



**Department of Humanities and Sciences
National Institute of Technology Goa
Farmagudi, Ponda, Goa - 403 401**

Course Title: Material Science

Subject Code: PH150

Credits: 3 (3-0-0)

Total hours: 46

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Course Outline

Module 1: Structure of Materials (6 hours)

Atomic structure and chemical bonding, Classification of solids, Periodicity in crystals, Crystal structure, Bravas lattices, Crystal systems, Crystallographic planes and Miller indices, Crystal structure analysis, Structure determination by X-ray diffraction, The Bragg law of X-ray diffraction, Crystal defects.

Module 2: Conductors and Resistors (4 hours)

The resistivity range, The free electron theory, Conduction by free electrons, Conductor and resistor materials, Superconducting materials.

Module 3: Semiconductors and Dielectrics (12 hours)

Semiconductors: Energy gap in solids, Intrinsic semiconductor, Extrinsic semiconductors, Semiconductor materials, Fabrication of integrated circuits, Semiconductor devices, p-n Junction diode theory, Bipolar junction transistor.

Dielectrics: Dielectric constant, Polarization, Field vector, Clussius-Mossotti equation, ferro-electric materials, Electrostriction, Piezoelectric effect, dielectric loss.

Module 4: Magnetic Materials (6 hours)

Magnetic materials, Diamagnetic materials, Paramagnetic materials, Ferromagnetic materials, Diamagnetism, Paramagnetism, Ferromagnetism, Antiferromagnetism, Ferrimagnetism, Soft & Hard Magnetic material and applications.

Module 5: Superconductivity (6 hours)

Superconductivity, Meissner effect, London penetration depth, Isotope effect, The BCS theory, Type-I superconductor, Type-II superconductors, Josephson effect and applications

Module 6: Advanced materials (12 hours)

Nanomaterials, Conducting Polymers, Meta materials, Fluorescent Materials. Principles of mesoscopic physics-size effect, Quantum confinement, and Coulomb blockade, Optical effects, Surface plasmon effects. Characterization techniques for nano size-SEM, AFM, TEM.

Text/Reference Books

1. William D. Callister, Jr, **Materials science and engineering an introduction**, John Wiley & Sons, Inc, 2007
2. V. Rajendran, A. Marikani ,**Materials Science**, Publisher Tata McGraw - Hill ducation Publishers.
3. S.L Kakani, Amit Kakani "Material Science" New age international Limited
4. Brain S. Mitchell "An Introduction to Materials for Engineering and science" Willey Interscience.
5. R. Balasubramanian, Materials Science and Engineering, Willey Interscience.
6. **V. Raghavan, "Material Science and Engineering "** PHI Publication.
7. Edward M Purcell, "*Electricity and Magnetism*"
8. Julius Adams Stratton, "*Electromagnetic Theory*" Tata McGraw - Hill Education Publishers.
9. Ali Omar, "Elements of Solid State Physics" Addition Wesley,2000
10. Frederick J. Milford, John R. Reitz, Robert W. Christy, "*Foundations of Electromagnetic Theory*" Addison Wesley Longman Publishers.
11. John W. Jewett, Raymond A. Serway, "*Physics for Scientists and Engineers*"Brooks/Cole publishers.
12. T. Pradeep, "*A Textbook of Nanoscience and Nanotechnology*", Tata McGraw Hill Education
13. Hans-Eckhardt Schaefer, "*Nanoscience: The Science of the Small in Physics, Engineering, Chemistry, Biology and Medicine*" Springer

Course objectives

1. Distinguish between crystal structures - in metallic materials
2. Correlate structure (i.e. crystal, microstructure) to mechanical/electrical/magnetic properties of a material and their characterization
3. Predict material response to external environment — mechanical or thermal conditions
4. Identify properties required for specific application
5. Propose mechanical and thermal conditions to tailor microstructure in order to modify properties....
6. Advanced materials their properties and applications

History

Historically periods of civilization are divided on the basis of material development

1. Stone age
2. Bronze age
3. Iron age
4. Plastic age
5. Silicon age

Importance of materials



Defense

Inter Continental
Ballistic Missile (ICBM)

Nose during re-entry gets
heated to in excess of 1500°C
**Material - Reinforced C-C
composite**



Popular products

Apple used metallurgy ideas
to sell its watch
by using **Al alloys,**
**gold –ceramics metal matrix
composite and stainless steel**

<http://gizmodo.com/the-crazy-metallurgy-apple-is-using-to-sell-its-watch-1690388081>

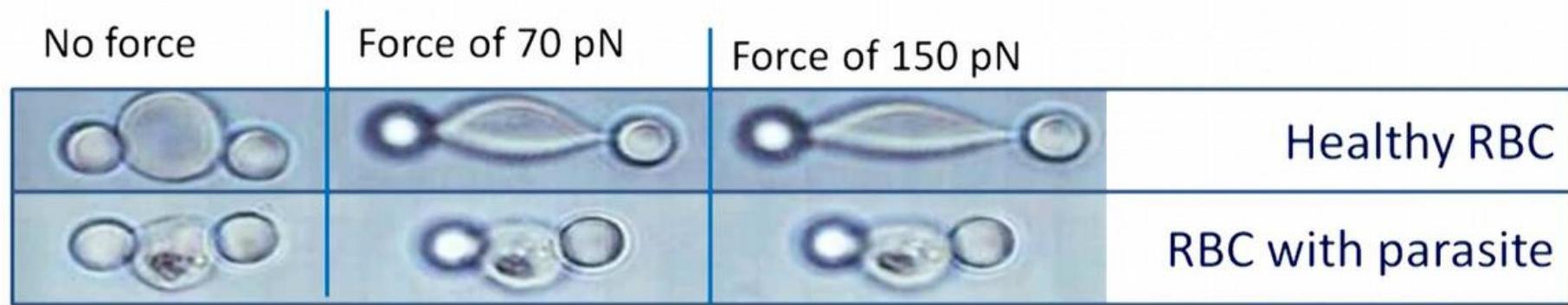
Space

GSLV MK-III

Cryogenic engines require
material to hold liquid
hydrogen and oxygen
Material - Ti alloys

Material behavior - Biotechnology

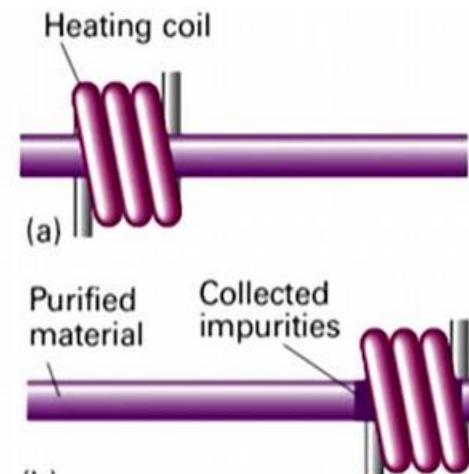
- Optical microscopy images of a healthy human RBC and RBC invaded by the malaria-inducing parasite *P. falciparum*.
- The cells are attached to glass beads at opposite ends and stretched by laser tweezers. The parasite-invaded cell loses its ability to stretch.



S. Suresh, J. Mater. Res., Vol. 21, No. 8, Aug 2006

Materials concepts in Electronics

- High purity Si are required for doping with trivalent or pentavalent elements to get p and n type extrinsic semiconductors respectively
- Zone refining is the technique to get high purity Si (99.999999%).
- The technique is entirely based on Metallurgical concept of phase diagram and non-equilibrium phase transformation .



http://faculty.chem.queensu.ca/people/faculty/mombourquette/Chem221/7_Phase-Diagrams/SolLiq.asp

A high-purity (99.999% = 5N) tantalum single crystal



Material – a human perspective

Annealed
415 MPa

4140 steel

Quenched
1100 MPa

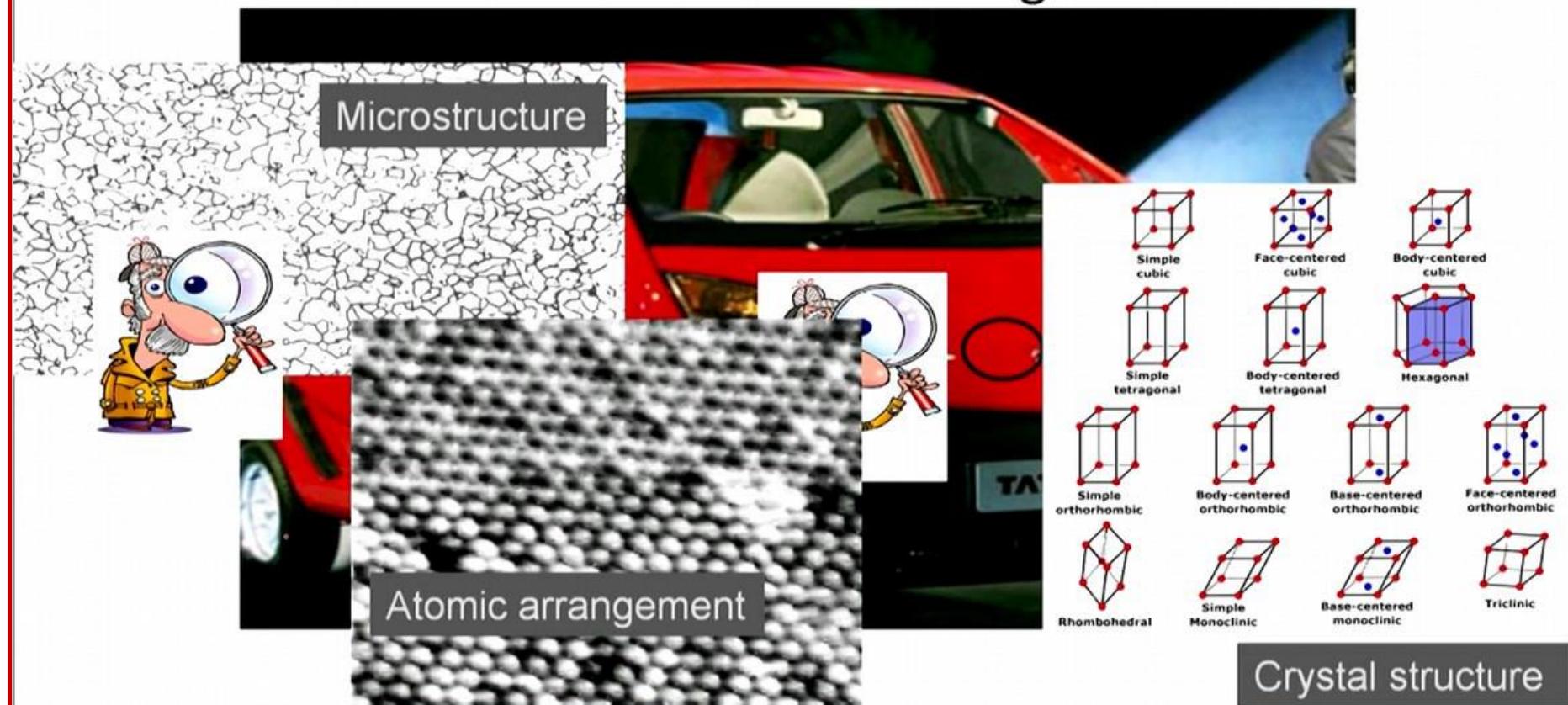
Fatigue – material fractures at the load lower than yield stress!!



Work hardening
Material strength improves by working



Structure at different length scale



Module 1: Structure of Materials

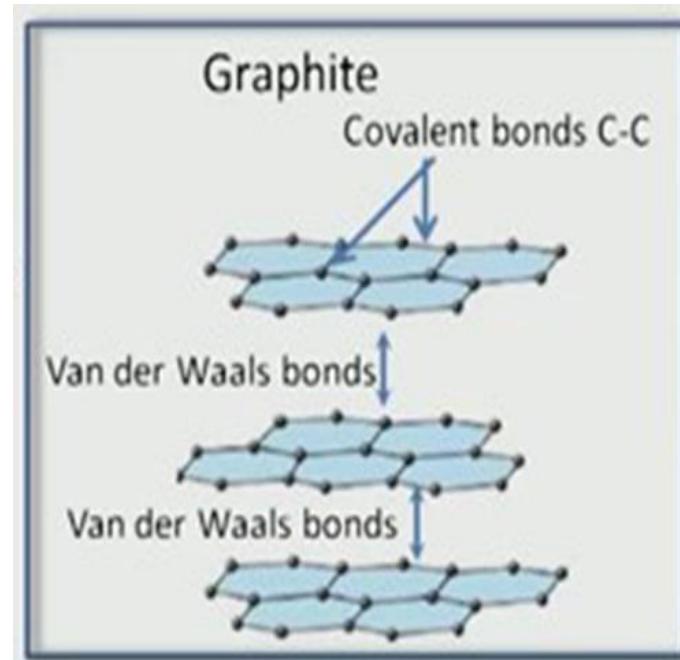
Atomic structure and chemical bonding, Classification of solids, Periodicity in crystals, Crystal structure, Bravas lattices, Crystal systems, Crystallographic planes and Miller indices, Crystal structure analysis, Structure determination by X-ray diffraction, The Bragg law of X-ray diffraction, Crystal defects.

Importance of atomic structure and bonding

- Atomic structure determines type of bonding
- Bonding decides properties of materials

For example

- ❖ In graphite carbon bond covalently in the plane (making a layer) and has van der Waals forces between the layers — Soft, layers can slide relative to each other
- ❖ In diamond the a carbon atom is covalently bonded to four other atoms — Hardest material known
- Metals have weaker metallic bonds
- Ceramics have stronger covalent or ionic bonds



Atomic structure

- An atom consists of a **nucleus (proton + neutron)** and **electrons** orbiting around it
 - ❖ Proton - is positively charged particle
 - ❖ Neutron — is neutral particle
 - ❖ Electron — is negatively charged particle
- Atomic number (Z) = Number of protons
- An atom is electrically neutral when No. of electrons = No. of protons
- Charge of an electron = -1.6×10^{-19} C

Atomic mass

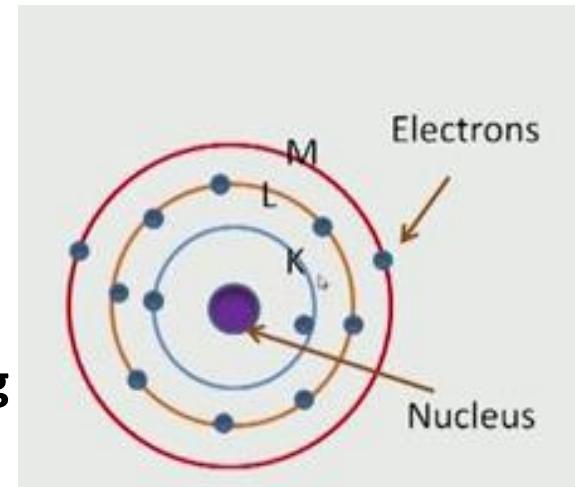
- Atomic mass is mass of protons + mass of neutrons (mass of electrons is not considered)
- Atomic mass unit (amu) = 1/12th of atomic mass of the carbon 12 (¹²C)
- 1 amu/atom = 1g/mol
- 1 mol of a substance = 6.023×10^{23} atoms
- For example, atomic weight of Fe is 55.85 amu/atom or 55.85 g/mol

Atomic model

1. Bohr model
2. Wave-mechanical model

Bohr model

- Bohr atomic model propose that electrons orbit around nucleus in discrete orbitals (K, L, M) having specific energy levels
- Position of electrons in the orbitals is well defined
- An electron can change orbit by emitting or absorbing a quanta of energy

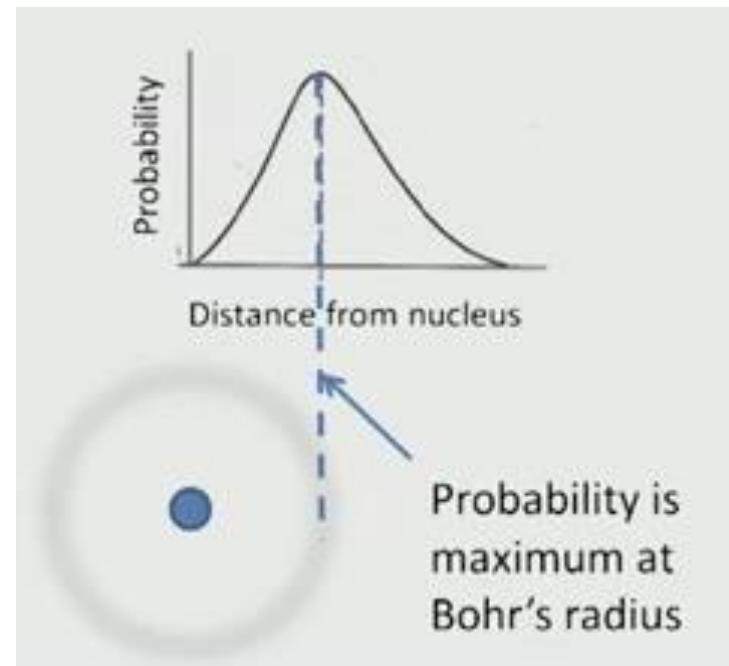


Bohr's Model

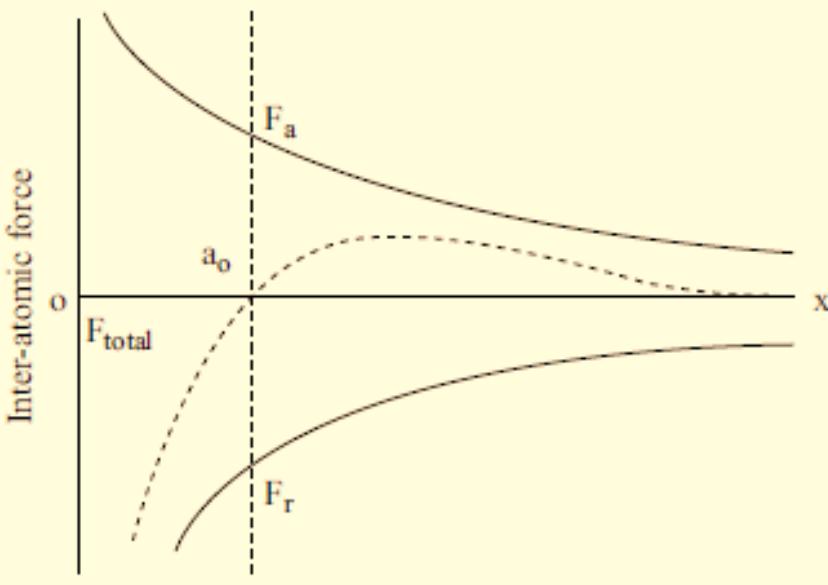
- could not explain the spectra of atoms containing more than one electron
- violates Heisenberg Uncertainty Principle — since Bohr's model predict both position and momentum at the same time

Wave — Mechanical model

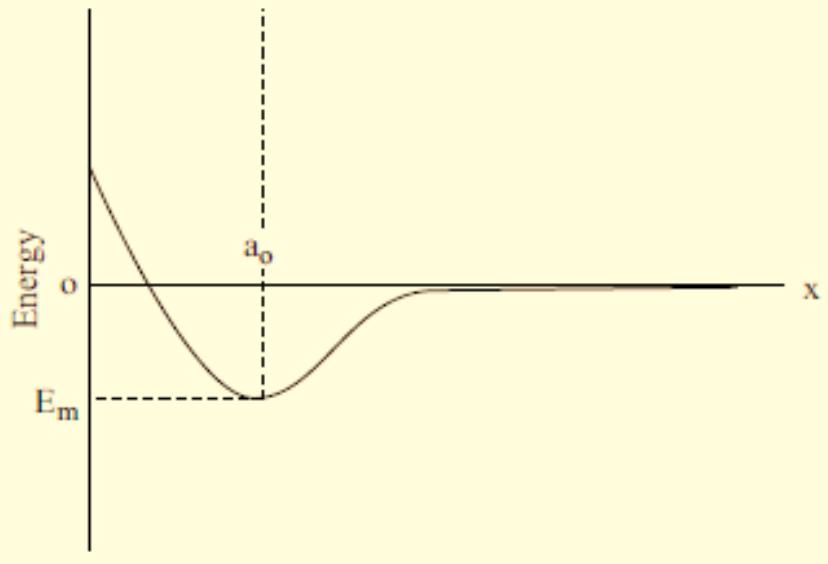
- Limitations of Bohr model was resolved by this model and electrons are considered to behave both **wave-like and particle-like**
- Electrons are no longer treated as a particle moving in discrete orbitals
- Position of an electron is described by a **probability distribution**



Atomic interaction



(a) Attractive, repulsive and total forces



(b) a_0 and E_m at zero resultant force

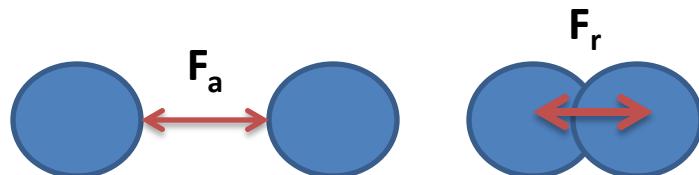
Attractive force due to electrostatic attraction between electrons and nucleus

Repulsive force

when separation is less than equilibrium — repulsion between nuclei (and electrons) of interacting atoms

At equilibrium separation net force is zero and potential energy is minimum

Higher bond energy , E_0
higher melting point
higher elastic modulus



Atomic bonding

Primary interatomic bonds

- Ionic
- Covalent
- Metallic

Secondary bonds

- van der Waals forces
- Hydrogen bonds

Ionic bonds

- Between metallic and nonmetallic atoms
- Metallic atom give valence electrons to the nonmetallic atom

Na atom (unstable)
Electrons – 2, 8, 1



Cl atom (unstable)
Electrons – 2, 8, 7



Eg: NaCl, KOH, MgO, MgCl₂....etc

Na⁺ ion (stable)
Electrons – 2, 8



Cl⁻ ion (stable)
Electrons – 2, 8, 8



Coulombic attraction – between two oppositely charged ions

The Coulombic interaction energy

$$U = -\frac{e^2}{4\pi\epsilon_0 R}$$

where **e** is the charge of the electron, ϵ_0 the permittivity of free space and **R** is the distance between the oppositely charged ions.

- The cohesive energy of NaCl per molecule is 7.9 eV

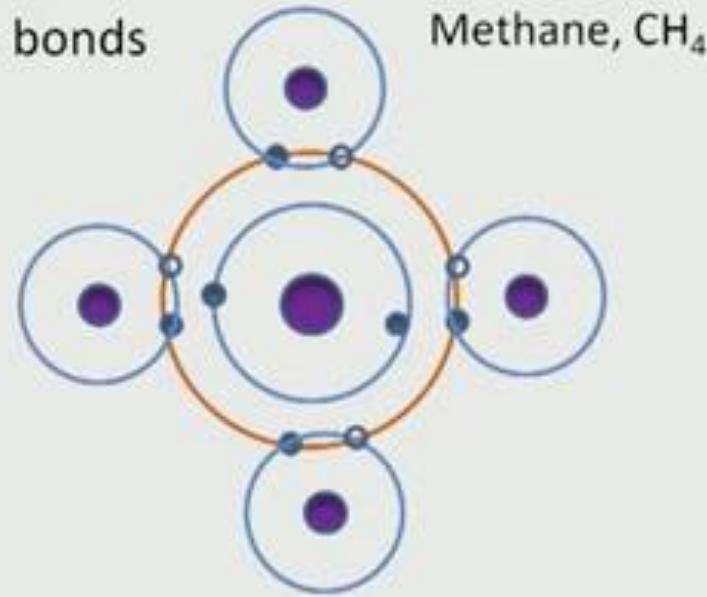
Covalent bonds

- In this type of bonding, atoms share their valence electrons to get a stable configuration
- Formed between atoms of similar electronegativity
- Diamond, silicon, germanium also have covalent bonds

C atom
Electrons – 2, 4

H atom
Electrons – 1

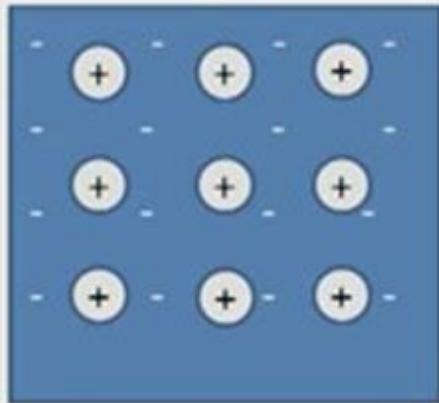
Sharing of electron
between one C atom
and four H atoms



The properties of covalent bonds

- (1) Covalent bond is directional.
- (2) Covalent bonding can be either very strong or very weak bonds, depending upon the atoms involved in the bond.
- (3) Covalent solids generally leads to low melting and boiling points compared to ionic solids, e.g., CCl_4 melting point is 296 K.
- (4) Nonpolar liquids like CCl_4 , benzene are good solvents for covalent molecules.
- (5) Covalent solids are hard, brittle and possess crystalline nature.
- (6) Different physical properties of the solid material are due to their bonding type

Metallic bonds



- Atoms (ions) have fixed position in the crystal
- Valence electrons are free to move as 'free electrons' forming an electron cloud
- The metallic bond arises out of the columbic attraction between these two oppositely charged species – the electron cloud and the ion cores
- Due to free electrons – very high conductivity

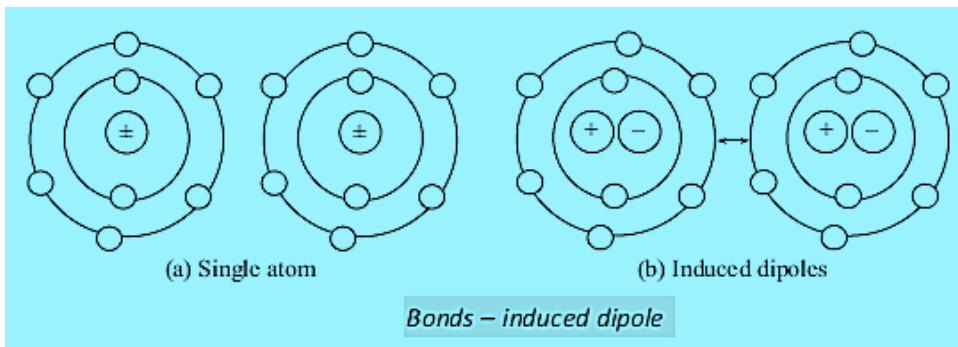
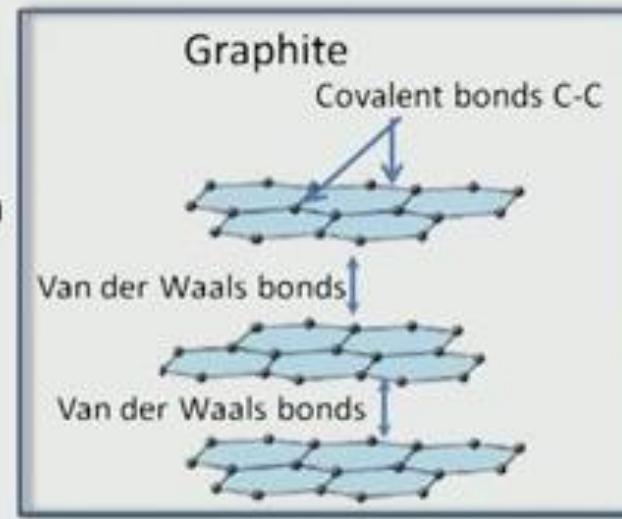
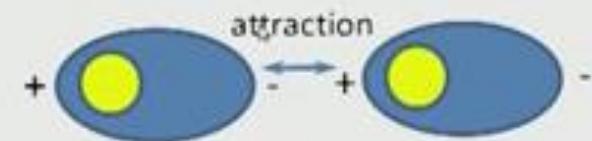
The properties of metallic bonds

- (1) The metallic bond is nondirectional in character.
- (2) Metallic bonds are good conductors, forming electron cloud and having high melting point and low ionisation energies.
- (3) Metallic crystals are ductile and strong due to the ability of the bond electrons to make and break bonds readily.
- (4) They have characteristic properties such as bright luster, high electrical and thermal conductivity, malleability, ductility and high tensile strength.
- (5) Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms.

Secondary bonding

van der Waals bonding

- Weaker in comparison to primary bonds, typically 10 kJ/mol
- Arise due to atoms or molecule dipoles which form due to separation of positive and negative species of an atom or molecule
- The bonding result from coulombic attraction between positive dipole (or negative) of one atom to the negative (or positive) of adjacent atom
- In graphite bonding between layers is van der Waals



Bonds – induced dipole

the cohesive energy due to the dipole – dipole interaction

$$U = 4 \varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

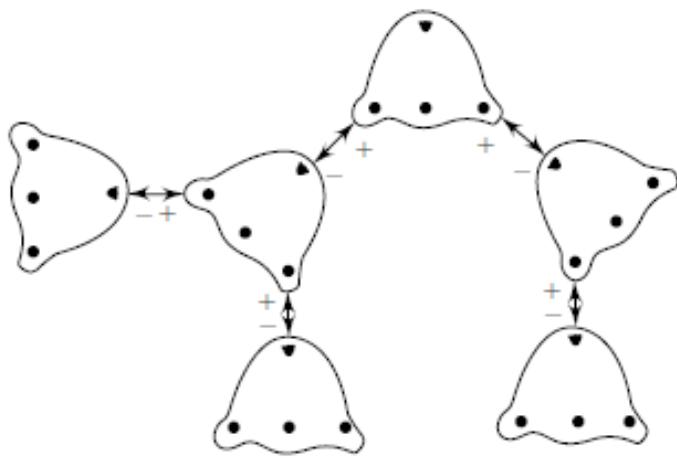
where R is the distance between the dipoles, ε and σ are characteristics constants.

The first and second term in the above equation represents **repulsive** and **attractive** potentials, respectively.

Secondary bonding

Hydrogen bonding

- Found in some molecules that have hydrogen as one of the constituent
- Electrostatic interaction between hydrogen and another atom of high electronegativity
- Water molecule is a good example of this bonding between hydrogen of one molecule with oxygen of another molecule



Hydrogen bonding - Water

The properties of the hydrogen bonds

- (1) Hydrogen bonds are directional and have low melting point.
- (2) Hydrogen bonded solids do not have any valence electrons and hence, they are solid insulators.
- (3) Hydrogen bonds are stronger than dispersion bonds but are weaker than primary bonds.
- (4) Hydrogen bonded solids may be crystalline or noncrystalline.
- (5) Hydrogen bonded solids are soluble both in polar and nonpolar solvents

Comparison of Various Types of Bonds

| Sr. No. | Properties | Ionic Bonds | Covalent Bonds | Metallic Bonds | Van der Waals Bond |
|---------|--------------------------|--|---|---|---|
| 1. | Bonding force | Electrostatic force between positive and negative ions | Mutual sharing of valence electrons between atoms | Electrostatic force between negative electron cloud and positive ions | Electrostatic force due to oscillating dipoles |
| 2. | Character of bond | Nondirectional | Directional | Nondirectional | Directional for dipole and hydrogen bonds. Nondirectional for dispersion bonds |
| 3. | Bond formation condition | One of the atoms has small number of valence electrons | Atomic orbitals of two atoms overlap | For elements having small number of valence electrons | Molecules forming dipoles |
| 4. | Bond energy | 150 – 370 kcal/mol | 125 – 300 kcal/mol | 25 – 200 kcal/mol | <10 kcal/mol |
| 5. | Conductivity | Low | Low | Good | Low |
| 6. | Hardness | High | Less | High | Poor |
| 7. | Density | Intermediate | Intermediate | High | Low |
| 8. | Melting point | Intermediate | High (if any) | High | Low |
| 9. | Examples | NaCl, MgO, etc. | Si, C, etc. | Al, Fe, Na, etc. | H ₂ O, Cl ₂ , etc. |

Classification of solids

Crystalline solids

Amorphous solids
Ex: Glass, rubber etc

→ Ionic crystals Ex: NaCl ,KCl

→ Covalent crystals Ex: Diamond, SiO₂

→ Molecular crystals Ex: naphthalene, anthracene, glucose

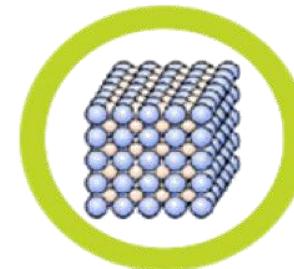
→ Metallic crystals Ex: All metallic elements
(Na, Mg,Cu,Au,Ag etc..)

→ Atomic solids - ex: frozen elements of Group 18

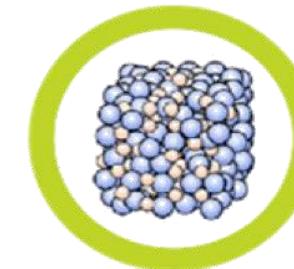
Crystalline solids are three-dimensional analogs of a brick wall. They have a regular structure, in which the particles pack in a repeating pattern from one edge of the solid to the other.

Amorphous solids (literally, "solids without form") have a random structure, with little if any long-range order.

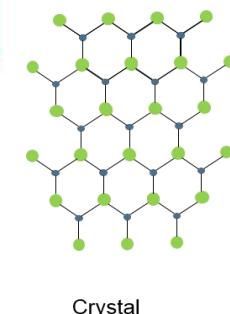
Crystalline Structure



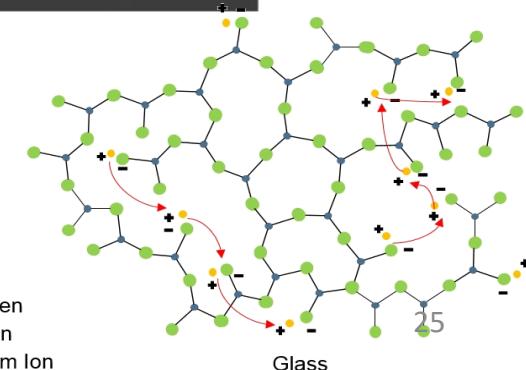
Amorphous Structure



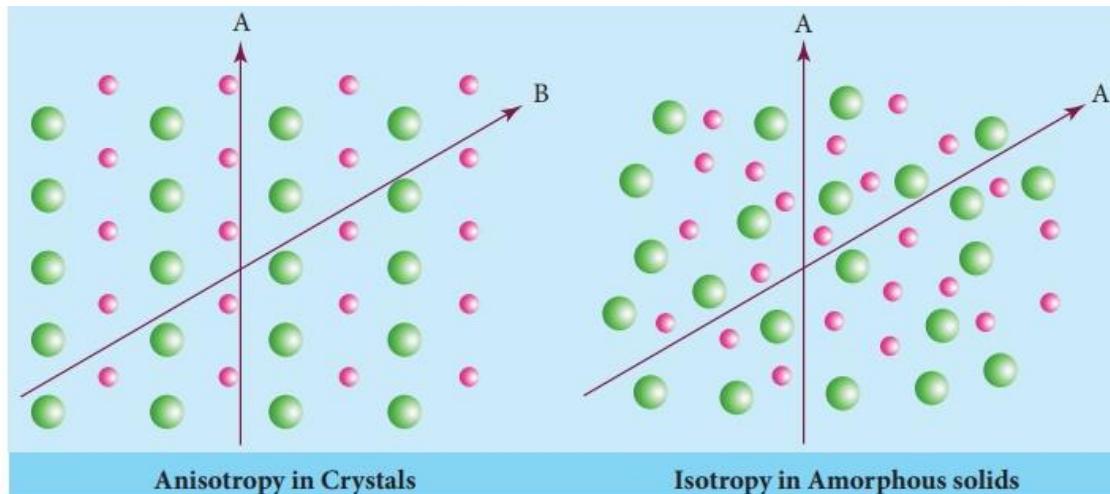
Difference in structure



Oxygen
Silicon
Lithium Ion



| S.no | Crystalline solids | Amorphous solids |
|------|--|---|
| 1 | Long range orderly arrangement of constituents. | Short range, random arrangement of constituents. |
| 2 | Definite shape | Irregular shape |
| 3 | Generally crystalline solids are anisotropic in nature | They are isotropic* like liquids |
| 4 | They are true solids | They are considered as pseudo solids (or) super cooled liquids |
| 5 | Definite Heat of fusion | Heat of fusion is not definite |
| 6 | They have sharp melting points. | Gradually soften over a range of temperature and so can be moulded. |
| 7 | Examples: NaCl , diamond etc., | Examples: Rubber , plastics, glass etc |



Lattice

- A lattice is a regular and periodic arrangement of points in three dimensions

Basis

To construct a crystal structure, some **basic arrangement** is to be fixed at each and every lattice point.

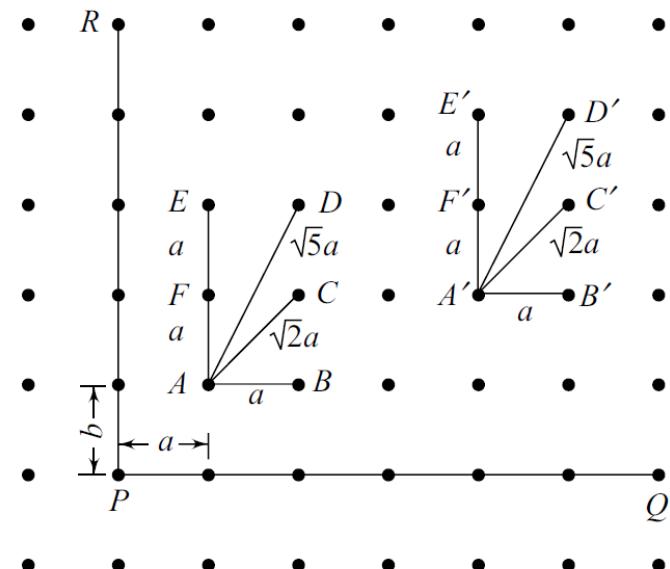
This basic arrangement is said to be a **basis**

Crystal Structure

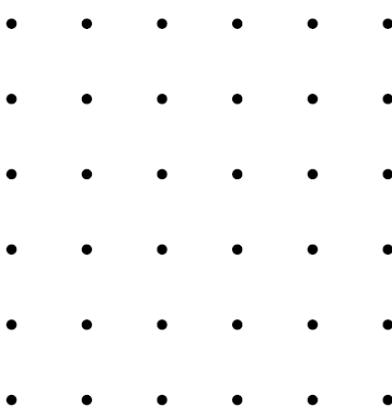
Obtained by arranging the **basis** in each and every **lattice point**

Crystal structure = lattice + basis

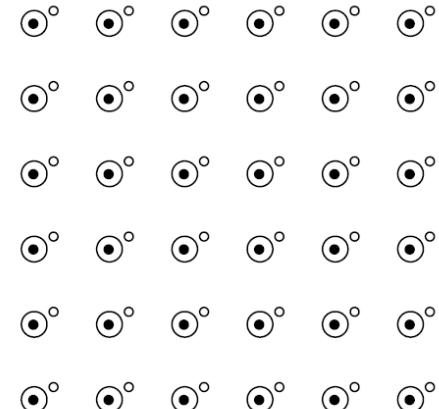
Lattice ➤ how to repeat
Basis ➤ what to repeat



A two-dimensional lattice



(a) Lattice



(b) Basis

(c) Crystal structure

Arrangement of basis and lattice point

Unit Cell

The smallest group of atoms which has the overall symmetry of a crystal, and from which the entire lattice can be built up by repetition in three dimensions.

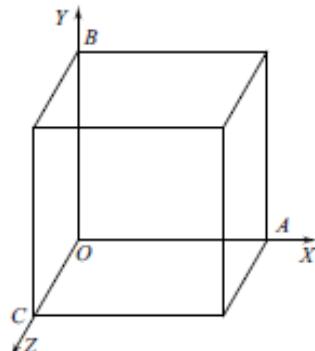
- A smallest unit
- Fundamental building block of a crystal structure

Primitives

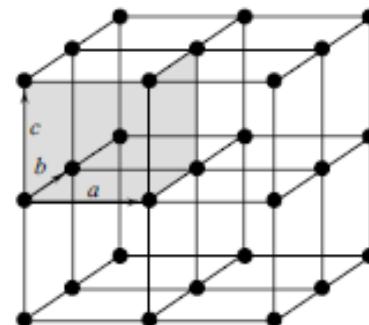
- Intercepts are known as primitives

Primitive Cell

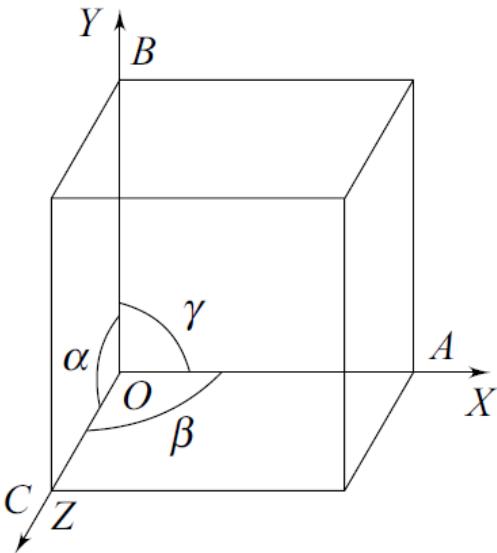
- Smallest unit cell in volume constructed by primitives.
- It consists of only one full atom.
- If a unit cell consists of more than one atom then it is not a primitive cell.
- A simple cubic unit cell is said to be a primitive cell



Primitives



Primitive cell of a space lattice



Crystallographic in unit cell

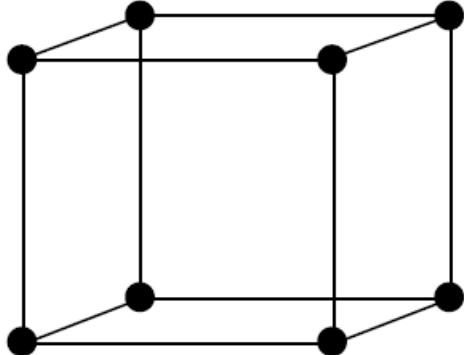
TYPES OF CRYSTALS

1. Cubic
2. Tetragonal
3. Orthorhombic
4. Monoclinic
5. Triclinic
6. Trigonal
7. Hexagonal

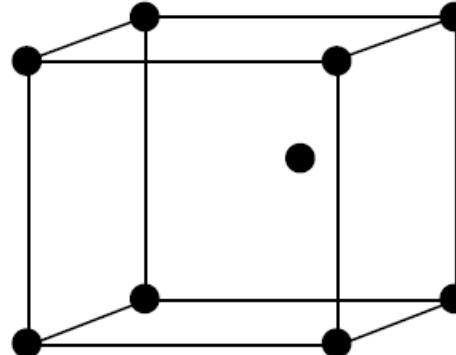
Bravais Lattices (Primitive (P), Body centred (I), Face centred (F) and base centred (C))

| Sr. No. | Name of the system | Relation between primitives and angles | Lattice symbols | No. of possible lattices | Examples | Lattice Parameters |
|---------|--------------------|--|------------------|--------------------------|---|---|
| 1. | Cubic | $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$ | P I F | 3 | Po Na, W, α - Fe Ag, Au, Pb | Interfacial angles and the corresponding intercepts |
| 2. | Tetragonal | $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$ | P I | 2 | TiO ₂ , SnO ₂ KH ₂ PO ₄ | |
| 3. | Orthorhombic | $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$ | P I F C | 4 | — PbCO ₃ , BaSO ₄ KNO ₃ , K ₂ SO ₄ α - S | |
| 4. | Monoclinic | $a \neq b \neq c$, $\alpha = \beta = 90^\circ \neq \gamma$ | P C | 2 | CaSO ₄ .2H ₂ O K ₂ MgSO ₄ .6H ₂ O | |
| 5. | Triclinic | $a \neq b \neq c$, $\alpha \neq \beta \neq 90^\circ \neq \gamma$ | P | 1 | K ₂ Cr ₂ O ₇ | |
| 6. | Trigonal | $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$ (but less than 120°) | P | 1 | Calcite, As, Sb, Bi | |
| 7. | Hexagonal | $a = b \neq c$, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ | P | 1 | SiO ₂ , AgI | |

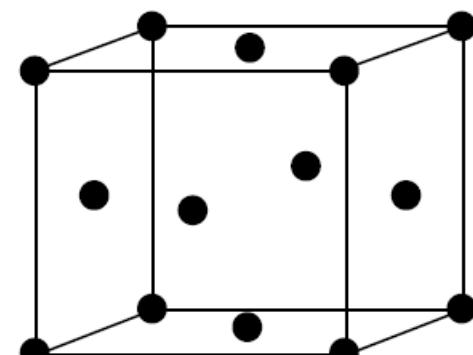
1. Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$)



Cubic primitive

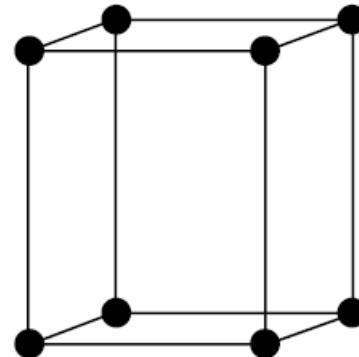


Cubic body centred

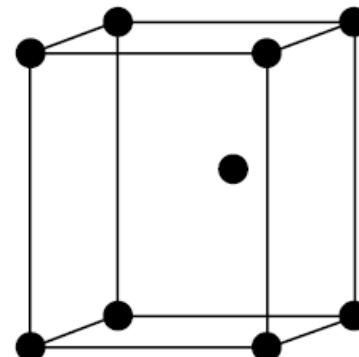


Cubic face centred

2. Tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$)

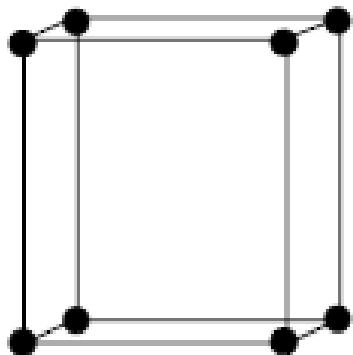


Tetragonal primitive

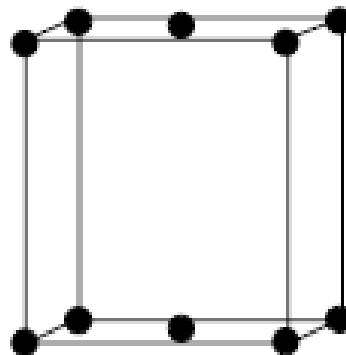


Tetragonal body centred

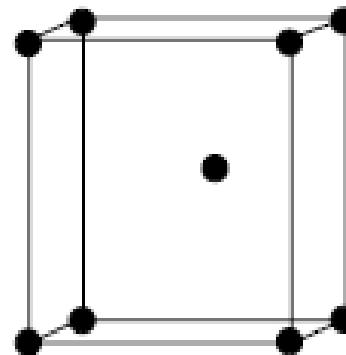
3. Orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$)



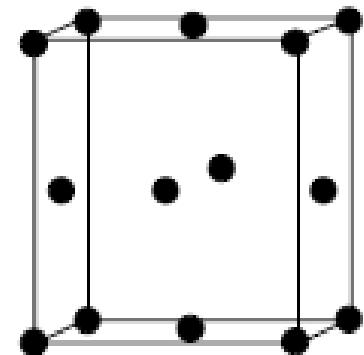
Orthorhombic
Primitive



Orthorhombic
Base centred

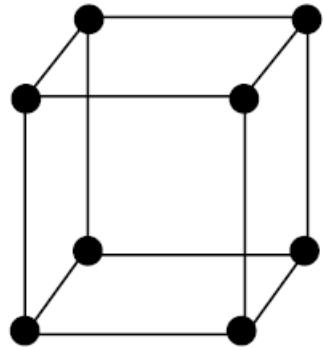


Orthorhombic
Body centred

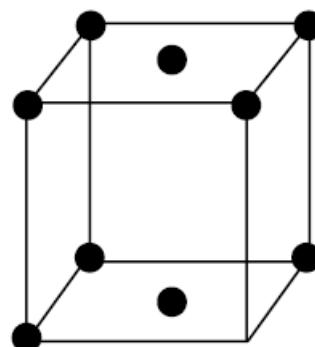


Orthorhombic
Face centred

4. Monoclinic ($a \neq b \neq c$, $\alpha = \beta = 90^\circ \neq \gamma$)

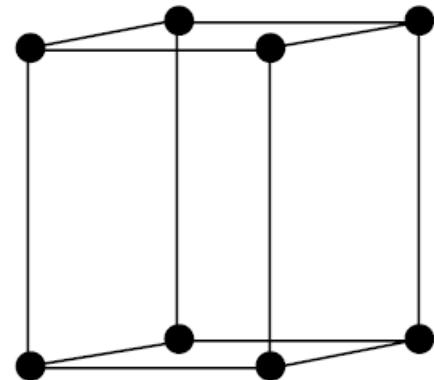
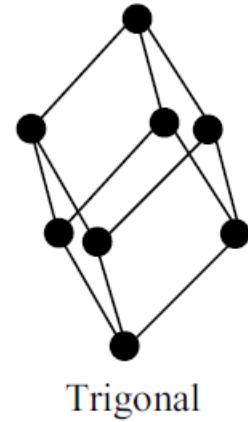
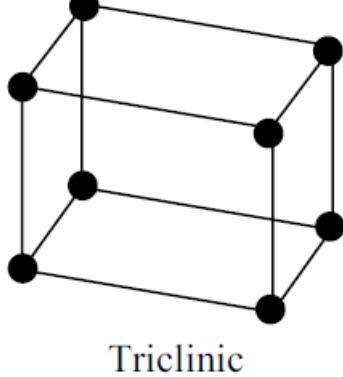


Monoclinic
Primitive



Monoclinic
Base centred

5. Triclinic $a \neq b \neq c,$
 $\alpha \neq \beta \neq 90^\circ \neq \gamma$
6. Trigonal $a = b = c,$
 $\alpha = \beta = \gamma \neq 90^\circ$
 (but less than
 120°)
7. Hexagonal $a = b \neq c,$
 $\alpha = \beta = 90^\circ$
 $\gamma = 120^\circ$



Trigonal and hexagonal P

Miller Indices

- Representation of crystal plane or direction

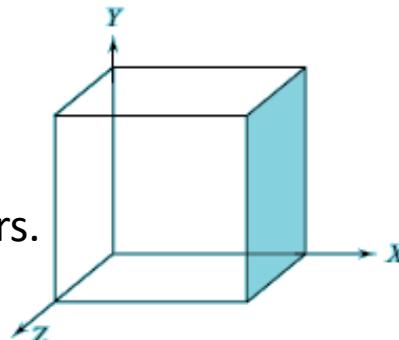
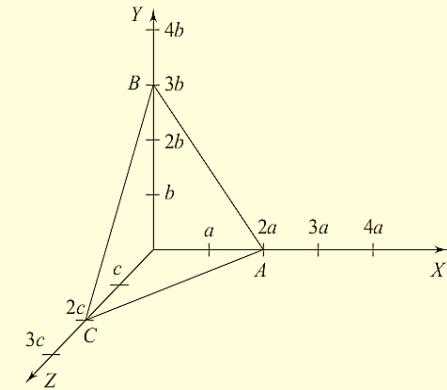
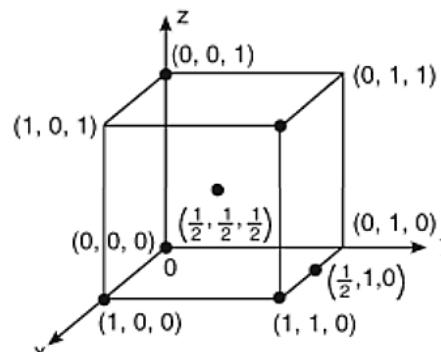
How to Find the Miller Indices of a Plane

- The intercepts made by the plane along X, Y and Z axes are noted.
- The coefficients of the intercepts are noted separately.
- Inverse is to be taken.
- The fractions are multiplied by a suitable number so that all the fractions become integers.
- Write the integers within the parentheses

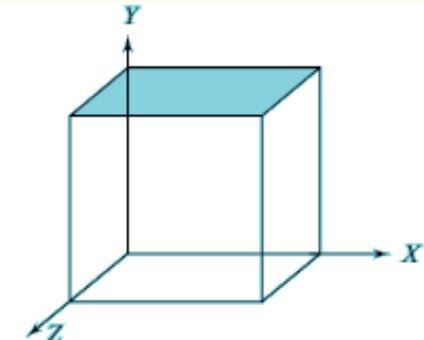
Eg: intercepts are $2a$, $3b$ and $2c$.

- The coefficients of the intercepts are 2, 3 and 2. The inverse are $1/2$, $1/3$, $1/2$.
- The LCM is 6. Multiply the fractions by 6, so that they become integers as 3, 2, 3.
- The integers are written within the parenthesis as (323)

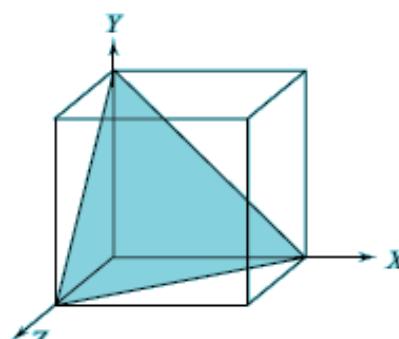
Relation between the interatomic distance a and the interplanar distance d



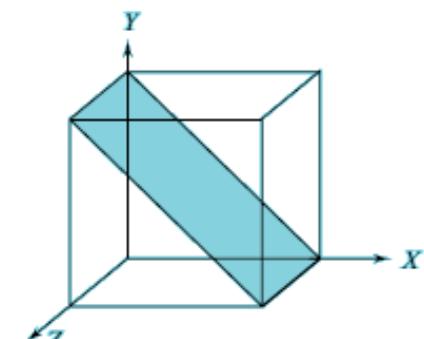
(a) (100) plane



(b) (010) plane



(c) (111) plane



(d) (110) plane

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

- (1) **Atomic Radius (r)** It is half the distance between any two successive atoms. For a simple cubic unit cell, the atomic radius

$$r = \frac{a}{2}$$

where a is the interatomic distance.

- (2) **Coordination Number** It is the number of nearest neighbouring atoms to a particular atom. For a simple cubic unit cell, the coordination number is 6.
- (3) **Packing Density** It is the ratio between the total volume occupied by the atoms or molecules in a unit cell and the volume of unit cell.

i.e.,

$$\begin{aligned} \text{Density of packing} &= \frac{\text{Total volume occupied by atoms in a unit cell}}{\text{Volume of the unit cell}} \\ &= \frac{\text{Number of atoms present in a unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}} \end{aligned}$$

1. Simple Cubic Crystal Structure

Unit cell volume (V): $V = a^3$ Coordination Number 6

Atomic Radius $r = a/2$

Effective number of atoms per unit cell, Z :

$$Z = Z_B + \frac{Z_F}{2} + \frac{Z_C}{8}$$

Z_B = Number of body centered atoms,

Z_F = Number of face centered atoms and

Z_C = Number of corner atoms

$$Z = Z_B + \frac{Z_F}{2} + \frac{Z_C}{8} = 0 + 0 + \frac{8}{8} = 0 + 0 + 1 \text{ atom / cell}$$

$$Z = 1 \text{ atom / cell}$$

The number of atoms present in a unit cell is 1.

Packing density

$$= \frac{1 \times (4/3) \times \pi r^3}{a^3}$$

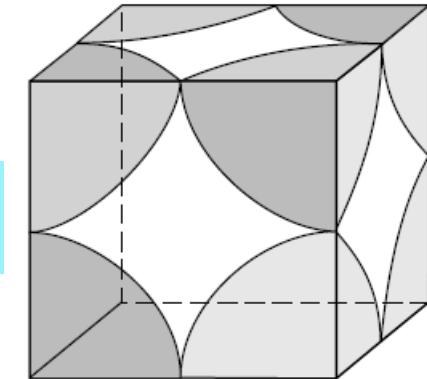
Substituting the value $r = a/2$

$$= \frac{1 \times (4/3) \times \pi (a/2)^3}{a^3}$$

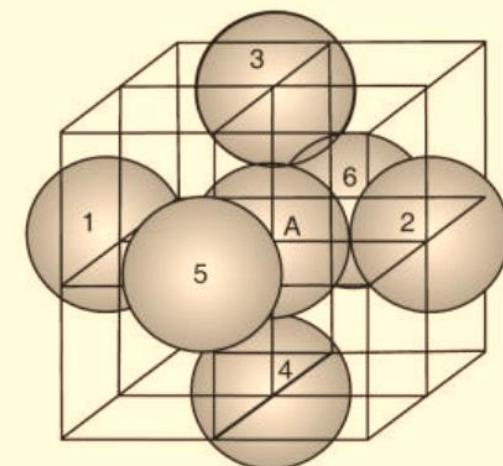
\therefore Packing density

$$= \frac{\pi}{6} = 0.52.$$

Therefore, packing density



Arrangement of atoms
in a SC unit cell



Determination of nearest neighbours. There are six close neighbours for any selected atom in a SC cell.

52 percent of the volume of simple cubic unit cell is occupied by atoms and the remaining 48 percent volume of the unit cell is vacant

2. Body Centred Cubic Structure

Unit cell volume (V):

$$V = a^3$$

Effective number of atoms per unit cell (Z):

$$Z = Z_B + \frac{Z_F}{2} + \frac{Z_C}{8}$$

$$Z = 1 + 0 + \frac{8}{8}$$

Z = 2 atoms/cell

Coordination Number, CN: 8

Atomic radius (R):

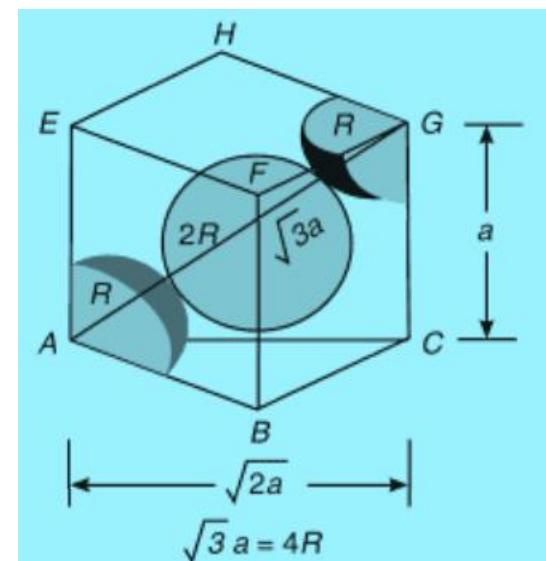
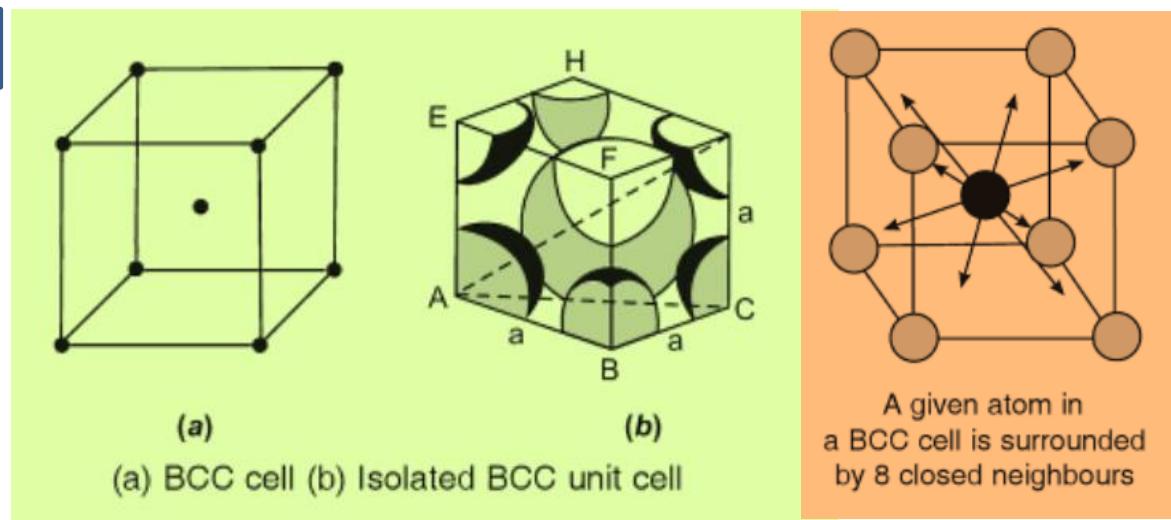
$$(AG)^2 = (AC)^2 + (CG)^2 = (AB)^2 + (BC)^2 + (CG)^2$$

$$AG = 4R \quad \text{and} \quad AB = BC = CG = a$$

$$(4R)^2 = 3(a)^2$$

$$4R = a\sqrt{3}$$

$$R = \frac{a\sqrt{3}}{4}$$



Determination of the relation between atomic radius and lattice edge in a BCC cell

The number of atoms present in a unit cell is 2.

$$\text{Packing density} = \frac{2(4/3)\pi r^3}{a^3}$$

Substituting the value of $r = (\sqrt{3}/4) a$

$$\begin{aligned}\therefore \text{Packing density} &= \frac{2(4/3)\pi \left[\left(\frac{\sqrt{3}}{4} \right) a \right]^3}{a^3} \\ &= \frac{\sqrt{3}\pi}{8} = 0.68\end{aligned}$$

68 percent of the volume of the body centred cubic unit cell is occupied by atoms and the remaining 32 percent volume of the unit cell is vacant

3. Face Centred Cubic Structure

Unit cell volume (V):

$$V = a^3$$

Effective number of atoms per unit cell (Z):

$$Z = Z_B + \frac{Z_F}{2} + \frac{Z_C}{8}$$

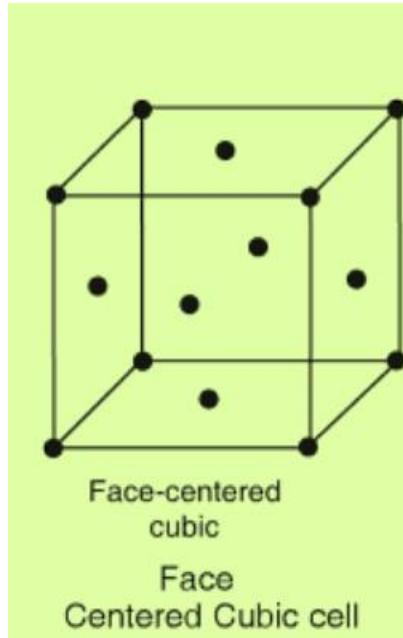
$$Z = 0 + \frac{6}{2} + \frac{8}{8}$$

$$Z = 4 \text{ atoms/cell.}$$

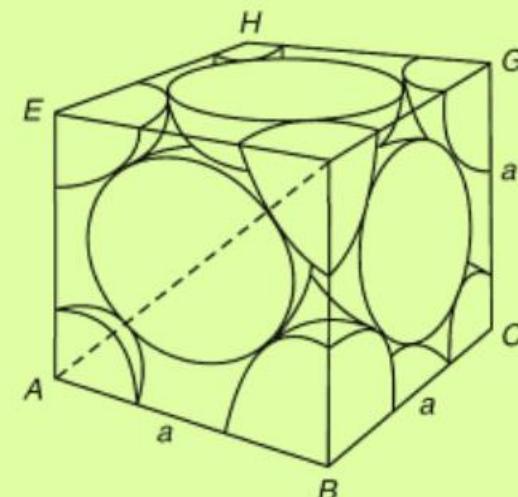
Coordination Number

- 4 atoms in the xy plane
- 4 atoms in the yz plane
- 4 atoms in the zx plane

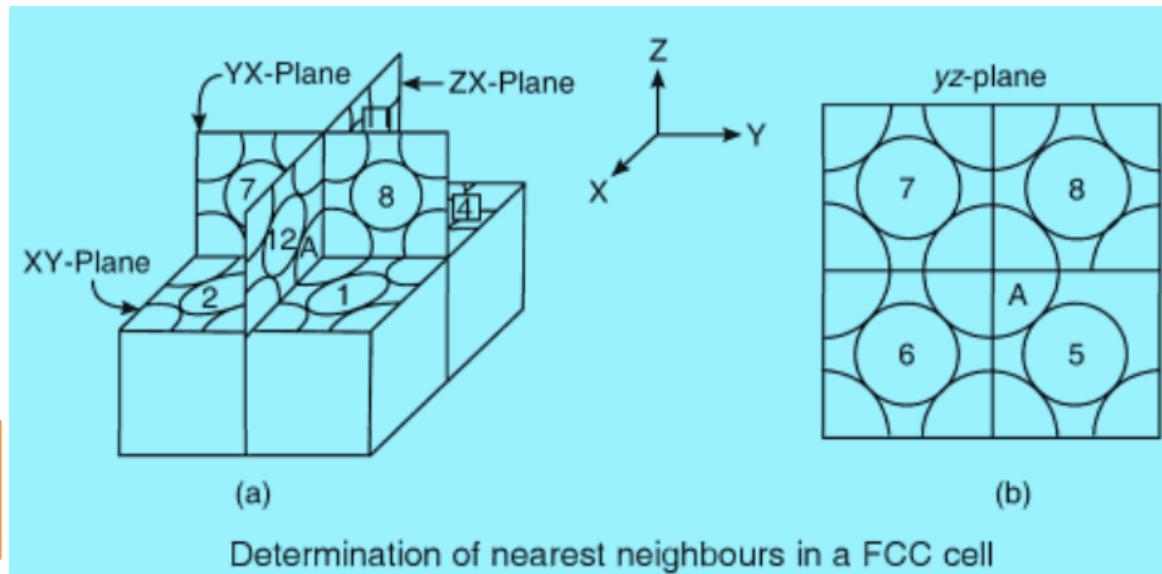
Coordination number = $4 + 4 + 4 = 12$



Face-centered cubic
Face Centered Cubic cell



Determination of effective number of atoms per unit cell.



Determination of nearest neighbours in a FCC cell

Atomic Radius

$$AF^2 = AB^2 + BF^2$$

$$AF = 4R \quad \text{and} \quad AB = a = BF$$

$$(4R)^2 = 2a^2$$

$$4R = a\sqrt{2}$$

$$R = \frac{a\sqrt{2}}{4} = \frac{a}{2\sqrt{2}}$$

the total number of atoms present in an fcc unit cell is 4

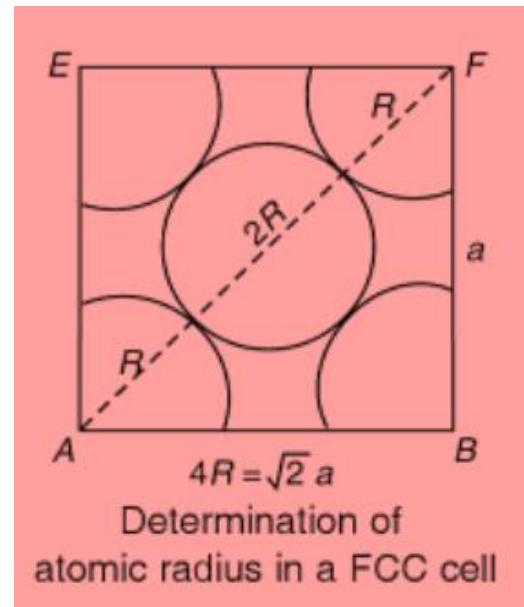
$$\text{Packing density} = \frac{4(4/3)\pi r^3}{a^3}$$

Substituting the value of $r = a/(2\sqrt{2})$

$$\therefore \text{Packing density} = \frac{4(4/3)\pi \times (a/2\sqrt{2})^3}{a^3} = \frac{\pi}{3\sqrt{2}}$$

the packing density of the fcc unit cell = 0.74

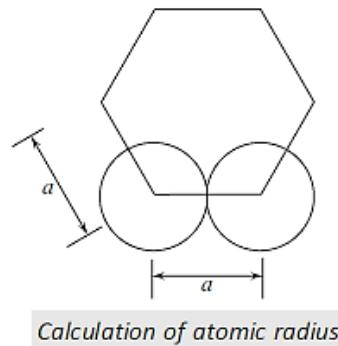
74 percent of the volume of an fcc unit cell is occupied by atoms and the remaining 26 percent volume of the unit cell is vacant



Hexagonal Closed Packed Structure

Atomic radius $r = a/2$

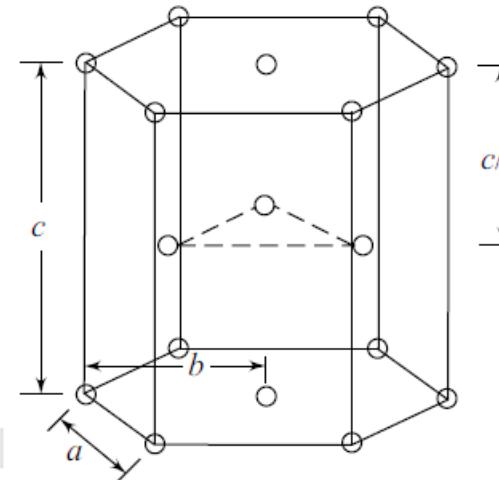
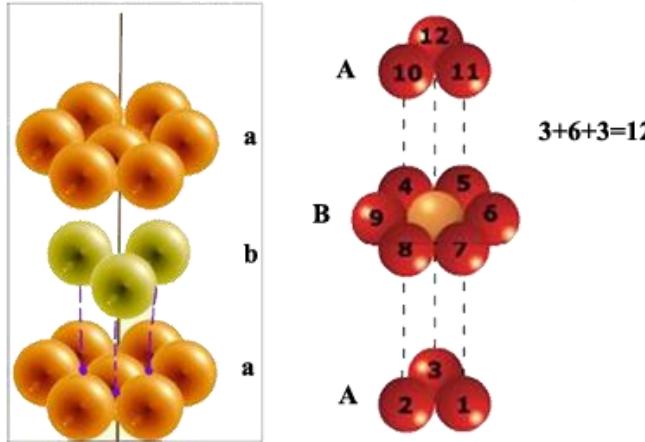
Effective number of atoms per unit cell (Z): 6



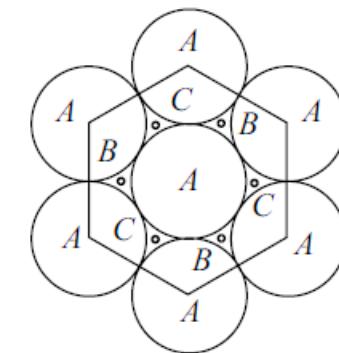
The total number of atoms present in a unit cell is $3/2$ (Bottom) + $3/2$ (Upper) + 3 (Middle) = 6.

Coordination Number 12

HCP-coordination number



(a) hcp unit cell



(b) Arrangement of atoms

$$= \frac{6(4/3)\pi r^3}{6(\sqrt{3}/4)a^2 c}$$

Packing density

Substituting the value of $r = a/2$

\therefore Packing density

$$= \frac{6(4/3)\pi(a/2)^3}{6(\sqrt{3}/4)a^2 c} = \frac{2\pi a}{3\sqrt{3}c}$$

Substituting the value of $c/a = \sqrt{(8/3)}$

\therefore Packing density

$$= \frac{2\pi}{3\sqrt{3}} \sqrt{\frac{3}{8}} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Therefore, the packing density of hcp unit cell

= 0.74.

74 percent of the volume of hcp crystal structure is occupied by atoms and the remaining 26 percent volume is vacant

The characteristics of the three types of cubic unit cells and the HCP cell

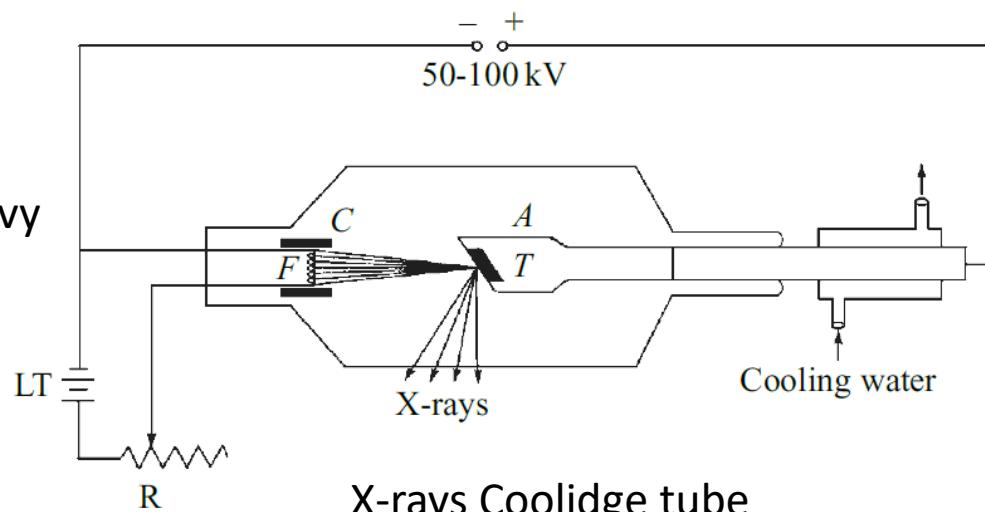
| Sr.No. | Characteristics | Unit Cell | | | |
|--------|------------------------------|---------------------|---------------------------|---------------------------|-----------------------------|
| | | SC | BCC | FCC | HCP |
| 1. | Unit cell volume, V | a^3 | a^3 | a^3 | $3\sqrt{2}a^3$ |
| 2. | Atoms per unit cell, Z | 1 | 2 | 4 | 6 |
| 3. | Atomic radius, r | $a/2$ | $a\sqrt{3}/4$ | $a/2\sqrt{2}$ | $a/2$ |
| 4. | Coordination number, CN | 6 | 8 | 12 | 12 |
| 5. | Atomic packing fraction, APF | $\pi/6$ = 0.52 | $\pi\sqrt{3}/8$ = 0.68 | $\pi/3\sqrt{2}$ = 0.74 | $\pi/3\sqrt{2}$ = 0.74 |
| 6. | Void space | 48% | 32% | 26% | 26% |
| 7. | Density, ρ | $\frac{M}{N_A a^3}$ | $\frac{2M}{N_A a^3}$ | $\frac{4M}{N_A a^3}$ | $\frac{\sqrt{2}M}{N_A a^3}$ |

X-Rays

- X-rays accidentally founded by Roentgen, in 1895
- X-ray highly monochromatic electromagnetic radiation
- The wavelength of X- rays ranging from 0.5 to 10 Å.
- The longer wavelength of the X-ray spectrum is known as soft X-rays
- X-rays of shorter wavelength are known as hard X-rays.

Generation of X-rays

X-rays are produced when a beam of fast moving cathode rays (electrons) strike a heavy target material such as tungsten or molybdenum



Mo → 0.71 Å
Cu → 1.54 Å
Co → 1.79 Å
Fe → 1.94 Å
Cr → 2.29 Å

Bragg's Law

Bragg's law stated relation between the wavelength (λ) of X-rays, the interplanar distance (d), and the glancing angle or incident angle (θ)

$$2d \sin \theta = n\lambda$$

where $n = 1, 2, 3, \text{ etc.}$, represents the order of the spectrum

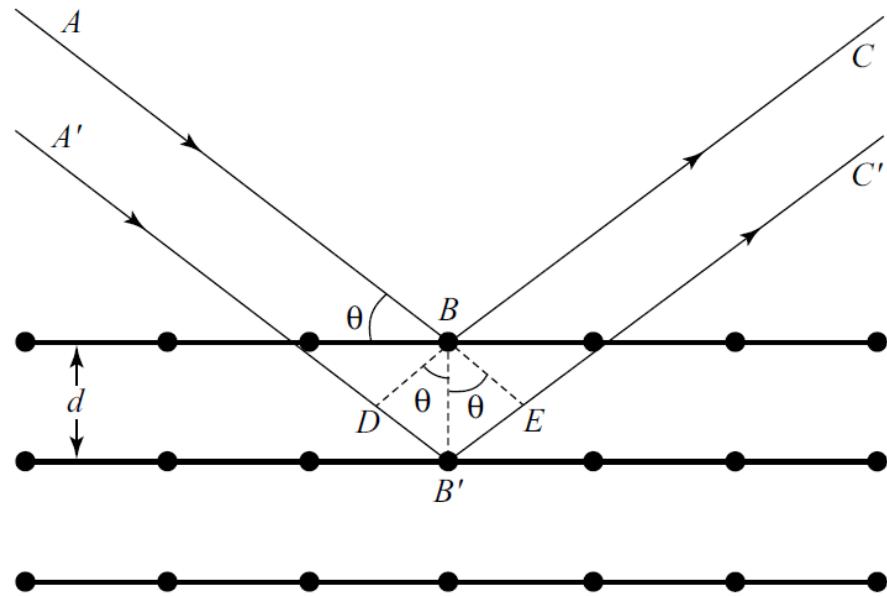
$$\sin \theta = DB'/BB'$$

$$DB' = BB' \sin \theta = d \sin \theta$$

$$B'E = d \sin \theta$$

Therefore, the path difference is given as,
 $d \sin \theta + d \sin \theta = 2d \sin \theta$

$$2d \sin \theta = n\lambda$$

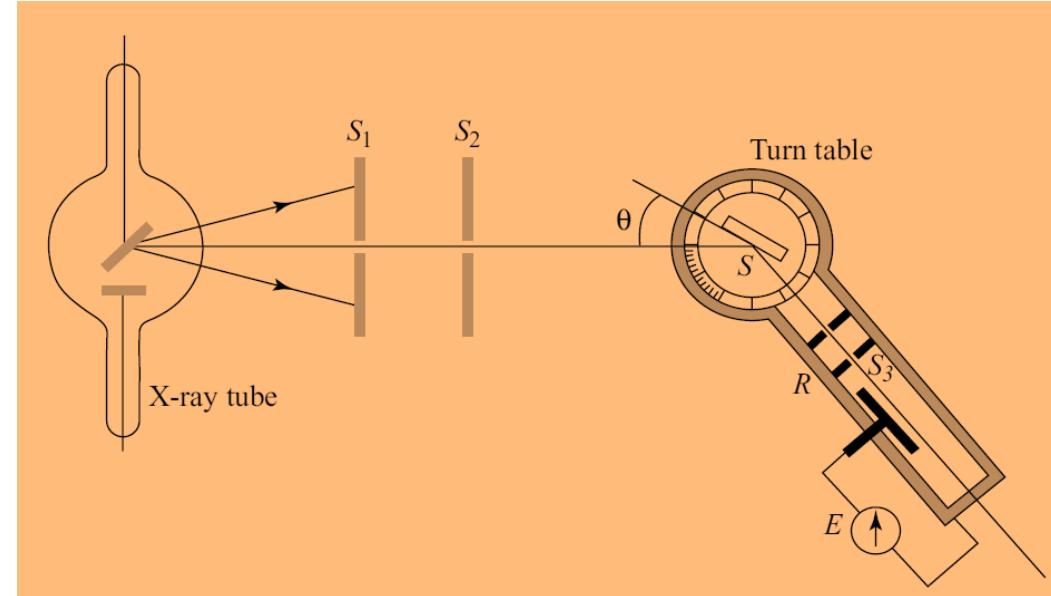


Braggs' spectrometer

- crystal is used as a reflection grating
- It is used to measure glancing angle θ

The spectrometer consists of two parts

- (1) A circular table
- (2) An ionisation chamber



$$2d \sin \theta = n\lambda$$

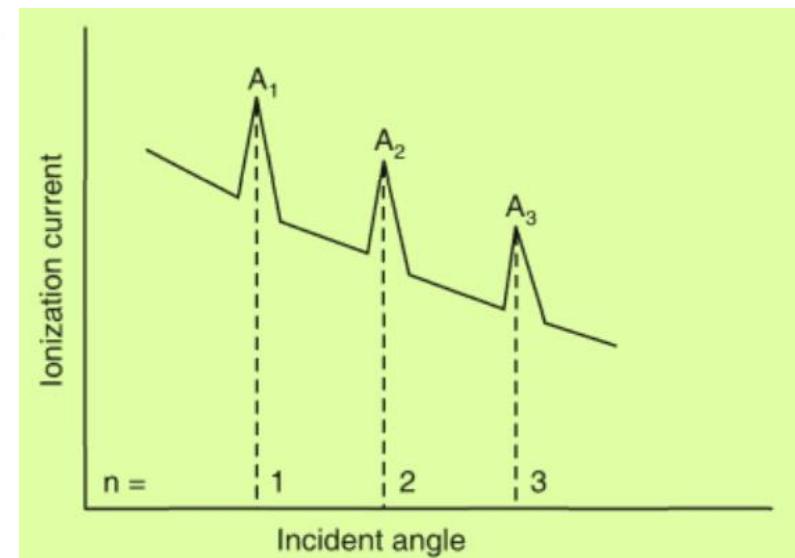
$$2d \sin \theta_1 = \lambda, \quad 2d \sin \theta_2 = 2\lambda \quad \text{and} \quad 2d \sin \theta_3 = 3\lambda$$

$$2d \sin \theta_1 : 2d \sin \theta_2 : 2d \sin \theta_3 = \lambda : 2\lambda : 3\lambda$$

$$\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$$

Determination of Lattice Constant:

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



Measurement of Wavelength of X-rays

The wavelength of X-rays is determined using brag's law. The glancing angle, θ , is experimentally determined from the graph. Therefore, the wavelength can be calculated by knowing d .

Calculation of d Let a be the distance between any two neighbouring atoms of the same kind and ρ be the density of the crystal.

Therefore,

$$\text{Mass of the unit cell} = \text{Volume} \times \text{Density}$$

For a cubic unit cell, the volume is a^3 .

Therefore,

$$\text{mass} = a^3 \rho$$

The mass of the unit cell

$$= \frac{\text{Number of atoms in a unit cell}}{\text{Avagadro's constant}} \times \text{Molecular weight}$$

$$= \frac{nM}{N_A}$$

i.e.,

$$\rho a^3 = \frac{nM}{N_A}$$

Therefore, the interatomic distance $a = \left[\frac{nM}{\rho N_A} \right]^{\frac{1}{3}}$

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

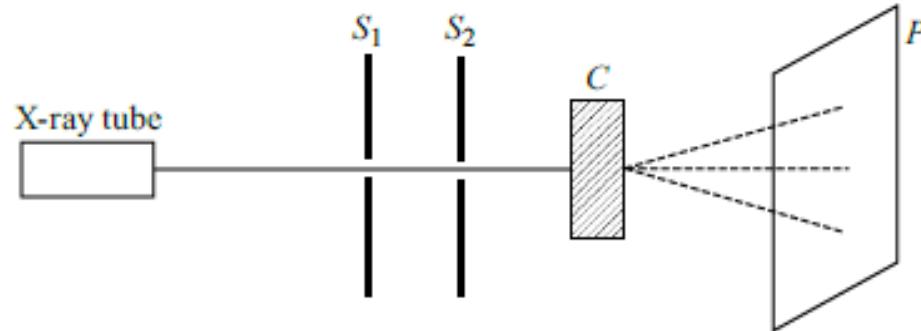
where h , k and l are the Miller indices of the plane and a the interatomic distance

DETERMINATION OF CRYSTAL STRUCTURE

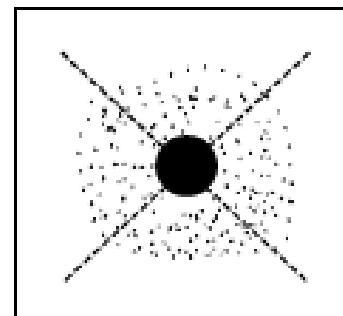
- (1) Laue's
- (2) Powder crystal
- (3) Rotating crystal

Laue's Method

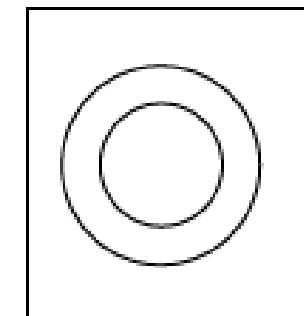
- Used to determine the crystal orientation
- Used to find the crystal is a single crystal or a polycrystalline material
- Not possible to determine the crystal structure and cell constants of the given crystal



Laue's method



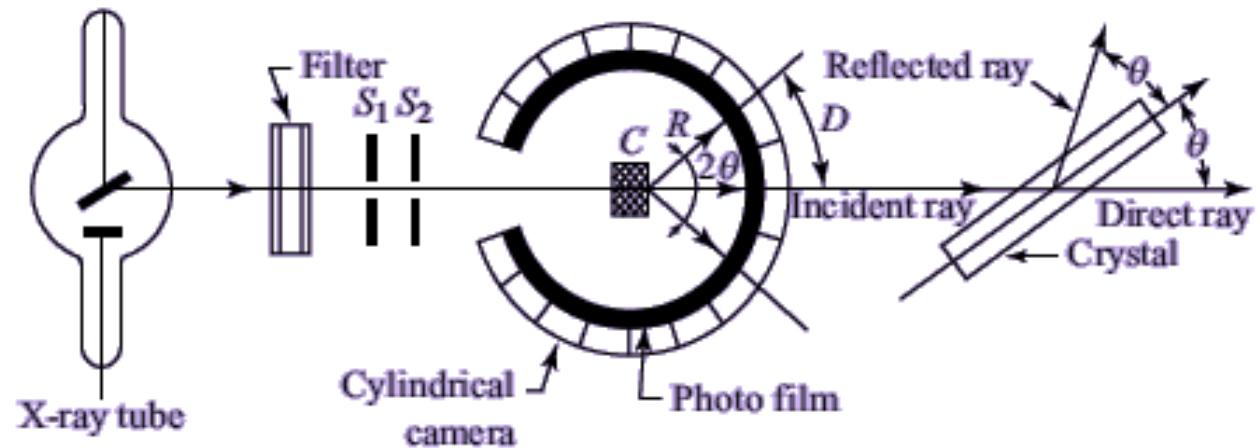
(a) Laue's spot



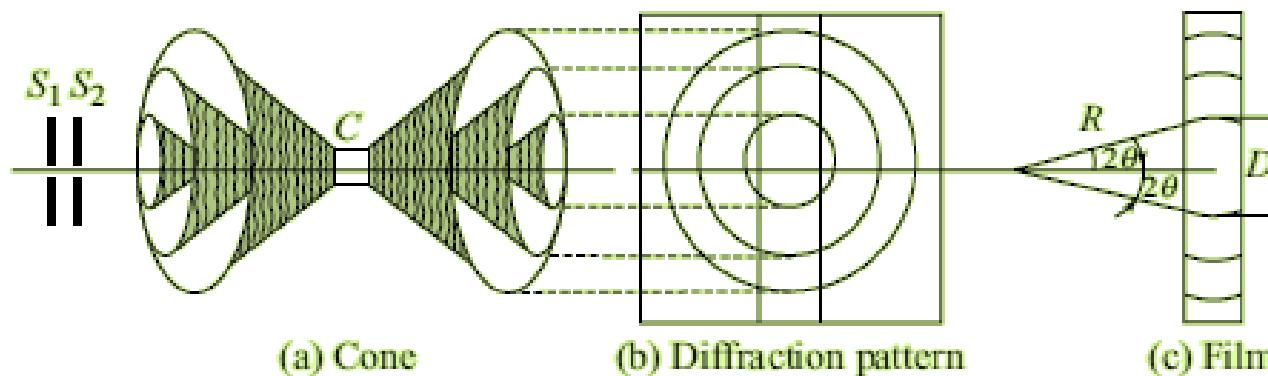
(b) Circular ring

Diffraction pattern

Powder Crystal Method



Powder diffractometer



Diffracted cones—Powder camera method

Distance D between two diffraction lines corresponding to a particular plane on the film is related to the Bragg's angle by the equation

$$4\theta = D/R \text{ radians}$$

Determination of Miller Indices—Powder Crystal Method

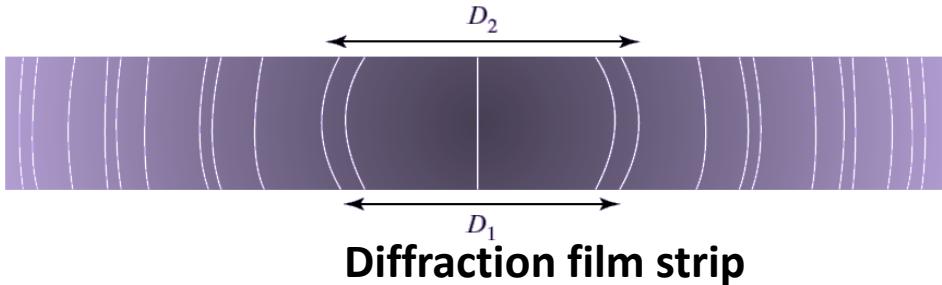
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Substituting the value of d in Bragg's equation

$$\frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin \theta = n\lambda$$

$$\begin{aligned} \sin^2 \theta &= \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2) \\ &= K^2 (h^2 + k^2 + l^2) \end{aligned}$$

| Sr. No. | Microscope reading | | Difference D | $v = D/4R$ | $\sin^2 v$ | $\sin^2 v = K^2 (h^2 \leq k^2 \leq l^2)$ | hkl |
|---------|--------------------|-------|----------------|------------|------------|--|-------|
| | Left | Right | | | | | |
| | | | | | | | |

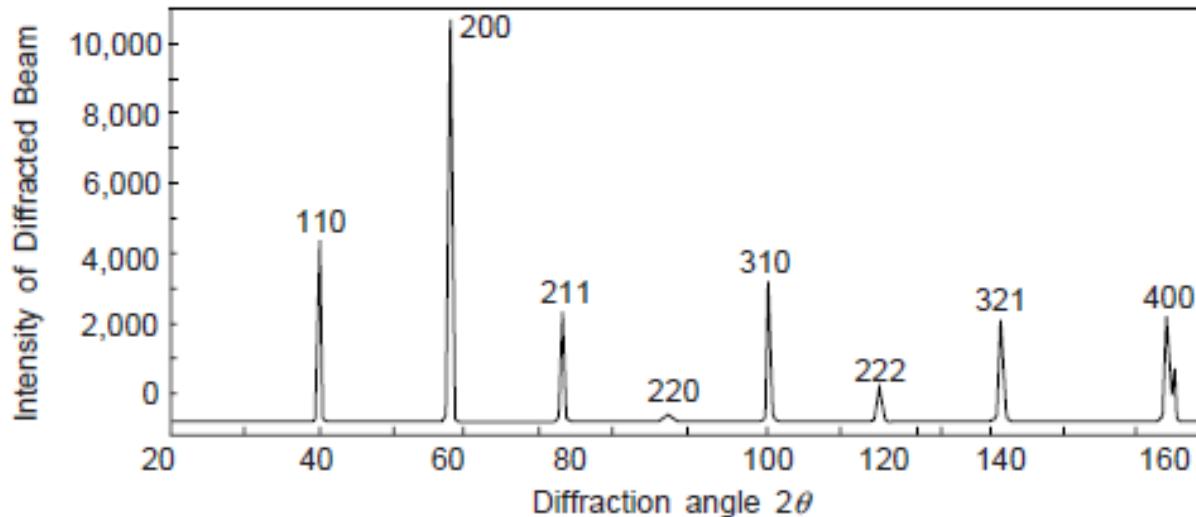


Advantages

- There is no need of single crystals because powder samples are used in this method.
- It is used to determine the Miller indices.
- The lattice parameters are accurately determined by measuring the spectrum at high angles.

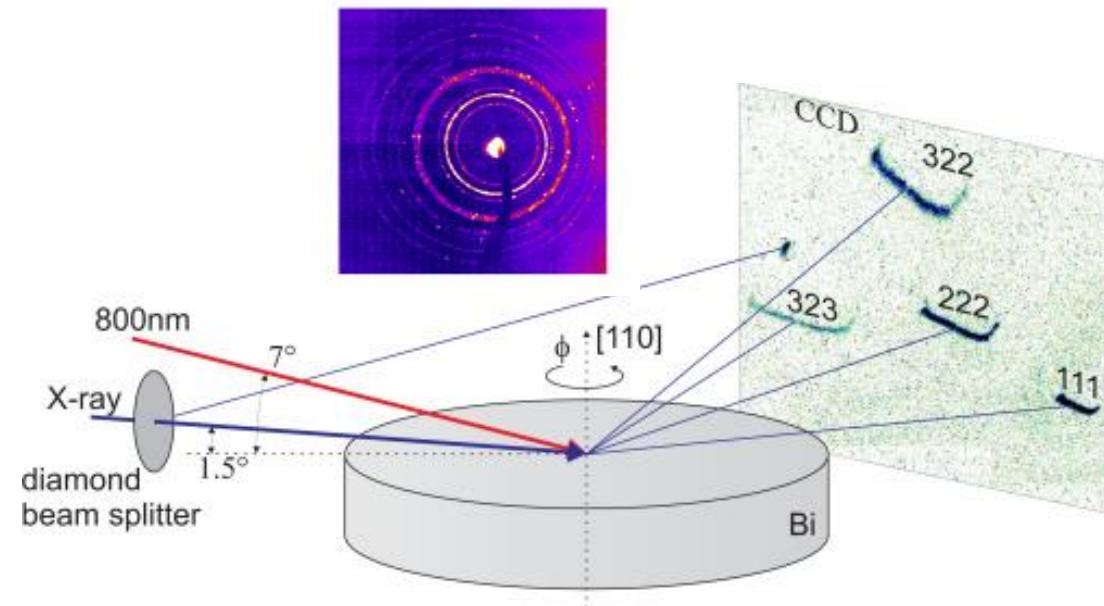
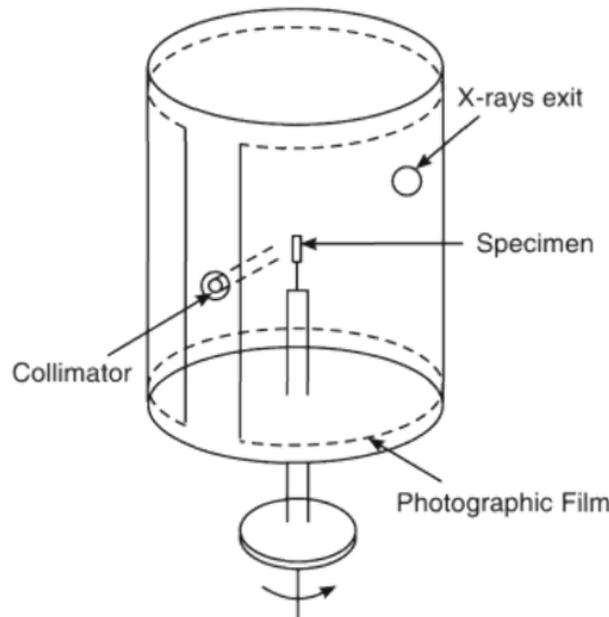
Limitations

The powder crystal method is not suitable for the determination of structure of crystals because of the multiplicity factor and the difficulty in indexing



Diffraction pattern intensity at various angles for tungsten

ROTATING CRYSTAL METHOD



Crystal defects

- In crystals, atoms or ions are arranged in a regular and periodic manner in three dimensions
- Natural crystals have some deviations from their regular arrangements

Any deviation in the crystal from the perfect periodic lattice or structure is known as *crystal imperfections* or *crystal defects*

The crystal imperfections can be classified on the basis of their geometry

1. Point defects (Zero dimensional defects)
2. Line defects or dislocations (One dimensional defects)
3. Surface imperfections or Planar defects (Two dimensional defects)
4. Volume defects (Three dimensional defects).

Why defect are important?

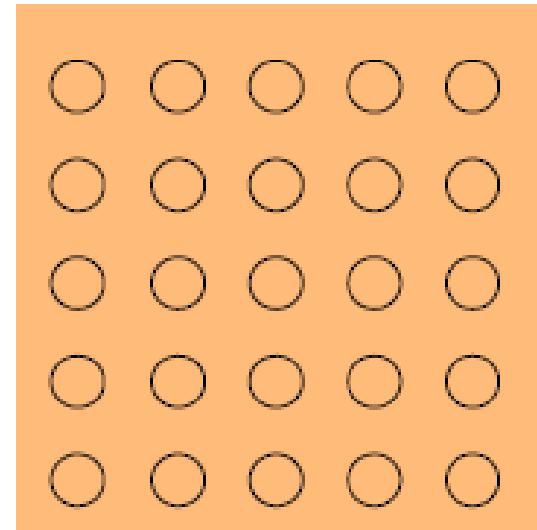
There are a lot of properties that are controlled or affected by defects, for example:

- Electric and thermal conductivity in metals (**strongly reduced by point defects**).
- Electronic conductivity in semi-conductors (**controlled by substitution defects**).
- Diffusion(**controlled by vacancies**).
- Ionic conductivity(**controlled by vacancies**).
- Plastic deformation in crystalline materials(**controlled by dislocation**).
- Colors(**affected by defects**).
- Mechanical strength(**strongly depended on defects**).

POINT DEFECT OR IMPERFECTION

- Imperfect at point-like regions in crystals
- Localised disruption of the lattice involving one or several atoms
- The size of the point imperfection is nearly one or two atomic distance

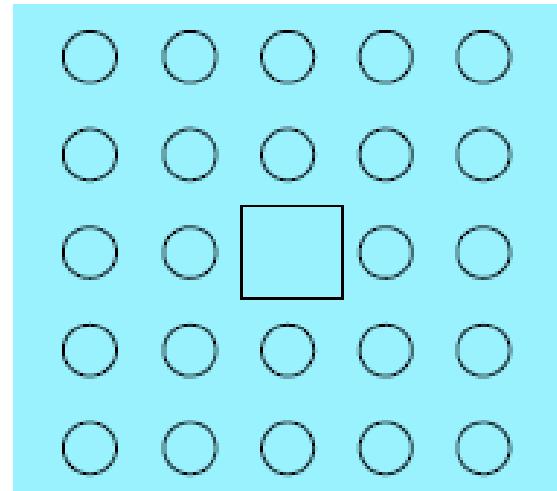
- (1) Vacancy defect
- (2) Substitutional defect
- (3) Interstitial defect
- (4) Frenkel defect, and
- (5) Schottky defect



Perfect crystal

Vacancy Defect

- The missing of an atom from the atomic site of a crystal is known as **vacancy**
- Vacancies are introduced into the crystal during **solidification** process
- The lattice vacancy is represented by a square □



Lattice vacancy

The number of lattice defects is proportional to the Boltzmann's factor, $\exp(-E_v/kT)$, where E_v is the average energy required to create such a vacancy.

Let N be the number of atoms per unit volume, then the vacancy concentration is

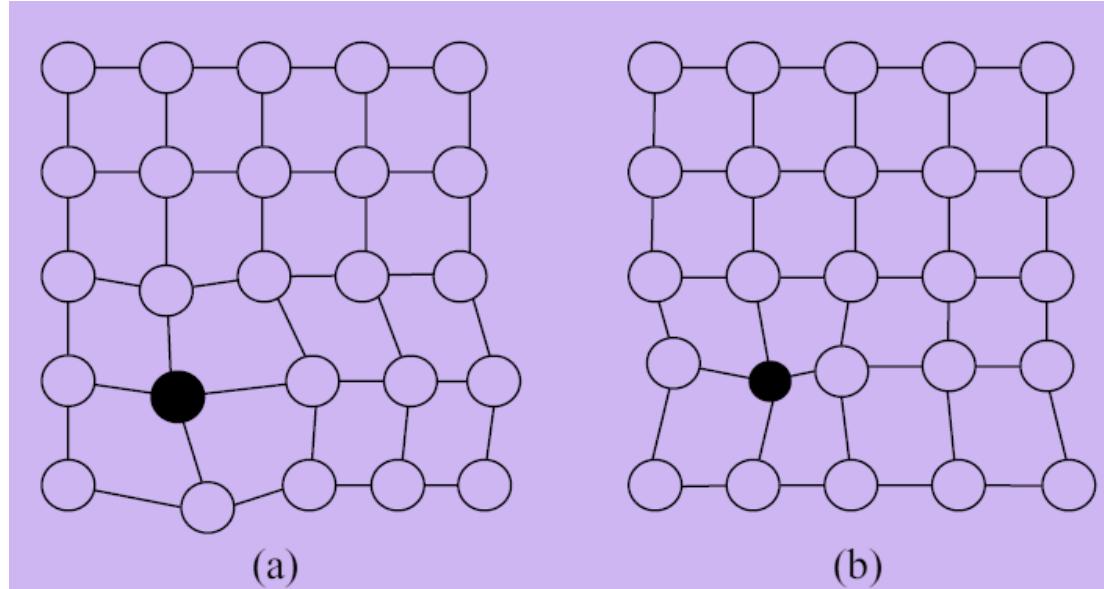
$$\frac{n}{N-n} = \exp\left(-\frac{E_v}{kT}\right)$$

We know that, the number of vacancy is less than the number of atoms per m^3 ($N \gg n$), above eq. can be written as,

$$n = N \exp\left(\frac{-E_v}{kT}\right)$$

Substitutional Defect

- A substitutional defect is produced when an atom is replaced by different types of impurity atom
- Eg. A pure crystalline metal with impurity atoms

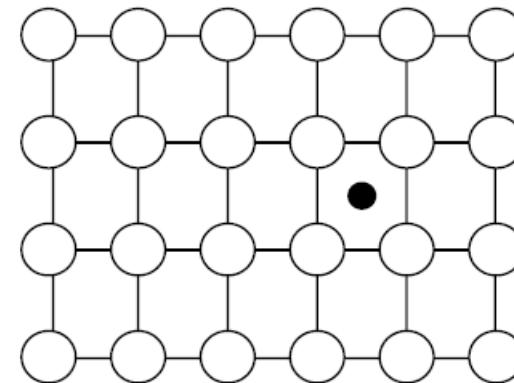


Substitutional defect produced due to the doping of impurities. Doping of (a) a big size atom produces lattice disturbances, and (b) a small size atom produces lattice disturbances

Interstitial Defect

- **Interstitial defect:** impurity atom or molecule occupies the intermolecular spaces in crystals
- Two or more atoms may share one lattice site
- Determined in some metals and semiconductors

An impurity atom can enter the interstitial position or void only when it is smaller in size when compared to the parent atoms



Interstitial defect

Schottky Defect

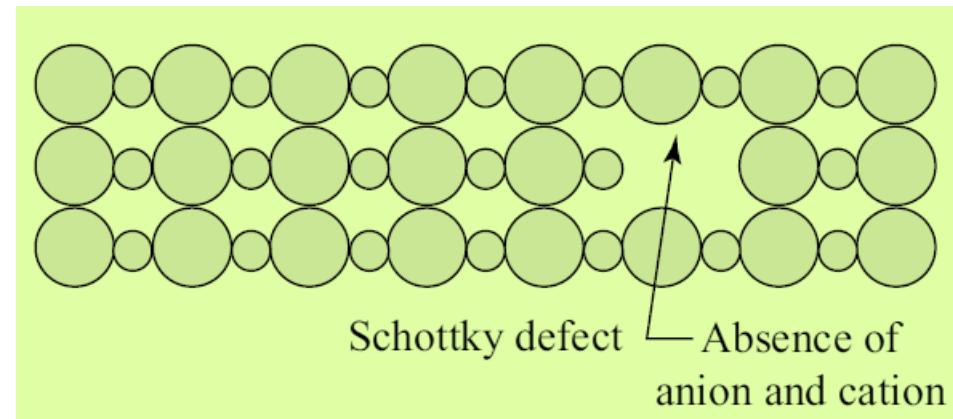
The missing of a pair of one anion and one cation from an ionic crystal is known as Schottky defect

Eg: alkali halides, NaCl, MgO

- The number of Schottky defects present in binary ionic crystals

$$n = N \exp\left(-\frac{E_S}{2k_B T}\right)$$

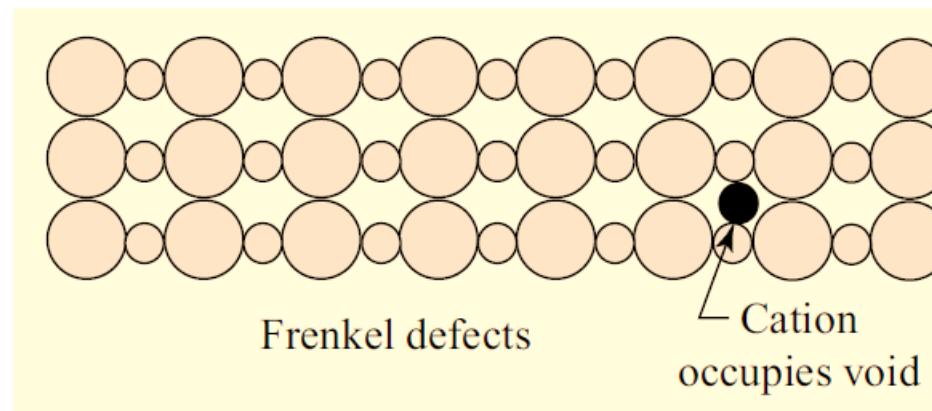
where N is the total number of cation-anion pairs, E_S is the average energy required to produce a Schottky defect and n the number of Schottky defects.



Frenkel Defect

Frenkel Defect: an ion leaves its position and occupies an interstice position

- A cation may get displaced from its position to an intermediate position because the cation size is smaller than the void space
- The anions do not get displaced because the size of the anion is larger than that of the void space
- Eg: pure silver halide



- The number of Frenkel defect in an ionic crystal is

$$n = \sqrt{NN_i} \exp\left(-\frac{E_f}{2k_B T}\right)$$

where E_f is the average energy required to displace a cation from its normal lattice position to an interstitial, N_i the number of interstitial sites and N the total number of cations

EFFECT OF POINT DEFECTS

Point defects are sources of distortion and cause residual strains in the lattice. But in some cases, they give rise to beneficial effects by improving mechanical and electrical properties of the materials.

- The addition of carbon atoms in iron increases its tensile strength.
- By changing impurities (carbon, manganese, chromium etc) or concentration of the impurities, various grades of steels are manufactured.
- Addition of copper atoms in gold increases its ductility so that it can be drawn into wires.
- Tin atoms substituted in copper lattice increase the bearing properties of copper.
- Pure germanium and silicon semiconductor materials are doped with pentavalent and trivalent impurities and as a result their electrical conductivity increases considerably.
- Copper atoms in silver increases the electrical resistivity of silver.
- Vacancies help the transport of atoms through the lattice for annealing etc purposes.

LINE IMPERFECTION

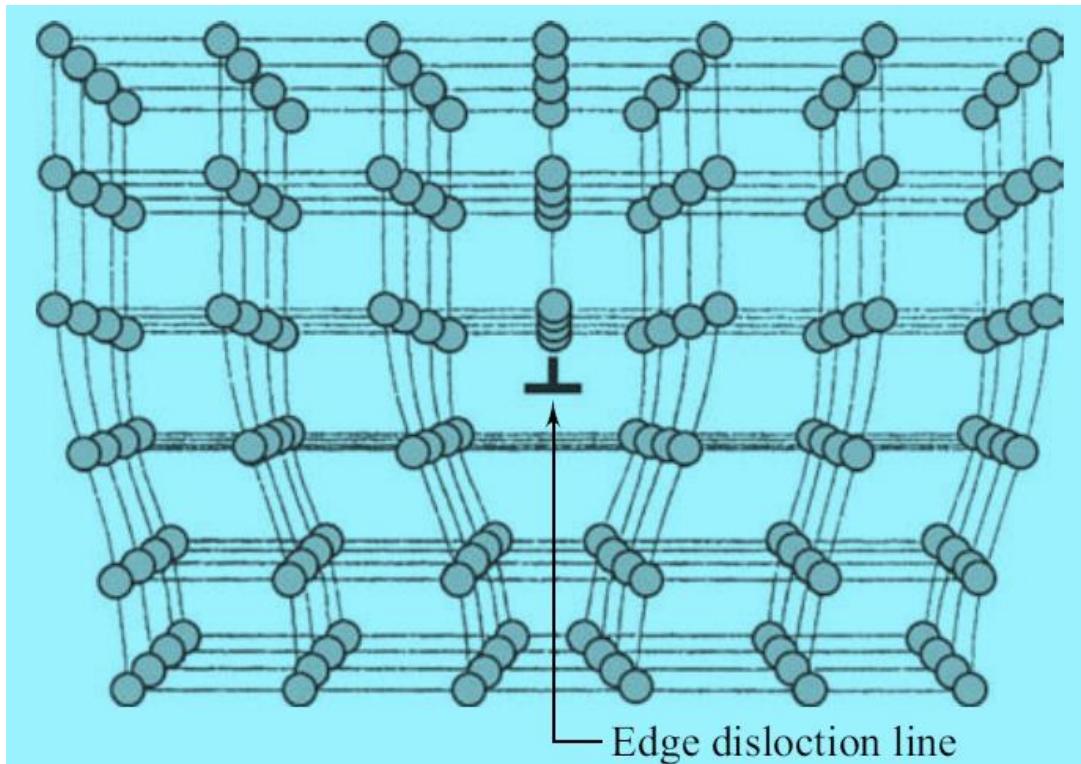
- An extra line of atoms is introduced in the crystal and causes the disturbance
- Imperfection along a line of the crystal is known as line imperfection (Dislocations)
- Disturbed region between two perfect parts of a crystal.
- A part-plane of atoms is displaced from its symmetrically stable position in the array.

Line imperfection

1. Edge dislocation
2. Screw dislocation

Edge Dislocation

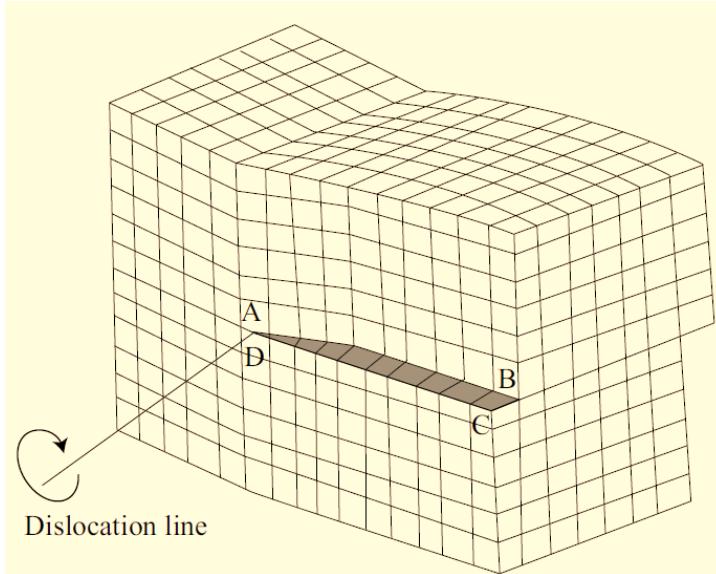
- Inserting a half plane of atoms between the regular planes of a crystal is known as **edge dislocation**
- **An extra layer of atom** is inserted from the upper portion of the crystal
- An extra layer of atoms is inserted from the **upper portion** of the crystal, it is represented by the letter, **⊥** (inverted Tee).
- An additional layer of atoms is inserted from the **bottom portion** of the crystal it is represented by the letter **T** (Tee).



Edge Dislocation

Screw Dislocation

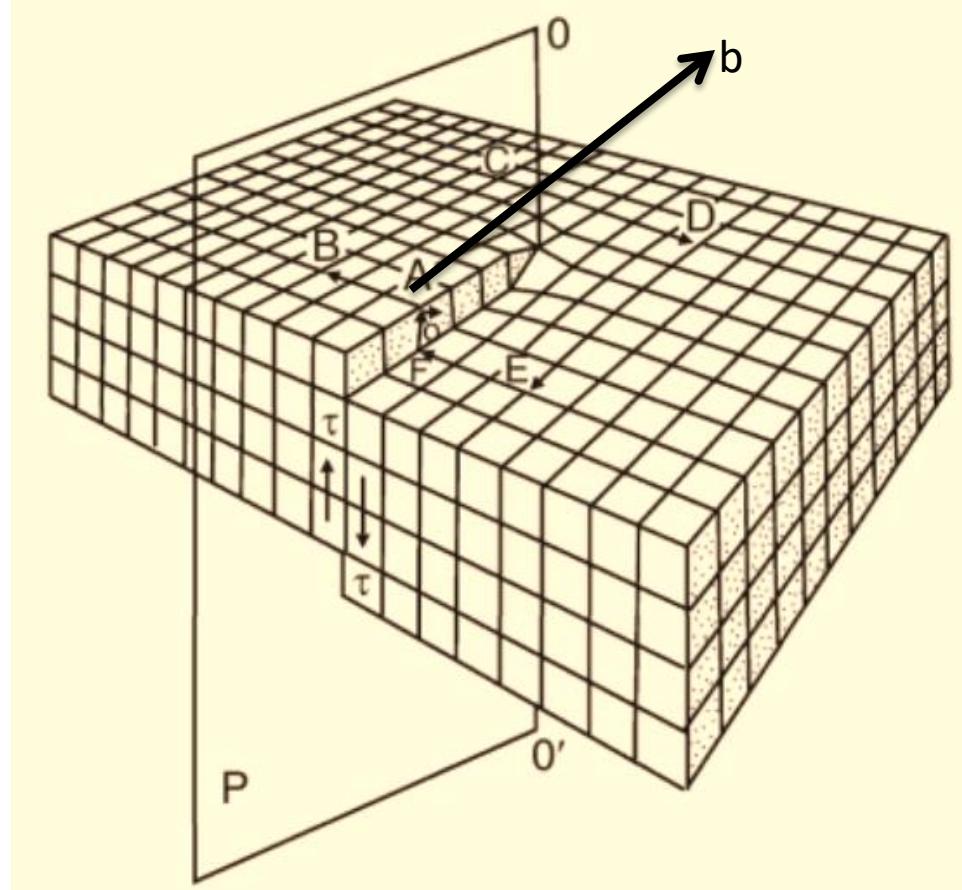
Screw dislocation: displacement of atoms in two separate perpendicular planes



Screw dislocation

The displacement of the atoms

$$r = \frac{b}{2\pi} \theta$$



where r is the displacement along the dislocation line and the angle θ is measured from a line perpendicular to the dislocation line.

Burgers Vector

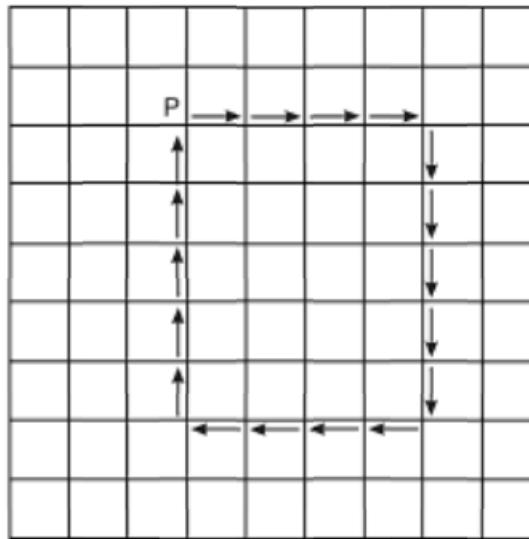
- A dislocation is characterized by considering an atomic circuit (**Burger circuit**) around the dislocation region.
- Dislocations are quantitatively described by the Burgers vector (**b**)
- It tells us the **direction** and the **magnitude** of the lattice distortion associated with a dislocation in a crystal.
- The Burger vector is **perpendicular** to the dislocation line in **edge dislocation** and **parallel** to the dislocation line **screw dislocation**.

Edge dislocation

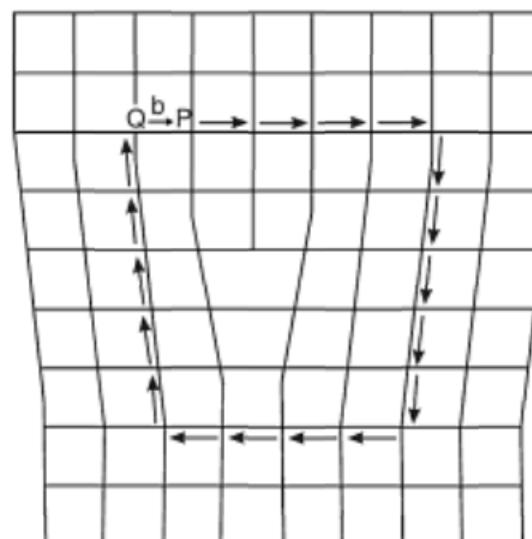
Burgers vector (BV) = QP = b

Screw dislocation

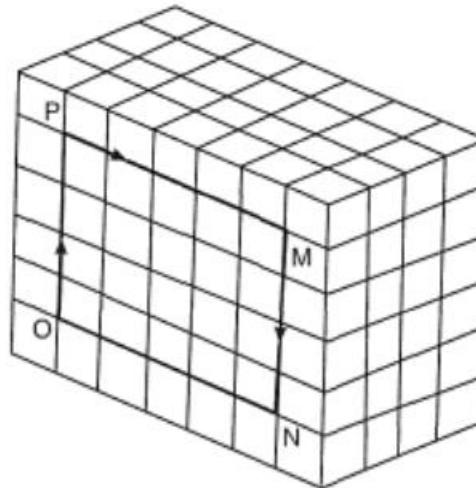
Burgers vector (BV) = b = FA



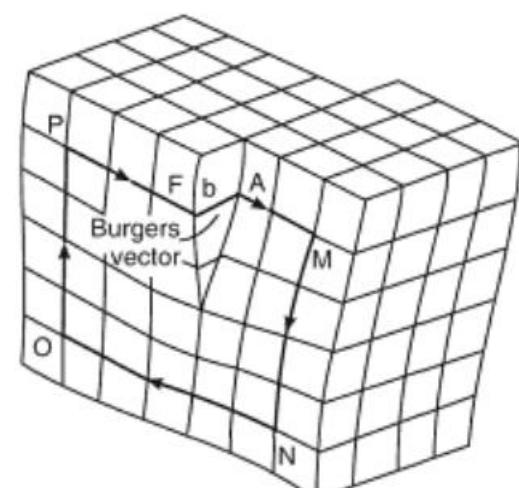
Perfect crystal



Crystal with edge dislocation



Perfect crystal



Crystal with screw dislocation

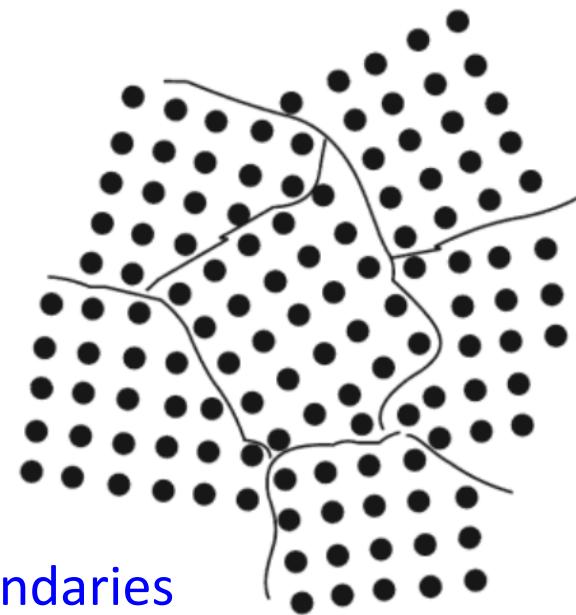
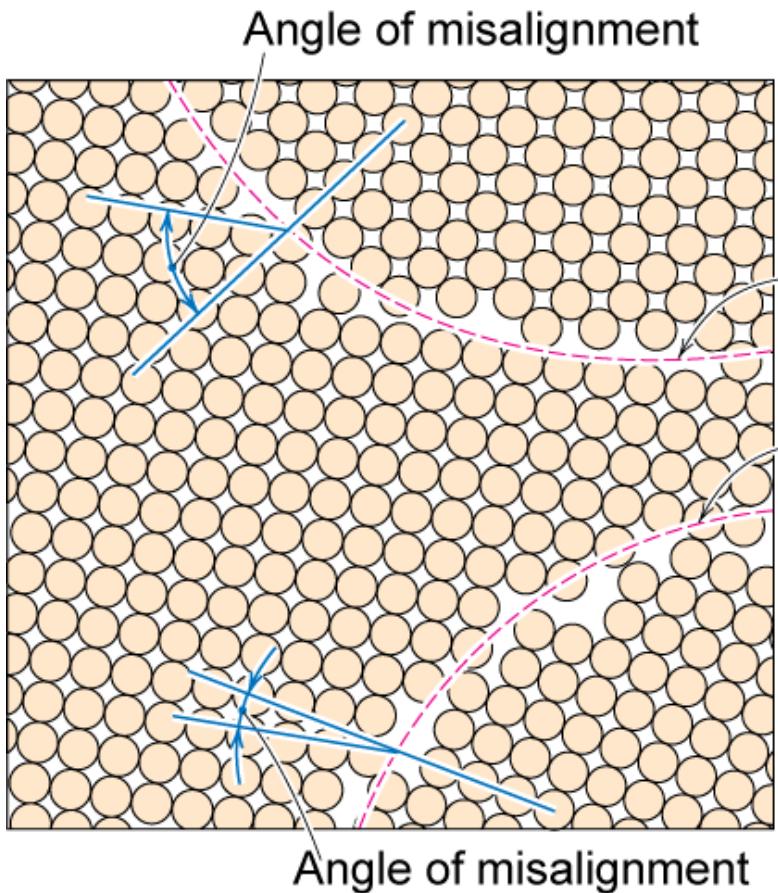
SURFACE DEFECT OR PLANAR DEFECT

The defect formed due to the change in the stacking of atomic planes on or across a boundary is known as surface defect

1. Grain boundaries
2. Twin boundaries
3. Stacking fault

Grain boundaries:

- are boundaries between crystals.
- are produced by the solidification process.
- have a change in crystal orientation across them.
- impede dislocation motion.



Grain Boundaries

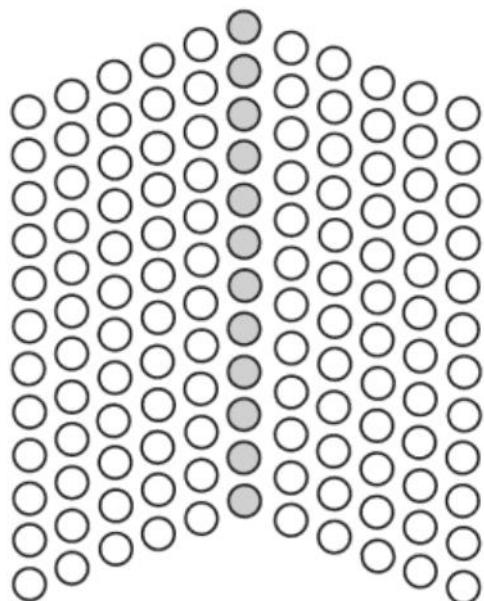
High-angle
grain
boundary

Small-angle
grain
boundary

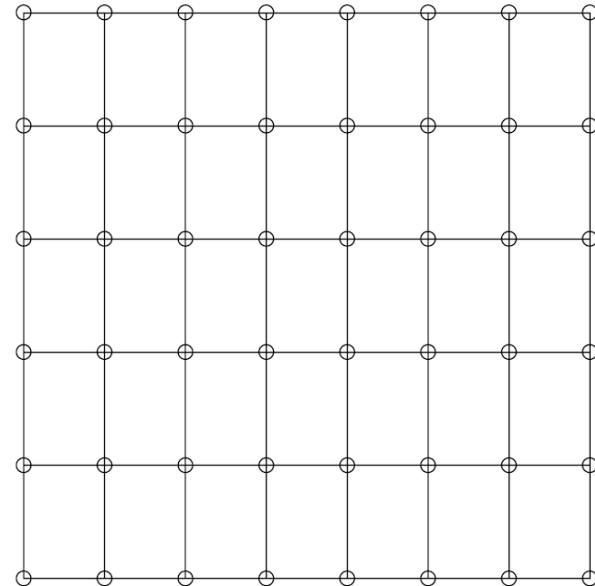
- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
 - high mobility
 - high diffusivity
 - high chemical reactivity

Twin Boundaries

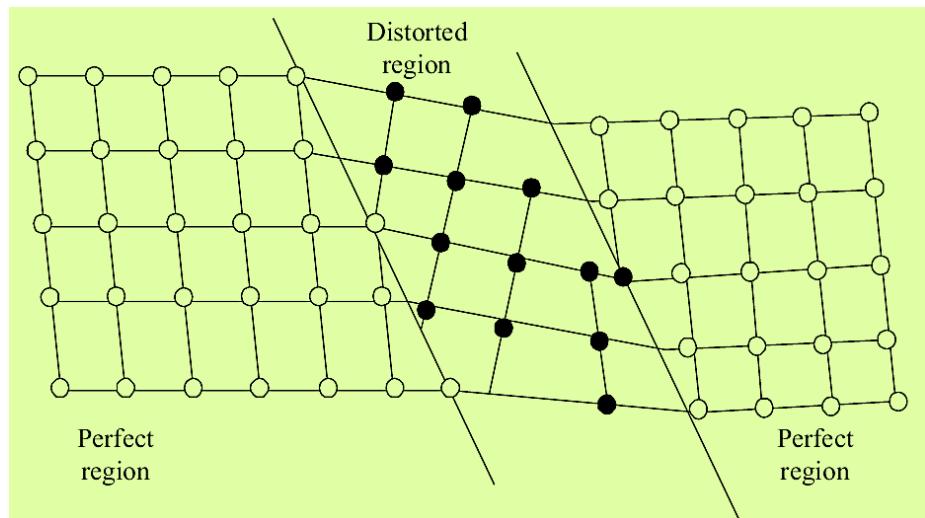
- Twinning is one of a plastic deformation which takes place along two planes
- The mirror plane is called as the twin boundary.
- Atoms on one side of a twin boundary are located in mirror-image positions of the atoms on the other side.
- Twin boundary is formed during the crystal growth or it may be the result of dislocation caused by an applied stress.



Twin boundaries



Before twinning – arrangement of atoms



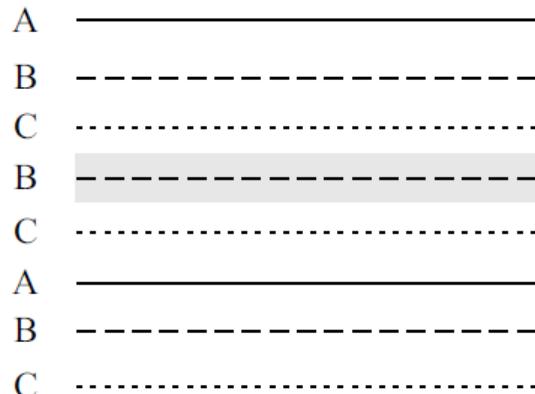
Twin boundaries

Stacking faults

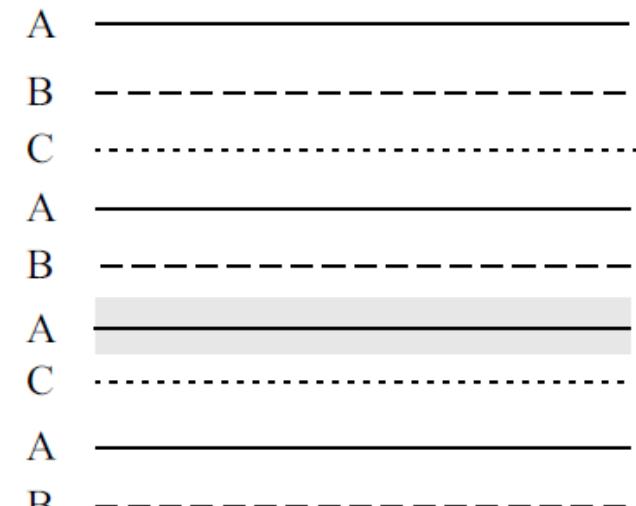
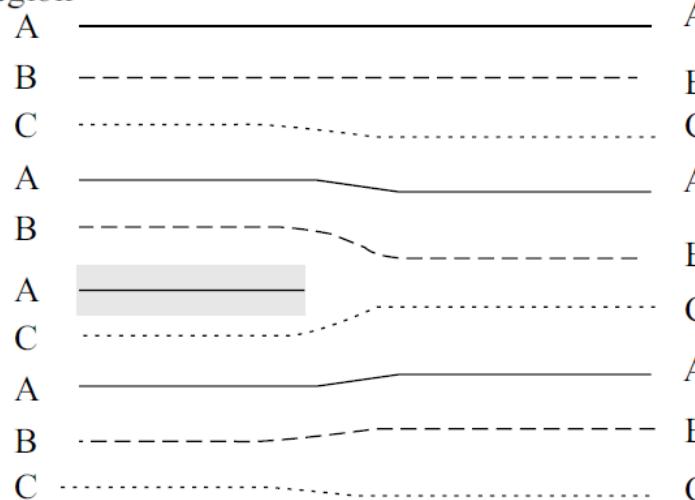
- Crystal is built by a stacking sequence of ABCABCABC... and so on.
- A stacking fault occurs, if the sequence goes wrong.

For FCC metals an error in ABCABC packing sequence

Ex: ABCABABC



- (a) In the regular stacking sequence, the layer A is absent at the shaded region



- (b) An extra layer of atom A is inserted at the shaded portion

- (c) The stacking fault is produced by inserting a layer A at the shaded portion and it terminates within the crystal

VOLUME DEFECT OR BULK DEFECT

Volume defects are Voids, i.e. the absence of a number of atoms to form internal surfaces in the crystal.

- Volume defects have similar properties to microcracks because of the broken bonds at the surface.
- Crack arises either during the growth of crystal or while using the crystal
- the crack arises due to a small electrostatic dissimilarity between the stacking sequences in metal

Thank you