Crystal Structures: Introduction, space lattice, basis, unit cell, lattice parameter,

Bravais lattices, crystal systems,

structure and packing fractions of simple cubic,

body centered cubic, face centered cubic crystals, directions and planes in crystals,

Miller indices, separation between successive [h k l] planes.

- Solids are broadly classified as either crystalline or non-crystalline.
- The crystalline type includes crystalline and polycrystalline.
- In a solid if the atoms are regularly arranged in three dimensions and if the environment about each atom is same then the substance is said to be in crystalline state.
- Non-crystalline substances are called 'Amorphous'
- In a solid if the atoms are arranged irregularly in 3D and the environment of each atom is not same then it is called as "Amorphous".


Amorphous   Crystal
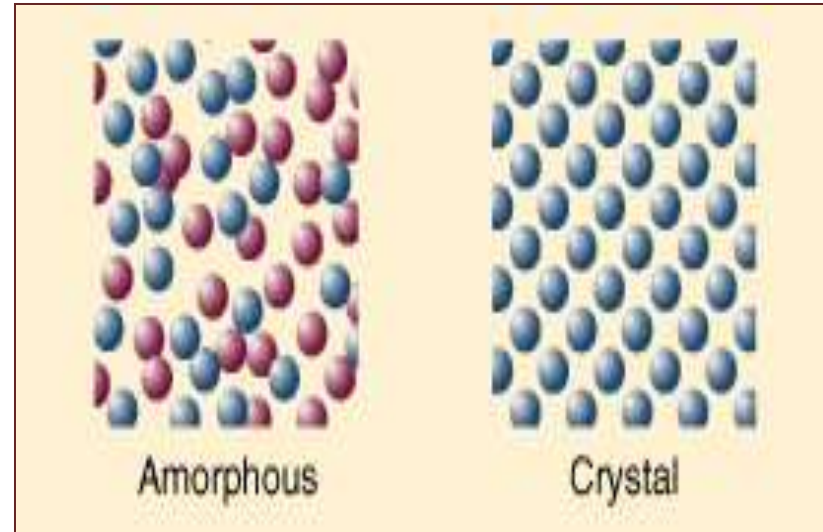
•The atomic arrangement in a crystal is called crystal structure.

•It is convenient to imagine periodic arrangements of points in space about which these atoms are located.

•Each lattice point in space may represent a single atom or group of atoms.

•This leads to the concept of space lattice.

•A space lattice is defined as an infinite array of points in three dimensional in which every point has the surroundings identical to that of the other point in the array.
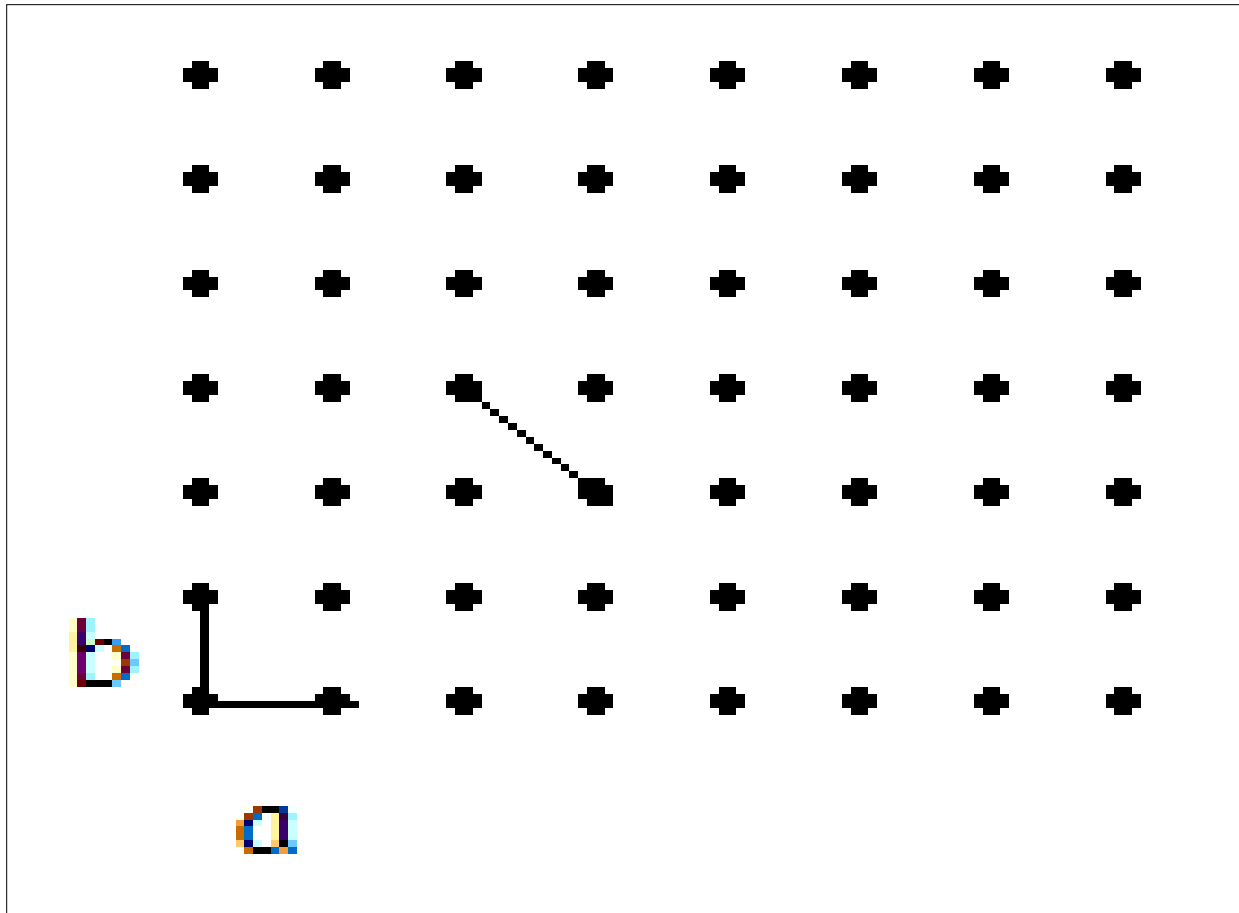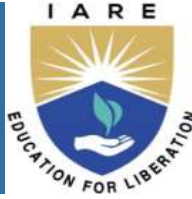
-     Consider a two dimensional array of lattice points as shown in figure.
-     By repeated translation of vectors a, b on the plane of the paper, we can generate the square array.
-     The magnitude of a and b are equal and can be taken to be unity. The angle between a and b is 900, a and b are called fundamental translational vectors that generate square array.
-     Let n1 be the number of translations of magnitude a in x-direction then its translation vector $\vec{T_1} = n_1 \vec{a}$
-     Let n2 be the number of translations of magnitude b in x-direction then its translation vector $\vec{T_2} = n_2 \vec{b}$
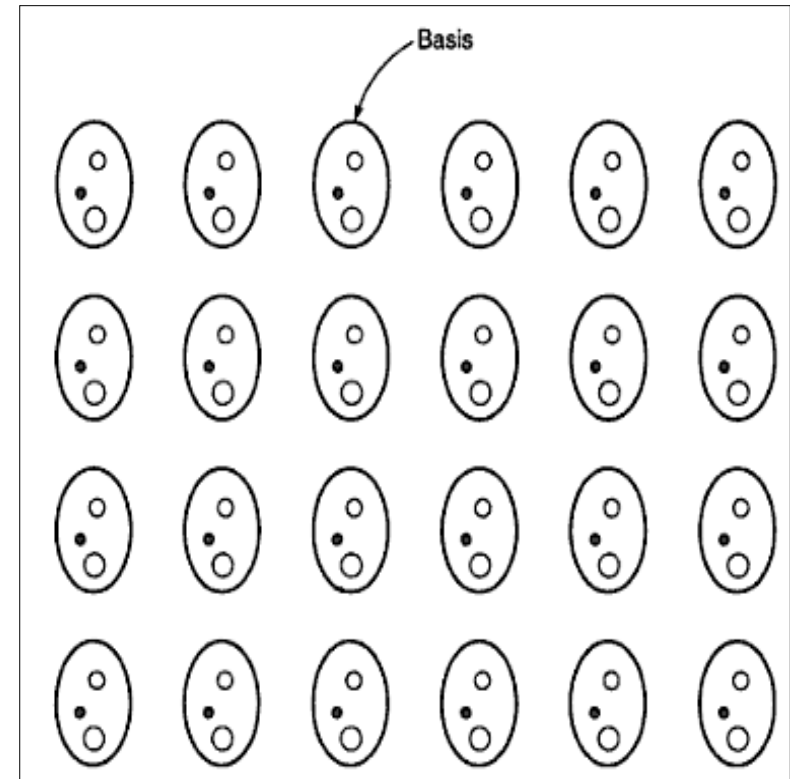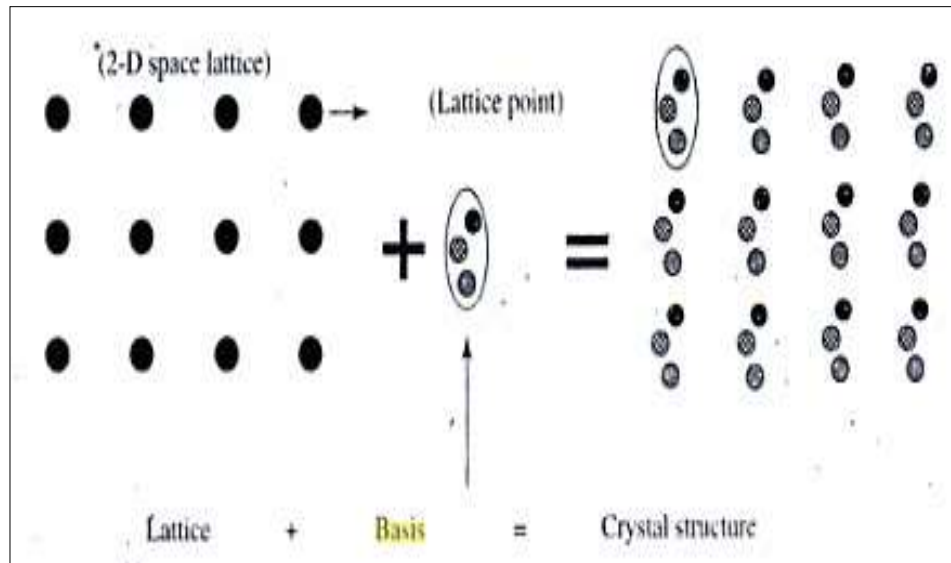
Let $\vec{T}$ be the resultant translation vector.

So, $\vec{T} = \vec{T_1} + \vec{T_2}$

$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$ where n_1 and n_2 are integers.

In 3-D $\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$

BASIS

Since a lattice point is an infinitesimal point in space it is an imaginary concept.

Now the crystal structure is formed by associating with every lattice point, a set of assembly of atoms or molecules or ions in identical composition, arrangement and orientation is called as basis which is shown above.

- A unit cell is the smallest geometrical figure, the repetition of which in 3Dimension will give the actual crystal structure.
- The choice of an unit cell may be of different types as shown in figure.
- A 2D unit cell is called parallelogram, in 3D it is called parallelepiped.
- Primitive Cell.
- Multiple Cell.
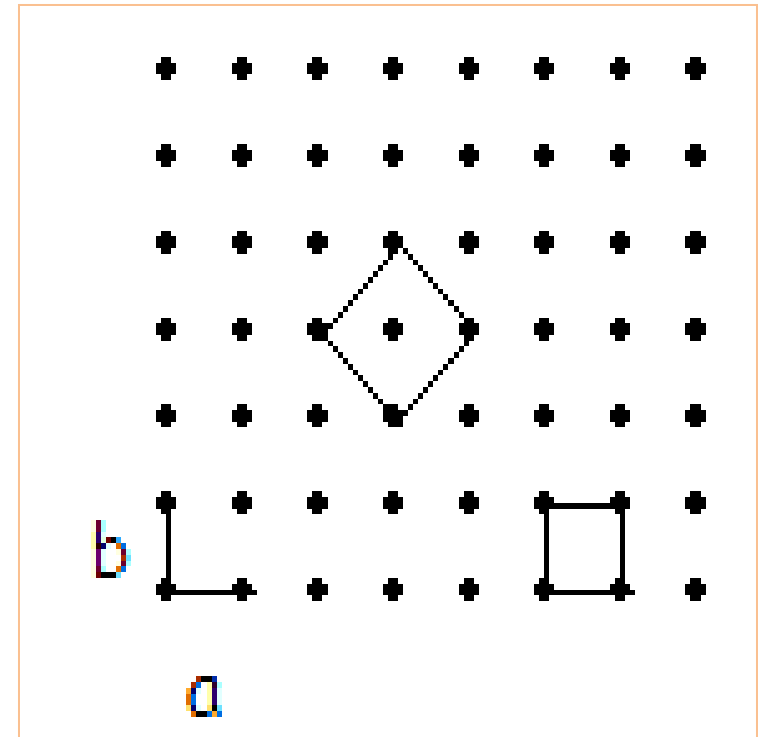
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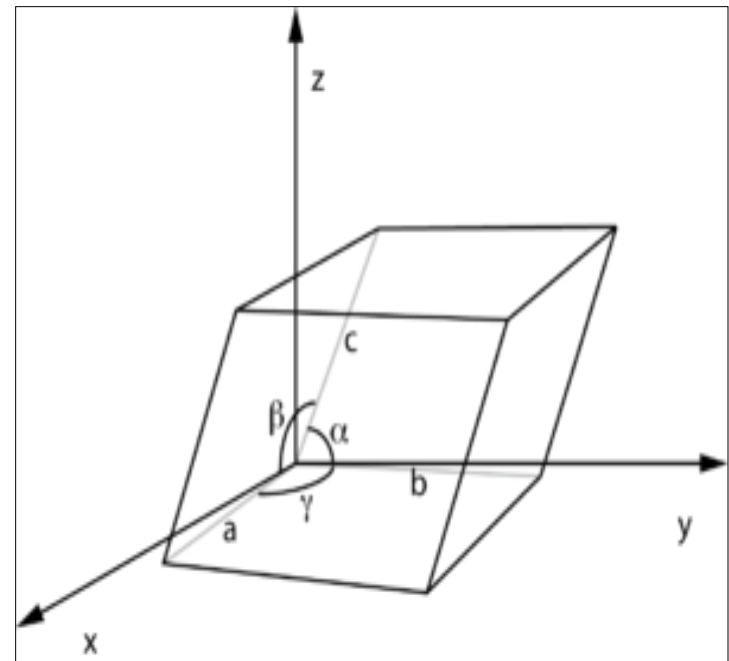
If we consider a unit cell described by three vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ referred as lattice parameters along the three different directions.

α, β, γ are interfacial angles between vectors $(\vec{b}, \vec{c})$, $(\vec{c}, \vec{a})$, $(\vec{a}, \vec{b})$ respectively.

A crystal structure is explained base on $\vec{a}$, $\vec{b}$, $\vec{c}$ and α, β, γ.

If we consider a cubic crystal then a=b=c: α= β= γ=90⁰.

Let ρ be the density of the molecules.

The volume of unit cell is V = abc = a³.

Mass of the unit cell = ρ.a³

Let 'M' be the molecular weight of the material, N_A, be the Avogadro's number which is 6.023×10^{23} mol^{-1}.

Mass of each molecule = $\dfrac{M}{N_A}$

Let us suppose that there are 'n' number of atoms or molecules in unit cell.

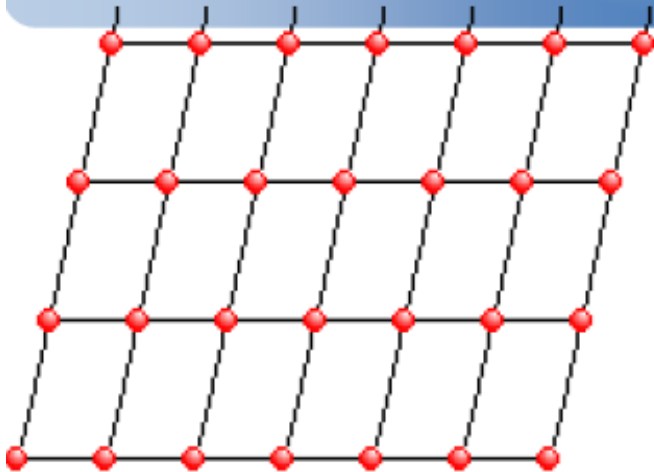Therefore, mass of unit cell = $\dfrac{nM}{N_A}$
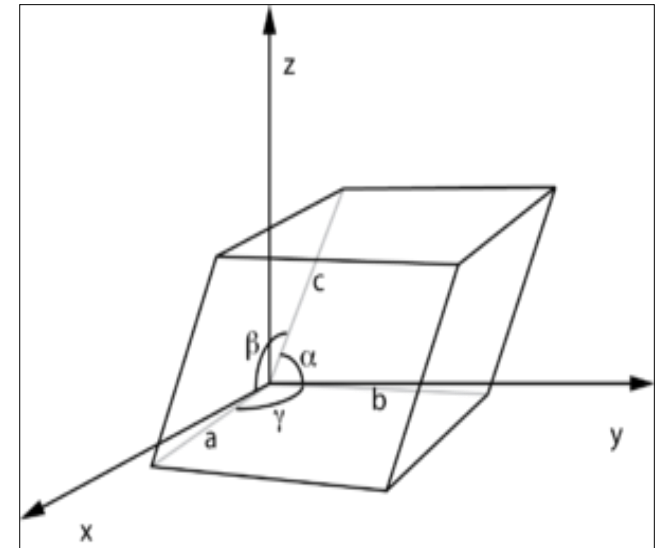
$$\rho.a^3 = \dfrac{nM}{N_A}$$

$$a^3 = \dfrac{nM}{\rho.N_A} \quad => \quad a = \left[\dfrac{nM}{\rho.N_A}\right]^{1/3}$$

4

Crystal Lattice

Bravais lattices:-

A 3D space lattice is generated by repeated translation of 3 non-coplanar vectors a, b, c.

There are only 14 distinguishable ways of arranging lattice points in 3D space.

These 14 space lattices are known as Bravais lattices.

As these are shown by Bravais, called as Bravais lattices.

According to Bravais, there are *14 possible types of space lattices* in the seven crystal systems; one triclinic, two monoclinic, one hexagonal, one trigonal, four orthorhombic, two tetragonal and three cubic.

Bravais Lattices

2 Dimensions : Five Bravais Lattices
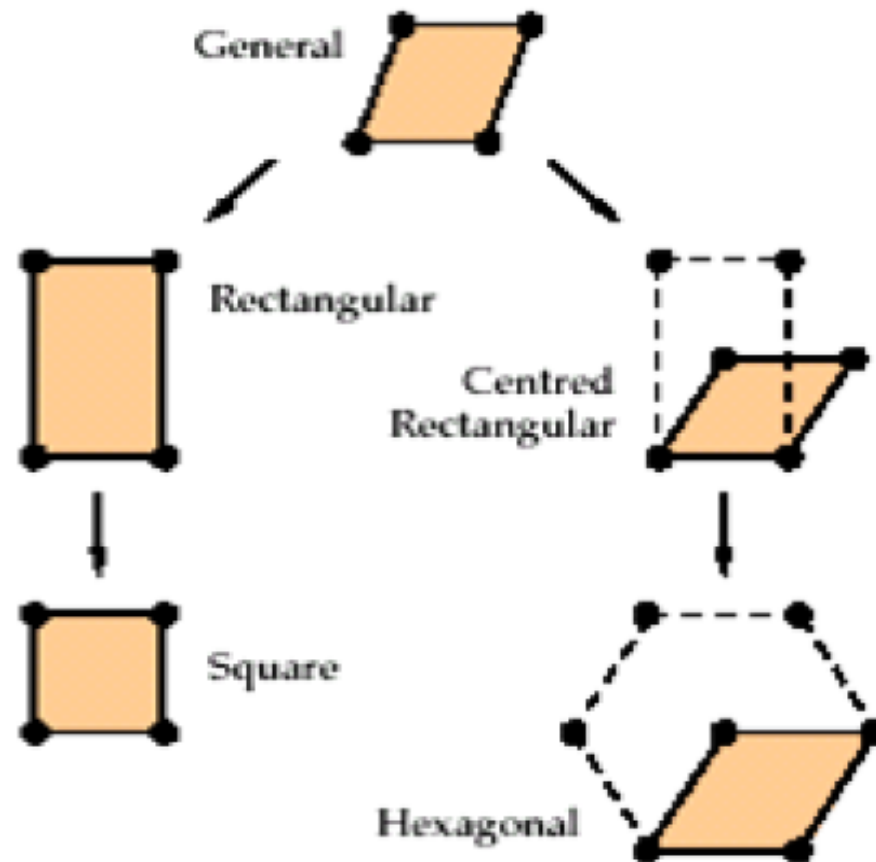
3 Dimensions : Fourteen Bravais Lattices
Only 14 ways of arranging the points in space
14 Space Lattices - Bravais Lattices
Belong to Seven Crystal Systems.

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ **14 Bravais Lattices**

A unit cell consists of only one full atom

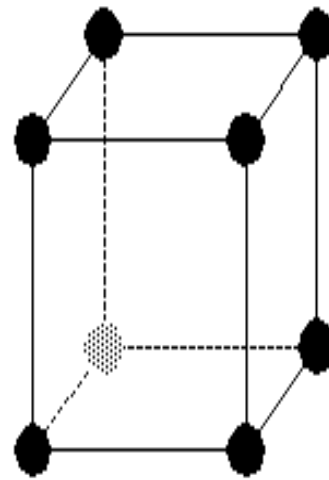A primitive cell got the points or atoms only at the corners

If a unit cell consists more than one atom, then it is not a primitive cell.

Example for primitive cell :

Simple Cubic (SC)

Examples for non-primitive cell :

BCC and FCC unit cell.
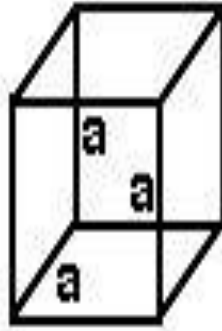

Primitive
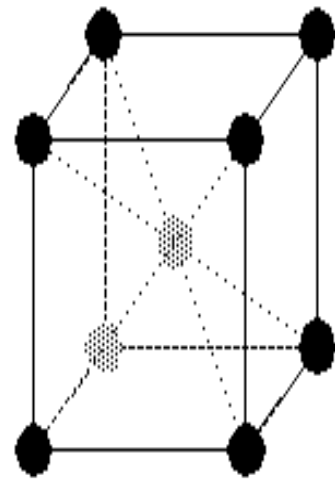
Body-Centered (bcc)
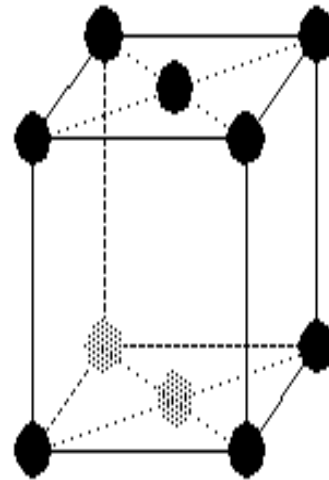
Side-Centered
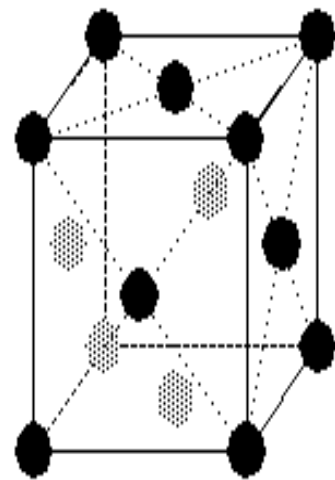
Face-Centered (fcc)
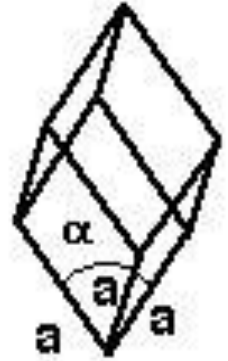
Seven Crystal Systems

Seven crystal systems:-
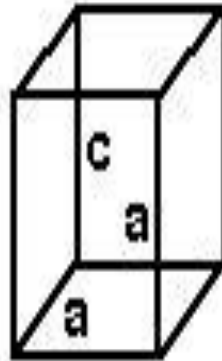
Cubic
$$a = b = c$$
$$\alpha = \beta = \gamma = 90°$$

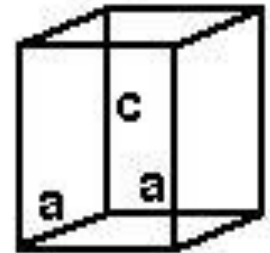Rhombohedral
$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90°$$

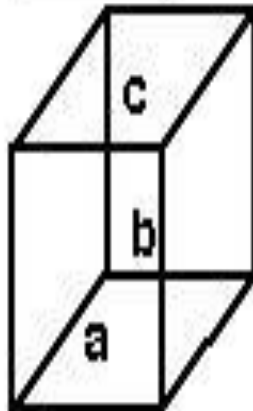Tetragonal
$$a = b \neq c$$
$$\alpha = \beta = \gamma = 90°$$

Hexagonal
$$a = b \neq c$$
$$\alpha = \beta = 90°$$
$$\gamma = 120°$$

Monoclinic
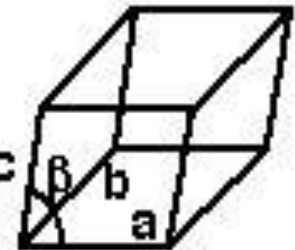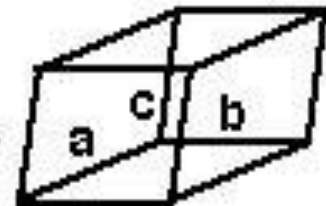$$a \neq b \neq c$$
$$\alpha = \gamma = 90° \neq \beta$$

Orthorhombic
$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90°$$

Triclinic
$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90°$$

Seven Crystal Systems and its Lattice Parameters

| Sr. No.	Crystal System	Axial length of Unit Cell	Inter axial angles	Number of Lattice in the system
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	2
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	4
4	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^0 \neq \gamma$	2
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	1
6	Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^0, \neq 90^0$	1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0, and\ \gamma = 120^0$	1

BRAVAIS LATTICE:

Bravais in 1948 showed that **14 types of unit cells under seven crystal systems** are possible.
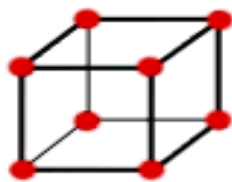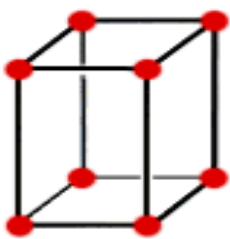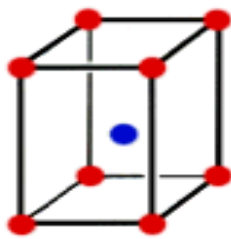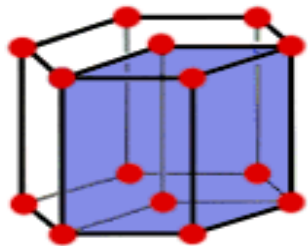

Simple cubic
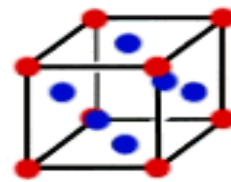
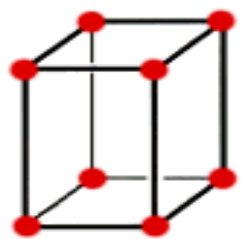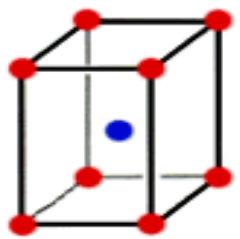Face-centered cubic
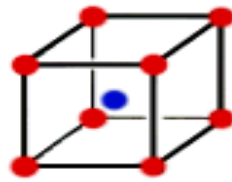
Body-centered cubic
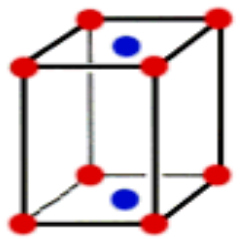
Simple tetragonal
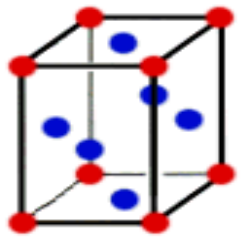
Body-centered tetragonal

Hexagonal

Simple orthorhombic
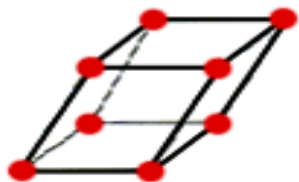
Body-centered orthorhombic

Base-centered orthorhombic
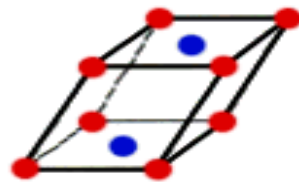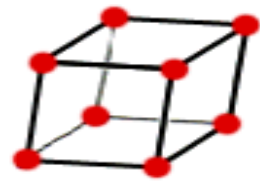
Face-centered orthorhombic

Rhombohedral

Simple Monoclinic

Base-centered monoclinic

Triclinic

14 Bravais Lattice divided into 7 Crystal Systems

S.N	Crystal System	Shape of UC	Bravais Lattices			
			P	**I**	**F**	**C**
1	Cubic	Cube	✓	✓	✓	
2	Tetragonal	Square Prism (general height)	✓	✓		
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓
4	Hexagonal	120° Rhombic Prism	✓			
5	Trigonal	Parallopiped (Equilateral, Equiangular)	✓			
6	Monoclinic	Parallogramic Prism	✓			✓
7	Triclinic	Parallopiped (general)	✓			

|	
P	Primitive
I	Body Centred
F	Face Centred
C	Base- Centred

Characteristics of unit cell

- **Number of atoms / unit cell**

- **Coordination number**

    No. of equidistant nearest neighbouring atoms to a particular atom

- **Atomic Radius (r)**

    Half the distance between the nearest neighbouring atoms

- **Atomic Packing Factor (APF) or Packing Density (PD)**

    Ratio of the volume occupied by the atoms in an unit cell (v) to the volume of the unit cell (V)
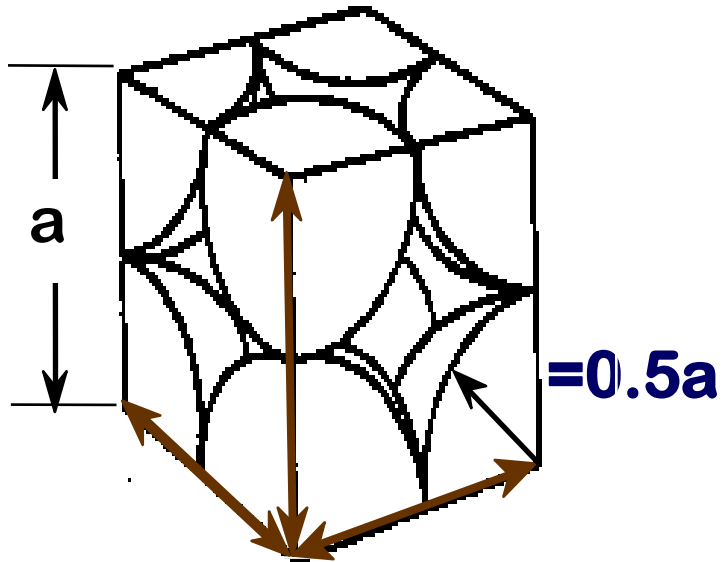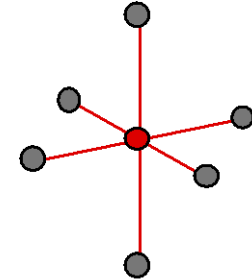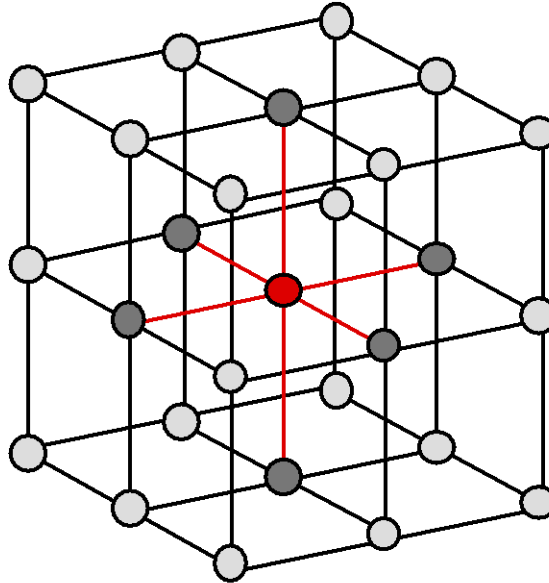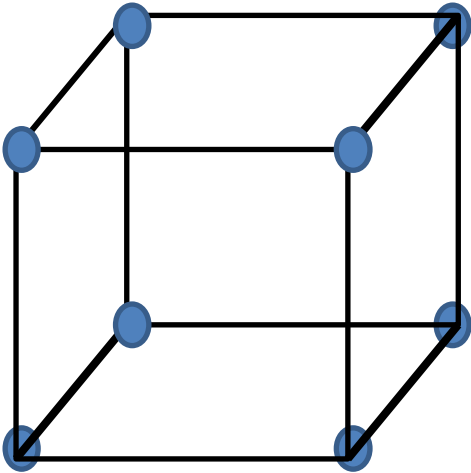
No. of atoms/unit cell	1
Atomic Radius	a/2
Coordination No.	6
APF	0.52

a

=0.5a

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Lattice Planes

- The crystal lattice may be regarded as made up of aggregate of a set of parallel equidistant planes passing through the lattice points, are known as lattice planes.

- The lattice planes can be chosen in many ways as shown in figure.

Lattice planes are generally parallel and equally spaced planes.

Generally, the lattice planes are characterized by miller indices and interplanar distance i.e., (h, k, l) and 'd' respectively.

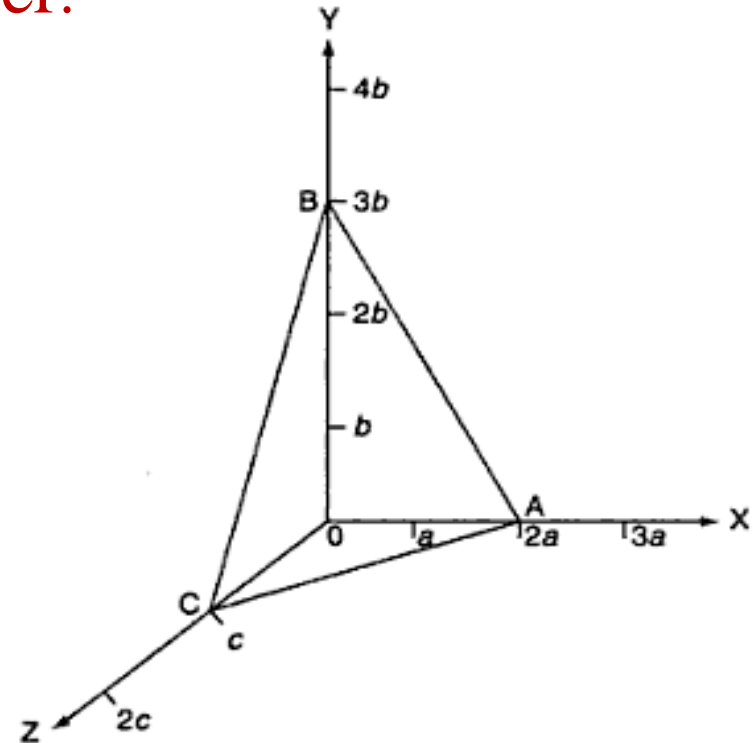Each family of lattice planes have an interplanar spacing of 'd'.
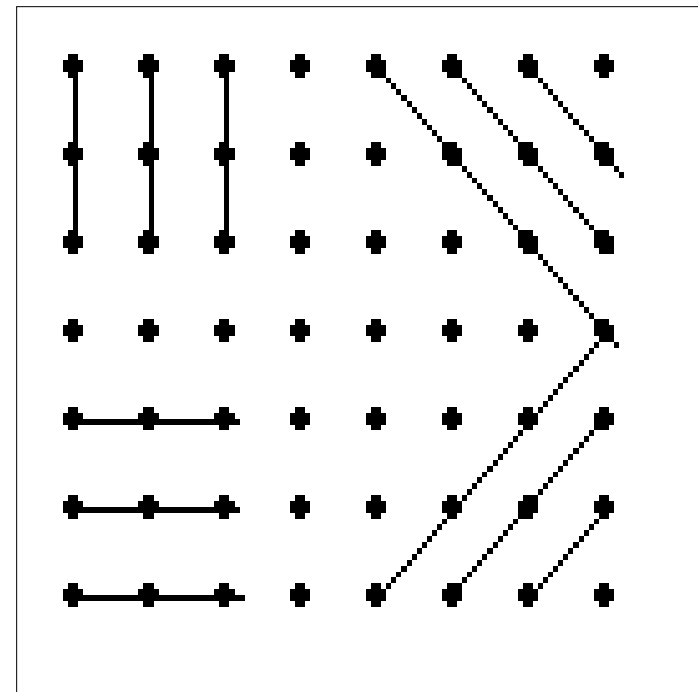
Miller Indices are three numbers used to label lattice planes.

Miller Indices were introduced in 1839 by the British mineralogist William Hallowes Miller.

The Miller index gives a mathematical description to explain lattice directions and lattice planes.

The Miller Indices are the three smallest possible integers which have the same ratios as the reciprocals of the intercepts of the plane concerned on the three axes.
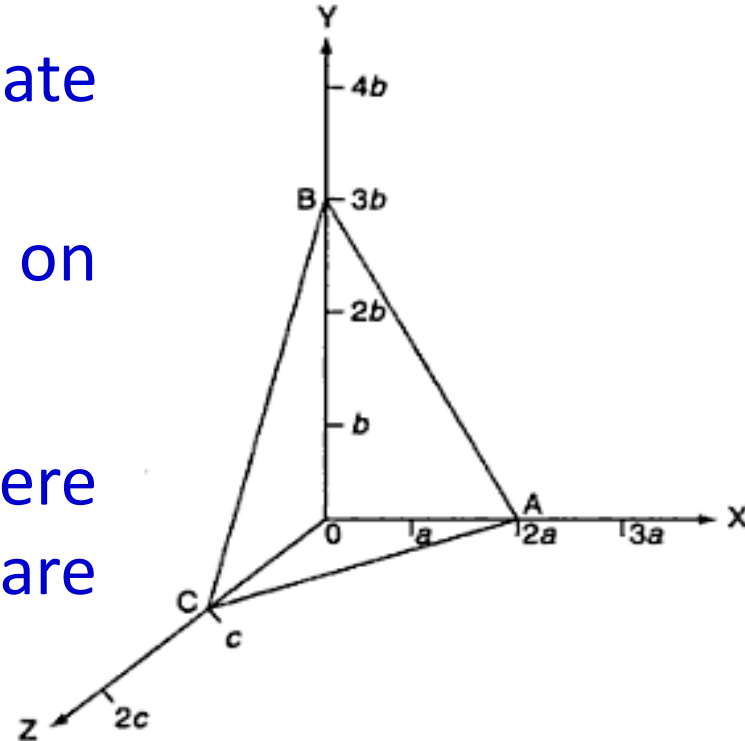
The rules for finding Miller Indices are:

Choose a system of three co-ordinate axes along the crystallographic axes.
First find the intercepts of plane on three axes in terms of primitives.

Let the intercepts are pa, qb, rc where a, b, c are primitives and p, q, r are integers or fractions.

Take the reciprocals of p, q, r i.e.,
Now Miller Indices h, k, l such that

$$h: q: l = \frac{1}{p} : \frac{1}{q} : \frac{1}{r}$$

MILLER INDICES

The below figure shows a plane making intercepts 2a, 3b, c along X, Y, Z directions.

The intercepts in multiples of lattice parameters are 2, 3, 1

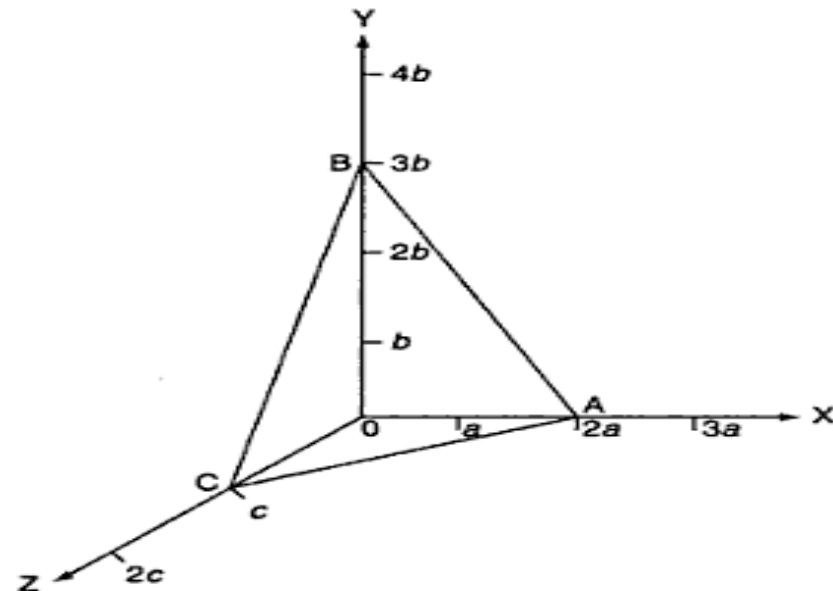The reciprocals of intercepts are $\dfrac{1}{2}, \dfrac{1}{3}, \dfrac{1}{1}$

Clear these fractions [by multiplying with LCM] to smallest integers having the same ratio as the fractions, enclose these integers in brackets.

$$\dfrac{1}{2} \times 6, \quad \dfrac{1}{3} \times 6, \quad \dfrac{1}{1} \times 6$$

$$3 \qquad\quad 2 \qquad\quad 6$$

So the miller indices are (3, 2, 6)

- **Step 1 :** Determine the intercepts of the plane along the axes

- **Step 2 :** Determine the reciprocals of these numbers.

- **Step 3 :** Find the *LCM* and multiply each by this *LCM*

- **Step 4 :** Write it in paranthesis in the form (h k l).
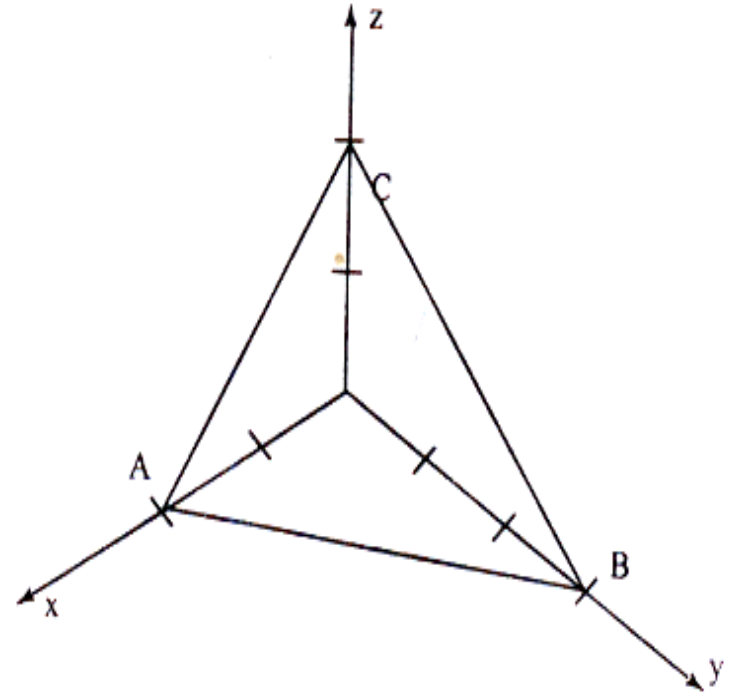
Step 1 : intercepts - **2a,3b and 2c**

Step 2 : reciprocals - **1/2, 1/3 and 1/2**.

Step 3 : LCM is '6'.
Multiply each reciprocal by lcm
we get, **3,2 and 3**.

Step 4 : Miller indices for the plane
ABC is **(3 2 3)**

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Important features of Miller Indices: -

All the parallel and equidistant planes have the same (h, k, l) value. So, Miller Indices (h, k, l) defines a set of parallel planes.

If any plane is parallel to one of the axes, then its intercept may be taken as infinity.

The plane passing through the origin is defined in terms of a parallel plane having non-zero intercepts.

If the Miller Indices of two planes are having the same ratio. For example (844), (422) and (211) are three planes, and then the planes are parallel to each other.

Miller's indices in cubic crystal (Silicon)
(100)   (110)   (111)
(200)   (Ī00)
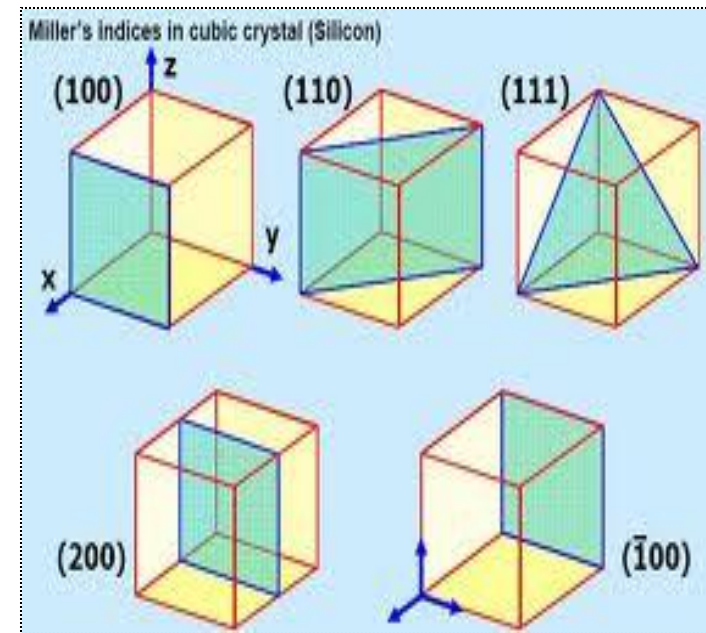
Miller Conventions: -

Generally a notation allows for distinction between a specific direction or plane and families of such.

Use the [ ] notation to identify a specific direction i.e., [1, o, -1].

Use the <> notation to identify a family of equivalent directions i.e., < 110>

Use the ( ) notation to identify a family of equivalent planes i.e., (111).

Use the notation { } to identify a family of equivalent planes i.e., {1, 2, 3}.

Co-ordination number: -

The co-ordination number is defined as the number of equidistant nearest neighbours that an atom has in a given structure.

More closely packed structures have greater co-ordination number.

Simply, co-ordination number of an atom is the number of atoms which it touches.

The co-ordination number of SC, BCC, FCC, HCP and Diamond are 6, 8, 12, 12, and 4 respectively

Lattice Points per cell: -

It represents the no. of atoms per unit cell.

For SC, BCC, FCC, HCP and Diamond, the values are 1, 2, 4, 6, and 8 respectively.

Nearest neighbour distance: -

The distance between the centers of two nearest neighbour atoms is called nearest neighbour distance.
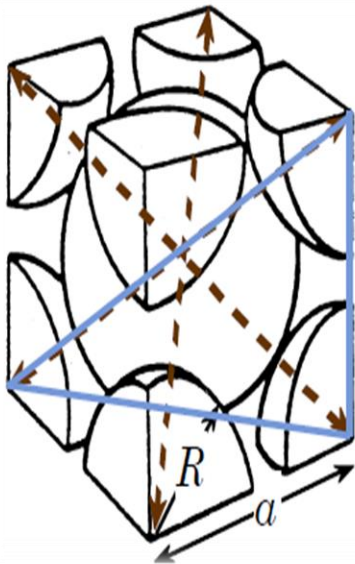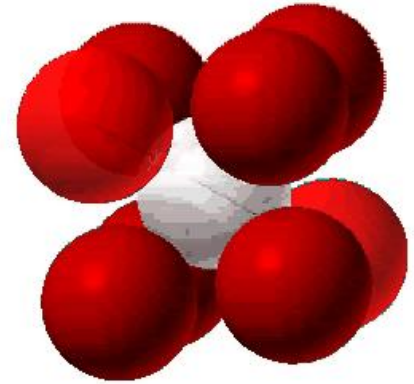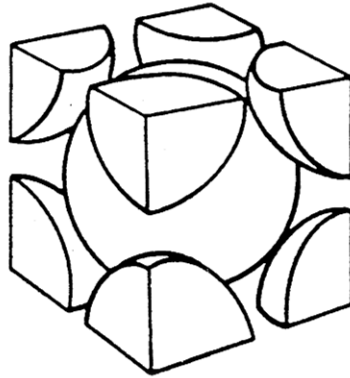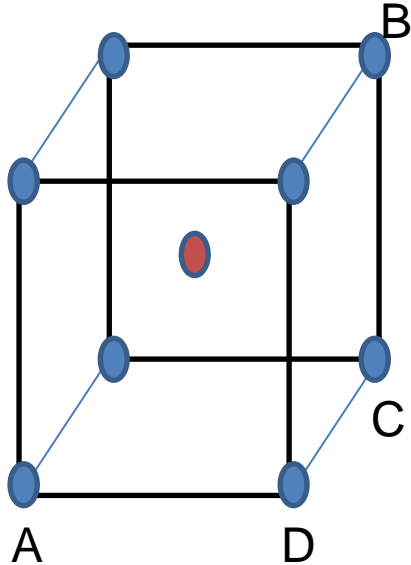
For SC, BCC, FCC, HCP and Diamond the nearest neighbor distance is a, √3a/2, a/√2, a, and √3a/4 respectively.

$$d = \frac{1}{\sqrt{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}}}$$

For cubic system $a = b = c$

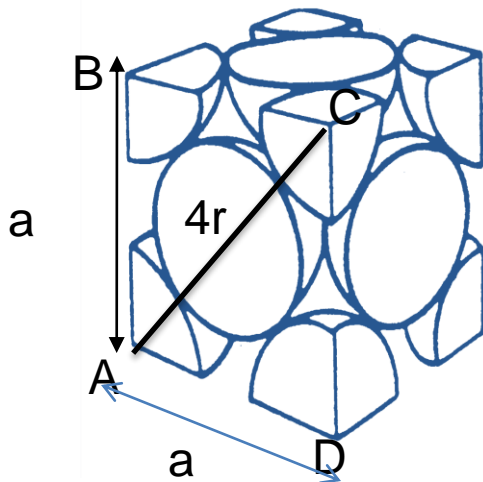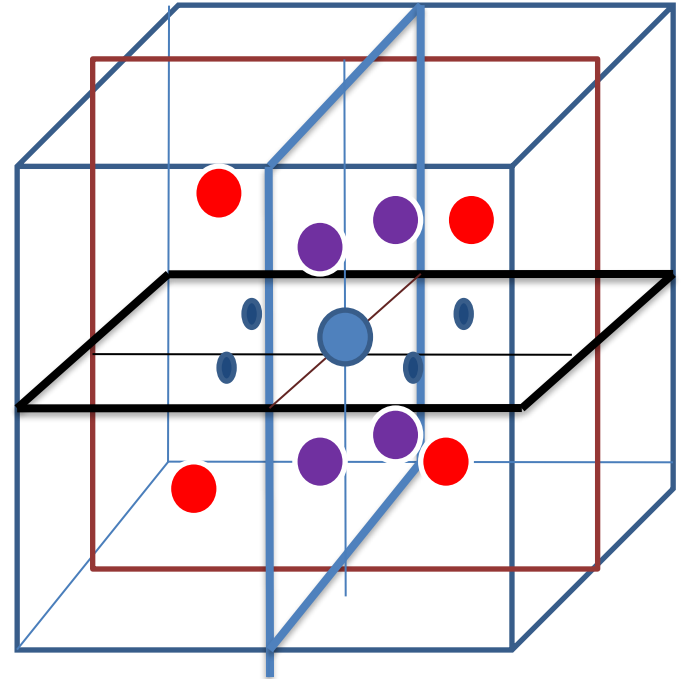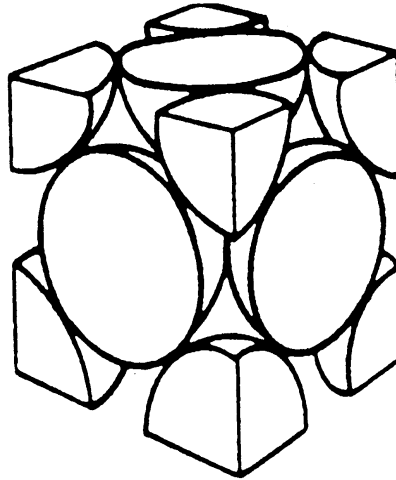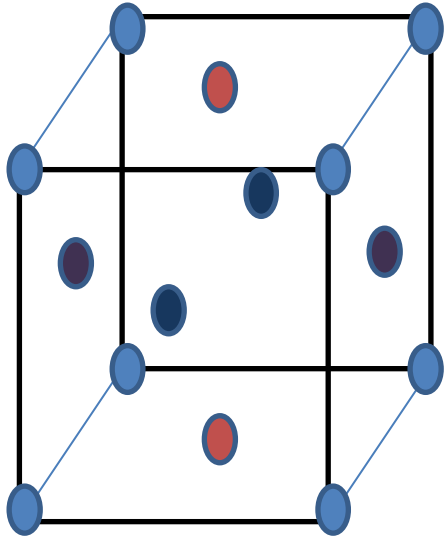$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Body Centered Cubic Structure (BCC)
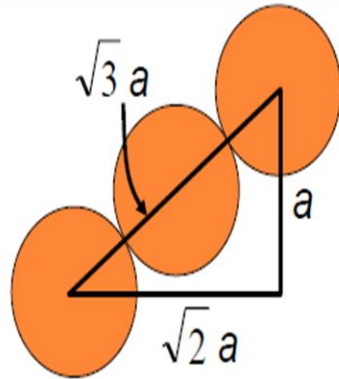
Close-packed directions:
length = $4R = \sqrt{3}\,a$

No. of atoms/unit cell	2
Atomic Radius	$\sqrt{3}\,a/4$
Coordination No.	8
APF	$\sqrt{3}\pi/8$ or 0.68

Face Centered Cubic Structure (FCC)

No. of atoms/unit cell	4
Atomic Radius	√2a/4
Coordination No.	12
APF	$\pi /(3\sqrt{2})$ or 0.74