

Crystal Physics

POOJA PREM

SOL
2110152.

- * classification of solids on the basis of arrangement of atoms and molecules
 - crystalline & non-crystalline
- * Crystalline solids: characterized by a regular, ordered arrangement of atoms, exhibit long range order
- * Non-crystalline / amorphous solids: characterized by a random arrangement of atoms, any regularity if present, exists only for a few atomic diameters, exhibit short range order.
- * Most solids are crystalline. Why? Energy released during the formation of an ordered structure is more than that released during the formation of an unordered structure. Crystalline solids are low energy in nature, thus preferred by most of the solids
- * When are amorphous solids formed? When the atoms do not have sufficient time to arrange themselves into a periodic fashion. e.g. plastic, rubber & glass.
- * Classification of crystalline solids: single crystalline and poly crystalline
Single crystalline \Rightarrow periodicity of atoms extends throughout the crystal.
Polycrystalline \Rightarrow consists of small aggregates of crystallites, randomly oriented, with well defined grain boundaries. Though the periodicity of the individual crystal may be interrupted at the grain boundaries, polycrystalline solids are more stable than single crystalline solids.
- * Crystalline vs. amorphous solids

crystalline	amorphous
1. periodic arrangement of atoms	1. irregular / random arrangement of atoms
2. long range order	2. short range order
3. sharp melting pt	3. melt over a range of temp.
4. anisotropic (have directional prop)	4. isotropic (no directional pr.)
5. esp can be cleaved giving regular surfaces	5. cannot be cleaved
6. quartz, mica, diamond	6. rubber, plastic, glass

* Crystallography: study of the geometry & physical properties of crystals.
Need: to understand the structure, electric, mechanical, thermal & optical properties.

Space lattice: an infinite array of points in 3D. Every point has surroundings identical to that of every other pt. in the surrounds

$$\text{for a 2D array: } \vec{r} = l\vec{a} + m\vec{b}$$

$$\text{for a 3D array: } \vec{r} = l\vec{a} + m\vec{b} + n\vec{c}$$

Basis: In order to obtain a crystal structure, it is necessary to place atoms / a group of atoms on the lattice point maintaining the same orientation throughout. It is these ~~gr.~~ atoms / group of atoms that is called the basis / motif and acts as a building unit / structural unit.

space lattice + base = crystal structure

Unit cell: smallest building block of a crystal consisting of atoms, ions and molecules.

geometry responsible for char. symmetric repetition in space produces a crystal lattice.

Lattice parameters: $a, b, c \Rightarrow$ axial lengths / translation vectors
 $\alpha, \beta, \gamma \Rightarrow$ interfacial angles

Primitive cell: a unit cell that contains only 1 lattice point effectively is called a primitive cell.

Note: all primitive cells are unit cells but not vice versa

Binaries Lattices

crystal system
cubic

tetragonal

orthogonal

monoclinic

triclinic

rhombohedral

hexagonal

Lattice types

S . B F

S B

S B F BA

S BA

S

S

S

S = simple

B = body centered

F = face centered

BA = base centered

Crystal Systems

crystal system

axial length

interfacial angles

examples

1. cubic

$a=b=c$

$\alpha=\beta=\gamma=90^\circ$

NaCl, CaF₂

2. tetragonal

$a=b \neq c$

$\alpha=\beta=\gamma=90^\circ$

Sn In

3. orthorhombic

$a \neq b \neq c$

$\alpha=\beta=\gamma=90^\circ$

sulphur, Topaz

4. monoclinic

$a \neq b \neq c$

$\alpha=\beta=90^\circ \gamma \neq 90^\circ$

Na₂SO₄, FeSO₄

5. triclinic

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90^\circ$

CuSO₄, K₂Cr₂O₇

6. rhombohedral

$a=b=c$

$\alpha=\beta=\gamma \neq 90^\circ$

calcite, anthracite

7. hexagonal

$a=b \neq c$

$\alpha=\beta=90^\circ, \gamma=120^\circ$

quartz, zinc

Miller Indices

- The crystal planes can be thought to be equidistant parallel planes passing through the lattice points
- Miller evolved a method to designate those parallel planes, by 3 nos h, k and ℓ called as Miller indices.
- They are defined as a set of whole numbers, obtained from the reciprocals of the coefficients of the intercepts made by the planes on the three axes.

Procedure to find Miller Indices

- Determine the intercepts of the plane on the crystallographic axes.
Let them be x' , y' , z' .
- Obtain the intercepts in terms of the lattice parameters.
Let them be p, q, r .
- Reciprocate them : $\frac{1}{p} : \frac{1}{q} : \frac{1}{r}$
- Find their LCM, so as to obtain a set of whole numbers.

Important features of miller indices

- All parallel sets of planes have the same miller indices
- If the intercept is -ve, the miller index is denoted by putting a bar over the number.

d Spacing or interplanar spacing in crystals

The perpendicular distance, or shortest distance d between successive parallel planes is called as the d spacing or interplanar spacing.

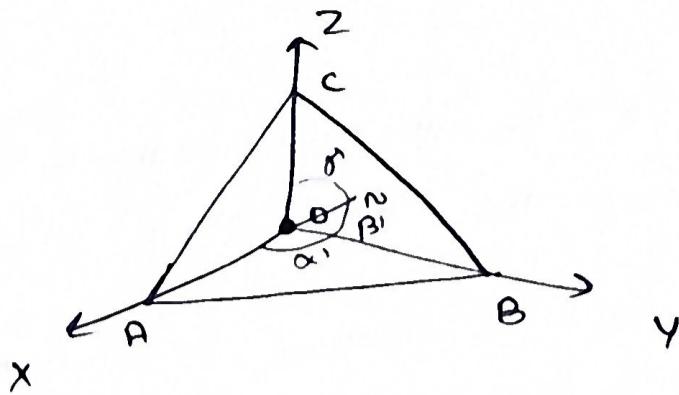
Consider a plane with Miller indices (hkl) . Let the intercepts be OA, OB & OC . The intercepts are proportional to the reciprocal of the Miller indices.

$$OA = pa \quad OB = qa \quad OC = ra$$

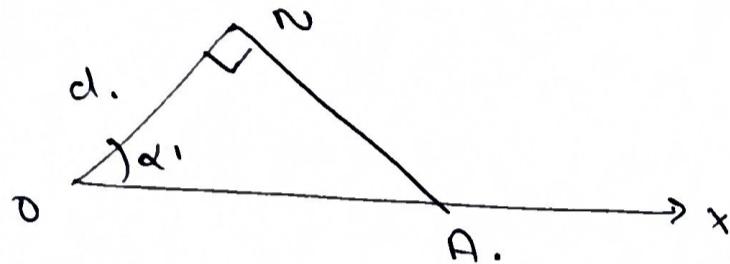
$$OA = \frac{a}{h} \quad \text{as} \quad p = \frac{1}{h}$$

$$OB = \frac{a}{k}$$

$$OC = \frac{a}{l}$$



ON is the normal drawn from the origin



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

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

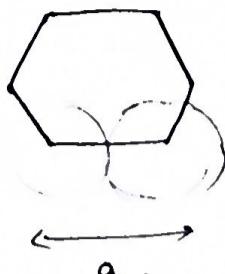
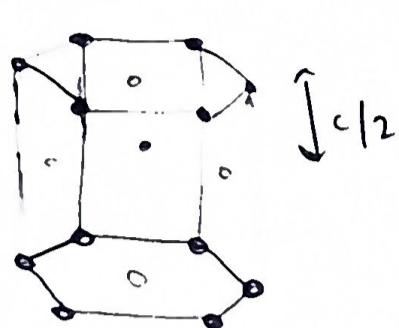
$$\cos \gamma' = \frac{dl}{a}$$

By the law of cosines, $\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$

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

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

Hexagonal Closed Packed Structure



- On the bottom layer, the central atom has 6 neighbouring atoms.
- At a height of $c/2$, there are 3 atoms, and the 3rd layer again has 1 central atom and 6 atoms around it.

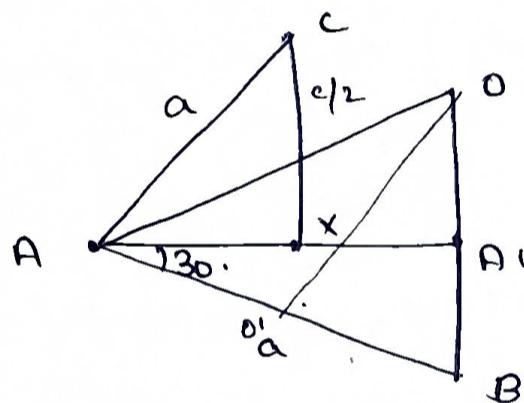
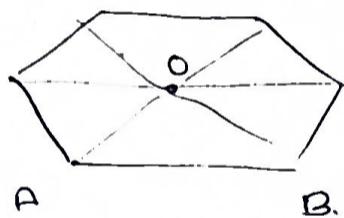
\therefore There are 12 atoms at the corner, 2 on the bases and 3 within the body

$$\text{coordination no} = 12$$

$$\text{no. of atoms per unit cell} = 6$$

$$\text{atomic radius : } a = 2r$$

To calculate c/a ratio



consider a $\triangle OAB$ from the hexagonal base.

$$\begin{aligned} AA' &= a \cos 30 \\ &= \frac{a\sqrt{3}}{2} \end{aligned}$$

$$AX = \frac{2}{3} AA'$$

$$AX = \frac{2}{3} \times \frac{\sqrt{3}a}{2} = \frac{a}{\sqrt{3}}$$

In the $\triangle ACX$, $AX^2 + CX^2 = AC^2$

$$\left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = a^2$$

$$\left(\frac{c}{2}\right)^2 = a^2 - \frac{a^2}{3} \quad \left(\frac{c}{2}\right) = \frac{2a^2}{3}$$

$$\left(\frac{c}{2}\right)^2 = \frac{2a^2}{3} \quad \text{--- (1)}$$

$$\frac{c^2}{4} = \frac{2a^2}{3}$$

$$\frac{c^2}{a^2} = \frac{8}{3}$$

$$\therefore c/a = \sqrt{\frac{8}{3}}$$

Packing factor:

$$\text{Volume of atoms in the unit cell} = 6 \times \frac{4}{3} \pi r^3$$

area of the base of the HCP cell:

$$= 6 \times \text{area of the equilateral } \Delta$$

$$= 6 \times \frac{\sqrt{3}}{2} a \times a \sin 60^\circ$$

$$= 3a^2 \times \frac{\sqrt{3}}{2} = \frac{3\sqrt{3}a^2}{2}$$

$$\text{height of the HCP structure: } c = \sqrt{\frac{8}{3}} a.$$

$$\text{Volume of the unit cell} = \frac{3\sqrt{3}a^2}{2} \times \frac{\sqrt{8}}{\sqrt{3}} \cdot a$$

$$= \frac{3a^3}{2} \cdot 2\sqrt{2} = 3\sqrt{2}a^3$$

$$\therefore \text{Packing fraction} = \frac{\text{volume of atoms in the unit cell}}{\text{Total volume of unit cell}}$$

$$= \frac{6 \times \frac{4}{3} \pi r^3}{3\sqrt{2}a^3}$$

$$= \frac{\frac{8}{3}\pi}{\frac{3\sqrt{2}}{2}} = \frac{\frac{8\pi}{3} \times \sqrt{2}}{\sqrt{2} + 2}$$

$$= \frac{6 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{3\sqrt{2}a^3} = 74\%$$

Properties of crystal structures

	SC	BCC	FCC	HCP
Unit cell volume	a^3	a^3	a^3	$3\sqrt{2} a^3$
No. of atoms per unit cell	1	2	4	6
Coordination number	6	8	12	12
atomic radius(r)	$a = 2r$	$a = \frac{4r}{\sqrt{3}}$	$a = 2\sqrt{2}r$	$a = 2r$
Packing factor	52%	68%	74%	74%
examples	α -potassium sodium chromium	iron sodium chromium	aluminium copper silver	magnesium zinc

Relation between lattice constant and density

Consider a cubic crystal of lattice constant $= a$
volume $= a^3$

$$\begin{aligned} \text{no. of atoms per unit cell} &= n \\ \text{mass of each unit cell} &= \rho \times a^3 \end{aligned}$$

$$\text{Avogadro's no.} = N$$

$$\text{mass of each molecule} = \frac{M}{N}$$

$$\text{mass of each unit cell for } n \text{ atoms} = n \times \frac{M}{N}$$

$$\Rightarrow \rho \times a^3 = \frac{n \times M}{N}$$

$$\boxed{\rho = \frac{nM}{a^3 N}}$$

($a^3 = V$, where vol. of the ~~any~~ unit cell is diff)

Diamond

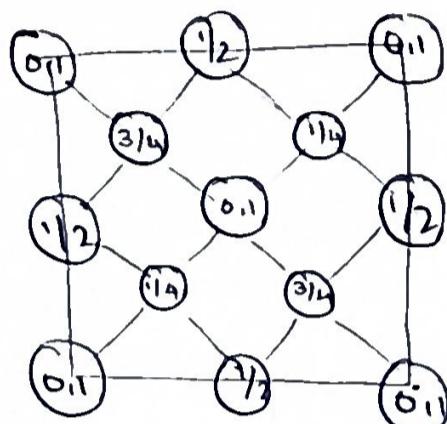
- has 2 interpenetrating FCC sublattices. One lattice has its origin at $(0,0,0)$ and another at $(a/4, a/4, a/4)$, $1/4$ th of the way along the body diagonal.

- The unit cell of diamond has 16 atoms in all.

corner : 8

Face : 6

inside : 4



- coordination no = 4

\Rightarrow very loosely packed

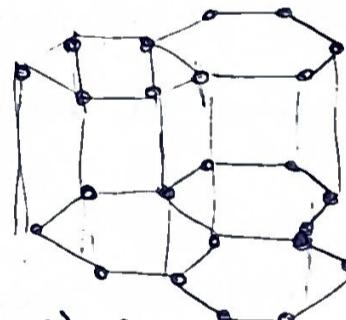
- no. of atoms per unit cell

$$\begin{aligned} &= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 \times 1 \\ &= 1 + 3 + 4 = \underline{\underline{8}} \end{aligned}$$

- atomic radius $\Rightarrow r = \frac{\sqrt{3}a}{8}$

- packing factor = 0.34

Graphite



- consists of an infinite arrangement of carbon atoms, possesses a layered structure.
- each plane : each carbon atom bonded to 3 others at a 120° angle honeycomb structure extends in 2 dimensions
- each layer connected by weak Van der Waals forces
- it is soft & slippery, has a value of < 1 on the Moh's scale.
- is used as a lubricant
- conducts electricity, as the electrons are free to move
- used as contact brushes in motors
- has a lower density than diamond
- absorbs light, appears black

Defects in solids

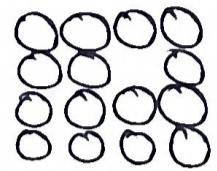
- Any deviation from the regular arrangement / perfect periodicity of the lattice arrangement is called a defect.
- Because of defects, the lattice arrays are no longer continuous but are rather broken up into blocks by discontinuities.
- Defects can be advantageous at times:
 - (i) chromium replacing a small portion of aluminium in aluminium oxide
 - (ii) 1 ppm doping of aluminium in silicon \Rightarrow p type semiconductor
 - (iii) 1 ppm doping of phosphorus in silicon \Rightarrow n type semiconductor
 - (iv) addition of copper to gold increases ductility
 - (v) carbon in iron \Rightarrow increased strength
 - (vi) tin in copper = bronze \Rightarrow increases bearing properties
- * Structure insensitive properties: not affected by presence of defects
 - (i) Stiffness
 - (ii) Electrical conductivity
 - (iii) Density
- * Structure sensitive properties: affected by presence of defects
 - (i) mechanical strength
 - (ii) magnetic strength
 - (iii) ductility
 - (iv) dielectric strength
 - (v) conduction

Point Defects

- They are point like imperfections.
- called zero dimensional defects

Characteristics

- (i) Local in its effect
- (ii) Internal energy increases (produces further distortion)
- (iii) Mechanical strength reduces
- (iv) Electrical resistance changes



① Vacancy Defect

- refers to an empty site in a crystal lattice
- can arise during imperfect packing of atoms during origin or from thermal vibrations at high temperature.
- At higher temperatures, the thermal energy due to vibration is high, and the probability of atoms jumping out of their sites is higher.

② Interstitial Defect

- occurs when an atom occupies an interstitial space.
 - For the small sized atom occupies the void without dislodging the parent atom.
 - can only happen when the atom is much smaller than the parent atom
- sizes : 0.414 \AA octahedral voids
0.225 \AA tetrahedral voids



③ Substitutional Impurities

- Another atom replaces the parent atom in the lattice
- Intentionally done during doping, such that aluminium / phosphorus replaces some silicon atoms



④ Frenkel Defect

- displacement of an ion from its position to an interstitial location
- defects in ionic crystals are subject to maintaining electrical neutrality
- anions are too big to fit into voids, mostly cations occupy the voids.
- e.g. in silver halides AgCl & CaF_2

5 Schottky Defect

- cations & anions are missing in pairs \Rightarrow electrical neutrality is maintained
- happens in alkali halides

6 Electronic Defects

- happens because of errors in charge distribution
- These defects are free to move around, leading to an increase in the electrical conductivity
- For eg. zinc ions may occupy interstitial spaces, leading to an increase in the positive charge. The other cations would have a surplus of negative charge.

Frenkel Defect

- Ions are displaced from their position in the lattice to an interstitial space.
- Cations occupy interstitial spaces due to their smaller size.

3. happens in silver halides, CaF_2

Schottky Defect

- A pair of cations & anions are missing
- Cations and anions are expelled in pairs

3. happens in alkali halides

Line Defects

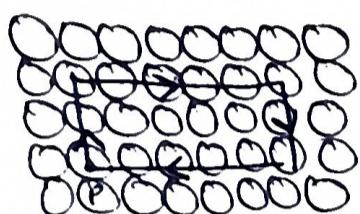
- line defects are one dimensional defects & are called dislocations. A dislocation is defined as the disturbed region between 2 substantially perfect portions of a crystal.

Characteristics

- In line defect, a particular part of a plane of atoms is disturbed / displaced from its symmetrically stable position
- responsible for slip, by which metals deform plastically

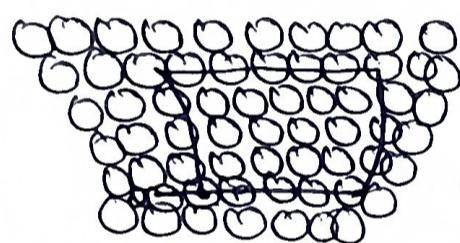
- It is also connected with other mechanical phenomena like creep, fatigue, yield point.
- The dislocation is the region between the slipped & unslipped portions of the plane. The Burgers vector represents the magnitude & direction of the strain component.

Burgers Vector



In a perfect crystal, the Burger circuit can be traced out as follows:

A distance of x is moved upwards from point P, then y distance towards the right, x distance downwards & y distance to the left. The point P is once again reached.

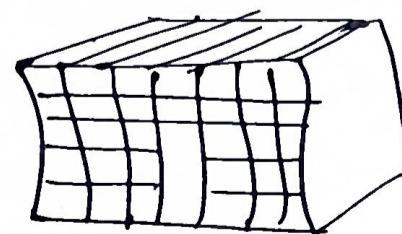
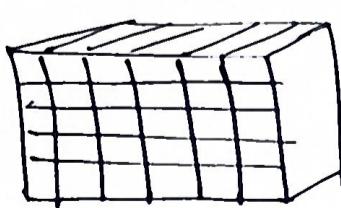
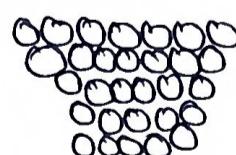


In an imperfect crystal, if the same Burger circuit is traced out again, the point P would not be reached.

∴ An additional distance of b would have to be moved to go back to the location.

The magnitude & direction of this step $\overrightarrow{QP} = b$ is called the Burgers vector.

Edge Dislocation



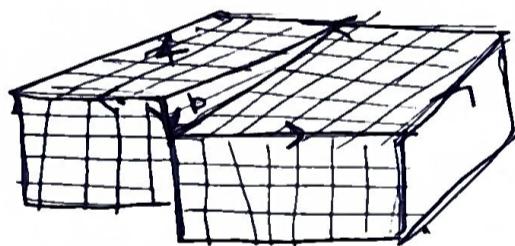
- If one of the vertical planes does not extend to the full length, but rather ends in between, it is called an edge dislocation.
- In a perfect crystal, all the atoms are at equilibrium positions and the bond lengths are equal.

In a crystal with an edge dislocation, the atoms are tightly packed together in the region above the edge dislocation & pulled apart in the region below.

- The bond length changes from an equilibrium value to either a higher or a lower value.
- The potential energy increases to a larger value.
- As the distortions are concentrated along the edge of the dislocated plane, they are called edge dislocations
 - represented by L and T, depending on whether the distortion is from the top or bottom
 - Burgers vector is \perp to edge dislocation.

Screw Dislocation

- refers to the displacement of atoms in one part of the crystal, w.r.t to another, forming a spiral ramp.
- Burgers vector is parallel to the screw dislocation.



Surface Defects

External Defects : • The surface of the crystal is an imperfection in itself.

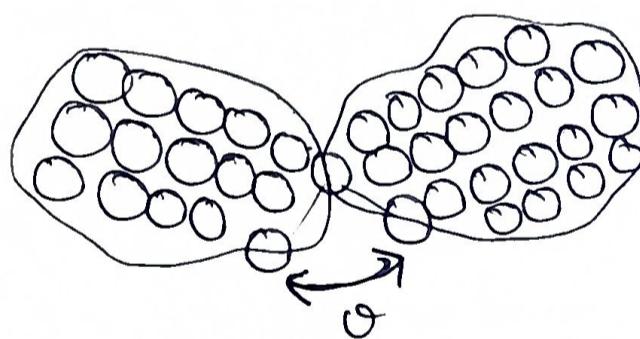
- The atoms on the surface have neighbours only on one side, while atoms in the middle, are completely surrounded by other atoms.
- The surface atoms have higher energy than the interior atoms in the interior.

Internal Defects -• They arise from a change in the stacking of atomic planes

- can be of diff. types : (i) grain boundaries
(ii) tilt boundaries
(iii) twin boundaries
(iv) stacking faults

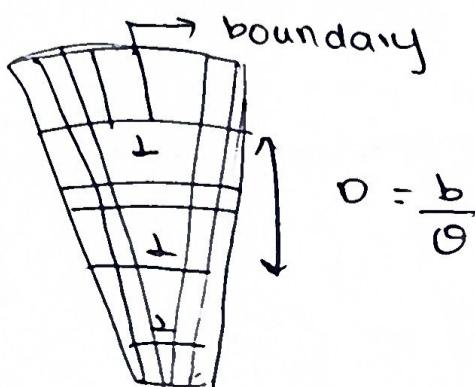
Grain boundaries : Polycrystalline alloys consists of an enormous no. of grains.

- Grain boundaries occur when imperfections are those imperfections that separate crystals of different orientations
- During solidification, new crystals are randomly oriented. They grow by the addition of atoms from adjacent regions, and eventually impinge on each other.
- When 2 parts of a crystal impinge on each other, the atoms are ~~forced~~^{in between} pulled in both directions
- They are forced to take up a compromising position in between.
- As a result, there is a boundary between the 2 parts.
- If the orientation diff. between neighbouring grains
 $> 10 - 15^\circ \Rightarrow$ high angle grain boundary
 $< 5^\circ \Rightarrow$ low angle grain boundary.



Tilt Boundary

- another surface defect, they are also called low angle boundary as the orientation difference between the different crystals is less than 10° .
- Comprises of edge dislocation stacked one on top of the other.
- angle / tilt calculated using = $\theta = \frac{b}{D}$

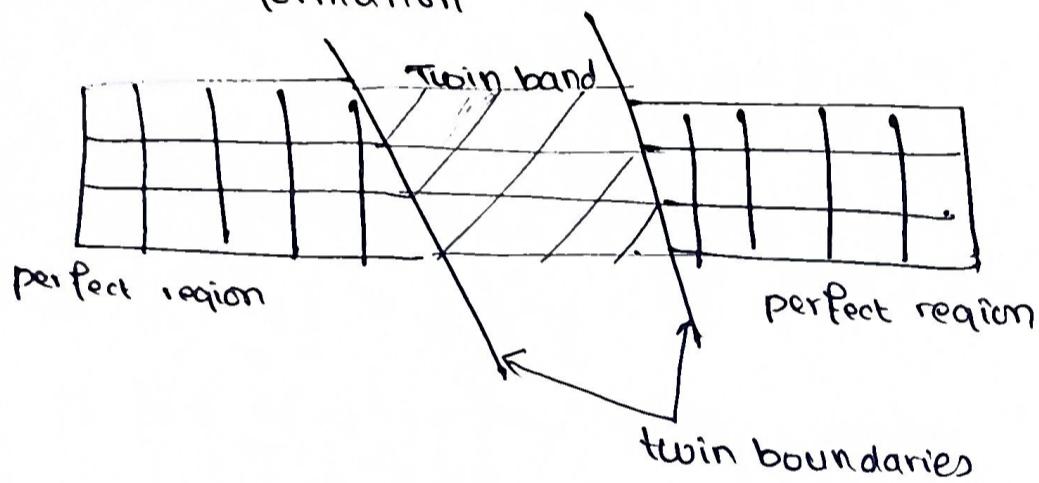


b = Burgers vector

D = avg. vertical distance
between dislocations

3. Twin boundaries

- Formed during the process of recrystallization
- The atomic arrangement is such that they are mirror images of each other, on either side of the twinned region.
- Twin boundaries occur in pairs such that the orientation change introduced by one is restored by another.
- Twin boundaries formed during
 - (i) mechanical working = mechanical twins
 - (ii) annealing after plastic deformation = annealing twins

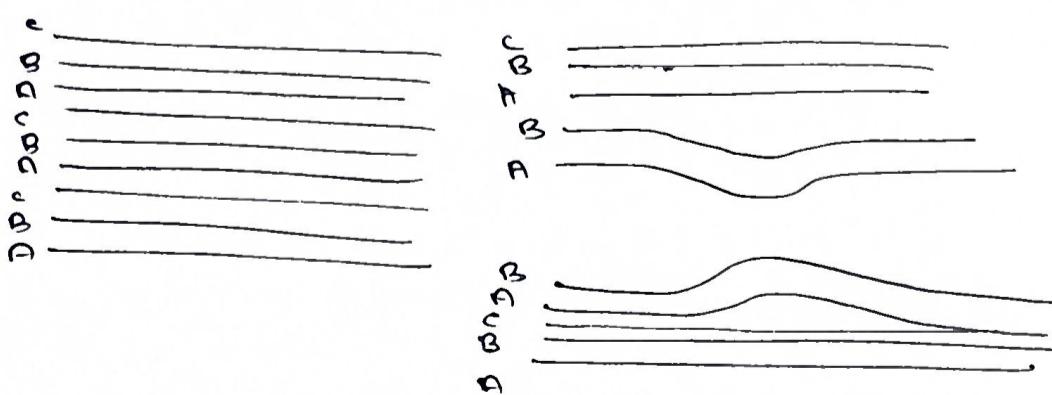


4. Stacking Faults: due to the improper sequencing of atomic planes
for e.g. FCC alloys have the arrangement ABC ABC ABC ABC

If there is a stacking fault, it may become:

ABC [AB AB] ABC

now it belongs to both the FCC & HCP structure.



Volume defects

- are called 3 dimensional defects
- volume defects like cracks may occur when there is only a small electrostatic dissimilarity between layers
- They can also be in the form of voids (clusters of atoms are missing)
- Pores: affect thermal, optical, mechanical properties
- Cracks: affect only mech. properties
- Foreign materials: mechanical, electrical, optical properties