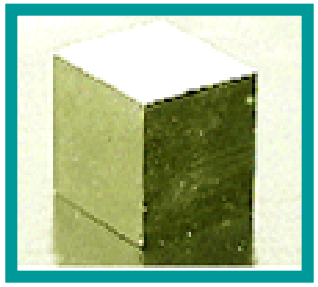
Crystals

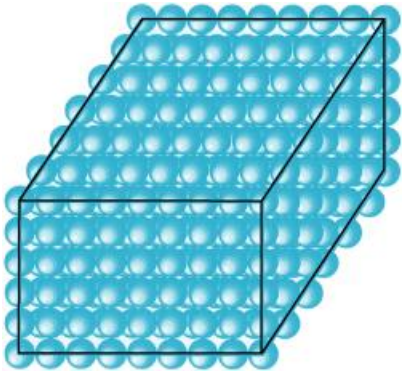
- **Solids consist of atoms or molecules** *executing thermal motion* **about an equilibrium position** *fixed at a point* **in space.**
- **Solids can take the form of crystalline, polycrystalline, or amorphous materials.**
- **Solids (at a given temperature, pressure, and volume) have stronger bonds between molecules and atoms than liquids.**
- **Solids require more energy to** *break the bonds.*

SOLID MATERIALS

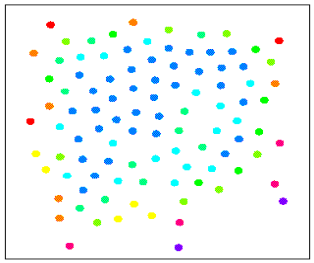
- CRYSTALLINE
  - Single Crystal
- POLYCRYSTALLINE
- AMORPHOUS (Non-crystalline)

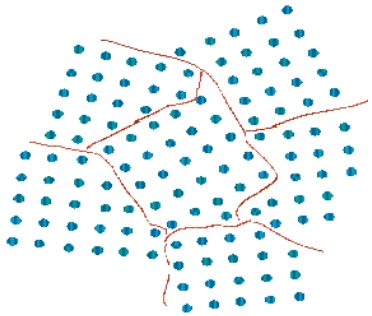


Types of Solids



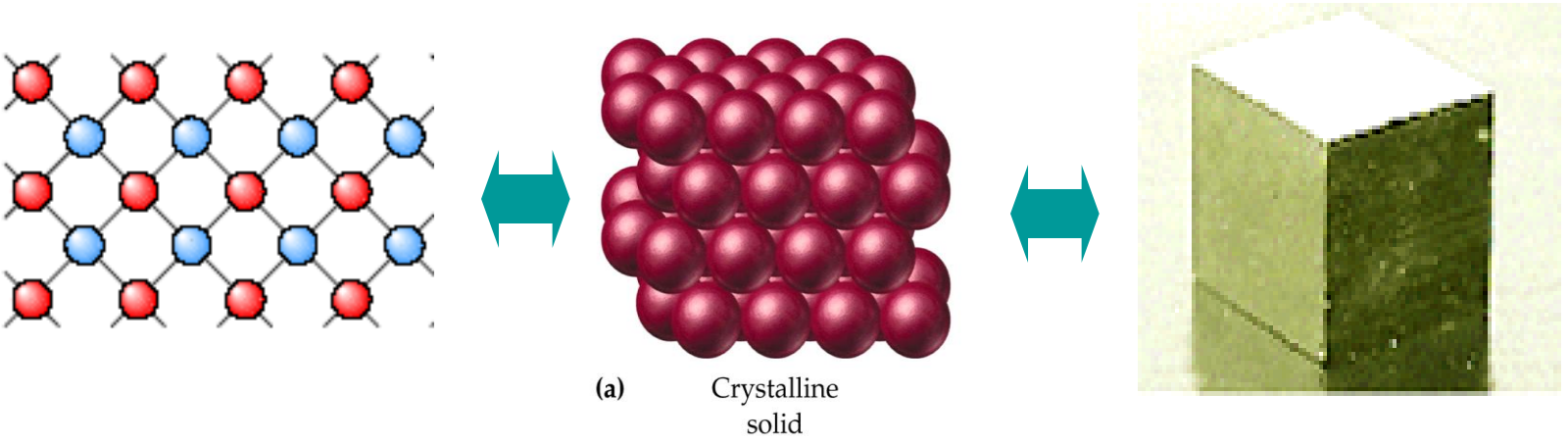
- Single crystal, polycrystalline, and amorphous, are the three general types of solids.
- Each type is characterized by the size of ordered region within the material.
- An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity.





Crystalline Solid

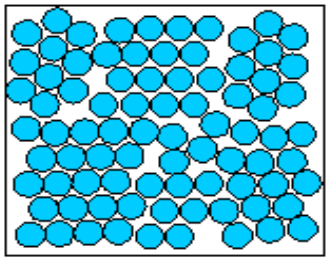
- **Crystalline Solid is the solid form of a substance in which the *atoms or molecules* are arranged in a definite, repeating pattern in three dimension.**
- **Single crystals, ideally have a high degree of order, or regular geometric periodicity, throughout the *entire volume of the material*.**



(a) Crystalline solid

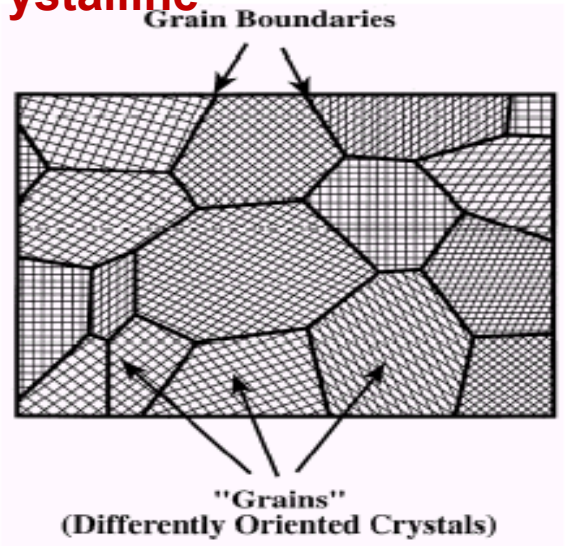
Polycrystalline Solid

- **Polycrystal is a material made up of an aggregate of** *many small single crystals* **(also called crystallites or grains).**
- **Polycrystalline material have a high degree of order over many atomic or molecular dimensions.**
- **These** *ordered regions,* **or single crystal regions, vary in size and orientation wrt one another.**
- **These regions are called as** *grains (domain)* **and are separated from one another by** *grain boundaries.* ***The atomic order can vary from one domain to the next.***
- **The grains are usually** *100 nm - 100 microns in diameter*. **Polycrystals with grains that are <100 nm in diameter are called nanocrystalline**



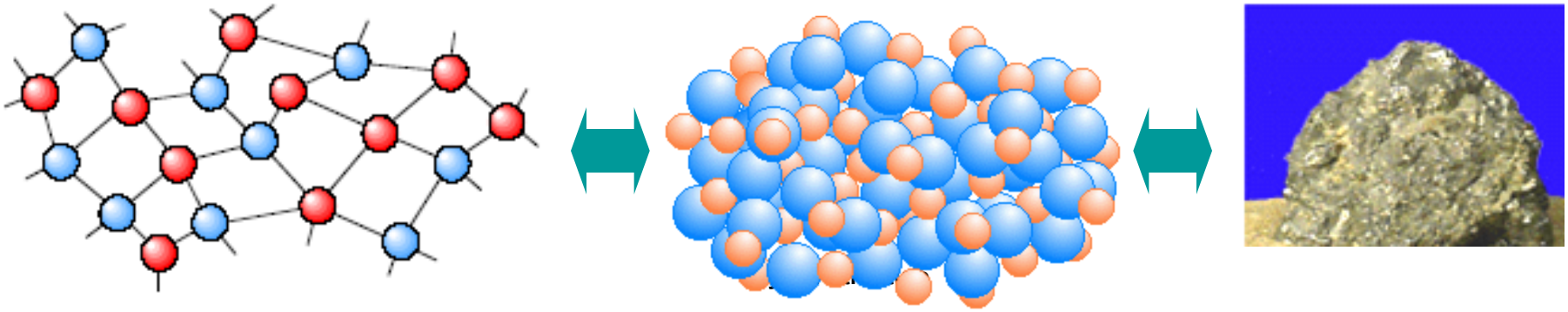
Polycrystalline Pyrite form (Grain)

Crystal Structure



Amorphous Solid

- Amorphous (Non-crystalline) Solid is composed of randomly orientated atoms , ions, or molecules that do not form defined patterns or lattice structures.
- Amorphous materials have order only within a few atomic or molecular dimensions.
- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples to amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicon can be used in solar cells and thin film transistors.



Distinction Between Crystalline and Amorphous Solids

Crystalline Solids

- Have a regular arrangement of particles
- Have different physical properties (thermal conductivity, electrical conductivity, refractive index etc.) in different directions i.e. Anisotropic
- Melting point is very sharp

Amorphous Solids

- Have completely random particle arrangement
- Have physical properties same in all directions, i.e. isotropic
- Do not have sharp melting point e.g. as the temperature of glass is gradually raised, it softens and starts flowing without any sharp change from solid state to liquid state

Why Crystallography

Crystallography is essential for solid state physics

- **Symmetry of a crystal can have a profound influence on its properties.**
- **Any crystal structure should be specified completely, concisely and unambiguously.**
- **Structures should be classified into different types according to the symmetries they possess.**

Why is there Interest in Solid State Physics?

Electronic Properties

- Transistors (the heart of EVERYTHING electronic)

Electron/Photon Interactions

- Laser Diodes, Photodiodes and CCDs

Electron/Phonon Interactions

- Piezoelectric materials

Electron Spin/Charge Interactions

- Spintronics, Quantum Computation

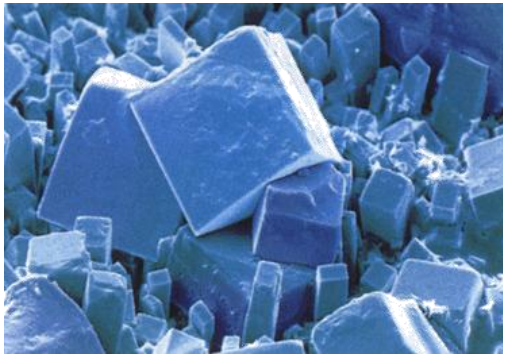
Highly-Correlated Electronic Systems

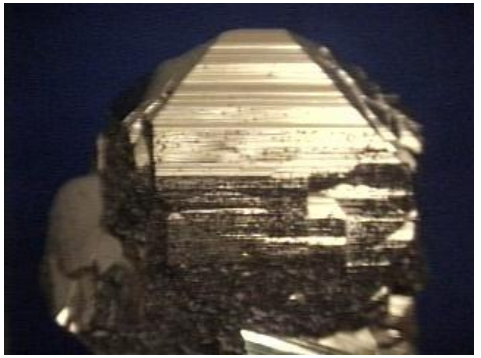
- Superconductors

CRYSTALLOGRAPHY

What is crystallography?

The branch of science that deals with the geometric description of crystals and their internal arrangement.



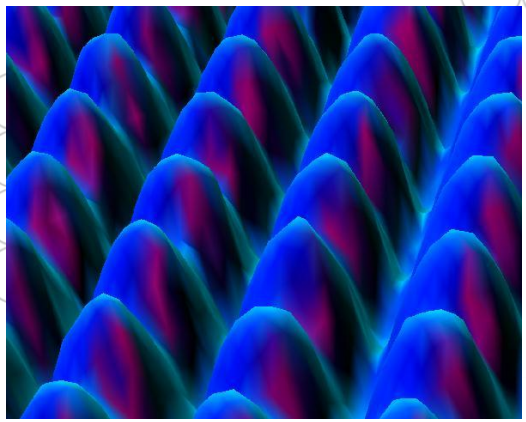


CRYSTAL LATTICE

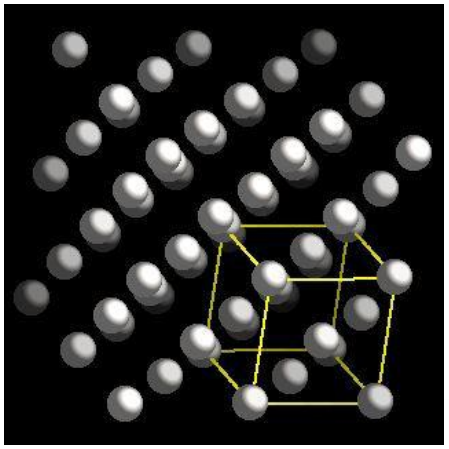
What is crystal (space) lattice?

In crystallography, only the geometrical properties of the crystal are of interest, therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom.

Platinum



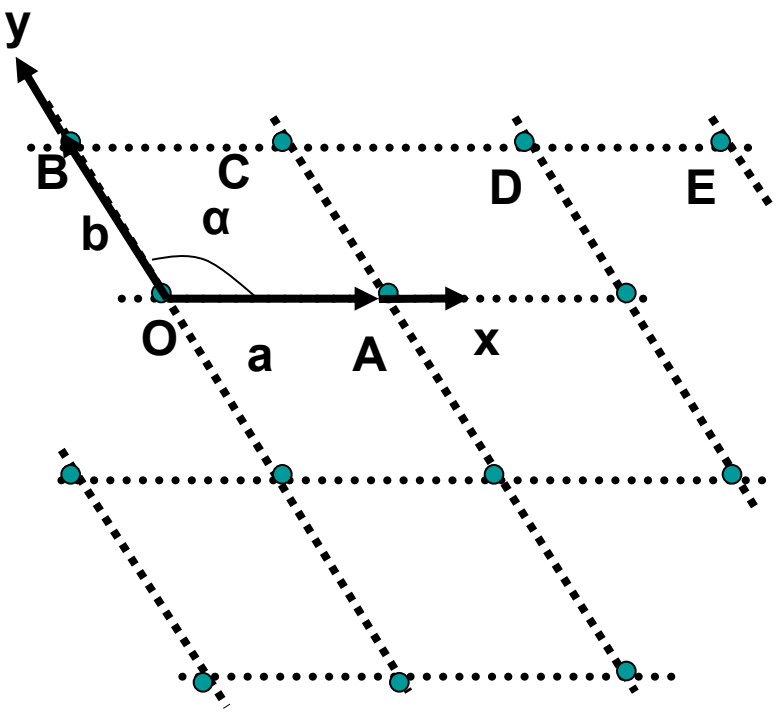
Platinum surface
(scanning tunneling microscope)



Crystal lattice and structure of Platinum

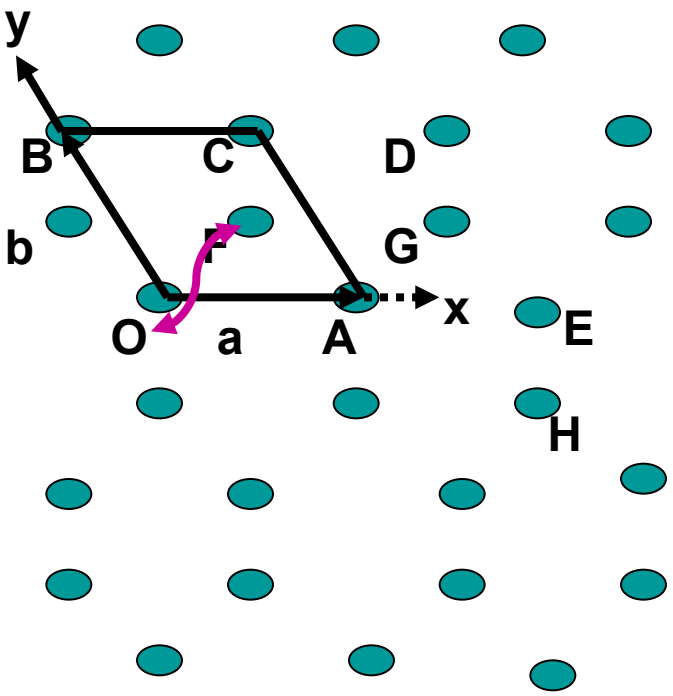
Crystal Lattice

- An infinite array of points in space,
- Each point has identical surroundings to all others.
- Arrays are arranged exactly in a periodic manner.

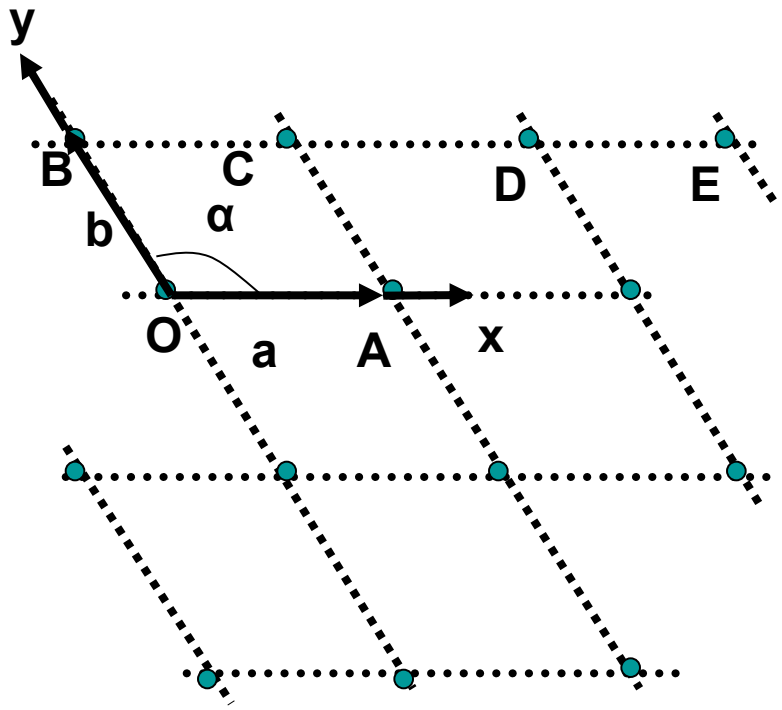


Basis

- A group of atoms which describe crystal structure



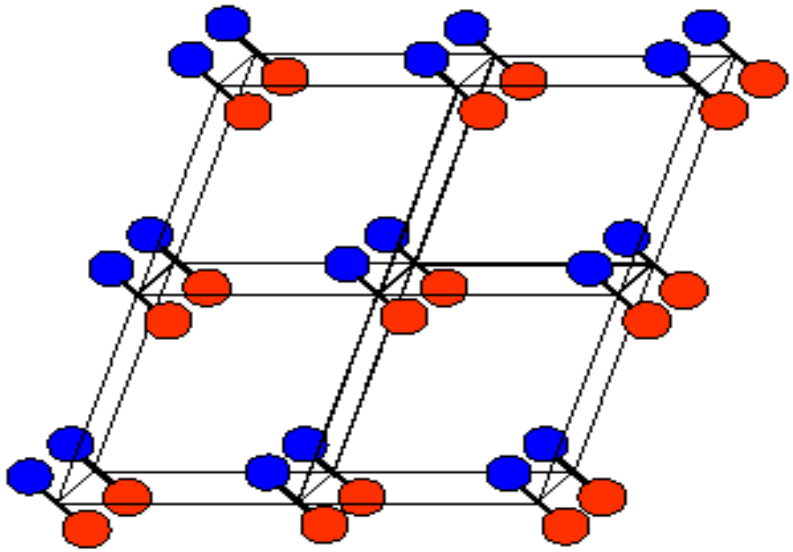
a) Situation of atoms at the corners of regular hexagons



b) Crystal lattice obtained by identifying all the atoms in (a)

Crystal structure

- **Don't mix up atoms with lattice points**
- **Lattice points are infinitesimal points in space**
- **Lattice points do not necessarily lie at the centre of atoms**



Crystal Structure = Crystal Lattice •+ Basis

Bravais Lattices

- Lattice points are located at the corners of the unit cells and, in some cases, at either faces or the center of the unit cell.
- 14 distinct arrangements of lattice points are possible. These unique arrangements of lattice points are known as the Bravais lattices.
- Concept of a lattice is mathematical and does not mention atoms, ions or molecules.
- One or more atoms can be associated with each lattice point

Bravais Lattice

- ✓ An infinite array of discrete points generated by a set of discrete translation operations described by

$$R = n_1 a_1 + n_2 a_2 + n_3 a_3$$

where n_i are integers and $\boldsymbol{a}_i$ are primitive vectors

- ✓ **14** Bravais lattices are possible in 3-dimentional space.
- ✓ These are obtained by combination of lattice system with lattice types
- ✓ Lattice system (crystal system): gives the information regarding the lattice parameters
- ✓ Lattice types: Gives the information about lattice points present in the unit cell.

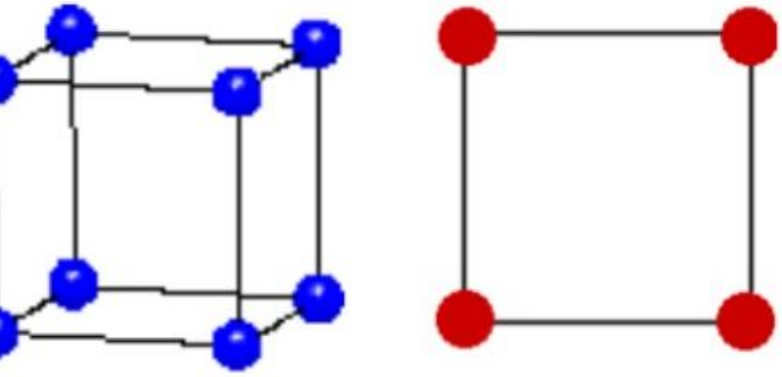
UNIT CELL

Primitive

- Single lattice point per cell
- Smallest area in 2D, or
- Smallest volume in 3D

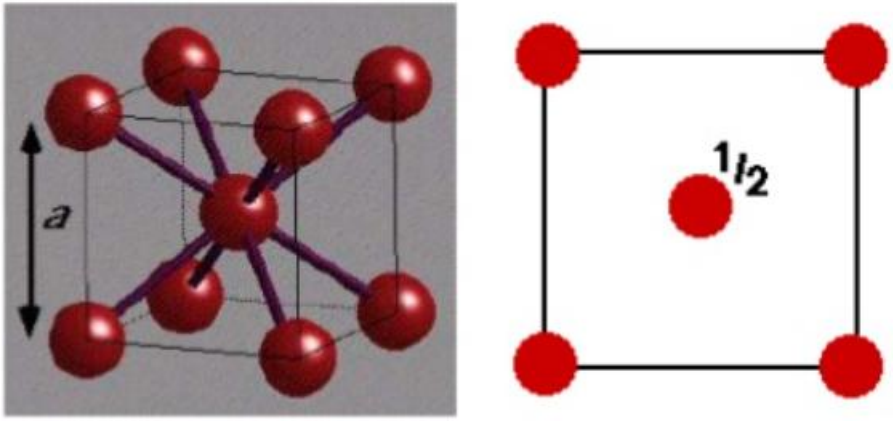
Conventional & Non-primitive

- More than one lattice point per cel
- Integral multibles of the area of primitive cell



Simple cubic(sc)

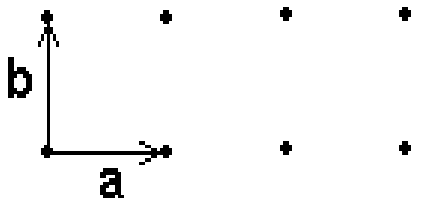
onventional = Primitive cell



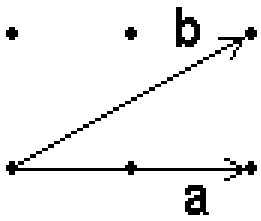
Body centered cubic(bcc)

Conventional ≠ Primitive cell

- **The primitive unit cell must have only one lattice point.**
- **There can be different choices for lattice vectors , but the volumes of these primitive cells are all the same.**



Primitive lattice vectors

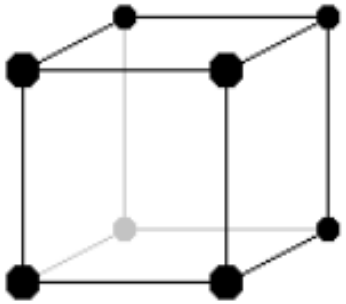


Non-primitive lattice vectors

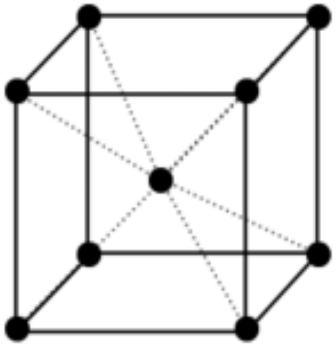
Primitive unit-cell: Consists of one lattice point
Non-primitive cell: More than one lattice points / unit cells
Volume of NP Cell = No of Motifs x Volume of Primitive Unit Cell

Lattice types

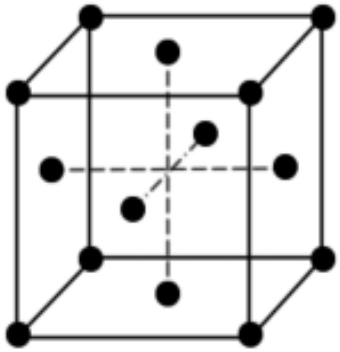
- Primitive (P)



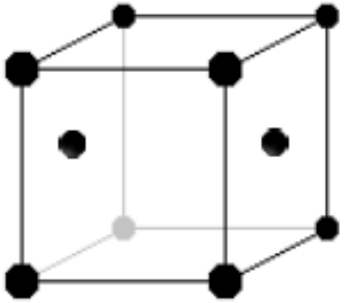
- Body centered (I)



- Face centered (F)



- Base centered (C)



14 Bravais lattices

Crystal system	Primitive (P)	Body centered (I)	Face centered (F)	Base centered (C)
Cubic	✓	✓	✓	×
Tetragonal	✓	✓	×	×
Orthorhombic	✓	✓	✓	✓
Monoclinic	✓	×	×	✓
Triclinic	✓	×	×	×
Rhombohedral	✓	×	×	×
Hexagonal	✓	×	×	×

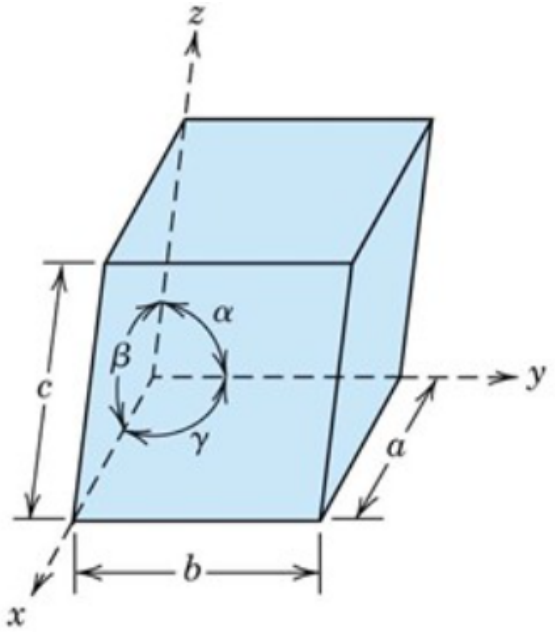
Crystallographic axes

- ✓ Axes resulted by the intersection of the three non-coplanar faces of the unit cell.
- ✓ The angles between these faces or crystallographic axes are known as interfacial or inter-axial angles.

Lattice parameters

- The lattice parameters include
  - Dimensions of the sides of the unit cell
  - Angles between the sides
  - The length is often given in nanometers (nm) or Angstrom (Å) units, where:

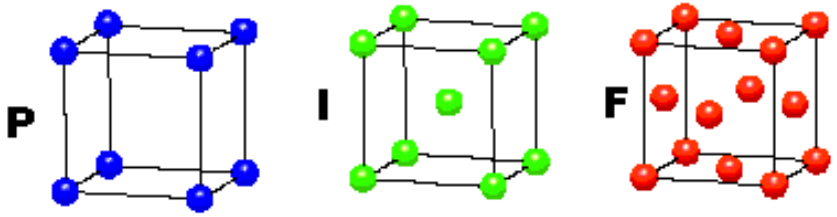
1 angstrom (Å) = 0.1 nm = 10^{-10} m = 10^{-8} cm



CUBIC

$a = b = c$

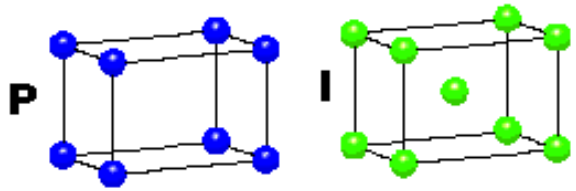
$\alpha = \beta = \gamma = 90°$



TETRAGONAL

$a = b \neq c$

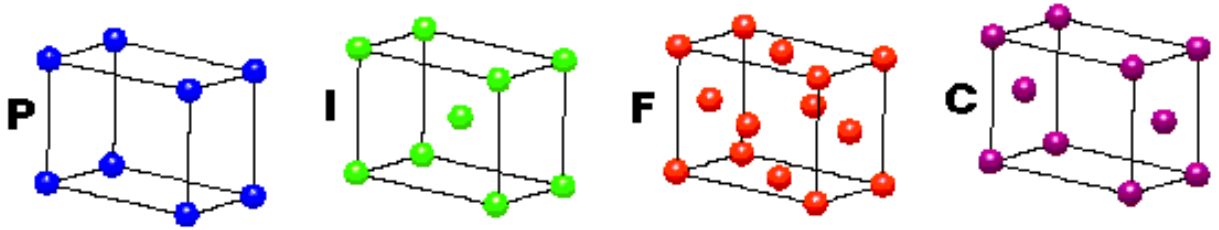
$\alpha = \beta = \gamma = 90°$



ORTHORHOMBIC

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

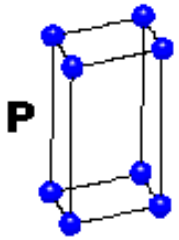


HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

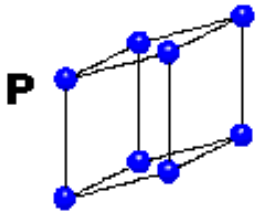
$\gamma = 120°$



TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

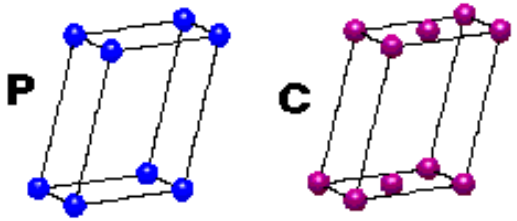


MONOCLINIC

$a \neq b \neq c$

$\alpha = \gamma = 90°$

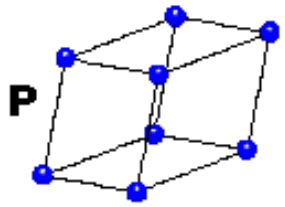
$\beta \neq 120°$



TRICLINIC

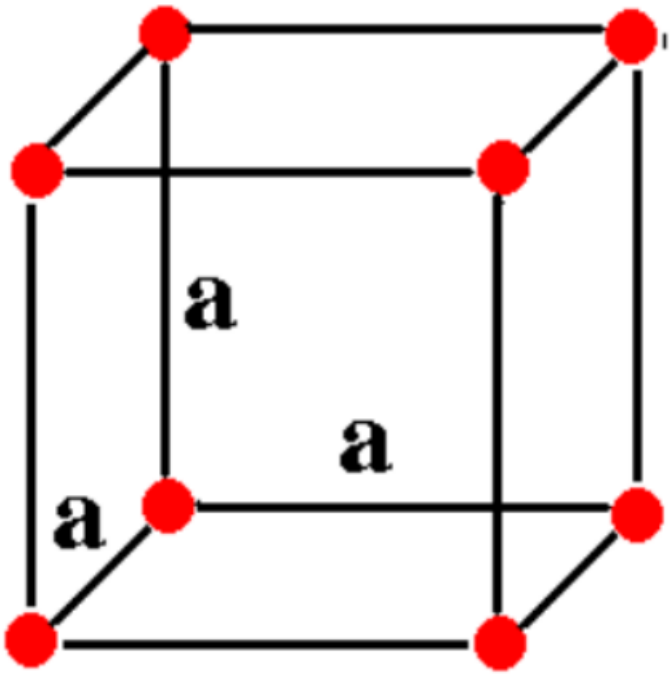
$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$



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

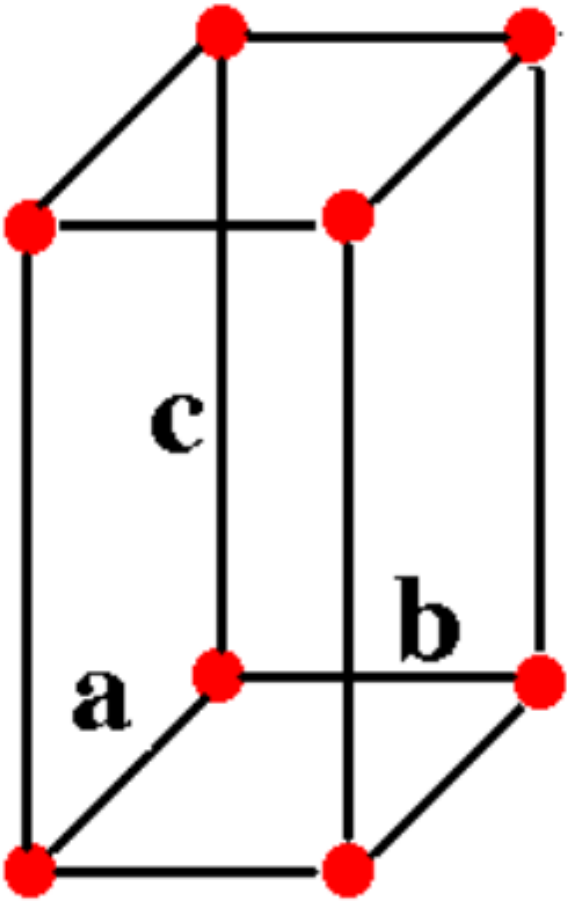
1. Cubic Crystal System



$a = b = c$

$\alpha = \beta = \gamma = 90°$

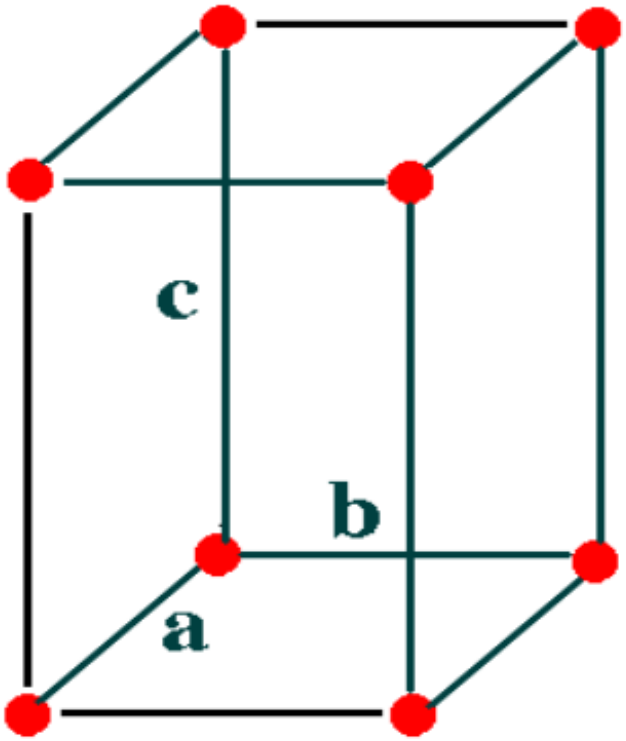
2.Tetragonal system



$a = b \neq c$

$\alpha = \beta = \gamma = 90°$

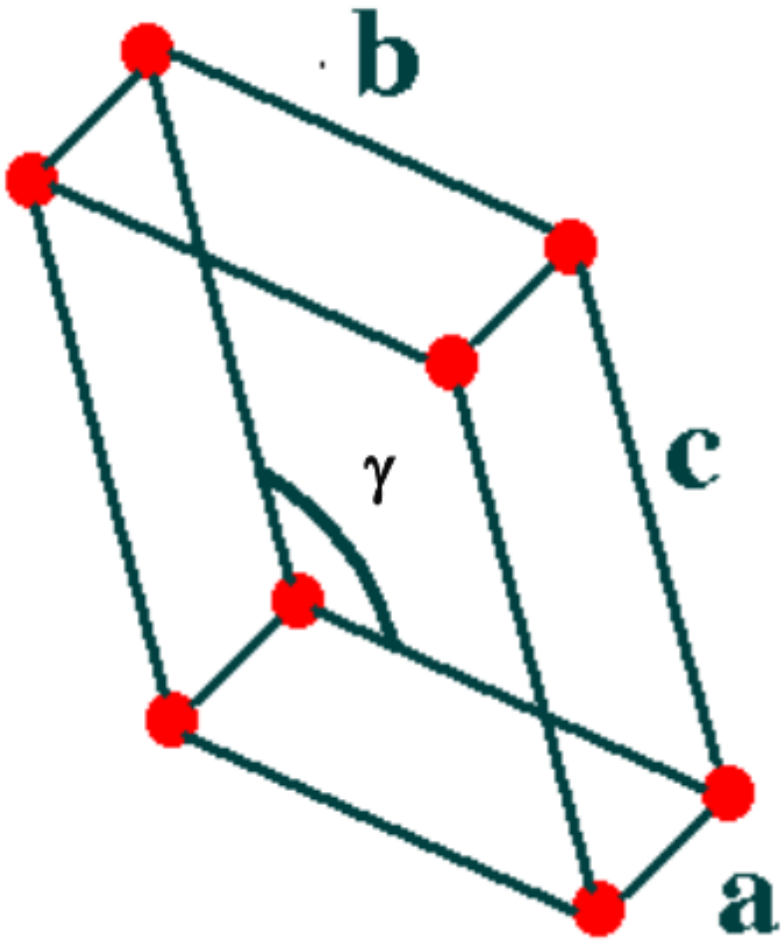
3. Orthorhombic system



$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

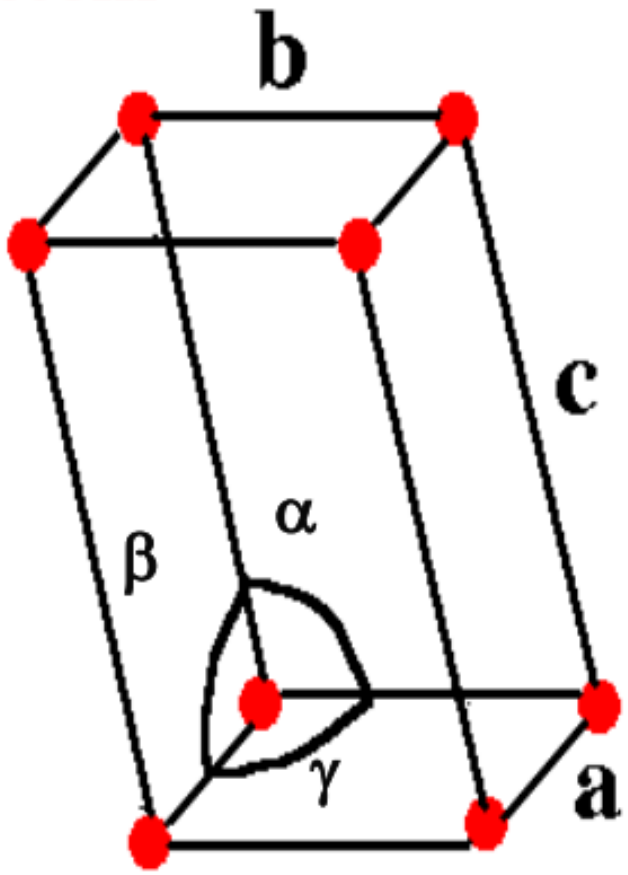
4. Monoclinic system



$a \neq b \neq c$

$\alpha = \gamma = 90°, \beta \neq 90°$

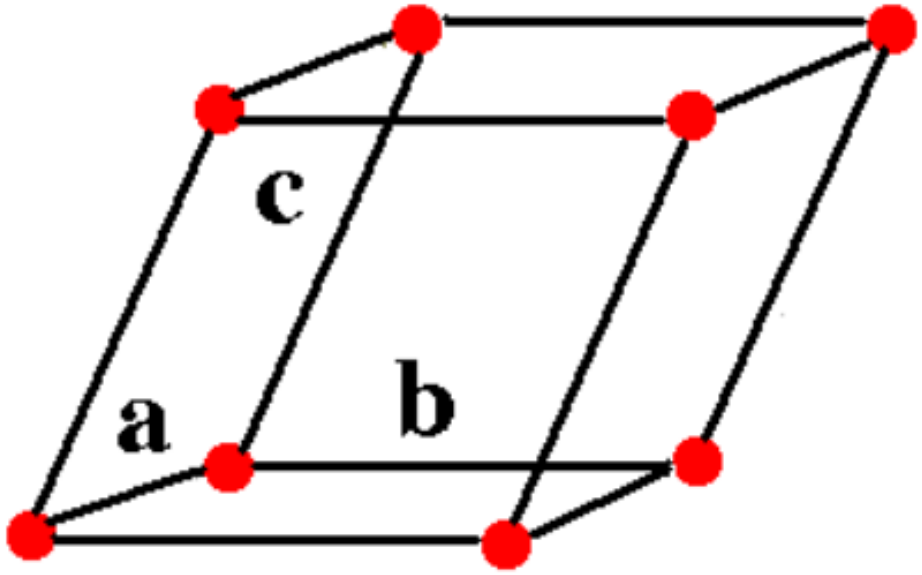
5. Triclinic system



$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$

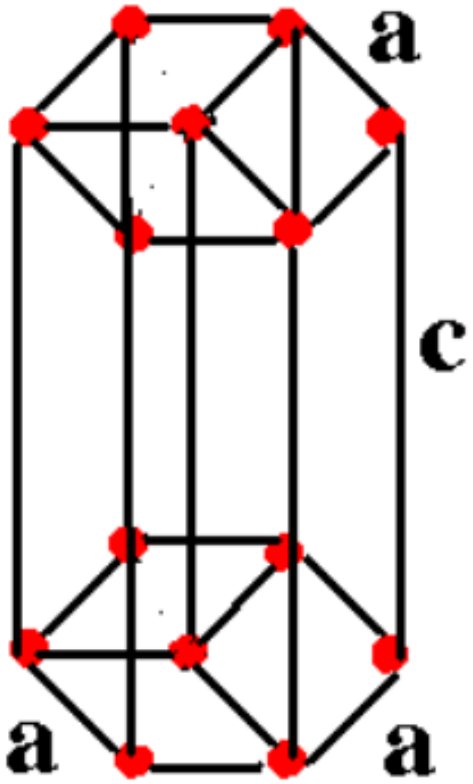
6. Rhombohedral (Trigonal) system



$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

7. Hexagonal system

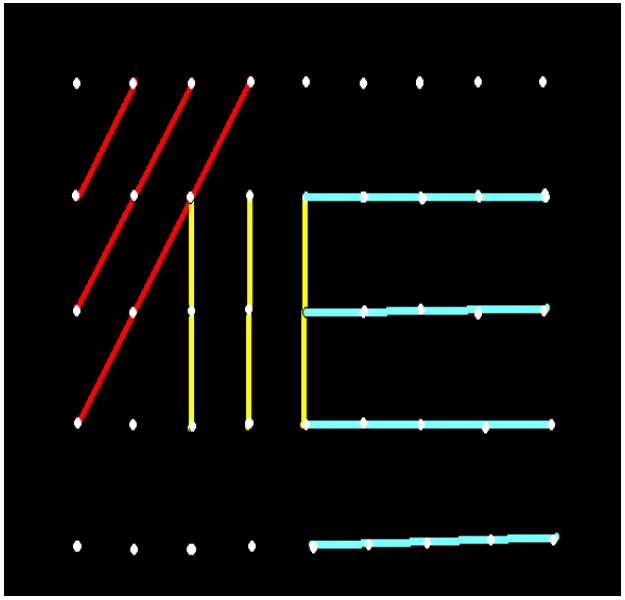


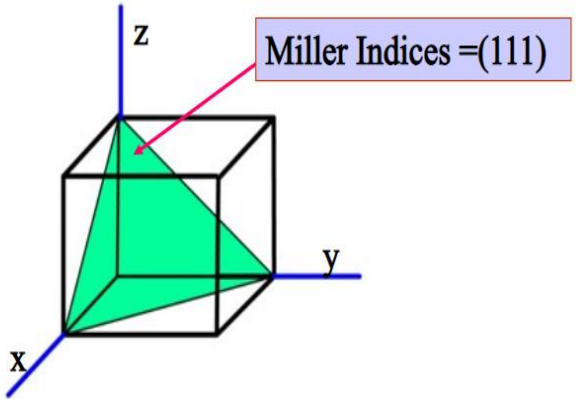
$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$

Miller Indices and lattice planes

The crystal lattice may be regarded as made up of an aggregate of set of parallel equidistant planes passing through the lattice points , which are known as " lattice planes"

Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice & are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.



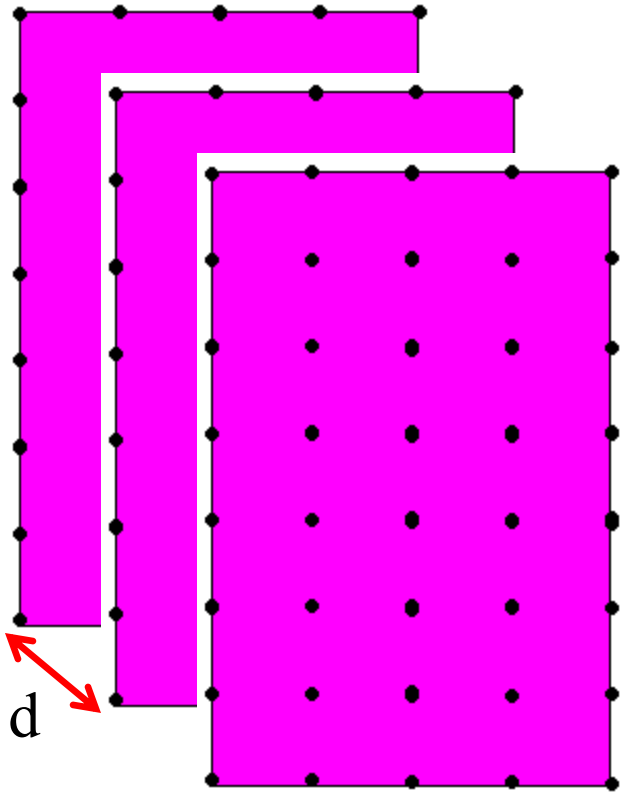


MILLER INDICES

- set of three possible integers represented as (h k l)
- reciprocals of the intercepts made by the plane on the three crystallographic axes
- designate plane in the crystal.

IMPORTANT FEATURES OF MILLER INDICES

- a plane parallel to the axes has an intercept of infinity (∞).
- a plane cuts an axis on the negative side of the origin, is represented by a bar, as ($\bar{1}$ 0 0).
- a plane passing through the origin have non zero intercepts
- All equally spaced parallel planes have same Miller indices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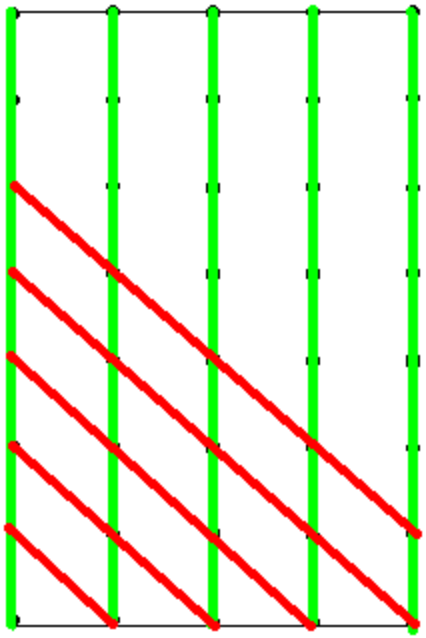
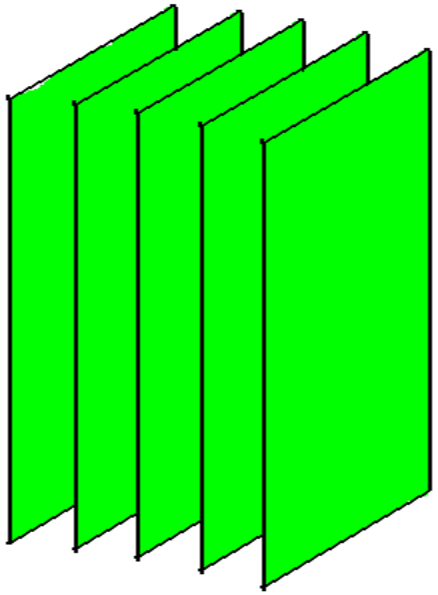
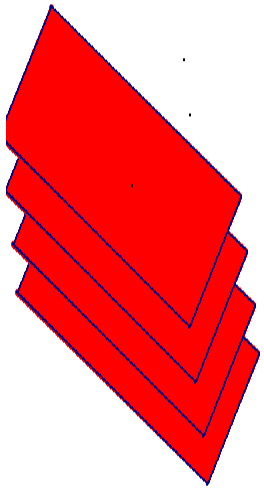






MILLER INDICES

Miller devised a method to represent a crystal plane or direction by using a set of three numbers written within the parentheses ( )

Steps to find Miller indices:

1.Find the intercepts along x,y and z axes of the plane

2.The coefficients of the intercepts are noted separately

3.Inverse is to be taken

4.The fraction are multiplied by a suitable number so that all the fractions become integers

5. Write the integers within parentheses

for example

ABC makes intercepts 2a, 3b and 2c

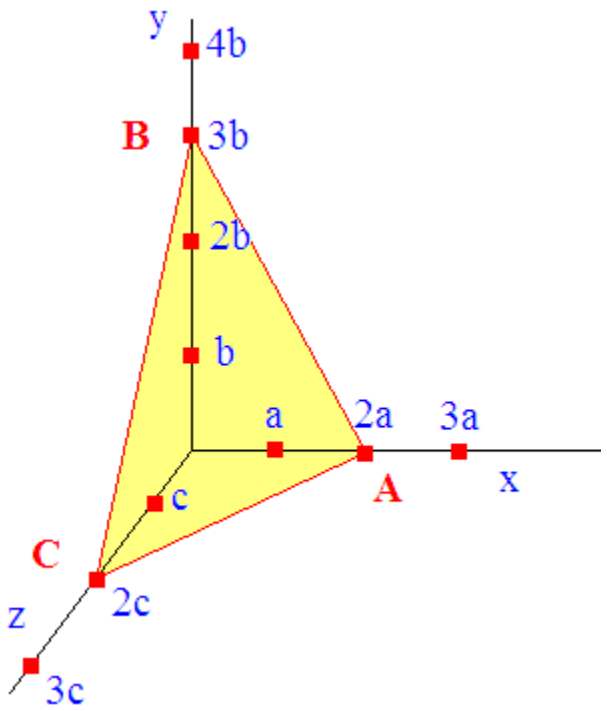
The coefficients are 2,3 ad 2

½ , 1/3 , ½

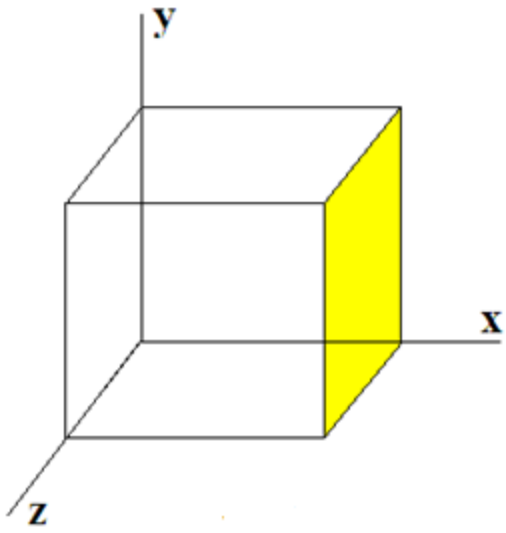
Multiply (LCM) by 6

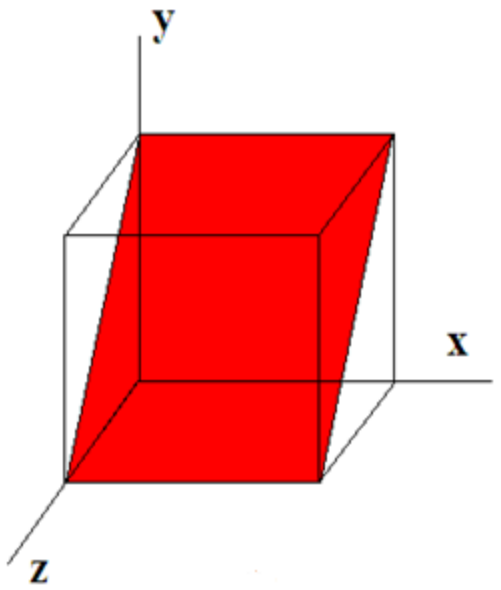
The integers are 3,2,3

Miller indices is (323)



- In a crystal lattice plane cuts intercepts 2a,3b and 6c along the three axes where a, b and c are the primitive vectors of the unit cell. determine the miller indices of the given plane
- obtain the miller indices of a plane which intercepts at a,b/2,3c is cubic unit cell. draw a neat diagram showing the plane


y
x
z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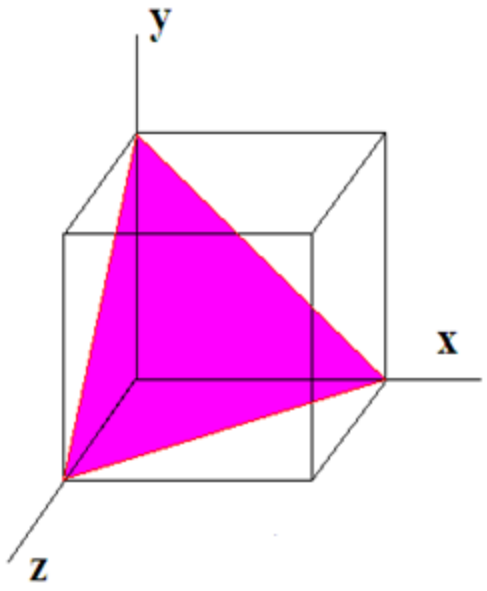
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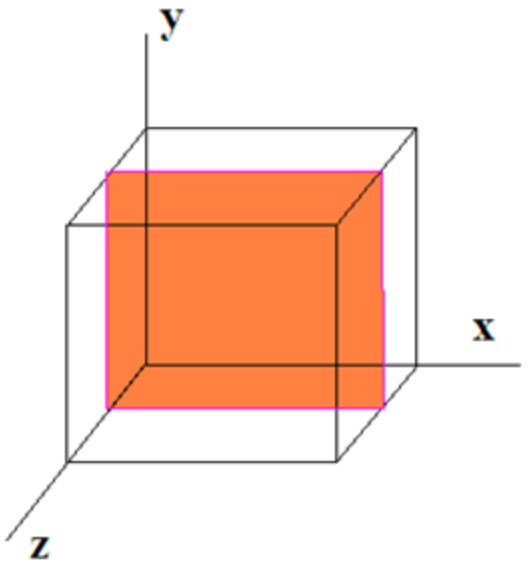
y
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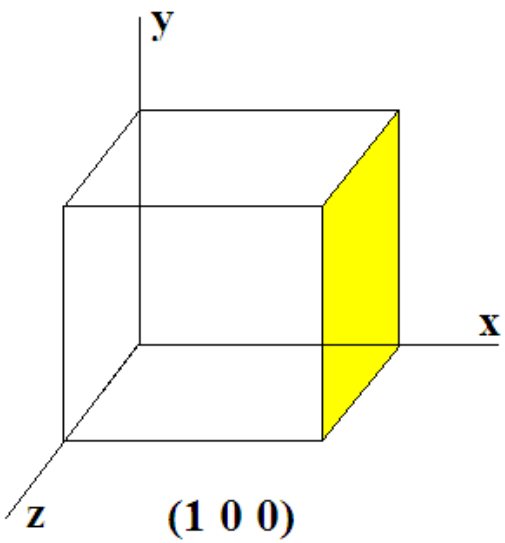
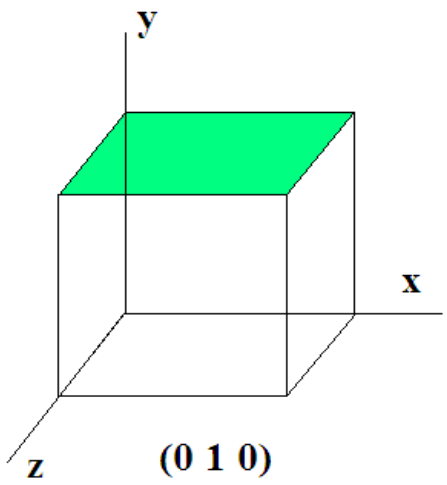
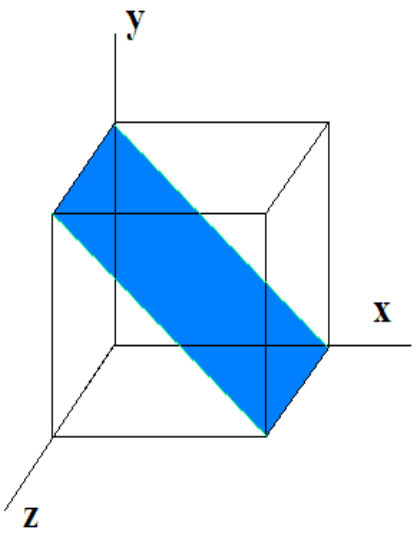


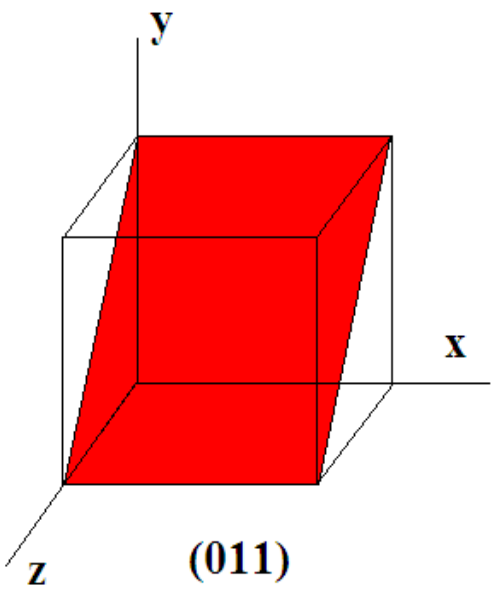
(1 0 0)



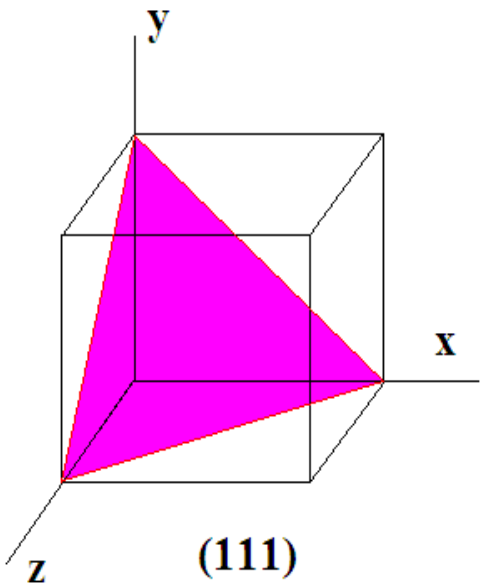
(0 1 0)



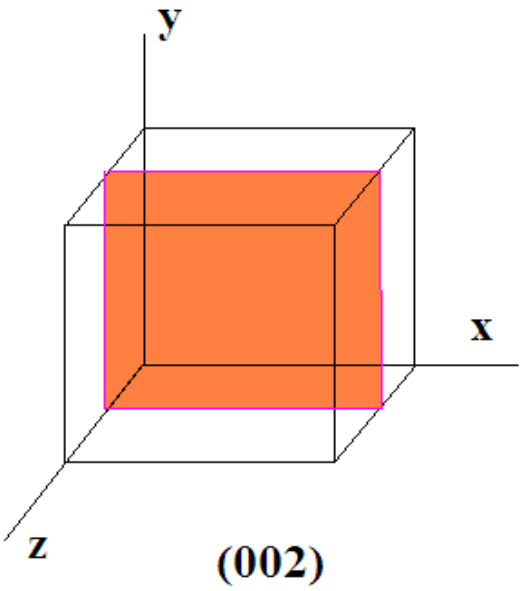
(110)



(011)

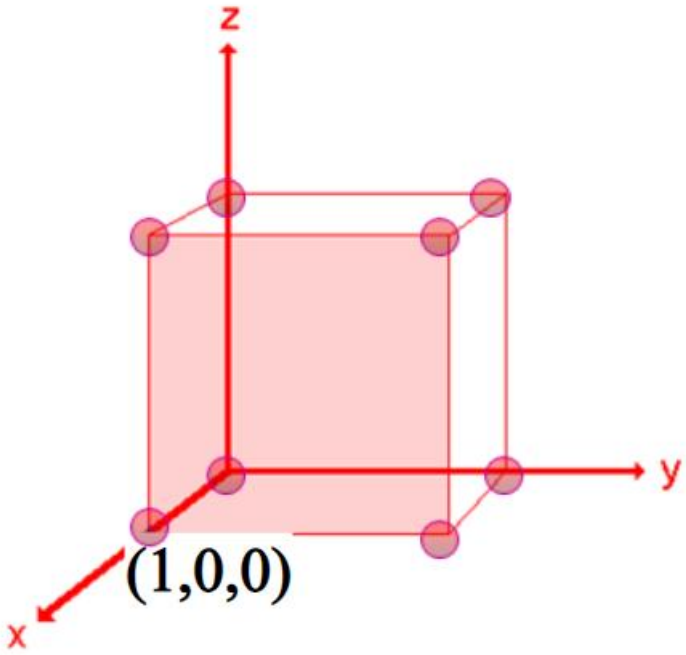


(111)



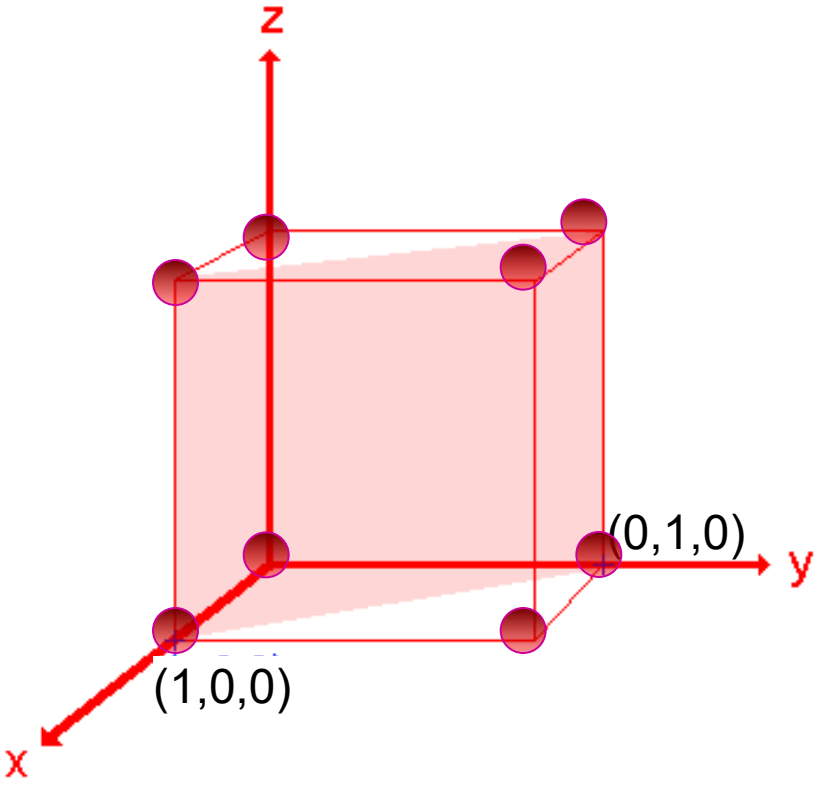
(002)

Example-1



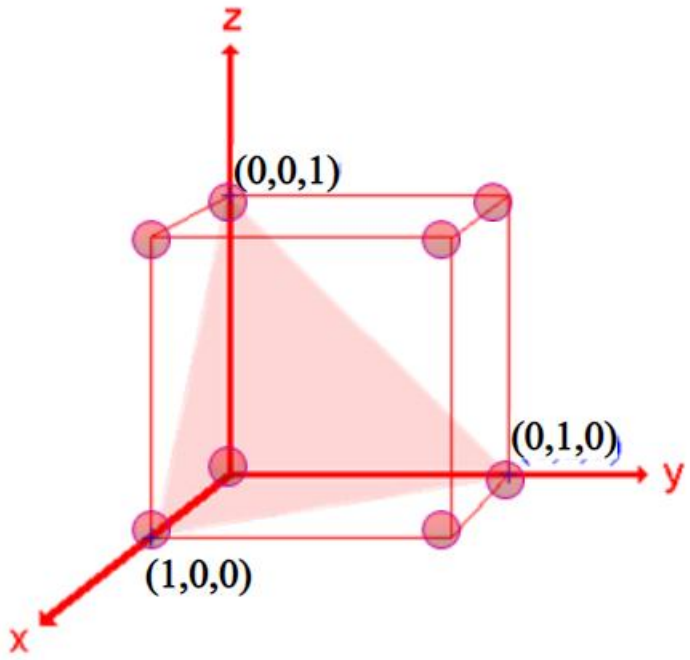
Axis	X	Y	Z
Intercept points	1	∞	∞
Reciprocals	1/1	1/ ∞	1/ ∞
Smallest Ratio	1	0	0
Miller İndices (100)			

Example-2



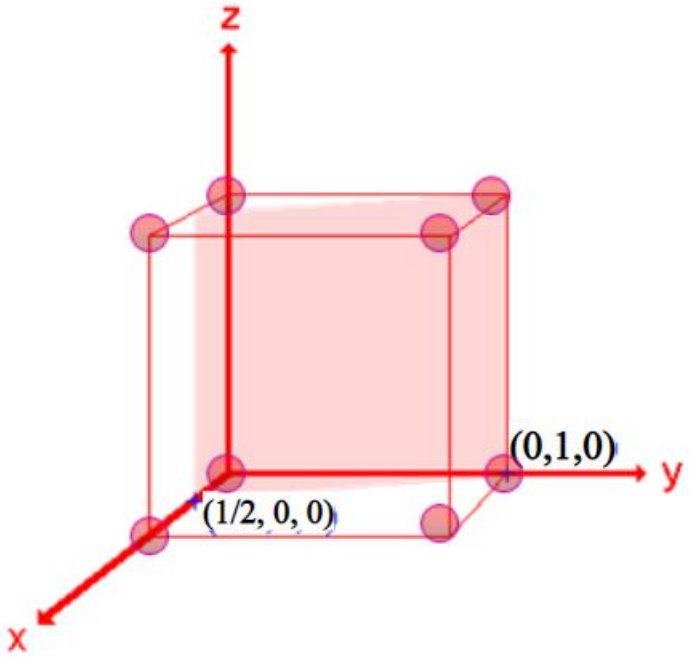
Axis	X	Y	Z
Intercept points	1	1	∞
Reciprocals	1/1	1/ 1	1/ ∞
Smallest Ratio	1	1	0
Miller İndices			**(110)**

Example-3



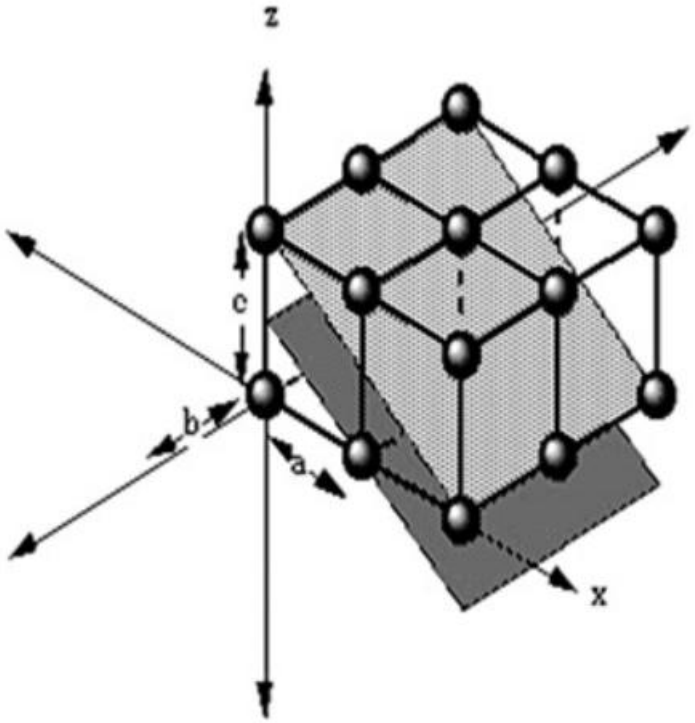
Axis	x	y	z
Intercept points	1	1	1
Reciprocals	1/1	1/ 1	1/ 1
Smallest Ratio	1	1	1
Miller İndices (111)			

Example-4



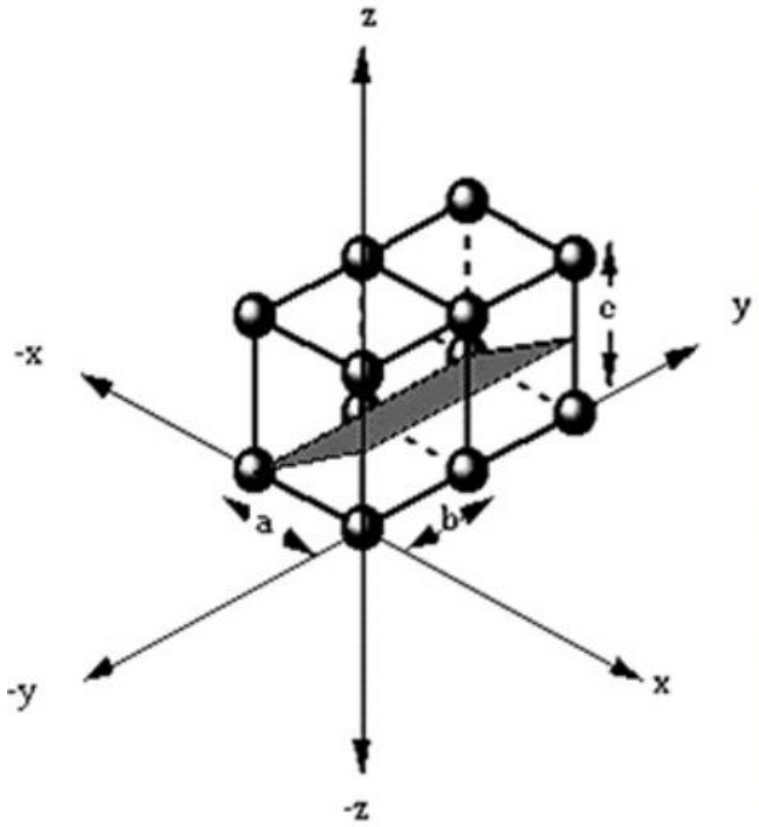
Axis	X	Y	Z
Intercept points	1/2	1	∞
Reciprocals	1/(½)	1/ 1	1/ ∞
Smallest Ratio	2	1	0
Miller İndices (210)			

Example-5



Axis	a	b	c
Intercept points	1	∞	½
Reciprocals	1/1	1/ ∞	1/(½)
Smallest Ratio	1	0	2
Miller İndices (102)			

Example-6



Axis	a	b	c
Intercept points	-1	∞	½
Reciprocals	1/-1	1/ ∞	1/(½)
Smallest Ratio	-1	0	2
Miller İndices			(1$\bar{0}$2)

Symbol	Meaning
(hkl)	A particular crystal plane
{hkl}	Family of equivalent planes
[uvw]	A particular crystallographic direction
<uvw>	Family of equivalent directions

- Planes that are crystallographically equivalent have the same atomic packing.
- Also, in cubic systems only, planes having the same indices, regardless of order and sign, are equivalent.
- Ex: {111}

$$= (111), (\bar{1}11), (1\bar{1}1), (11\bar{1}), (\bar{1}\bar{1}\bar{1}), (\bar{1}\bar{1}1), (\bar{1}1\bar{1}), (1\bar{1}\bar{1})$$

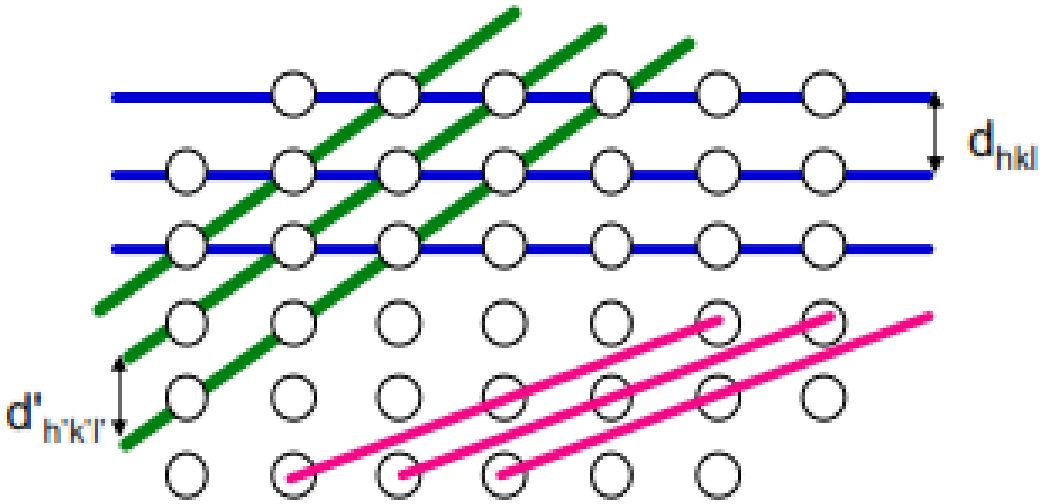
Ex: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$

Inter-Planar Spacing, d_{hkl}, and Miller Indices

The inter-planar spacing ($\mathbf{d_{hkl}}$) between crystallographic planes belonging to the same family (h,k,l) is denoted ($\mathbf{d_{hkl}}$)

Distances between planes defined by the same set of Miller indices are unique for each material

2D



Interplanar distance (or) ‘d’ spacing in cubic lattice

Definition: The distance between any two successive planes is called d spacing or interplanar distance.

Let us consider a cubic lattice of length ‘a’ with two planes ABC and A′ B′ C′. Let d1 and d2 be the distance between the origin and the first (ABC) and second plane (A′ B′ C′). Let d be the distance between the two planes ABC and A′ B′ C′

Let us assume that the second plane lies in the origin. So we can find the distance between the origin and first plane instead of finding the distance between the two planes.

The plane AB makes the intercepts OA,OB and OC on X,Y and Z axis respectively.

$OA:OB:OC = \frac{1}{h} : \frac{1}{k} : \frac{1}{l}$

Multiply by lattice constant “a”

$OA=\frac{a}{h}$ $OB=\frac{a}{k}$ $OC=\frac{a}{l}$

Interplanar Spacing

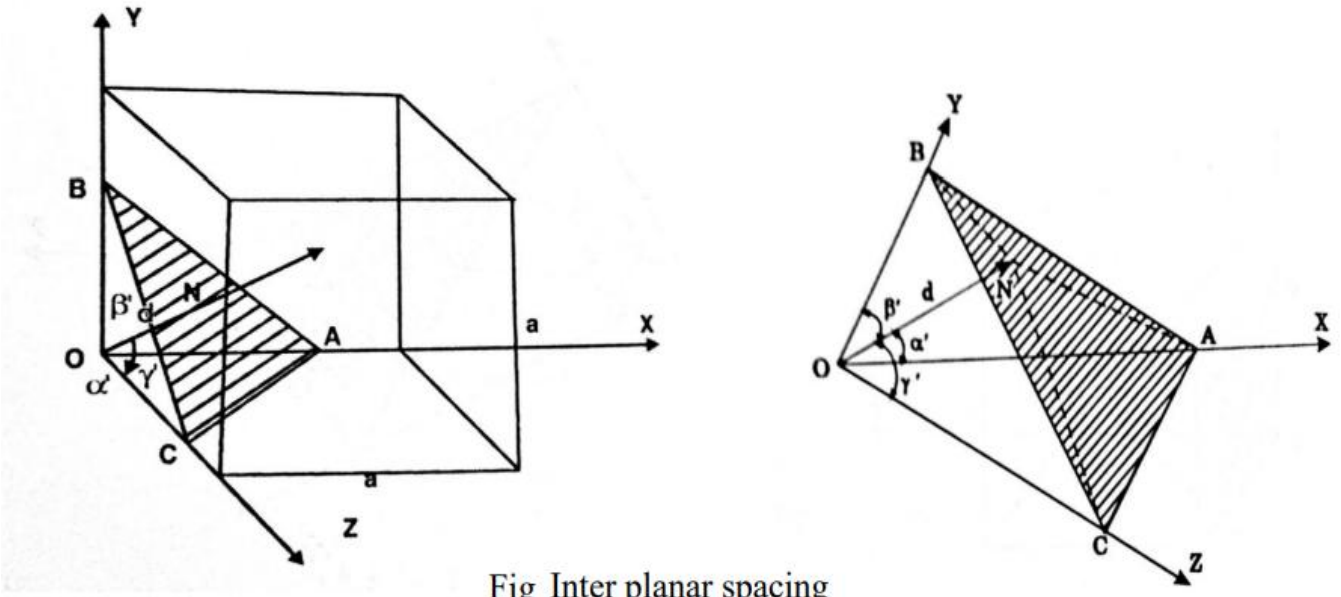


Fig Inter planar spacing

From the figure

$$\cos\alpha' = \frac{ON}{OA} = \frac{d}{\frac{a}{h}} = \frac{dh}{a}$$

$$\cos\beta' = \frac{ON}{OB} = \frac{d}{\frac{a}{k}} = \frac{dk}{a}$$

$$\cos\gamma' = \frac{ON}{OC} = \frac{d}{\frac{a}{l}} = \frac{dl}{a}$$

According to the law of conservation of energy

$$\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$$

$$\left(\frac{dh}{a}\right)^2 + \left(\frac{dK}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$$

$$\frac{d^2h^2}{a^2} + \frac{d^2k^2}{a^2} + \frac{d^2l^2}{a^2} = 1$$

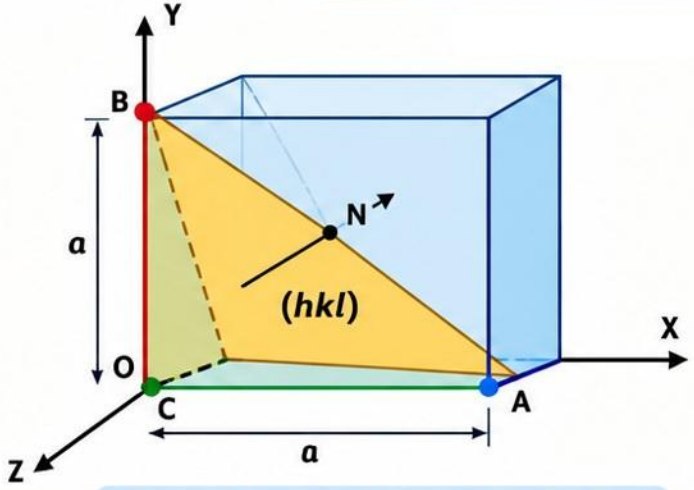
$$\frac{d^2}{a^2}(h^2 + k^2 + l^2) = 1$$

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

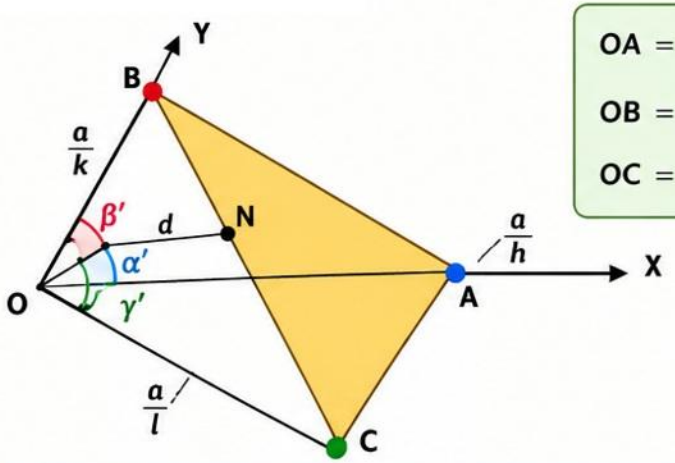
$$d = \frac{a}{\sqrt{(h^2+k^2+l^2)}}$$

The above equation gives the expression for interplanar spacing d.

Interplanar Spacing (d) in a Cubic Crystal



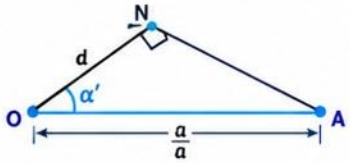
3D view of a cubic lattice with plane (hkl)



Triangle OAB, OBC and OAC (separate triangle view)

$$OA = \frac{a}{h} \text{ (on X-axis)}$$
$$OB = \frac{a}{k} \text{ (on Y-axis)}$$
$$OC = \frac{a}{l} \text{ (on Z-axis)}$$

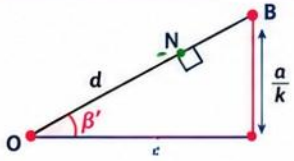
1. Triangle O–N–A (X-direction)



$$\cos\alpha' = \frac{ON}{OA} = \frac{d}{\frac{a}{h}}$$

$$\cos\alpha' = \frac{dh}{a}$$

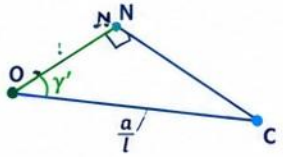
2. Triangle O–N–B (Y-direction)



$$\cos\beta' = \frac{ON}{OB} = \frac{d}{\frac{a}{k}}$$

$$\cos\beta' = \frac{dk}{a}$$

3. Triangle O–N–C (Z-direction)



$$\cos\gamma' = \frac{ON}{OC} = \frac{d}{\frac{a}{l}}$$

$$\cos\gamma' = \frac{dl}{a}$$

4. Combine using direction cosines

$$\cos^2\alpha' + \cos^2\beta' + \cos^2\gamma' = 1$$

Substitute:

$$\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$$

$$\frac{d^2}{a^2}(h^2 + k^2 + l^2) = 1$$

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

Final Formula

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

where,

d_{hkl} = interplanar spacing

a = lattice constant

h, k, l = Miller indices

- OA, OB, OC are the intercepts of the plane (hkl) on the X, Y and Z axes respectively.
- The perpendicular distance between two successive parallel planes is d (interplanar spacing).
- The three triangles are used to obtain the direction cosines and hence the relation for d.

Remember:
For a cubic crystal, $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

◑ $\theta = 2\theta$

ex) in a cubic system (100) peak position for CsCl (4,1 Å)

If x-ray wavelength is 1.54 Å ,

→ $$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{4.1}{\sqrt{1}} = 4.1\,\text{Å}$$

$$\sin\theta = \frac{\lambda}{2d} = \frac{1.54}{8.2} = 0.188$$

$$\therefore \theta = 10.8^\circ$$

$\therefore$ (100) peak is at $\theta = 10.8^\circ$

$\therefore$ detected between position $2\theta = 21.6^\circ$