS:

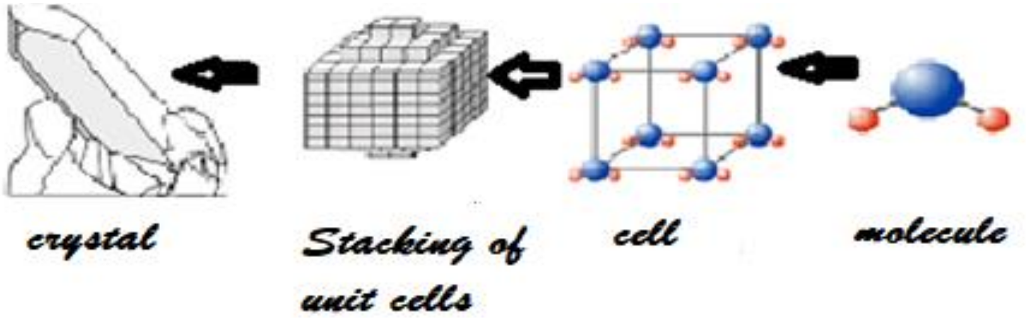
Crystals diffract X-rays in specific directions, a phenomenon known as X-ray diffraction. The reflection image, recorded on film or analyzed by an X-ray detector, is a crucial property for crystals. It allows to:

- 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.
- Analyzing the electron density in the crystal lattice.
- Recognizing the crystal symmetry and dimensions of the unit cell.

The behavior of crystals towards X-rays contrasts with the behavior of non-crystalline solids (amorphous solids), liquids, or gases.

II.2.1. CRYSTAL:

A crystal is a solid material with multiple flat surfaces (polyhedral) formed by the periodic arrangement of atoms or molecules. It can be described by the repetition along three reference directions of a primary atomic unit known as the unit cell.

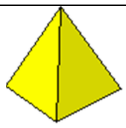
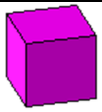
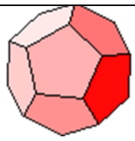


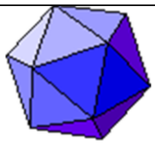
II.2.2. POLYHEDRON:

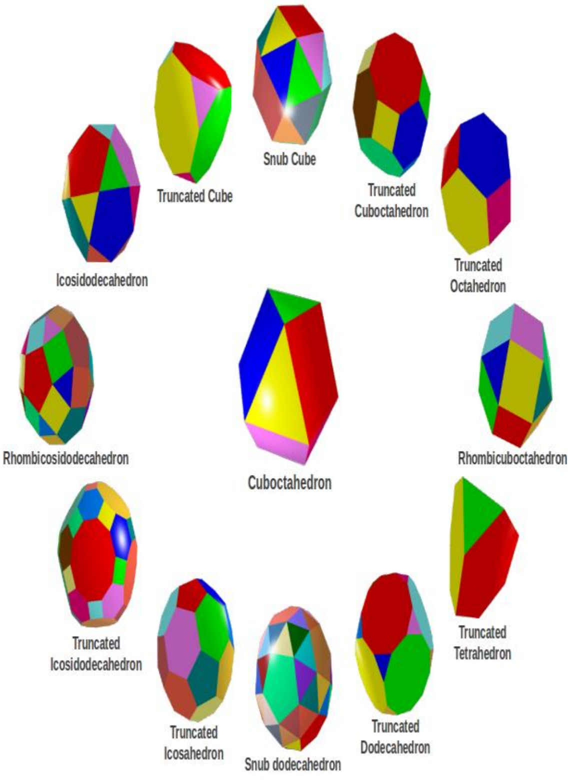
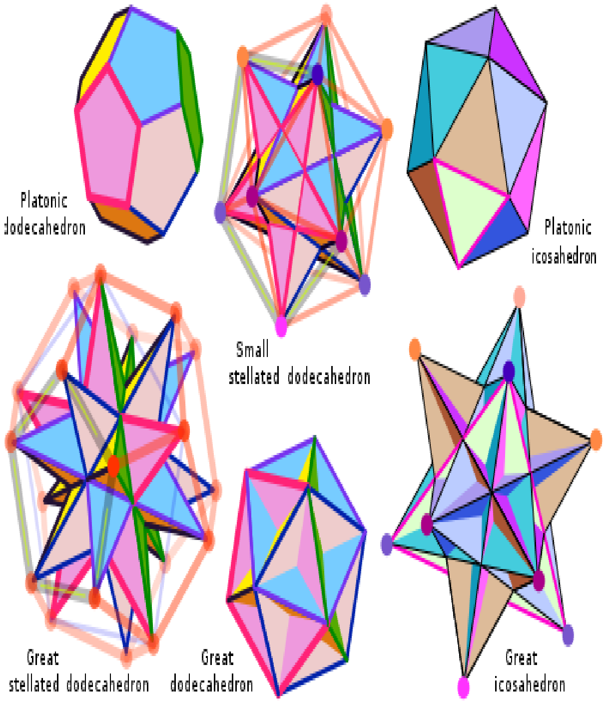
The observation of gemstones such as calcite and quartz reveals that many of these crystals are characterized by flat, regular surfaces intersecting at sharp angles, following an unusual symmetry. They display cubes, pyramids, or prisms, or more complex shapes with flat faces called polyhedra.

A polyhedron (poly: many, hedron: face or base) is a three-dimensional geometric shape with flat faces and straight edges.

Polyhedrons of Platon

Polyhedron	Name	Faces	Vertices	Edges
	Tetrahedra	4	4	6
	Hexahedra (Cube)	6	8	12
	Octahedra	8	6	12
	Dodecahedra	12	20	30

	Icosahedra	20	12	30

<table>
<tr><th>Archimede polyhedra</th><th>Kepler-Poinsot polyhedra</th></tr>
<tr><td>
</td><td>
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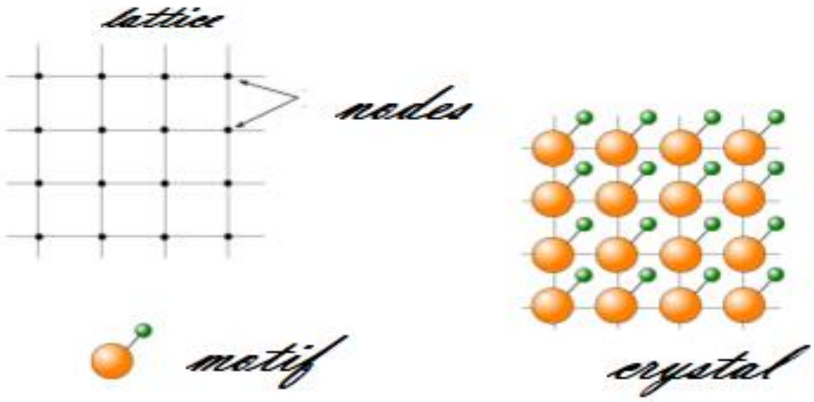
II.2.3. CRYSTALLINE LATTICE:



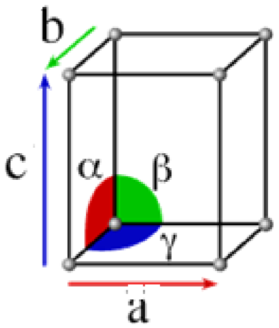
Crystalline solid matter consists of a large number of particles (ions, atoms, and molecules) arranged at specific points in space called nodes. The crystalline lattice is formed by a periodic arrangement of particles in three spatial directions.

The transmission vector is:

T= u. a + v. b+ w. c (u و v و w three integers).

a, b, and **c** are the three periods along the three spatial directions in the space Ox, Oy, and Oz, respectively.

II .2.4. CELL:



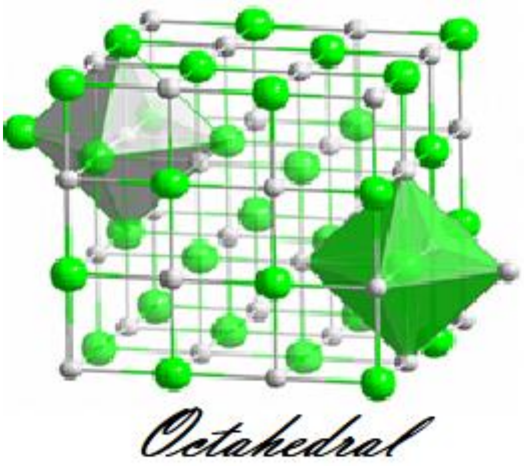
The unit cell is the smallest constituent (smallest volume) that corresponds to parallel surfaces, and it is defined by three lengths a, b, and c, which are the periods along the axes Ox, Oy, and Oz, respectively, and three angles α, β, and γ. Using this unit cell, we can completely fill the crystal space without leaving gaps.

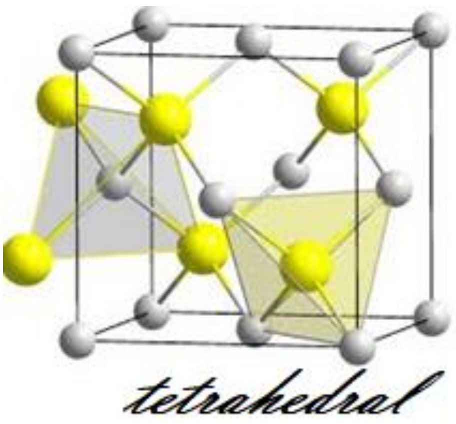
II. 2.4.1. MOTIF :

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.2.4.2 : 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

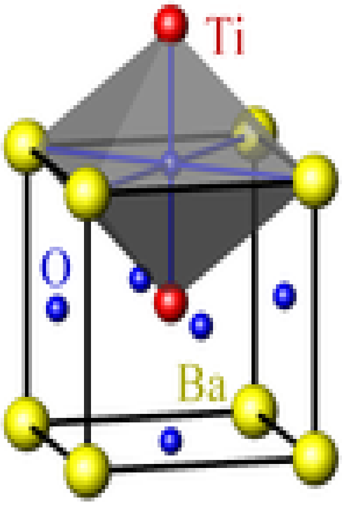




The most common ones are tetrahedral sites, defined by 4 atoms, and octahedral sites, defined by 6 atoms.

The occupancy of these sites by different chemical species influences the crystal's properties, including its electrical, magnetic, and optical characteristics. Understanding the distribution of particles within crystallographic sites is essential for comprehending the behavior and functionality of crystalline materials.

II .3.4.2. LA COORDINATION NUMBER:



The coordination number of the central motif in a crystal is the number of nearest surrounding motifs in space connected to this central motif. It is also referred to as coordination index. **Example:** in Barium Titanate (BaTiO3):

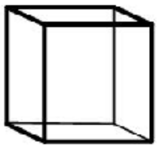
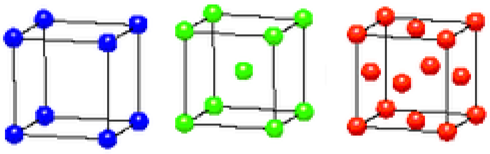
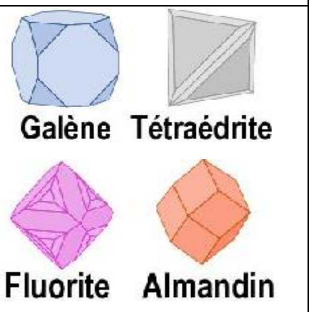
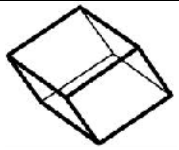
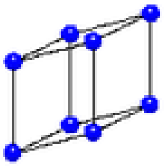
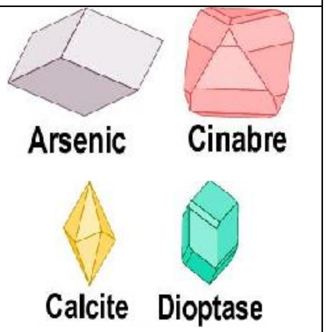
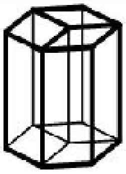
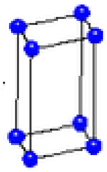
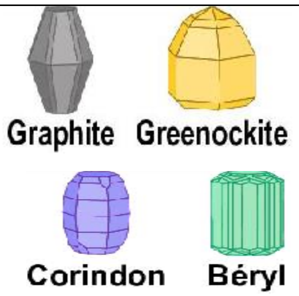
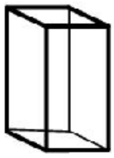
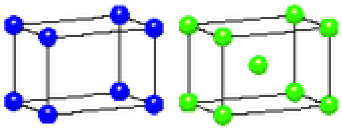
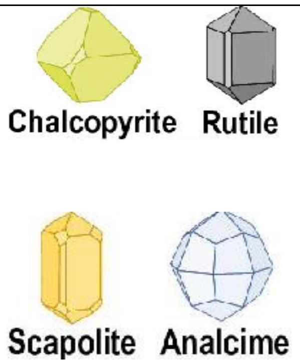
- Titanium (Ti) is coordinated with 6 adjacent oxygen (O) ions arranged in an octahedral configuration, and its coordination number is 6.
- Barium (Ba) is coordinated with twelve adjacent oxygen (O) ions arranged in a cuboctahedral configuration, and its coordination number is 12.
- Oxygen (O) is coordinated with two adjacent Ti ions and four Ba ions in a distorted octahedral arrangement, and its coordination number is 2 + 4.

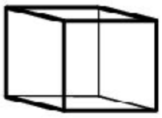
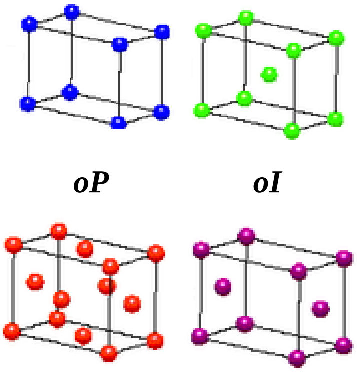
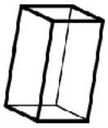
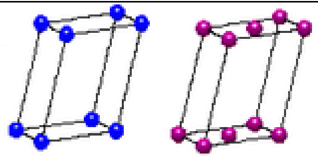
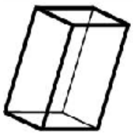
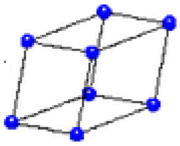
II.2.5.CRYSTALLINE SYSTEM:

A crystal is described using a system of three axes characterized by lengths a, b, and c along the axes, and the angles α, β, and γ formed by these axes. These axes represent the edges of the unit cell where the origin of the axes is taken as a node in the lattice.

Long before the commencement of crystal studies, through theoretical mathematical exploration of possible structures exhibiting periodicity in all three spatial directions, Auguste Bravais (1848) demonstrated that there are only 14 possible types of structures, which are variations of only 7 crystal systems. The 7 crystal systems are created by placing different possible combinations of linear parameters for the cell dimensions a, b, c, and the angular parameters α, β, γ.

In nature, there are only 7 fundamental forms with multiple facets (7 primitive cells allowing for the infinite structural construction of crystals). However, if they share the same crystal system, they differ in their dimensions – the length, width, and height of the lattice specific to each chemical crystal shape.

Crystalline system	Bravais system	exemples
 **Cubic(C)** $a = b = c$ $\alpha = \beta = \gamma = 90°$	 ***cP*** ***cI*** ***cC***	
 **Rhomboédric or trigonal** $a = b = c$ $\alpha = \beta = \gamma \neq 90°$	 ***R***	
 **Hexagonal** $a = b \neq c$ $\alpha = \beta = 90° \quad \gamma = 120°$	 ***hP***	
 **Tetragonal** $a = b \neq c$ $\alpha = \beta = \gamma = 90°$	 ***tP*** ***tI***	

 **Orthorombic** a ≠ b ≠ c α = β = γ = 90°	 ***oP*** ***oI*** ***oF*** ***oB***	 Bornite Boracite Baryte Bertrandite
 **Monoclinic** a ≠ b ≠ c α = γ = 90° β≠120°	 ***mP*** ***mC***	 Pyrrhotite Monazite Stilbite Neptunite
 **Triclinic** **(Anorthic)** **No conditions** a ≠ b ≠ c α ≠ β ≠ γ ≠ 90°	 ***aP***	 Turquoise Cyanite Albite Rhodonite

The seven 3D crystal systems or primitive unit cells are denoted by a two-letter symbol. The first letter (lowercase) designates the crystal system: '***a***' for anorthic or triclinic, '***m***' for monoclinic, '***o***' for orthorhombic, '***t***' for tetragonal, '***h***' for hexagonal, '***c***' for cubic, and oddly, no letter for trigonal or rhombohedral. The second letter (uppercase) indicates the type of cell, where '***P***' stands for primitive, '***I***' for body-centered, '*F*' for face-centered, and 'A' (plane b-c), '***B***' (plane a-c), and '***C***' (plane a-b) for base-centered cells. The exception to this rule is the rompbohedral or trigonal system which is indicates by the symbol ***R***

Crystalline solid matter can exist in one or more crystalline forms that correspond to different arrangements of atoms or ions in the lattice. These various crystalline forms are called allotropes. This is the case, for example, with diamond and graphite, which are two interrelated forms or allotropes of carbon. The phenomenon of allotropy corresponds to a change in the crystal structure under the influence of temperature and pressure.

<u>Exemples :</u>

- Minerals generally belong to the cubic (***c***) or hexagonal (***h***) crystal system, most of them have a closely packed crystalline structure (***cI, cF, hI***),.

- Alkali metals (Li, Na, K, Rb, Cs, etc.) crystallize in the body-centered cubic (*cI*) system.

- Noble metals such as Au, Ag, Cu, Al, Pb, Ni, Pt crystallize in the face-centered cubic (***cF***) system.

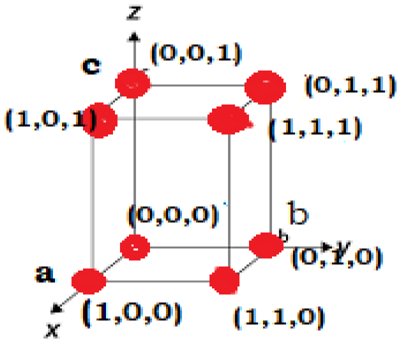
- Some transition metals and alkaline earth metals have a hexagonal structure.

- Noble gases Ne, Ar, Kr, Xe, as well as CO_2 and O_2, crystallize in the ***cF*** system.

- Depending on pressure and temperature conditions, there are 11 stable crystalline forms of water. Ice I, with a hexagonal system, is stable under normal temperature and pressure conditions. Ice III crystallizes in a cubic system at 0 degrees Celsius under pressures close to 3,108 pascals.

II.3. CRYSTALLOGRAPHIC COMPUTATIONS:

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*.



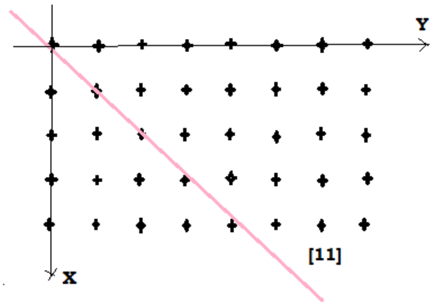
II.3.1. DIRECTIONS IN CRYSTALLINE LATTICE:

A vector in the space lattice possesses two key attributes: its length and direction. When we choose a translation vector, represented by '**t**' in the space lattice, we are essentially specifying a direction within the crystal lattice.

According to international agreements, the direction of a row in the crystal lattice is determined by the equation:

$$\mathbf{t}=u\mathbf{a}+v\mathbf{b}+w\mathbf{c}$$

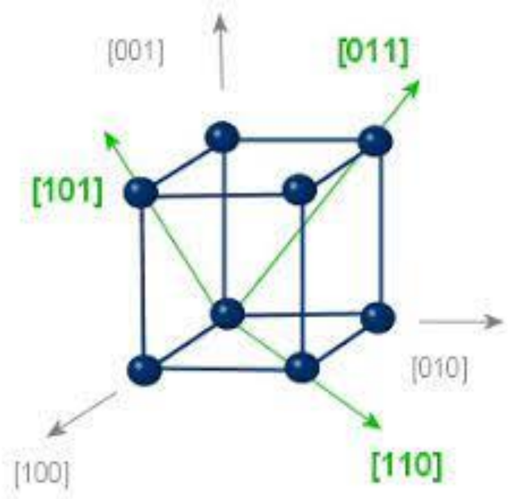
This direction is defined by the line segment connecting the origin to the endpoint of the vector.

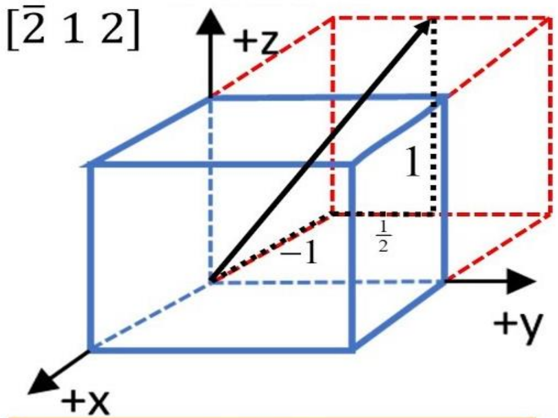


Directions within crystal lattices are commonly denoted using a special symbol. Specifically, the direction parallel to the vector '**t**' is represented by [uvw] (Miller's indices), where (u, v, w) are the smallest integers proportional to the components of the vector '**t**'. It is important to note the use of square brackets and the absence of commas between the components. If a component is negative, the minus sign is consistently placed above the corresponding integer. Additionally, if any of the integer components exceed 9, it is customary to introduce a narrow space between the numbers.

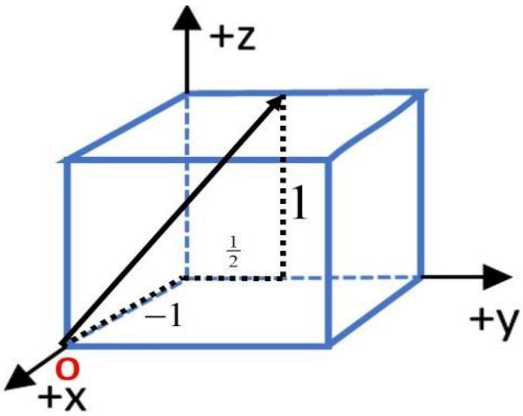
All lines parallel to the vector [uvw] and equidistant form a family of this vector.

Examples: $[110], [111], [\bar{1}22], [3\bar{1}2], [0\ 12\ 4]$.





OPTION A
Draw another unit cell behind the current one (x axis represents in and out)



OPTION B
Move origin along the x axis (due to the negative x index)

II.3.2. PLANES IN CRYSTALLINE LATTICE:

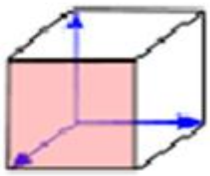
The lattice plane (crystal plane) is defined according to the equation:

$$h \cdot x + k \cdot y + l \cdot z = m$$ (h,k *and* l are integers).

It is represented as (*hkl*) (Miller's indices) within brackets without commas.

Regarding *h*, *k*, and *l*, they are the points that intersect the axes *ox*, *oy*, and *oz* respectively by the plane referred to as (*hkl*) at the points ***a*/*h***, **b/*k***, **c/*l*** respectively.

Examples:



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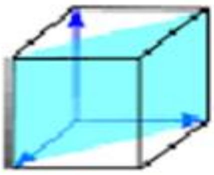

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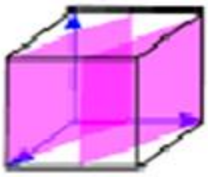

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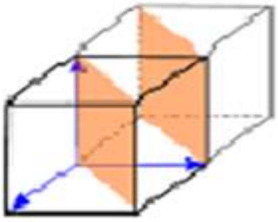
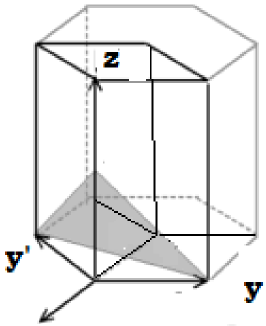


(110)

The three Miller indices (*hkl*) are used for all crystal systems (6 systems) except the hexagonal system. For the hexagonal system, four indices ((*hkk'l*) are employed (Miller-Bravais indices) due to the hexagonal lattice symmetry, which does not manifest with the simple cubic lattice based on the diamond structure. The fourth index, *k'*, is obtained by considering an additional axis *oy'*, which is the outer bisector of the angle xôy. Consequently, the axes *ox*, *oy*, *oy'* are 120 degrees apart from each other.

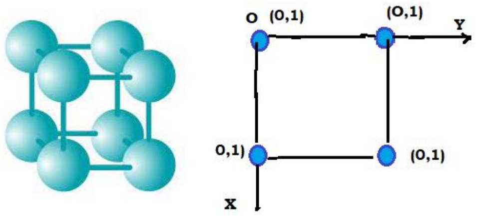


plan ($11\bar{2}2$)

Projecting the unit cell onto a plane:

The projection onto a specific plane (which can be the XY plane, XZ plane, YZ plane, or a lattice plane defined by (*hkl*) is determined by the coordinates X, Y, and Z.

Example: Projecting the simple cubic unit cell onto the XY plane (001)



Activity: Providing the projection of each Bravais lattice system onto the XY plane (homework)

II.3.3. DISTANCE BETWEEN TWO POINTS IN CRYSTALLINE LATTICE:

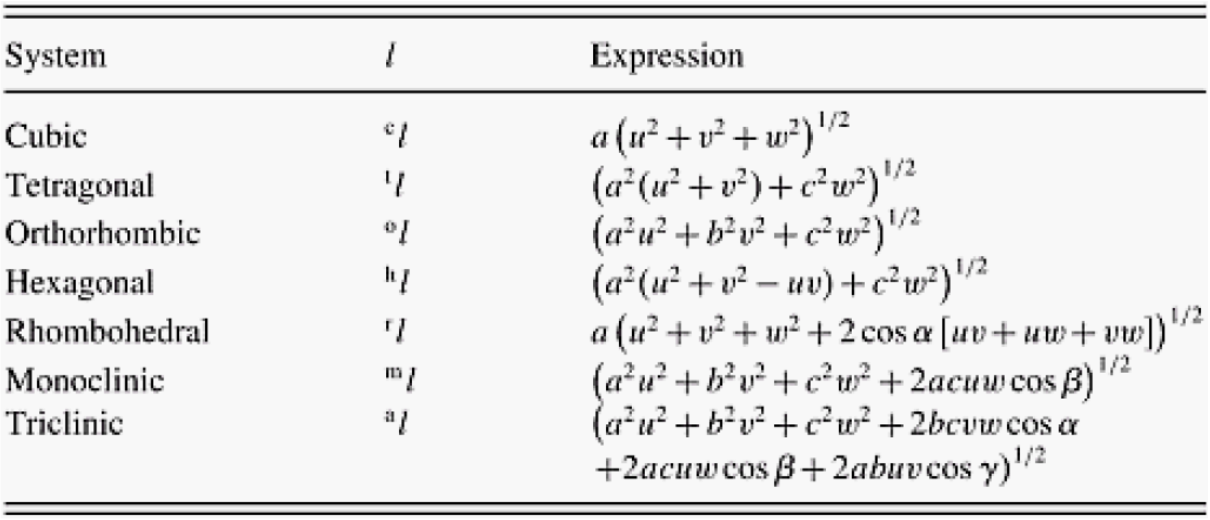
For two pints **P$_1$**(u$_1$,v$_1$,w$_1$) and **P$_2$** (u$_2$,v$_2$,w$_2$), the distance D between them is calculated using this following formula:

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

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

the distance between the origin O (0,0,0) and a point P (u,v,w) is the length of the vector [uvw]

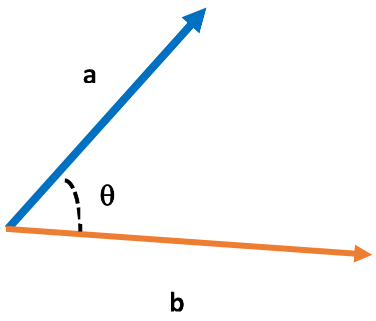
Table 1: the expressions for the length of vector [uvw] in seven system:



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.3.3. 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**:



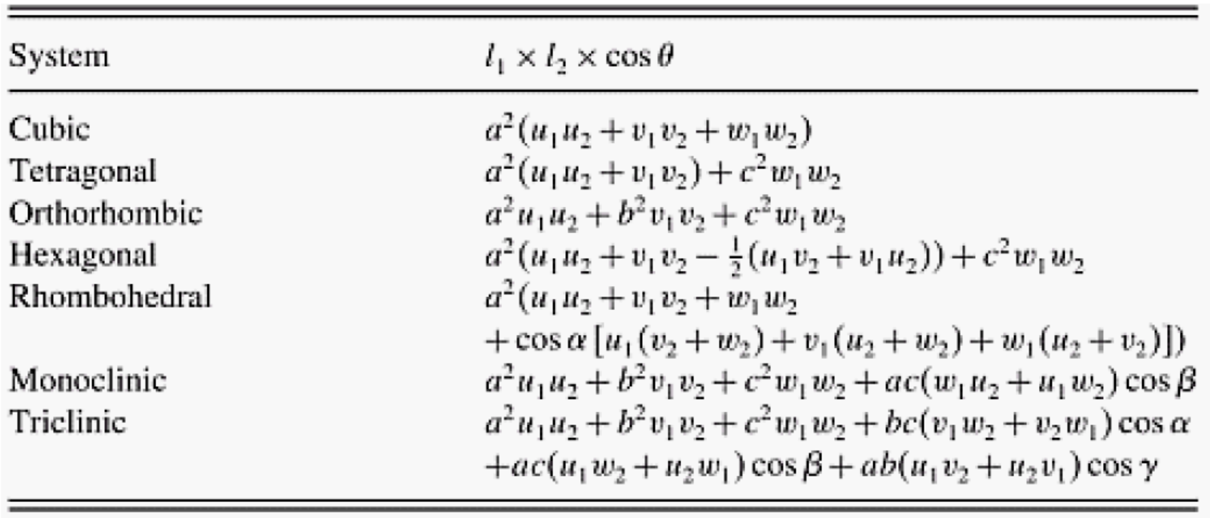
$$a * b = |a||b|cos\theta$$

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.

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.



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	$a^2u_1u_2+b^2v_1v_2+c^2w_1w_2+bc(v_1w_2+v_2w_1)\cos\alpha$ $+ac(u_1w_2+u_2w_1)\cos\beta+ab(u_1v_2+u_2v_1)\cos\gamma$

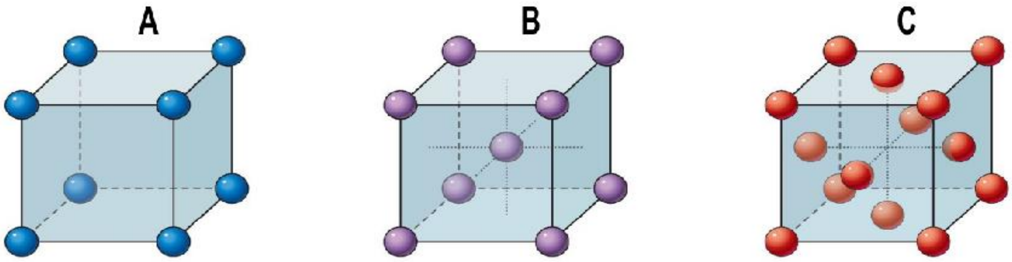
II.3.4. THE CRYSTAL DENSITY:

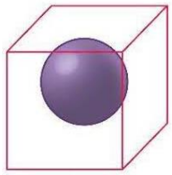
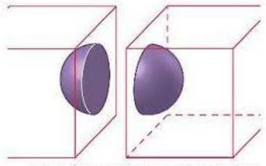
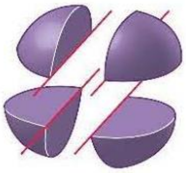
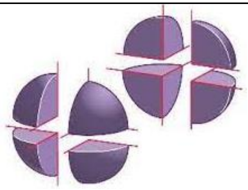
II.3.4.1. MULTIPLICITY:

The multiplicity ***z*** of the crystal cell represents the number of motifs belonging to this cell.

- We say a lattice is simple if it contains only one node (having nodes only at the corners).
- We say a lattice is complex if it contains multiple nodes (having more nodes either at the body center, the face centers, or the centers of opposite faces).
- The smallest crystal cell used to describe the entire crystal is called the primitive cell.

Example: For the cubic system, there are three structures.:



The number of cells that share the atom	The position of the atom in the cell	The contribution of the atom in the cell
	Center	1
	Centrer of faces	1/2
	Center of the Edge	1/4
	Corners	1/8

II.3.4.2. THE COMPACTNESS OR PACKING DENSITY:

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.

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

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:

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

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

$$\boldsymbol{\tau = C \times 100}$$

II.3.4.3. THE CRYSTAL DENSITY:

As we know the density formula is:

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

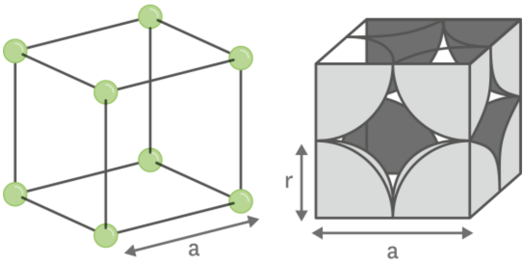
for the crystalline cell we have:

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

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.

Examples:

- A detailed study of the elements present in nature reveals that most mineral crystals belong to cubic or hexagonal lattice structures.



Example 1:

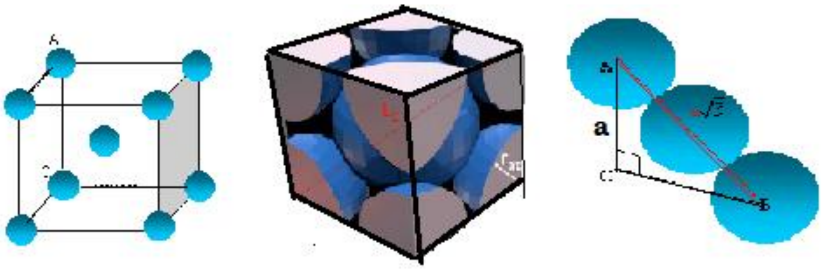
In the case of a simple cubic cell, for example, the spheres are located only at the corners with a multiplicity of z=1. The cell volume is given by:

$$\mathbf{V} = \mathbf{a^3} = \mathbf{(2r)^3}\ (a = 2r). \Rightarrow \mathbf{V} = \mathbf{a^3} = \mathbf{(2r)^3} = \mathbf{8r^3}$$

$$C = \frac{\frac{4}{3}\pi r^3}{8r^3} = 0,52$$

$$\tau = 0,52 \times 100 = 52\%$$

Example 2 :



In the case of a body-centered cubic lattice (***cI***), for example, the spheres are located at the corners of the cube plus one at the center, giving z=2. The spheres are in contact along the [111] direction, which is the main diagonal of the cube (atoms at the corners do not touch each other

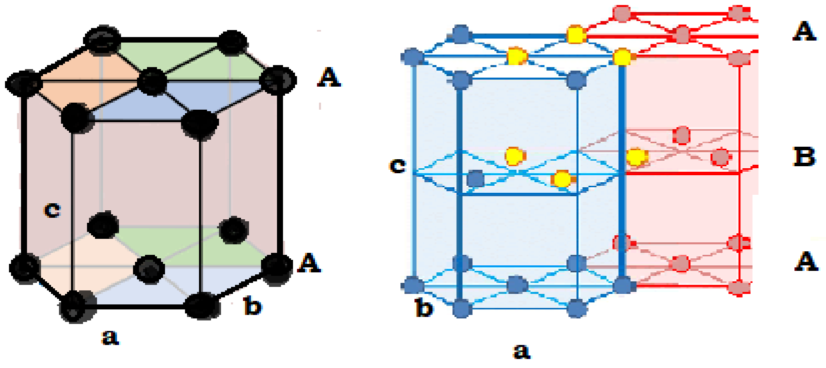
$$a\sqrt{3} = 4r \Rightarrow a = \frac{4r}{\sqrt{3}}$$

$$V = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$$

$$C = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0,68$$

$$\tau = 0,68 \times 100 = 68\%$$

Example 3 :



It should be noted here that there are two types of hexagonal systems. The first type is simple hexagonal: the layer sequence is AAA... The second type is close-packed hexagonal, where the layer sequence is of the type ABAB....

The hexagonal shape consists of six basal triangular prisms or three certain base prisms, and thus the total volume is the sum of these volumes.

We assume that **a=b= 2r**

$$V \quad = a \times a \times c \times \sin 120$$

The cell contains 14 motifs, but some of these motifs are shared with neighboring cells. Each of the six vertices is shared with six cells, and the two motifs in the lower and upper faces are shared between two cells. Therefore, the cell's coordination number is:

$$Z = 12 \times (1/6) + 2 \times (1/2) = 2 + 1 = 3$$

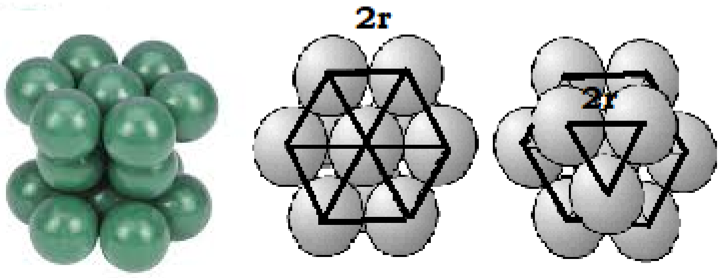
II.4. SOME EXAMPLES OF CRYSTAL STRUCTURES:

The Crystals are discovered in the form of polyhedral, and sometimes a combination of both. However, their crystalline development typically starts from a polyhedral form according to Pauli's law (crystal atoms always adopt behaviors that consistently align with the minimum energy of the cell, under specific dynamic thermal conditions)

II.4.1. METALLIC CRYSTALS

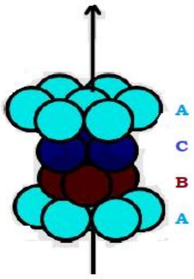
Most minerals have a densely packed or semi-densely packed crystalline structure of identical spheres. This results in three main structures: ***cF***, ***hCP*** (Hexagonal Close Packing), and ***cI*** (Body-Centered Cubic).

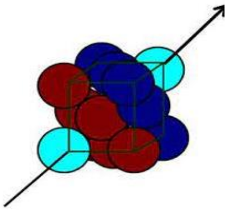
In the first level, each sphere is in contact with 6 neighbors and is placed in the center of a regular hexagon with a side length of r2, and the hexagon's vertices occupy the lattice points. These voids interlock with each other to occupy the smallest volume. If a second layer B of identical spheres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

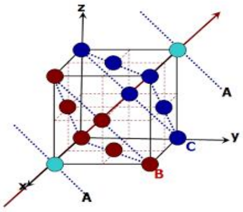


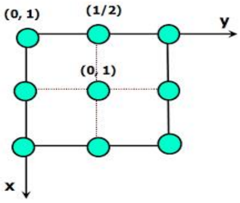
The close packing of spheres gives rise to two types of structures: face-centered cubic) or hexagonal close-packed. These two types of close-packing structures differ in the number of consecutive layers. We have seen the stacking of two consecutive layers, A and B. A third layer, C, can be added to these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

1. 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.



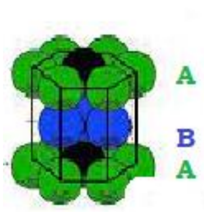


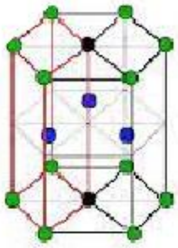


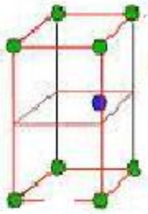


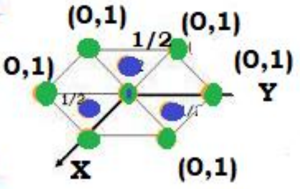
The initial lattice ($a = b = c$ and $\alpha = \beta = \gamma = 90$) contains atoms at the eight corners of the cube and at the centers of the six faces. The geometric coordinates (XYZ) for these positions are: (000) (100) (010) (001) (110) (101) (011) (111) - (1/2 1/2 0) (1/2 0 1/2) (0 1/2 1/2) (1/2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

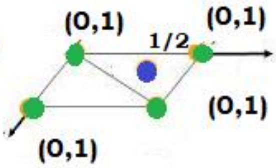
2. The HCP (Hexagonal Close-Packed) structure occupies the C layer positions in the voids of the B layer, dropping vertically above the spheres of the A layer.







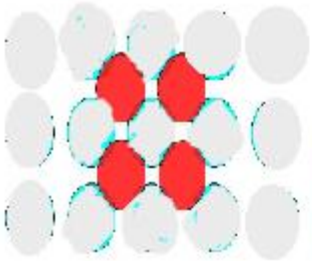


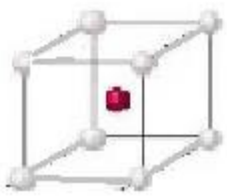


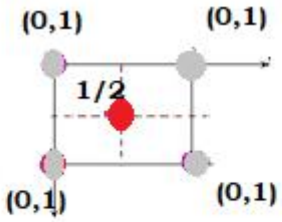
The initial cell describing the Hexagonal Close-Packed lattice ($a = b \neq c$; $\alpha = \beta = 90°$ and $\gamma = 120°$) contains atoms at the eight corners and one atom in the center. The geometric coordinates (XYZ) for these atoms are:

(000) (100) (010) (001) (110) (101) (011) (111) - (2/3 1/3 1/2) ou (1/3 2/3 1/2)

3. 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.







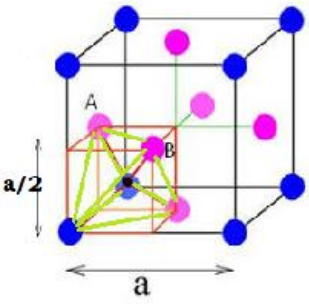
The specified geometric coordinates (XYZ) for the atomic positions in Cell ***cI*** are: (000) (100) (010) (001) (110) (101) (011) (111) (1/2 1/2 1/2).

Insertion in the crystalline lattice:

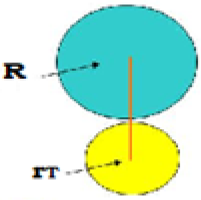
The presence of empty spaces in metal crystals makes it possible to introduce smaller particles, thereby obtaining insertion compounds such as metal alloys like iron-carbon alloys (cast iron and steel). The introduction of carbon makes it possible to modify the mechanical properties of iron.

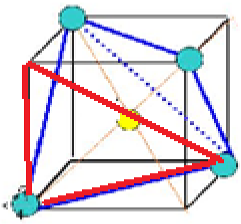
Example 1 : system cF

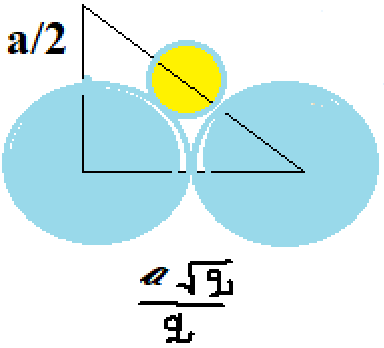
The central cubic lattice contains eight tetrahedral sites that correspond to the centers of the eight smaller cubes with a side length of �/2a/2. The geometric reference coordinates for these sites are (1/4, 1/4, 1/4), (3/4, 1/4, 1/4), (1/4, 3/4, 1/4), (3/4, 3/4, 1/4), (1/4, 1/4, 3/4), (3/4, 1/4, 3/4), (1/4, 3/4, 3/4), and (3/4, 3/4, 3/4).



supposing r_T is the maximum radius of the atom T that can be accommodated in a tetrahedral site without distorting the lattice.







From the diameters of the smaller cubes, we can obtain the following:

$$\boldsymbol{R + r_T = \frac{1}{2}x.. (1)}$$

$$\boldsymbol{x^2 = \left(\frac{a}{2}\right)^2 + \left(\frac{a\sqrt{2}}{2}\right)^2 \ldots (2)}$$

$$\boldsymbol{x^2 = \frac{3a^2}{4} \ldots (3)}$$

$$=> \boldsymbol{x = \frac{a\sqrt{3}}{2}} \ldots (4)$$

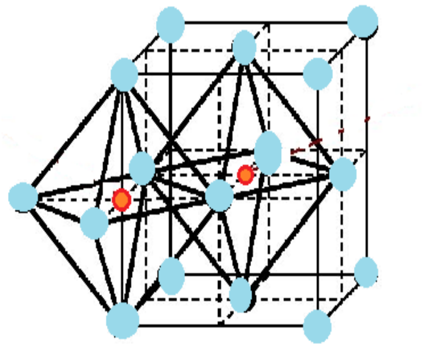
$$(1) + (4) \Rightarrow \; R + r_T = \frac{1}{2}\frac{a\sqrt{3}}{2} \Rightarrow$$

$$\text{And we know that: } 2R = \frac{a\sqrt{2}}{2} \Rightarrow a = \frac{4R}{\sqrt{2}}$$

$$R + r_T = \frac{a\sqrt{3}}{4} = \frac{4R\sqrt{3}}{4\sqrt{2}} = R\frac{\sqrt{3}}{\sqrt{2}} \Rightarrow r_T = R\left(\frac{\sqrt{3}}{\sqrt{2}} - 1\right)$$

$$r_T = 0,225R$$

The face-centered cubic (***cF***) lattice also contains 4 octahedral sites: one at the center of the cube and one at the midpoint of each of the 12 edges. r_O is the maximum half-radius of an **O** atom that can be accommodated in an octahedral site (square-based bipyramid) of the ***cF*** structure without distorting the unit cell. The site is located at the center of the square.



$$r_O + R = \frac{a}{2} \; et \; 2R = \frac{a}{\sqrt{2}} \Rightarrow r_O = 0,414R$$

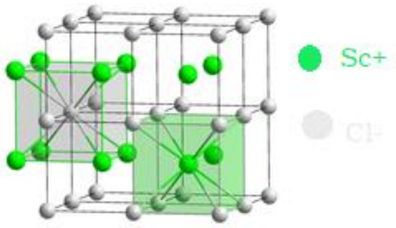
. II.4.2. IONIC CRYSTALS:

Ionic crystals consist of two interpenetrating lattices separated by the ionic bond length ℓ: the cationic lattice and the anionic lattice. The ionic bond length is taken as the sum of the ionic radius of the cation and anion: $\ell = r^+ + r^-$.

As anions are larger than cations, those determining the type of stacking place cations in the interstitial sites of the anionic lattice.

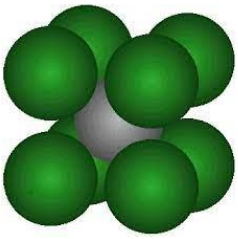
Example: CsCl structure

In the **CsCl** structure, the negatively charged chloride ions (**Cl$^-$**) form a simple cubic lattice (***cP***). The Secium cations (**Cs$^+$**) occupy the center of the cube. This structure corresponds to two interpenetrating simple cubic lattices, each shifted by a type of translation (**1/2, 1/2, 1/2**).



- ***Multiplicity***: The primary lattice contains 8 chloride ions (**Cl$^-$**), each contributing 1/8, and one cesium cation (**Cs$^+$**) at the center. The number of CsCl units per lattice is: ***z*=1.**

- ❖ ***Coordination:*** Each **Cs^+** cation is surrounded by 8 Cl^- anions located at the same distance **a√3/2**. Similarly, each **Cl^-** anion is surrounded by 8 **Cs^+** cations at the same distance. Consequently, the coordination number is 8 for both, resulting in a coordination of 8-8.

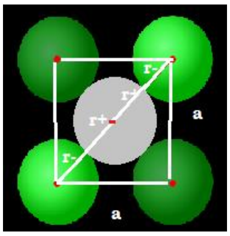


  - ❖ ***Compactness:*** Similar to the calculation for metallic crystals, the packing in **CsCl** is such that the volume of the unit cell is equal to the sum of the volumes of the ions.

$$\boldsymbol{C = \frac{\frac{4}{3}\pi(r_{Sc} + r_{Cl})^3}{a^3}}$$

- ❖ ***Condition for the presence of an ScCl type structure*:**

The adjacent **Cl^-** ions must not touch each other. Therefore, **a ≥2r** $^-$. The Cs^+ cations are placed in the sites between the anions.



$$2r^+ + 2r^- = a\sqrt{3}$$

$$\Rightarrow \; a = \frac{2(r^+ + r^-)}{\sqrt{3}} > 2r^- \Rightarrow \frac{r^+}{r^-} \geq \sqrt{3} - 1 \;\; \Rightarrow \frac{r^+}{r^-} \geq 0{,}732$$

$$\frac{r^+}{r^-} < 1 \Rightarrow \mathbf{1} > \boldsymbol{\frac{r^+}{r^-}} \geq \mathbf{0{,}732}$$

II.4.3. COVALENTE CRYSTALES:

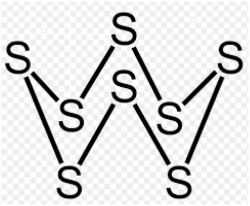
The covalent crystals are large molecular crystals in which atoms or groups of atoms form the lattice framework. There are three types of covalent molecular crystals:

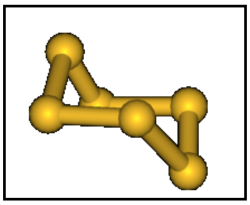
1. Linear or mono-dimensional molecules, such as "soft" sulfur, $PdCl_2$, $CuCl_2$, $CuBr_2$, and many polymers. Chains are linked to each other through van der Waals or hydrogen bonding.

2. Large di-dimensional or planar molecules with a structure resembling sheets, such as graphite.

3. tri-dimensional molecules evolving in all three spatial directions, examples include diamond, silicon, and germanium.

Example 1 : mono-dimensional structure « S »





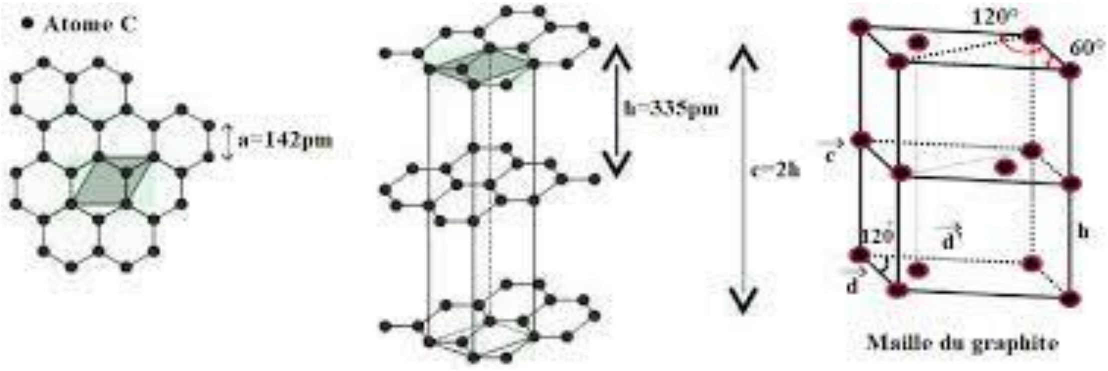
Sulfur occurs in nature in various allotropes, with the most abundant forms being:

- **Orthorhombic (α-Sulfur):** Rectangular parallelipiped crystals (S8).
- **Monoclinic (β-Sulfur):** Monoclinic crystals (S8).
- **Hexagonal (γ-Sulfur):** Hexagonal crystals (S6).

Sulfur exhibits the phenomenon of catenation, forming long chains of sulfur atoms that, when closed, give rings ranging from 6 to 20 atoms. In the α and β forms, the sulfur molecule (S8) forms a ring with 8 sulfur atoms, and it has bond angles between the bonds measuring 105°. In the hexagonal form, the molecule (S6) forms a ring of 6 atoms in a chair-like shape.

Example 2 : di-dimensional structure « Graphite » :

Carbon exists in several allotropes, with the most well-known being graphite and diamond. Graphite crystallizes in the form of regularly spaced layers or sheets. In these sheets, each carbon atom is surrounded by 3 other atoms. They are arranged at the vertices of regular hexagons on the plane, with a separation of approximately 1.42 Å.



Three atoms from the B-plane fall onto three vacancies in the A-plane in an A-B-A type structure. The distance between the two sheets is 3.4 Å. Cohesion between the layers is ensured through van der Waals bonds. The structure of graphite can be described as a hexagonal lattice (a = 1.42 Å and c = 6.8 Å).

- ***Multiplicity:***

z = 12x1/6 + 2x1/2 + 3 = 6

- ***Coordination*** :

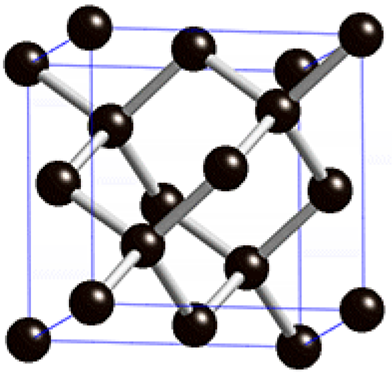
The carbon coordination is 3: each carbon atom is surrounded by 3 other atoms located in the same plane. The hybridization is sp2, and the angle between two C--C bonds is 120°.

- ***Compactness*** **:**

$$C = \frac{6\frac{4}{3}\pi r_c^3}{ca^2 \sin 120} \; and \; r_c = a/2$$

Example 3 : tri-dimensional structure :

In diamond, carbon atoms form four saturated covalent bonds with no free electrons. The structure of diamond can be described as a cubic unit cell of carbon atoms centered on the faces, with carbon atoms located at the half positions of each face.



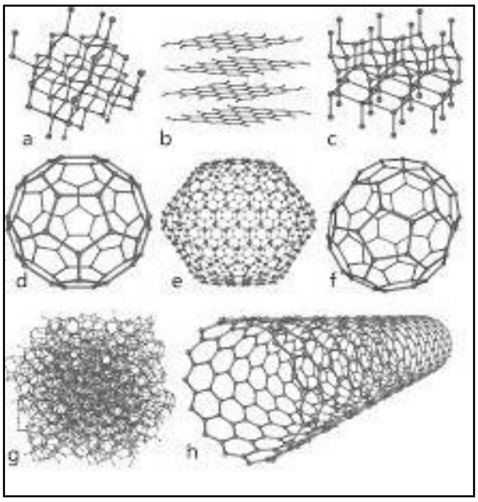
- ***Multiplicity :***

8× 1/8 + 6× 1/2 + 4 = 8

- ***Coordination*** :
- Carbon coordination: Each carbon atom is surrounded by 4 other atoms located at the vertices (corners) of a tetrahedron. The angle between two C-C bonds is **109.471°.**
- ***Compactness :***

$$C = \frac{8\frac{4}{3}\pi r_c^3}{a^3} \; therefore \; 2\, r_c = \mathrm{a}\sqrt{3}/4$$

Notes :



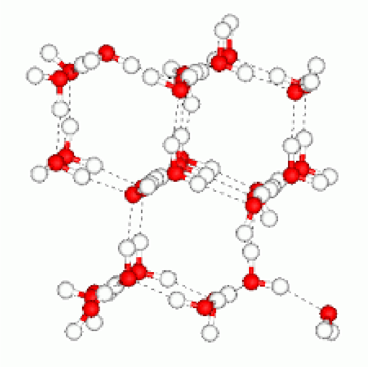
Recently, new types of carbon structures have been synthesized, including fullerenes. Fullerenes are molecular assemblies with various sizes and arrangements such as C_{20}, C_{60}, C_{70}, ... C_{540} in d, f, e, g shapes. They resemble graphite (b) with sheets composed of interconnected hexagonal rings, but they also contain pentagonal and sometimes heptagonal rings, preventing the sheet from being flat.

II.5. MOLECULAR STRUCTURES:

Molecular crystals are crystalline solids composed of motifs of molecules, such as ideal gases (e.g., hydrogen, nitrogen, oxygen, iodine) or diatomic molecules like carbon dioxide ($CO2$). The bonds within these molecules are covalent

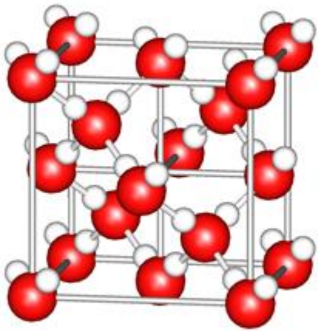
Example the ice :

the glass has 14 allotropic structures



At ordinary atmospheric pressure and up to a pressure of about 0.2 gigapascals (2000 bars), ordinary ice molecules form a crystalline structure following a hexagonal lattice, stabilized by hydrogen bonds. The stable form at 0 degrees Celsius under atmospheric pressure (up to a pressure of about 2000 bars) is a hexagonal type described as a network derived from two compressed hexagonal structures separated by c 3/8. Hexagonal lattice: a=452pm, c=737pm.

The structure has low compression, and therefore, the density of ordinary ice is less than that of water (917 kg/m3 for pure ice at 0 degrees Celsius, standard atmospheric pressure).



Under pressures higher than 3 kilobars, another ice structure (Ice III) is obtained at temperatures close to 0 degrees Celsius. It is derived from the structure of diamond. Oxygen atoms occupy the same positions as carbon atoms in diamond. Each red sphere represents an oxygen atom in a water molecule. Oxygen atoms form a cubic F lattice (a = 635). Each hydrogen atom is placed between two oxygen atoms at specific distances, forming O-H distances of 98 or 177 pm depending on whether it is a sigma bond (98 pm) or a hydrogen bond (177 pm).

Homework :

1. Provide the projections on the XOY plane for all the crystal structures studied in this part of the chapter
2. Calculate their volumetric mass.