

- (1) Bonding forces & energies of a system of two atoms
- Attraction - Long range force
  - Repulsion - Short range force
  - Bond length  $A_0$  = Equilibrium (Resultant force = 0)  
(Stable system)

$$F_{\text{attr}} = A/g_N \quad \left\{ \begin{array}{l} N > M \text{ for all systems} \\ g_N = \text{Distance} \end{array} \right.$$

$$F_{\text{rep}} = -A/g_M$$

$$F_{\text{res}} = F_{\text{attr}} + F_{\text{rep}}$$

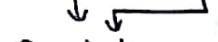
$$\bullet E = - \int F \cdot dg \quad , \quad F_{\text{res}} = 0 \text{ corresponds to minimum potential energy.}$$


---

### \* Types of Bonds → Potential Energy Surface

#### • Primary bonds

↳ Ionic, Covalent, Metallic



Crystals  
are hard  
but brittle

(Since ~~opposite~~  
repulsive forces  
increase rapidly)

#### • Secondary bonds

↳ Fluctuating <sup>Due to atom</sup>  
induced dipole bonds

↳ Polar molecule  
induced dipole bond

↳ Due to strong  
differences in  
induced charges  
(ex: HF)

(Free electron clouds)

Metallic are  
also non  
directional

⇒ Ionic bonds are non directional →  
Metallic are also non directional

↳ Covalent bonds are directional  
(Metallic bonds → unsaturated covalent bonds)

### \* Crystal Structures:

- Single crystal - Need to avoid thermal stress when the crystal is being formed.  
(long range order)  
(Thermal stress leads to deformations)
- Poly crystalline - Simple to form (due to thermal stress etc)  
(short range order)  
(Grains in crystal where regularity is maintained within grains, grain boundaries)  
↳ Thermal stress is high.
- Non crystalline - Grain boundaries are really small compared to cell size.  
(Amorphous)

- Crystal properties are direction dependent whereas amorphous material properties are not.

\*  $\Rightarrow$  Lattice + Basis  $\rightarrow$  Crystal structure.

↓                      ↓  
 Network of imaginary points      Basis unit of atoms / ions etc

- 14 Bravais lattices  $\rightarrow$  7 crystal systems

(Primitive unit cells - only corners present in lattice)

$\Rightarrow \underbrace{a, b, c}_{\text{Edge lengths}}, \underbrace{\alpha, \beta, \gamma}_{\text{Angles}} = \text{Parameters of unit cell}$

### \* Crystal Systems

- Cubic  $\rightarrow$  ~~Body centered~~, Face centered, Body centered
- Tetragonal  $\rightarrow$  ~~Body centered~~, Primitive, Body
- ~~Orthorhombic~~  $\rightarrow$  Primitive, Body, Face, Side
- Monoclinic  $\rightarrow$  Primitive, Side
- Triclinic  $\rightarrow$  Primitive
- ~~Orthorhombic~~  $\rightarrow$  1
- Trigonal  $\rightarrow$  Primitive
- Hexagonal  $\rightarrow$  Primitive

### \* Miller Indices (Direction)

- For any direction, the ratios of  $x, y, z$  intercepts
- ex:  $[110], [213]$  within cubic unit cells.

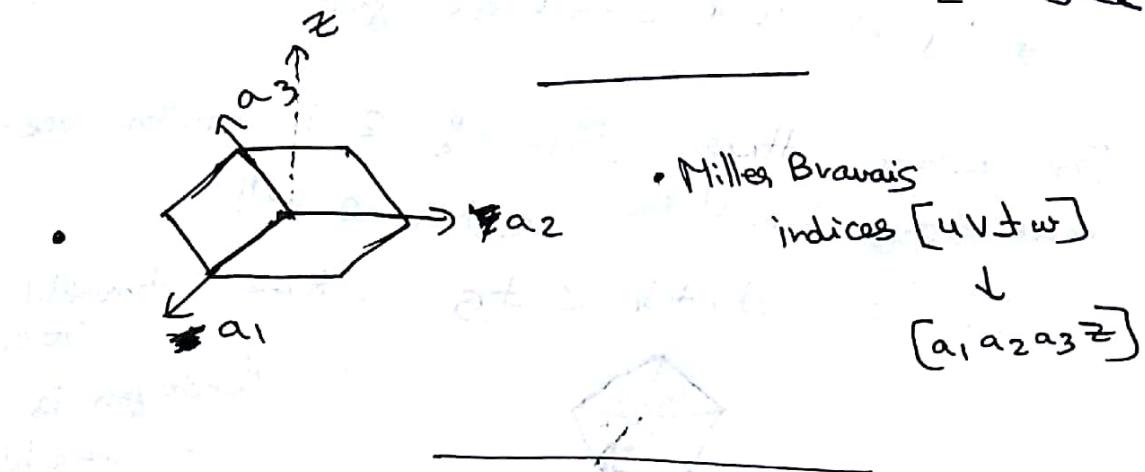
(Normalize by largest value)

(-ve values are shown with  $\bar{c}$ )

ex:  $[1\bar{2}3] \Rightarrow 1 \text{ in } x, -2 \text{ in } y, 3 \text{ in } z$

\* (Choose origin such that you stay within the unit cell)

- \*  $\Rightarrow$  Hexagonal use Bravais-Miller indices (4 value representation on)
- Note: Equivalent directions are ones having same interatomic spacing. ex  $[1\bar{2}3]$ ,  $(\bar{3}21)$ ,  $[\bar{2}13]$  etc.



### ③ Space Lattice:

- Infinite array of imaginary points in which every point has identical environment.
  - It is described by the unit cell.
  - Translation vector  $T$  connects any 2 points in the arrangement,  $T = h_1 \bar{a} + h_2 \bar{b} + h_3 \bar{c}$  where  $h_i$  = integer &  $\bar{a}, \bar{b}, \bar{c}$  are primitives of unit cell (vectors)
- $\Rightarrow$  Lattice + Basis = Crystal structure

### \* $\Rightarrow$ 2D Lattice:

- |                            |  |
|----------------------------|--|
| 4 fold rotational symmetry | 1) Square lattice (square unit cell)   |
| 2 fold                     | 2) Rectangular lattice (rectangular unit cell)                                     |
| 2 fold                     | 3) Rectangular lattice (face centered rectangular)                                 |
| 3 fold                     | 4) Diagonal lattice (diagonal unit cell) ( $a=b, \alpha=120^\circ$ )               |
| 2 fold<br>symmetry         | 5) Parallelogram lattice (diagonal unit cell) ( $a \neq b, \alpha \neq 90^\circ$ ) |

- Primitive unit cell  $\rightarrow$  1 atom in a cell

## \* Crystallographic restriction theorem:

\* Crystals cannot be formed by objects with 5, 7 or 8 fold or higher order fold rotational axes but only by objects of 2, 3, 4 & 6 fold rotational symmetry.

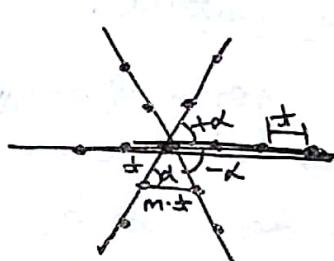
- For space lattices, sum of 2 translation vectors must be a translation vector as well,

$$\text{e.g.: } t_1 + t_4 \neq t_5 \therefore \text{Not a translation vector}$$



$\therefore$  Pentagon is not a space lattice

$\Rightarrow$  For a ~~shape with angled~~,



$$\cos \alpha = \frac{m}{2}$$

$$\therefore \cos \alpha = \frac{m \pm 1}{2}$$

$$m = -2$$

$$\alpha = 180^\circ$$

2 fold

$$m = -1$$

$$\alpha = 120^\circ$$

3 fold

$$m = 0$$

$$\alpha = 90^\circ$$

4 fold

$$m = 1$$

$$\alpha = 60^\circ$$

6 fold

$$m = 2$$

$$\alpha = 0^\circ$$

1 fold

(every object has this)

( $360^\circ$  rotation gives the same)

## 3D Space lattice:

- Triclinic — most asymmetric structure

$$a \neq b \neq c \Rightarrow \alpha \neq \beta \neq \gamma \neq 90^\circ$$

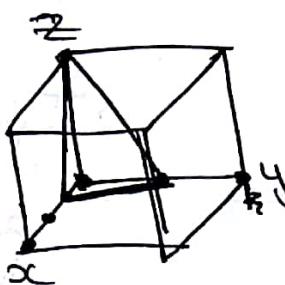
- Exhibits anisotropy (direction dependent properties)



## \* Crystallographic directions & planes:

- Miller indices for directions  $[uvw] \rightarrow$  Represent orientation

~~ex:  $(\bar{2} \ 2 \ \bar{1})$~~



If side length =  $a$

Intercepts: Consider  
~~length~~

~~1/2, 1, 1~~

~~2, 3, 2~~

- The indices represent the normal to the plane present within the cube

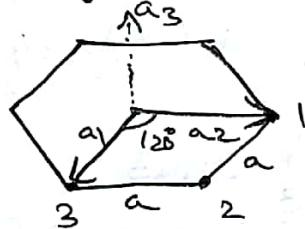
$\Rightarrow$  Normal  $[x \ y \ z] \rightarrow$  Plane with intercepts  $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

$\Rightarrow$  Equivalent planes are planes having same planar density.

ex:  $(101), (110), (011)$  are equivalent since (# of atoms / area) is the same.

## \* Braavais Miller indices: (Hexagonal)

- If we use normal miller indices



$\Rightarrow$  Point 1  $\Rightarrow (0, 1, 0)$  } Not equivalent  
Point 2  $\Rightarrow (1, 1, 0)$  }  
All axes should be equivalent.

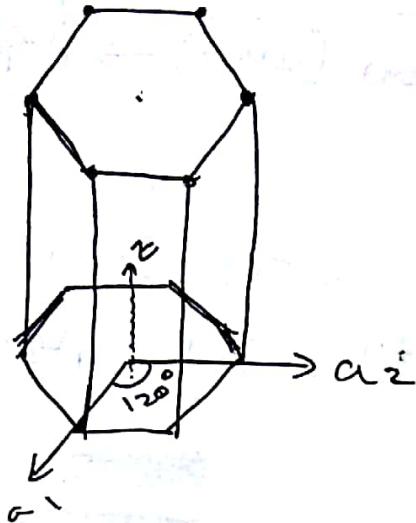
$\Rightarrow$  We move to these 4 indices,

$$u = \frac{1}{3}[2u' - v'] \quad t = -(u+v)$$

$$v = \frac{1}{3}[2v' - u'] \quad w = w'$$

(where  $u', v', w'$  are the previous)

(4) \*



Miller indices of sides

$(100)$   $\Rightarrow \Rightarrow$

$(110)$

$(010)$

Normal  
directions

→ Take intersections of plane with each axis and then the inverse gives us the miller indices for sides -  
(Assignment for example)

⇒ Metals are mostly FCC or BCC metallic crystals

ex: Al, Cu, Au, Pb

ex: Na, K,  $\alpha$ -Fe, Hg

a) FCC - Atoms are in contact along the face diagonal.  
(Unit cell side length =  $a$ )

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

$$\Rightarrow 2a = a/\sqrt{2}$$

\* • Coordination number = 12 } For a given atom there are 12 atoms that are the nearest neighbors

• No. of atoms per unit cell =  $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

$$\text{Atomic packing factor (APF)} = \frac{n \times \frac{4}{3} \cdot \pi r^3}{a^3} = 0.74 \quad (26\% \text{ void})$$

b) BCC - Atoms are in contact along the body diagonal

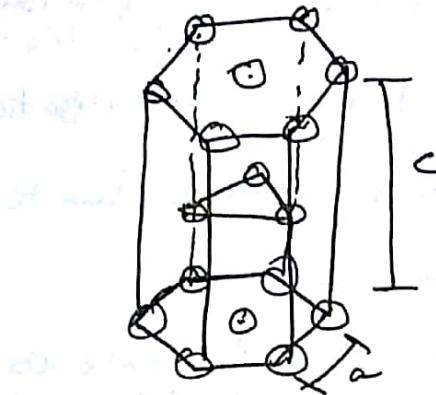
$$\rightarrow 4a = \sqrt{3}a, 2a = \frac{\sqrt{3}a}{2}$$

$\Rightarrow$  Coordination number = 8

- No. of atoms per unit cell =  $8 \times \frac{1}{8} + 1 = 2$
  - Atomic packing factor = 0.68
- 

### c) HCP:

- Hexagonal but with extra plane in the center with 3 atoms.



(Volume of hexagon)  
 $= 6 \times \frac{\sqrt{3}}{4} a^2 \times c$

( $a = 2r$  for packing since atoms touch each other)

- Each corner shared with 6 unit cells.

No. of atoms per unit cell =  $2 \times (6 \times \frac{1}{6})$

$$+ 2 \times (\frac{1}{2})$$

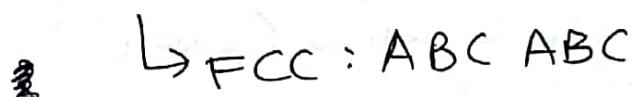
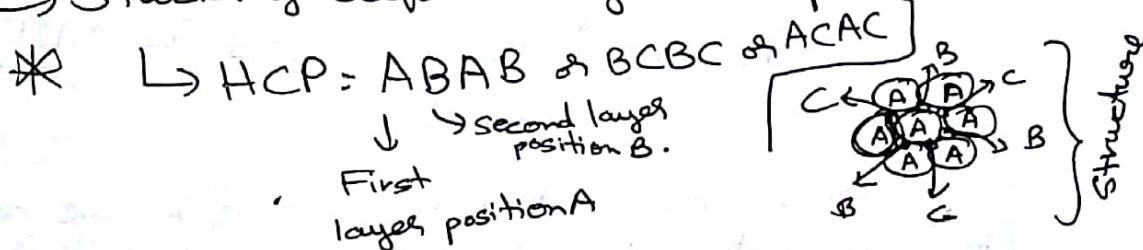
$$+ 3 = 6$$

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

$$= 0.74$$

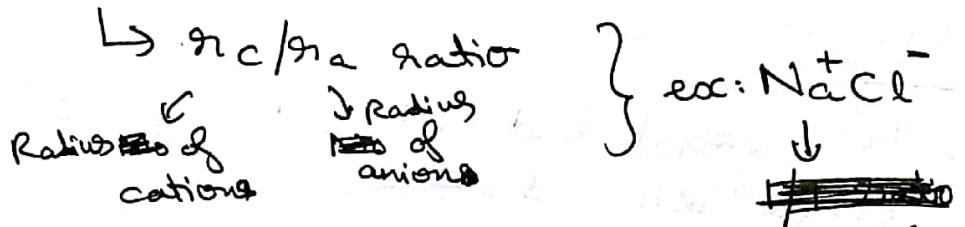
$(\frac{c}{a} = 1.63)$ ,  
 (For hexagonal).

$\Rightarrow$  Stacking sequence of atomic planes



## \* Ceramic crystals:

- Ionic characteristic:  $\text{escp} \left( 1 - 0.05(x_A - x_B) \right) \times 100$
- Based on charge

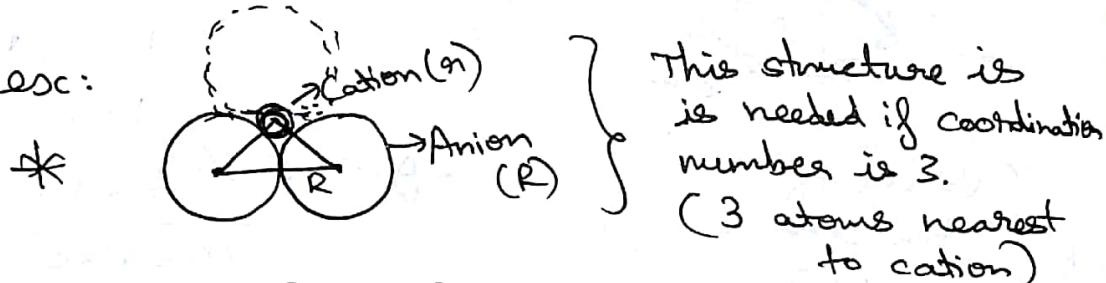


(Radius ratio & charge of an ion)

→ No. of anions near a cation & vice versa  
 & gradient ratios  
 \* are important for charge neutralization.

(Anion radius is generally larger due to electron cloud)

a) esc:



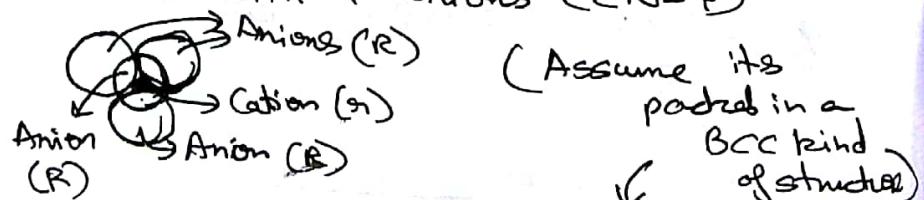
$$\cos 30^\circ = \frac{R}{R+r_2} = \frac{\sqrt{3}}{2}$$

$$\Rightarrow r_2 = \left( \frac{2-\sqrt{3}}{\sqrt{3}} \right) R = 0.155R$$

∴ Minimum <sup>radius</sup> ratio for CN=3 is 0.155.

b)

esc: For a coordination number of 4, we need  
 \* the cation to be larger so that it is in contact with 4 anions (CN=4)



$$R+r_2 = \frac{\sqrt{3}a}{2}$$

• 2 Anions are in contact along face diagonal  $\Rightarrow 2r_2 = \sqrt{2}a$

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

$$\therefore R + r = \frac{\sqrt{3}}{\sqrt{2}}R, \quad r = \left(\frac{\sqrt{3}}{\sqrt{2}} - 1\right)R$$

$\therefore$  Minimum radius ratio for CN=4 is 0.225

c) ec: For coordination number of 6



- Anions contact along face diagonal  $\rightarrow 2R = \sqrt{2}a$
- $a = R + r$  since cation & anion are in contact along side.

$$\therefore \frac{r}{R} = (\sqrt{2} - 1) = 0.414$$

Minimum radius ratio for CN=6 is 0.414

d) ec: For coordination number of 8

$\rightarrow$  Minimum radius ratio for CN=8 is



Note: NaCl  $\rightarrow$  CN=6, 4 sodium ions & 4 chloride ions per unit cell.

\* FCC of { (FCC) }  
 Na & FCC  $\hookrightarrow$  Edge centers & body center filled as well.  
 Cl are merged.

• CsCl  $\rightarrow$  Simple Cubic

Simple cube of Cs & simple cube of Cl merged

• ZnS (FCC) — Combination of Zn FCC & S FCC  
 (Covalent bonds)  $\hookrightarrow$  Diamond & Silicon have same  
 (All C) (All Si) structure.

- $\text{CaF}_2$ :  $\text{F}^-$  present at corners, edge centers, face centers & body centers

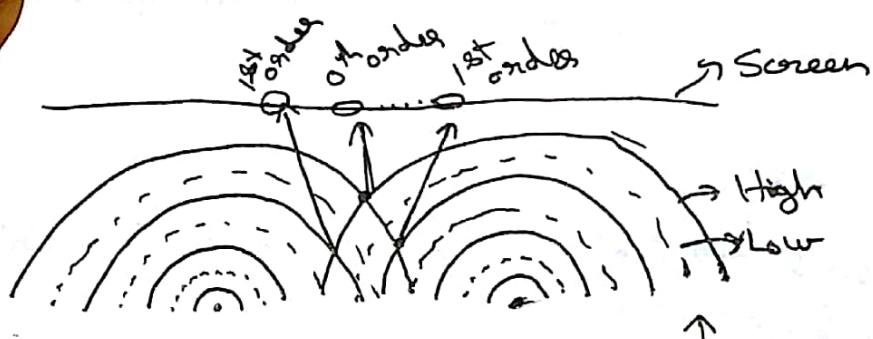
Ca present at 4 centers of cell  
Split into 8 cells.

- CN for F is
- CN for Ca is

- (5) • Structures of graphite & diamond.
- ↓
- Wander-walk bonds across layers (Hexagonal)
- ↳ FCC  $\leftarrow$  Combination of 2 FCCs.  
(Electric insulator, heat conduction)

## \* Reciprocal Lattices:

- X-Ray diffraction is used to observe structure.  
↳ The wavelength of X-Rays is comparable to the interatomic distances in crystals hence we use X-Ray diffraction.



- Intersections of two high crests creates a high spot else it's a low spot.

- This gives us the fringe pattern

\*  $\rightarrow$  A plane wave in the direction:  $e^{\frac{i\vec{k}\cdot\vec{r}}{}}$

$$\begin{aligned}\vec{r} &= \text{Distance,} \\ \vec{k} &= \text{Wave vector } (\lambda)\end{aligned}$$

- Wave vector  $\vec{k} = \text{Normal to wave fronts}$   
Wave front  $\vec{n}$   $\rightarrow$  Wave vector.

- Let  $\bar{R} = n_1 a_1 + n_2 a_2 + n_3 a_3$  be the translation vector of our crystal. (Periodicity  $\bar{R}$ )  $\rightarrow n_1, n_2, n_3$  are integers

$\hookrightarrow$  We observe that plane wave also has periodicity of  $\bar{R}$ .

$$\therefore e^{i(\bar{k} \cdot \bar{R})} = e^{i\bar{R}(\bar{n} + \bar{R})}$$

$$\Rightarrow e^{i\bar{k}} = e^{i\bar{k}\bar{R}}$$

$$\Rightarrow e^{i\bar{k}\bar{R}} = 1, \bar{k} \cdot \bar{R} = 2\pi m$$

- \* Assume  $\bar{k} = k_1 b_1 + k_2 b_2 + k_3 b_3$

Reciprocal lattice vectors

$$\Rightarrow b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}$$

$$b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)}$$

$$b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)}$$

Using these values, we find a solution.

$$\bar{k} \cdot \bar{R} = (k_1 b_1 + k_2 b_2 + k_3 b_3) \cdot (n_1 a_1 + n_2 a_2 + n_3 a_3)$$

$$= k_1 n_1 \cdot 2\pi \frac{(a_2 \times a_3) \cdot a_1}{(a_2 \times a_3) \cdot a_1}$$

$$+ k_2 n_2 \cdot 2\pi \frac{(a_3 \times a_1) \cdot a_2}{(a_3 \times a_1) \cdot a_2}$$

$$+ k_3 n_3 \cdot 2\pi \frac{(a_1 \times a_2) \cdot a_3}{(a_1 \times a_2) \cdot a_3}$$

+ 0  $\rightarrow$  Rest of the cross terms are zero

$$\therefore \bar{k} \cdot \bar{R} = 2\pi (k_1 n_1 + k_2 n_2 + k_3 n_3) = 2\pi m$$

Should be integer

Such  $\bar{k}$  satisfies the condition.  $\therefore k_1, k_2, k_3$  should be integers to be a valid wave vector  $\bar{k}$ .

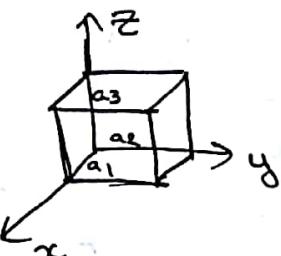
- These lattices of wave vectors (forming a plane wave with same periodicity as lattice) are known as reciprocal lattices. We see reciprocal lattice as diffraction pattern.
- Reciprocal of simple cube = simple cube.

→ Reciprocal of FCC = BCC

→ Reciprocal of BCC = FCC

esc: Reciprocal lattice of S.C = S.C

\* \*



$a_1 = a_2 = a_3 = a$  } Lengths

$$\Rightarrow a_1 = a\hat{x}, a_2 = a\hat{y}, \\ a_3 = a\hat{z}$$

$$\Rightarrow b_1 = \frac{2\pi(a_2 \times a_3)}{a_1 \cdot (a_2 \times a_3)} = \frac{2\pi(a\hat{y} \times a\hat{z})}{a\hat{x} \cdot (a\hat{y} \times a\hat{z})} \\ = \frac{2\pi a^2}{a^3} \hat{x} \\ = \frac{2\pi}{a} \hat{x}$$

Note:

## ⑥ Pol

\* • Mole

• Cr

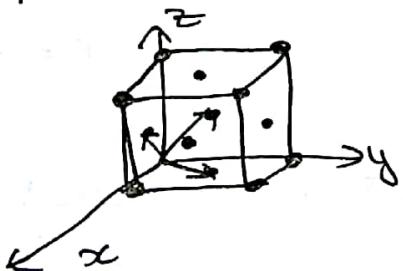
An

Similarly  $b_2 = \frac{2\pi}{a} \hat{y}, b_3 = \frac{2\pi}{a} \hat{z}$

We can see that these form a reciprocal lattice that is also a simple cube.

esc: Reciprocal lattice of FCC = BCC

\* \*



$a_1, a_2, a_3$  are vectors to the 3 nearest face centers

$$\rightarrow a_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}, a_2 = \frac{a}{2}(\hat{y} + \hat{z}), \\ a_3 = \frac{a}{2}(\hat{x} + \hat{z})$$

known periodicity  
as lattice  
as diffraction pattern.

$$\Rightarrow b_1 = \frac{2\pi (a_2 \times a_3)}{a_1 \cdot (a_2 \times a_3)}$$

$$a_2 \times a_3 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & a/2 & a/2 \\ a/2 & 0 & a/2 \end{vmatrix} = \hat{x} \cdot \left(\frac{a^2}{4}\right) + \hat{y} \left(\frac{a^2}{4}\right) - \hat{z} \left(\frac{a^2}{4}\right)$$

↙  
Direction of  $b_1$

$\therefore a_1 \cdot (a_2 \times a_3) \rightarrow$  Just a number.

} Lengths

$$a_2 = a\hat{y},$$

$$a_3 = a\hat{z}$$

$$(a\hat{y} \times a\hat{z})$$

$$\hat{x} \cdot (a\hat{y} \times a\hat{z})$$

$$\frac{2\pi a^2}{a^3} \hat{x}$$

$$\frac{2\pi}{a} \hat{x}$$

$$\frac{2\pi}{a} \hat{z}$$

form a  
also a

$\Rightarrow$  We can see that  $\frac{a^2}{4} (\hat{x} + \hat{y} - \hat{z})$  points to a body center. Similarly  $b_2$  &  $b_3$  point to other body centers.

Reciprocal of FCC = BCC.

Note:  $a_1, a_2, a_3$  of BCC are lines joining origin to 3 nearest body centers.

## ⑥ Polymers:

- Molecules are the basis for the structure.
- They form linear chains
- Crystallinity - Orderliness - Density is ~~high~~ high
- Amorphous - Density is low.

BCC

,  $a_3$  are  
to the 3  
face centers

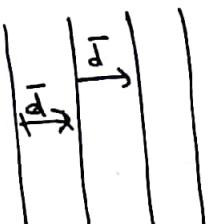
$$a_2 = \frac{a}{2} (\hat{y} + \hat{z})$$

$$= \frac{a}{2} (\hat{x} + \hat{y})$$

$$\frac{S_c | S_S - S_a |}{S_s | S_c - S_a |} \times 100 = \text{Percent crystallinity}$$

### Note:

\* For a set of parallel planes in the crystal there exists a reciprocal lattice vector  $\vec{k}$  to planes and has shortest length  $2\pi/d$ . ( $d$  = interplanar spacing)

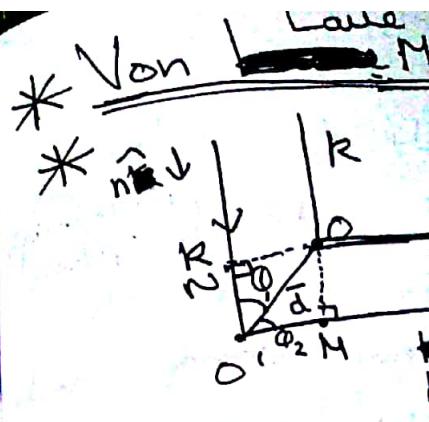


$$e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot(\vec{r}_1 + \vec{d})} \\ \Rightarrow \vec{k} \cdot \vec{d} = 2\pi m$$

Reciprocal wave vector (lattice vector)

$$\therefore \vec{k} = \frac{2\pi}{d}, \frac{4\pi}{d}, \frac{6\pi}{d}, \dots \\ =$$

- In reciprocal lattices, a set of planes are represented with a point & the direction.



Total path diff

$$= d \cos \theta_1 + d$$

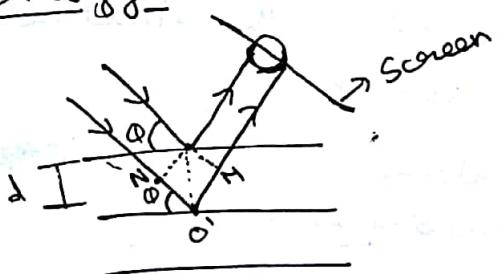
$$\Rightarrow \vec{d} \cdot \hat{\vec{k}} =$$

$$\vec{d} \cdot (\hat{\vec{n}} -$$

$$\vec{d} \cdot (\hat{\vec{n}} -$$

Distance b/w planes.

### Bragg's



Path difference is -  
 $NO' + O'M$   
 $= 2d \sin \theta$

Path difference  
should be an  
integral multiple  
of wavelengths

- To get constructive interference on the screen to get a bright spot

(Planes diffracting light are parallel to the Bragg's planes)

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

Equivalence of B

$$K =$$

$$k^2 =$$

$$\Rightarrow K^2 =$$

$$\Rightarrow \frac{1}{2} K =$$

planes in the crystal lattice vector of length  $2\pi/d$ . ( $d$  = interplanar spacing)

$$\vec{r} = e^{i\vec{k} \cdot (\vec{r} + \vec{d})}$$

$$\vec{k} \cdot \vec{d} = 2\pi m$$

$$k = \frac{2\pi m}{d}$$

$$\frac{6\pi}{d} \dots$$

a set of planes in a point by the

Path difference is,

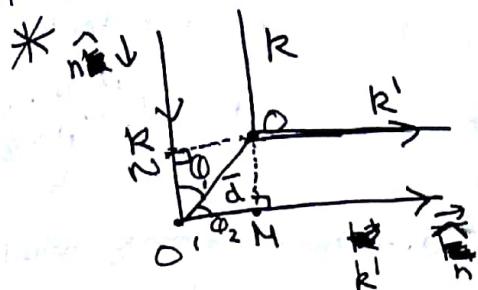
$$N\vec{o}' + O'M = 2d \sin \theta$$

To get constructive interference on the screen to get a bright spot

Planes diffracting light are parallel to the Bragg plane

$$N\vec{o}' = n\lambda$$

### \* Von Laue Method:



Path difference is  $N\vec{o}' + O'M$

$$6N\vec{o}' \rightarrow \cos \theta_1 = \frac{O'M}{d}$$

$$N\vec{o}' = d \cos \theta_1$$

$$\cos \theta_2 = \frac{O'M}{d}$$

Total path diff

$$= d \cos \theta_1 + d \cos \theta_2 = d\hat{n}_1 - d\hat{n}_2 \quad O'M = d \cos \theta_2$$

$$\Rightarrow \vec{d} \cdot \hat{n}_1 = \vec{d} \cdot \hat{n}_2 = m\lambda \quad \begin{matrix} \text{Corresponds} \\ \text{to the} \\ \text{total path diff} \end{matrix}$$

$$\vec{d} \cdot (\hat{n}_1 - \hat{n}_2) = m\lambda \quad \text{For constructive interference.}$$

$$\vec{d} \cdot (\hat{n}_1 - \hat{n}_2) = m\lambda, \quad \frac{2\pi}{\lambda} \vec{d} \cdot (\hat{n}_1 - \hat{n}_2) = m\lambda \times \frac{2\pi}{\lambda} = m\lambda \times \frac{2\pi}{X}$$

Distance b/w planes.

$$\vec{d} = R_{||} \quad = 2\pi m$$

$$\vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m$$

$$\vec{i} \cdot \vec{R} \cdot (\vec{k} - \vec{k}') = 1 \quad \begin{matrix} \text{Shows that} \\ \text{* reciprocal lattice} \\ \text{vector } \vec{R} \text{ should} \end{matrix}$$

Equivalence of Bragg's and Von Laue (Uploaded material for details)

$$\vec{K} = \vec{k} - \vec{k}', \quad \vec{k}' = \vec{k} - \vec{K}$$

$$k'^2 = k^2 + K^2 - 2\vec{k} \cdot \vec{K} \quad \therefore k'^2 = k^2$$

~~$$\vec{K}^2 = 2\vec{k} \cdot \vec{K} = 2\vec{k} \cdot \vec{K}$$~~

~~$$\vec{K}^2 = 2\vec{k} \cdot \vec{K} = 2\vec{k} \cdot \vec{K}$$~~

$$\vec{K}^2 = \vec{k} \cdot \vec{K}$$

Component of incident wave  $\vec{k}$  along reciprocal lattice vector  $\vec{K}$  is half the length of  $\vec{K}$

## \* Ewald's sphere:

- Sphere of radius = magnitude of incident wave
- Drawn in reciprocal lattice - (set of points indicating planes)
- All reciprocal lattice points on the sphere indicate direction along which diffracted rays can undergo constructive interference

## ⑦ Laue Method: (Cont)

- X-rays  $\xrightarrow{\text{Monochromatic}}$  Focus Sharpener  $\rightarrow$  Crystal  $\rightarrow$  Interfere & displayed on screen
  - $2d \sin\theta = n\lambda$        $\left. \begin{array}{l} \uparrow \\ \text{Distance between planes} \end{array} \right\} \theta = \text{Angle of diffraction}$
- Can be found easily using the experimental setup.

- Orientation of single crystal can be found.*
- Based on symmetry of patterns, internal symmetry of the crystal can be found
  - Interplanar spacing however, can't be found.  $\lambda$  of X-rays has a range  $\lambda_{\min}$  to  $\lambda_{\max}$ . Now these give us 2  $d$ 's  $\rightarrow$  giving us 2 Ewald spheres

$$\text{Note: } R_{xyz} = \frac{2\pi}{d_{xyz}}$$

✓

Use  $R_{xyz}$  to draw the reciprocal lattice

↓  
Interplanar spacing

( $x, y, z = \text{Miller indices of plane}$ )

All reciprocal lattice points (sliding in that range satisfy)

side of incident  
lattice - (points wave  
pointe on the  
ection along which  
can undergo  
us)

Crystal  $\rightarrow$  Interfere  
le of  
raction  
& displayed  
on screen

sily using the  
mental setup.

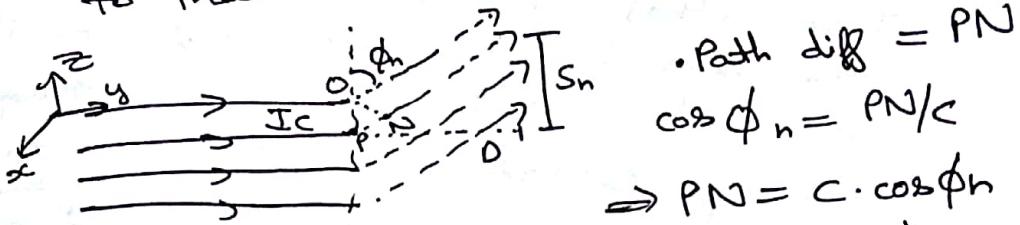
of patterns, internal  
crystal can be found  
however, can't be  
s a orange & into  
we us 2 d's  $\rightarrow$  inter  
giving us 2 small  
spheres

All reciprocal  
lattice points  
(slide in that  
orange satisfy  
 $(x,y,z) = \text{Miller}$   
indices of  
plane)

$(x,y,z) = \text{Miller}$   
indices of  
plane)

## \* Rotating crystal method:

- $\phi$  is not fixed, but variable so we would be able to analyze the crystal better.
- To find dimension of the crystal along a certain axis, we send X Rays perpendicular to that axis.



$$\text{Path diff} = PN$$

$$\cos \phi_n = PN/c$$

$$\Rightarrow PN = c \cdot \cos \phi_n$$

$$= n\lambda$$

(For constructive  
interference)

? (Diffracted ray at  
screen at central spot  
is the ?)

$$\tan(\frac{90}{2} - \phi_n) = \frac{Sn}{D}, \cos \phi_n = \frac{Sn}{D}$$

$$\Rightarrow \frac{Sn}{D} = \frac{n\lambda/c}{\sqrt{1 - \frac{n^2\lambda^2}{c^2}}}$$

$$\Rightarrow c = \frac{n\lambda (R^2 + Sn^2)^{1/2}}{Sn}$$

(R = Distance  
of screen  
from  
crystal)

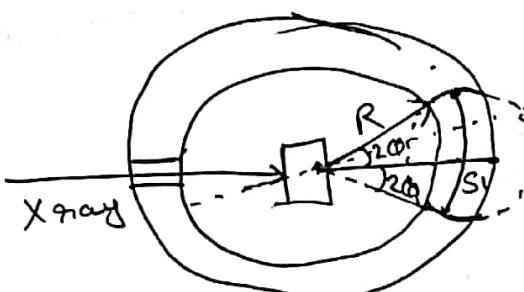
- Similarly calculate a, b - This would give us dimensions of crystal. (Unlike Laue which doesn't)

## Powder Method: (Details in slides)

- Use powder instead of a single oriented crystal. Consists of all the possible kinds of orientations of the planes. For each  $(hkl)$  we have all possible orientations w.r.t incident ray.

- This method won't produce spots on the film but creates rings on the film instead.  $\rightarrow$  Each ring corresponds to a certain  $hikl$ , } Corresponding to one lattice point.

Fixed  $\theta$   
but in  
all possible  
orientations  
w.r.t incident  
ray.  
(Set of  
planes in  
crystal)



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

$$\begin{aligned} \bullet S_1 &= R(4\pi) \\ \Rightarrow \theta &= S_1/4R \\ \bullet d_{hkl} &= \frac{n\lambda}{2\sin\theta} \end{aligned}$$

$\Rightarrow$  This allows us to find  $d$ ,  $\theta$  etc but we still need to find  $h, k, l$

## \* Geometrical structure factor:

- Only specific values of  $h^2 + k^2 + l^2$  and other conditions on  $h, k, l$  lead to constructive interference. These conditions change from system to system. (Details in slides) ( $K$  = Reciprocal lattice vector)

$$(S_h = \sum_{j=1}^n e^{iKd_{hj}}) \rightarrow \text{Using these conditions,}$$

Sum of amplitudes  
of waves scattered at structure factors  
every lattice point.

(Slides details) Lead to certain fixed values of  $h, k, l$  values of  $h^2 + k^2 + l^2$

single possible kinds  
For each orientation

(8)

Spots on rings on the ring correspond to one lattice point (Set of planes in crystal)

$$R(4\pi) = \frac{S}{4R} = \frac{n\lambda}{2\sin\theta}$$

$\theta$  etc but we

factors:  
of  $h^2 + k^2 + l^2$   
on  $h, k, l$  lead to different Miller indices. These come from system to system (K = Reciprocal lattice vector)

Using these conditions we get only certain fixed values of  $h^2 + k^2 + l^2$

$$\frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2\sin\theta} \quad (\text{if } n=1)$$

$$\Rightarrow 2\lambda \sin\theta = n\lambda \quad \{ \text{we have}$$

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

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

$$\Rightarrow \frac{\sin^2\theta}{h^2 + k^2 + l^2} = \frac{n^2 \lambda^2}{4a^2}$$

LHS must be constant for all  $\theta$ .

$\therefore$  Different values of  $h^2 + k^2 + l^2$  are permitted.

ex: BCC structure can be considered as 2 simple cubic structures on 2 intersecting lattices on 2 basis atoms. (Side length =  $a$ )

$$\bullet d_1(0,0,0) \text{ & } d_2(a/2, a/2, a/2)$$

$\rightarrow$  If incident ray is scattered by  $d_1$  &  $d_2$

$$S_k = e^{i d_1 k} + e^{i d_2 k}$$

$$* = e^0 + e^{i \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})} \cdot \frac{2\pi}{a} (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \\ = 1 + e^{i\pi(n_1 + n_2 + n_3)}$$

If  $n_1 + n_2 + n_3 = \text{even} = 2n$

$$S_k = 1 + 1 = 2 \quad \{ \text{Constructive}$$

If  $n_1 + n_2 + n_3 = \text{odd} = 2n+1$

$$S_k = 1 - 1 = 0 \quad \{ \text{Destructive}$$

$(n_1 + n_2 + n_3)$  depends on sum of Miller indices of the plane (reciprocal lattice vector)

- A point in the diffraction pattern indicates a set of planes.

BCC:

Diffraction occurs when  $h+k+l = \text{even}$

$$h^2 + k^2 + l^2 = 2, 4, 6, 8, 10, 12, 16, \dots$$

FCC:

Diffraction occurs when  $h, k, l$  each must be either even or all odd

$$h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, \dots$$

→ In Bragg's model →  $\theta = \text{Bragg angle}$   
then

$$2\theta = \text{Diffraction angle}$$

Bragg peaks are observed at certain values of  $\theta$  for a cubic crystal. We assign Miller indices to each such spot.

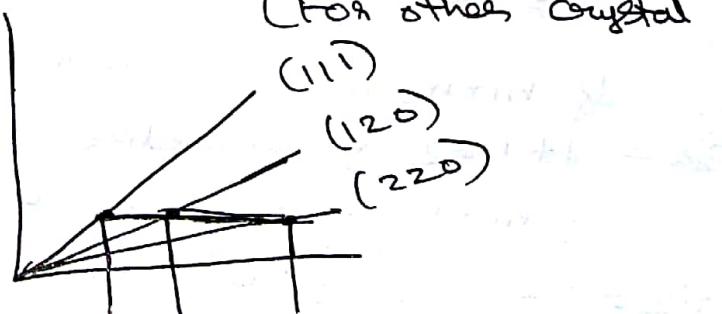
→ From  $\frac{\sin^2 \theta}{h^2 + k^2 + l^2} = \frac{n^2 \lambda^2}{4a^2}$  { We know  $\lambda, n=1$ ,  $\theta$  so we can figure out  $h, k, l$ .

→ Interplanar spacing is

$$d = \frac{h\lambda}{2 \sin \theta}$$

? Hull-Davey charts

(For other crystal systems apart from cubic)



## \* Crystal Imperfections

- Many properties of crystals are structure sensitive. (Some are structure insensitive)

ex: Magnetization of materials is based on the structure → Mechanical properties like toughness, yield strength, conductivity of semiconductors (increased by adding impurities) are also based on structure.

### Types of defects:

- 1) Point defects - irregularity confined to a single lattice point
- 2) Line defects
- 3) Surface defects
- 4) Volume defects

I)

#### \* Point Defects:

##### \* i) Vacancy defect:

(Formation of vacancy is exothermic)  
• Thermodynamically favourable process.

• Gibbs free energy  $G = H - TS$

Entropy  $S$  is higher  $\rightarrow$   
Gibbs free energy is lower.

\*  $\Rightarrow$  Vacancy concentration  $\propto$  temperature  
$$n_v = N_e \frac{e^{-H/kT}}{kT} \quad \left\{ \begin{array}{l} \text{# of vacant sites per unit volume} \\ \text{# of vacant sites per unit volume} \end{array} \right.$$
  
$$\text{# of vacancies per unit volume.}$$
  
( $H$  = Enthalpy of formation,  
- energy required to create 1 vacancy)

##### \* ii) Impurity defect:

ex: Al in Si, C in Steel.  
Impurity defect  $\rightarrow$  Interstitial site  
 $\rightarrow$  Substitutional site  
(switch with another)

- Depends on the ratio of radii:  $\frac{r_A - r_C}{r_C} < 15\%$   
 Leads to substitutional  $\leftarrow$  Radii are similar  $\leftarrow$   $r_A - r_C$
- Similar  $EN^-$  values, same FCC Substitutional crystal structure

(a)

(Yield strength & tensile strengths

↳ Resistance of material to plastic deformation)

- Hard magnetic materials — permanent magnets
- Soft magnetic materials — can be easily magnetized (pure materials)

Note: Self interstitial point defects where same atom is present additionally at an interstitial point. This is not thermodynamically favorable

- \* • Size of interstitial site

↳ FCC:  $r = 0.414R$   
 BCC:  $r = 0.291R$  } we know

⇒ If impurity is at interstitial site

↳ But its radius  $<$  site size

↳ We have a tensile

field region  
 (bonds expand)

↳ Radius  $>$  site size

↳ We have a compressed field region  
 (bonds compressed)

i) BCC:



(tetrahedral site)

$$(R+r)^2 = \frac{a^2}{4} + \frac{a^2}{16}$$

$$\Rightarrow R+r = \frac{\sqrt{5}}{4}a \Rightarrow \sqrt{3}a = 4R \quad (\text{In BCC})$$

radii:  $\frac{r_A + r_C}{2}$   
 are  $r_C < \frac{r_A + r_C}{2} \times 15\%$   
 same FCC Substitution  
 Crystal structure  
 (elastic deformation)

permanent magnets  
 can be easily magnetized

affects where same  
 ionically at an interstitial  
 thermodynamically favorable

$R$   
 $IR$ } we know

interstitial site

radius < site size

we have a tensile  
 field region  
 (bonds expand)

site size

we have a compressed  
 field region  
 (bonds compressed)

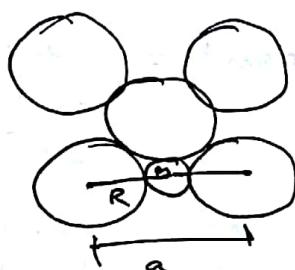
octahedral site)

$$\frac{r^2}{4} + \frac{r^2}{16}$$

$$\frac{\sqrt{5}}{4}a, \quad \sqrt{5}a = 4R \quad (\text{In BCC})$$

$$\therefore r = (\sqrt{3} - 1)R = 0.291R$$

ii) FCC:



$$R + 2r + R = a$$

$$\Rightarrow 4R = \sqrt{2}a \quad (\text{In FCC})$$

$$\therefore r + R = \frac{2R}{\sqrt{2}}$$

$$\therefore r = (\sqrt{2} - 1)R = 0.414R$$

- Quantity of impurity added in terms of weight percent and atom percent.

\* Q) If Iron BCC lattice constant is 0.2866 nm,

$$a = 0.2866 \text{ nm}$$

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

$$\Rightarrow R = \frac{\sqrt{3}}{4} \times 0.2866 \text{ nm}$$

$$r = 0.291 \times \frac{\sqrt{3}}{4} \times 0.2866 \text{ nm}$$

$$= 0.035 \text{ nm}$$

L) If Iron FCC lattice constant is 0.3571 nm

$$\text{then } a = 0.3571 \text{ nm} \quad \Rightarrow r = 0.414R \\ 4R = \sqrt{2}a \quad \rightarrow r = 0.414 \text{ nm}$$

$$\rightarrow r = 0.414 \text{ nm}$$

$$\cdot \text{Atom percent} = \frac{n_{m-1}}{n_{\text{host}} + n_{m-1}} \times 100$$

$$\text{Weight percent} = \frac{m_1}{m_1 + m_2} \times 100$$

Quantity  
of  
the  
impurity.

## II) Dislocation

- \* • Föhrer defect

i) E

- \* • In BCC : There are 24 interstitial sites and each contributes to 2 unit cells

$$\therefore \text{ex: Atom percent} = \frac{24 \times \frac{1}{2}}{24 \times \frac{1}{2} + 2} \times 100 \rightarrow \begin{array}{l} \text{Interstitial} \\ \text{filled.} \end{array}$$

$\approx 85\%$

- \* • In FCC : There are 12 interstitial sites and each contributes to 4 unit cells

$$\therefore \text{ex: Atom percent} = \frac{12 \times \frac{1}{4}}{12 \times \frac{1}{4} + 1} \times 100 \rightarrow \begin{array}{l} \text{along} \\ \text{edges} \end{array}$$

$+ 1$

$$\frac{12 \times \frac{1}{4} + 1}{12 \times \frac{1}{4} + 1} \times 100 \rightarrow \begin{array}{l} \text{one} \\ \text{site} \\ \text{at} \\ \text{center} \end{array}$$

$+ 4$

$$\approx 50\% \rightarrow \begin{array}{l} \text{FCC} \\ \text{has} \\ \text{4 atoms} \end{array}$$

$\therefore$  BCC distorts more if impurities are 100%.

### iii) Frenkel & Schottky defect : (In ionic crystals)

- Frenkel defect when anion is displaced and put in interstitial site. (seen in metals as well)  
(No charge issues since displacement is small)

- Schottky defect when cation is removed and to maintain charge, an anion is also removed. As  $T \uparrow$ , more of this is seen.

Applying shear force

ii) S

## II) Dislocations: (Line defects)

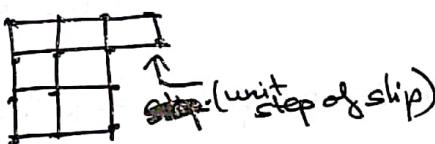
- Formed when materials are subject to plastic deformation etc.

### \* i) Edge dislocations: (Examples in slides)

- When a set of atoms along a line are removed, adjacent atoms bend in to fit in shape. Edge dislocation line = the line where atoms are missing.
- Burgers vector = Step size (magnitude) (Details in slides) that is not traversed if we consider a closed path on crystal, this additional path is burgers vector. If parallel to edge then it's an edge dislocation



⇒ On applying shear force, the shape changes creating an additional slip plane (Instead of deformed shape from earlier)



(Burgers vector  
is perpendicular  
to dislocation  
line)

⇒ Peierls - Nabarro stress  $\propto$  Interplanar spacing  
 $\sigma = c \exp\left(-\frac{kd}{b}\right)$   
 Stress developed.  $\propto$  Step size

### ii) Screw dislocations: (Slides for images)

- Generated due to plastic deformation - An entire volume is shifted by a certain amount.
- Dislocation line & burgers vector can be calculated. Burgers vector is parallel to the dislocation line.

### iii) Mixed dislocations:

- Burgers vector can be oriented in any way w.r.t dislocation vectors.

## III) Surface defects:



i) External surface: Since atoms on ~~surface~~ have a lack of coordination number

ii) Grain boundary: Grains where they join, we have defects. These are chemically active regions.

(Formed by series of edge dislocations to change grain orientation)

(Tilt boundaries)

iii) Twin boundary: Mirrored structures present, boundary separating is called twin boundary.

(Generally seen in ceramics)

? iv) Stacking point defect:

⑩

- Note:- Ceramics are brittle  $\rightarrow$  Not malleable (No plastic deformity)
- Magnitude of burgers vector determines the amount of dislocation.
  - Materials break when a large force is applied and dislocations are present. (Anion-anion & cation-cation repulsions cause this)
  - Directions that have large linear atomic density are preferable for plastic deformation
  - Planes having larger planar atomic density is preferable for plastic deformation.

Q) Calculate the length of Burgers vector in FCC copper. The lattice parameter of copper is  $0.3615\text{ nm}$

\* In the FCC structure,

- $\rho d_{(100)} = \frac{2}{a^2}$  { Planar density along plane (100)}

$$\rho d_{(110)} = \frac{2}{\sqrt{2}a^2}$$

$$\rho d_{(111)} = \frac{2/\sqrt{3}}{\sqrt{6}} \times (\sqrt{2}a)^2 = \frac{4}{\sqrt{3}a^2}$$

$$3 \times \frac{1}{6} + 3 \times \frac{1}{2} = 2 \text{ atoms}$$

- Here largest pd is found at (111), :- this is where deformation is preferred.

- The slipping happens along  $[110] \rightarrow$  Interface direction and hence Burgers vector = minimum distance b/w two atoms  $= \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$

$$(a = 0.3615\text{ nm})$$

## Electrical properties of materials:

- Metals: Sea of electrons (electron gas) & positive ions. There are mobile charge carriers. Good reflectors of light as well.
- Multiple models proposed.

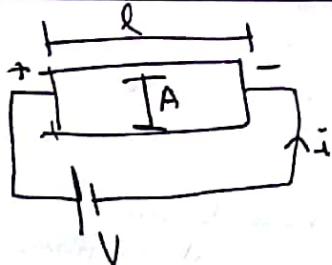
### Draude:

- Independent  $e^-$  (No  $e^- - e^-$  interactions)
- Free  $e^-$  (No  $e^- - \text{Ion}$  interactions)

} Assumptions made.

- Assumptions made
- Collisions between  $e^-$  & ions are elastic collisions.
  - Velocity of  $e^-$  after collision is dependent on T of the region where collision occurred.
  - Probability of collision  $\propto 1/\text{Relaxation time}$  (Mean collision time)  
(Mean free path = Distance travelled between 2 collisions)
  - Should be comparable to atomic distance.

$\Rightarrow$  Draude developed a model based on these assumptions.



$$i = \frac{V}{R}$$

$$\Rightarrow \frac{V}{l} = \frac{iR}{l} = \frac{i \cdot R}{A \cdot l} \cdot A$$

- $\frac{V}{l} = E$   $\rightarrow$  Potential electric field intensity.

$= J \cdot \rho \rightarrow$  Resistivity  
(Resistance of unit area per unit length)  
 $\downarrow$   
Current density

$$\Rightarrow E = J \cdot \rho \rightarrow \text{Micro} \quad \left\{ \text{Ohm's Law.} \right.$$

$$V = iR \rightarrow \text{Macro}$$

- If electron density of material is ' $n$ '.
- Drift velocity ( $v_d$ ) = Velocity of  $e^-$ .

$\hookrightarrow v_d \cdot dt \cdot n$   $\left\{ \begin{array}{l} \text{Total distance} \\ \text{advanced by all } e^- \text{ in } dt \text{ time.} \end{array} \right.$

$\rightarrow (-e) \cdot n \cdot v_d \cdot dt$   $\left\{ \text{Total charge moved per unit area in } dt \text{ time.} \right.$

$\Rightarrow (-e) \cdot n \cdot v_d \cdot dt \cdot A$   $\left\{ \text{Total charge through area of cross-section } A. \right.$

$i = -e \cdot n \cdot v_d \cdot A$   $\left\{ \text{Charge per time.} \right.$

$J = -e \cdot n \cdot v_d$   $\rightarrow$  Drift velocity

- Drift velocity = const velocity of  $e^-$  in material once attractive forces by repulsive collision forces are balanced

⑪

(we focus only on the valence electrons and don't really care about the core electrons)  $\rightarrow$  All valence ~~electrons~~ take part in conduction.

- Another assumption
- Maxwell-Boltzmann distribution - To find  $\# e^-$  with velocity  $v$
  - A velocity 'v' can be possessed by any number of electrons (no restrictions)

$$\Rightarrow F = Ee$$

$$ma = -Ee$$

$$m\left(\frac{v-u}{t}\right) = -Ee$$

,  $v$  = Drift velocity here  
 $u$  = Velocity after collision  
 (random and hence  $\rightarrow 0$ )  
 $t = \approx 3$  Mean free time

$$\therefore \frac{mv_d}{t} = Ee$$

$$V_d = \frac{-EeT}{m}, J = -envd$$

$$J = \frac{n e^2 T}{m} \cdot E$$

we know,  $J = \sigma E$

$$E = J \rho, \frac{E}{\rho} = J$$

$$\therefore J = \frac{n e^2 T}{m} \cdot E = \sigma \cdot E$$

$$\therefore \boxed{\sigma = \frac{n e^2 T}{m}}$$

$\Rightarrow$  Wiedemann-Franz law:

$$\frac{k}{\sigma} \propto T$$

(The proportionality constant he suggested was not considered correct since Drude had different results)

## 2) Sommerfeld Theory:

- Use principles of quantum theory here along with Pauli's exclusion principle.
- $\Psi_e(x, y, z, \chi)$   $\xrightarrow{\text{Position.}}$  Clockwise & Anticlockwise spin

$\rightarrow$  Indep  $e^-$  approach & free  $e^-$  approach similar to Drude.

$$\text{Ground state } \nabla^2 \Psi + \frac{2m}{\hbar^2} \cdot E \Psi = 0$$

- Metal is a 3D potential box.  $-V=0$  inside box  $V=V_0$  outside box

- Usually, we assume boundary conditions as  $e^-$  can't exit box. Here we assume that exiting from a face,  $e^-$  enters from the opposite face instantaneously. (Continuous box basically)
- (Running wave solution)  $\rightarrow$  Progressive wave solution.

$$\Psi(x) = \Psi(x+L)$$

$$\Psi(x, y, z) = \Psi(x+L, y, z)$$

$$\Psi(x, y, z) = \Psi(x, y+L, z)$$

$$\Psi(x, y, z) = \Psi(x, y, z+L)$$

- Solution is, (without boundary conditions)

\*  $\Psi(r) = \frac{1}{\sqrt{V}} e^{ik\bar{r}}$  where  $\bar{r} = (x, y, z, \chi)$

$E = \frac{\hbar^2 k^2}{2m}$   $\rightarrow \left( \frac{1}{2} mv^2 \text{ (Equivalent)} \right)$

$\Rightarrow$  Applying boundary conditions,

$$e^{ik_x x} = e^{ik_x(x+L)}$$

$$\Rightarrow e^{ik_x L} = 1, k_x L = 2\pi n_x$$

$$\Rightarrow k_x = \frac{2\pi}{L} \cdot n_x$$

$$\text{Similarly } k_y = \frac{2\pi}{L} \cdot n_y$$

$$k_z = \frac{2\pi}{L} \cdot n_z$$

?  $\Rightarrow E = \frac{\hbar^2}{2m} (n_x^2 + n_y^2 + n_z^2)$

- Each energy state can contain  $2e^-$ .

- Degenerate states  $\rightarrow$  States with the same energy.

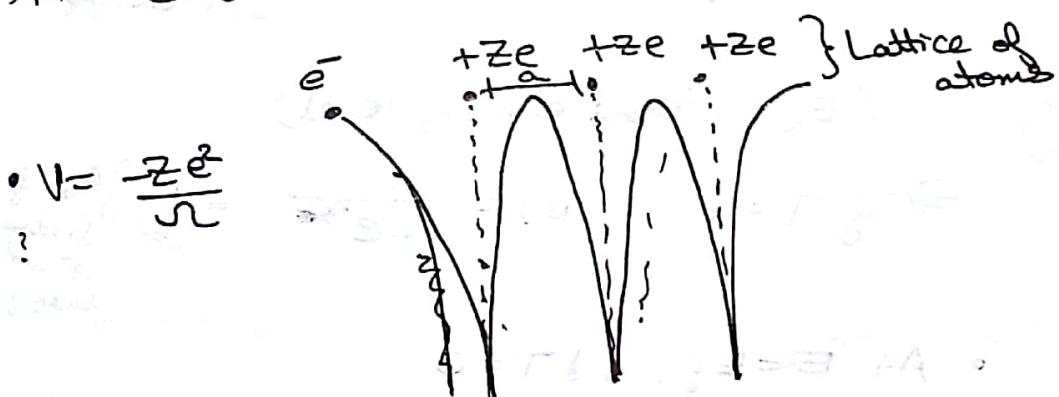
$n_x$	$n_y$	$n_z$	
1	0	0	Degenerate state (6 $e^-$ total)
0	1	0	
0	0	1	Degenerate state (6 $e^-$ total)
1	1	0	
1	0	1	$\{ 2e^-$ (Non-degenerate state)
0	1	1	
1	1	1	

- Highest energy level occupied by electrons is called the Fermi energy level.
- Only electrons belonging to the Fermi energy level participate in conduction since they have free energy levels above to excite to. (Main difference from Drude)

$\Rightarrow$  This however means that all materials should be conductors but this is incorrect, this is due to the assumption that no  $e^-e^-$  interactions etc are present.

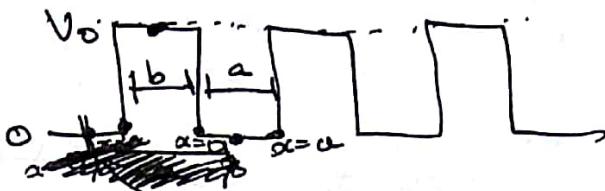
### Kronig - Penny Model:

- Consider  $e^-N$  interactions,



- This is how the PE of  $e^-$  varies if we consider a 1D case. (this has a periodic nature)  
(Periodicity = ' $a$ ')  $\rightarrow$  Interatomic spacing.

- This is simplified to binarized PE values as  $\psi$  &  $V_0$  -



If  $e^-$  needs to move across it needs to pass these PE barriers of  $V_0$ .

- $\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \rightarrow \textcircled{1}$

$$0 < x < a$$

- $\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V_0] \psi = 0 \rightarrow \textcircled{2}$

Let,  $-b < x < 0$

$$\alpha^2 = \frac{2m}{\hbar^2} E, \quad p^2 = \frac{2m}{\hbar^2} [V_0 - E]$$

- The solution to this is,  $\psi = A e^{-ikx} + B e^{ikx}$

$$\psi = C e^{-ikx} + D e^{ikx}$$

Solutions for  $\textcircled{1}$  &  $\textcircled{2}$

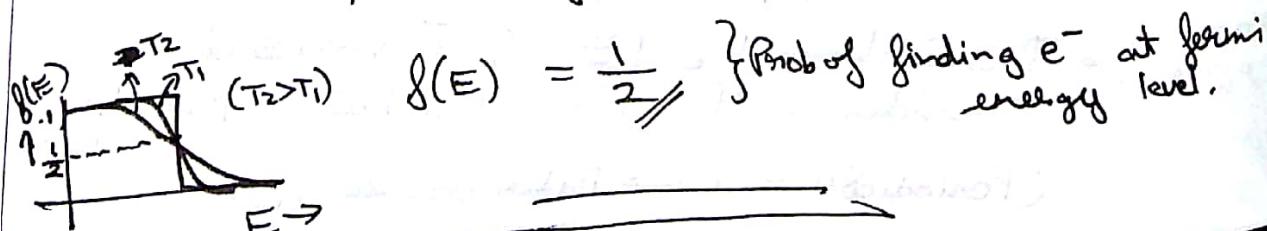
(1) Note: Fermi-Dirac distribution (Sommerfeld cont)

$$f(E) = \frac{1}{1 + e^{\frac{E-E_F}{kT}}} \quad \left. \begin{array}{l} \text{Probability} \\ \text{of finding an electron} \\ \text{with energy } E. \end{array} \right.$$

( $E_F$  = Fermi energy level)

$$\Rightarrow \text{If } T=0, \quad f(E) = \frac{1}{1 + e^{\infty}} = 1 \quad \left. \begin{array}{l} \text{Prob of} \\ \text{finding } e^- \text{ with} \\ \text{energy } < E_F \end{array} \right.$$

- At  $E = E_F$ , and  $T \neq 0$



$\Rightarrow$  Conditions  $\psi_1, \psi_2$  need to satisfy are,

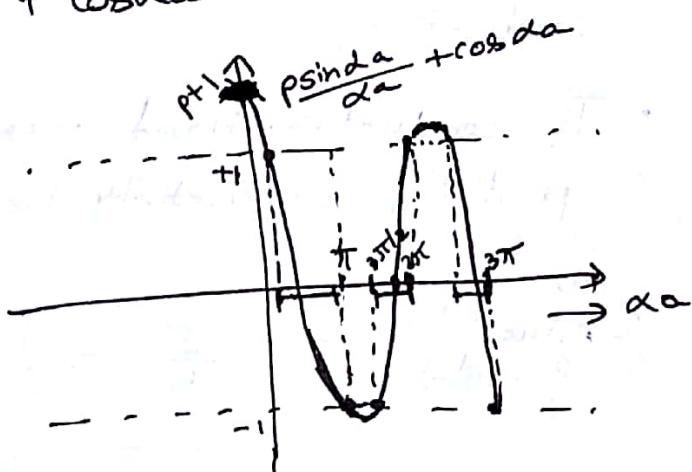
$$\left( \frac{mV_{ob}}{\hbar^2 \alpha} \right) \sin \alpha a + \cos \alpha a = \cos k a$$

Let,  $P = \frac{mV_{ob}a}{\hbar^2}$  } Strength of potential barrier

$$\Rightarrow \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a \quad \xrightarrow{\pm 1 \text{ are limits}}$$

sol:  $P = \frac{3\pi}{2}$

H = Allowed energy bands.



$$(\lim_{\alpha a \rightarrow 0} \frac{P \sin \alpha a}{\alpha a} = P)$$

- The ranges where function is between -1 to 1 is allowed region & rest is forbidden region.

As  $\alpha a \uparrow$ , width of allowed energy bands ↑.

i) Now, if  $P=0$  (Neglecting electron nuclear interactions)

$$\cos \alpha a = \cos k a$$

$$\alpha a = ka$$

$$\alpha = k$$

$$\alpha^2 = \frac{2mE}{\hbar^2} = k^2$$

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{What we get in de Broglie}$$

ii) Now if  $P=\infty$ ,  $\alpha a = n\pi$ ,  $\alpha^2 = \frac{n^2 \pi^2}{a^2}$

$$\sin \alpha a = 0$$

$$\Rightarrow \frac{2mE}{\hbar^2} = \frac{n^2 \pi^2}{a^2} \quad E = \underbrace{\frac{n^2 \pi^2 \hbar^2}{2ma^2}}_{\text{What we get in Sommerfeld}}$$

Scanned by CamScanner

## \* Energy Bands : (Metals)

- In metals  $\rightarrow$  we have partially filled valence bands as well as completely filled valence bands.
- $\Rightarrow$  Gap between conduction & valence bands determines conductivity.
- If conduction band overlaps valence band  
? partially, conductivity increases.

$$\text{Conductivity of metal } \sigma = \frac{J}{E} = \frac{n e V_d}{E} = n e M$$

↑  
Influenced { Mobility of  
by amount electron  
of impurities  
in metal.

## Mattissone's rule: (Plots in slides)

$$\rho = \rho_T + \rho_{\text{Imp}} + \rho_{\text{Deformation}}$$

} Resistivity of  
a metal.  
Due to thermal properties Major factors of  $\rho$  } So used to change resistivity of metal.

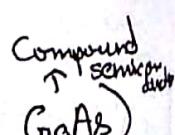
$$\Rightarrow \rho_T = \rho_0 + \alpha T$$

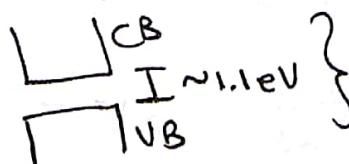
$$\Rightarrow \rho_{\text{Imp}} = A c_i (1 - c_i)$$

Concentration of impurity in atom %

## \* \* Semiconductors:

i) Intrinsic — Pure (ex: Silicon, germanium, 

  
GraAs



Band gap is

small. Based on temp, as  $T \uparrow$ , conductivity increases

(unlike metals where opposite happens)

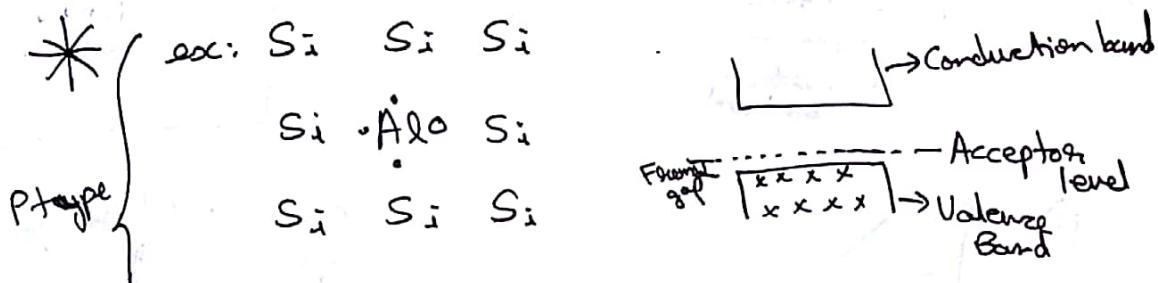
$$\sigma = n e \mu_n + p e \mu_p$$

↓                      ↓  
Mobility of  $e^-$       Mobility of hole

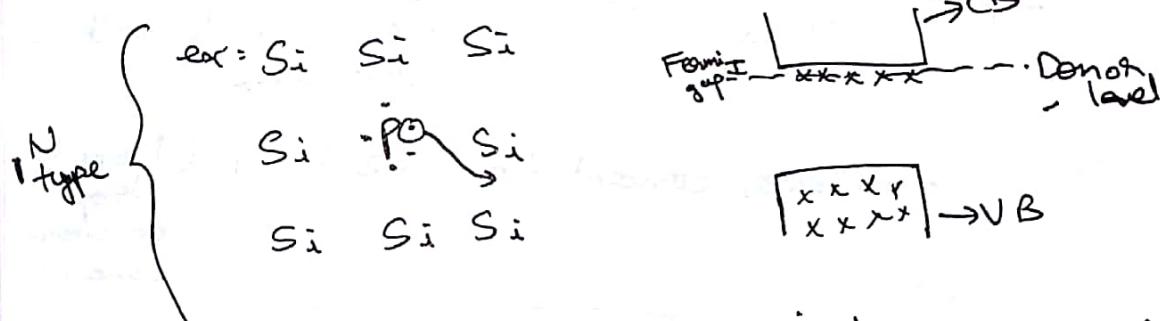
} For semiconductors  
( $\mu = V_d/E$ )?  
 $(\mu_n > \mu_p$   
generally)

$$\sigma = n_i e (\mu_n + \mu_p) \quad ('; n = p = n_i')$$

ii) Extrinsic - Mixed (Doped semiconductors)



- Hole concentration is large since  $e^-$  get excited from valence to acceptor level easily.

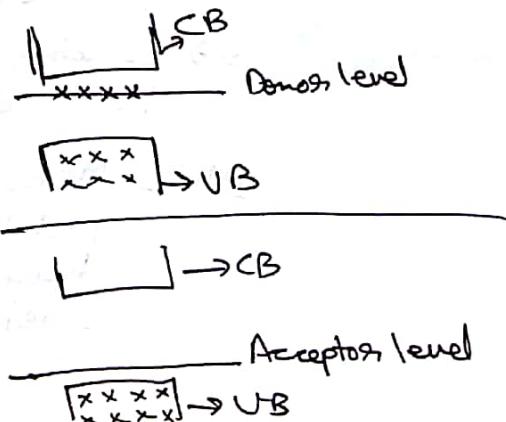
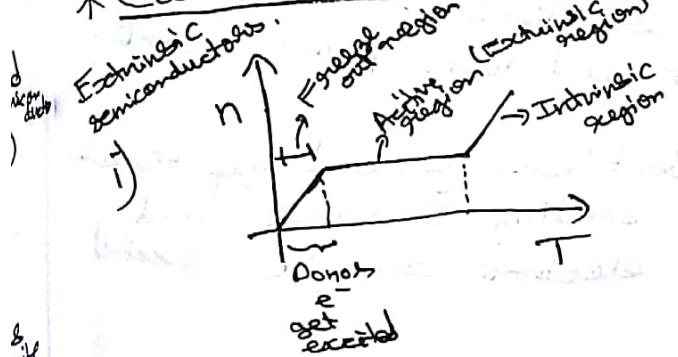


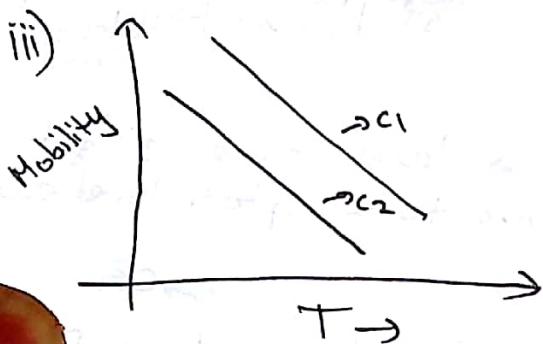
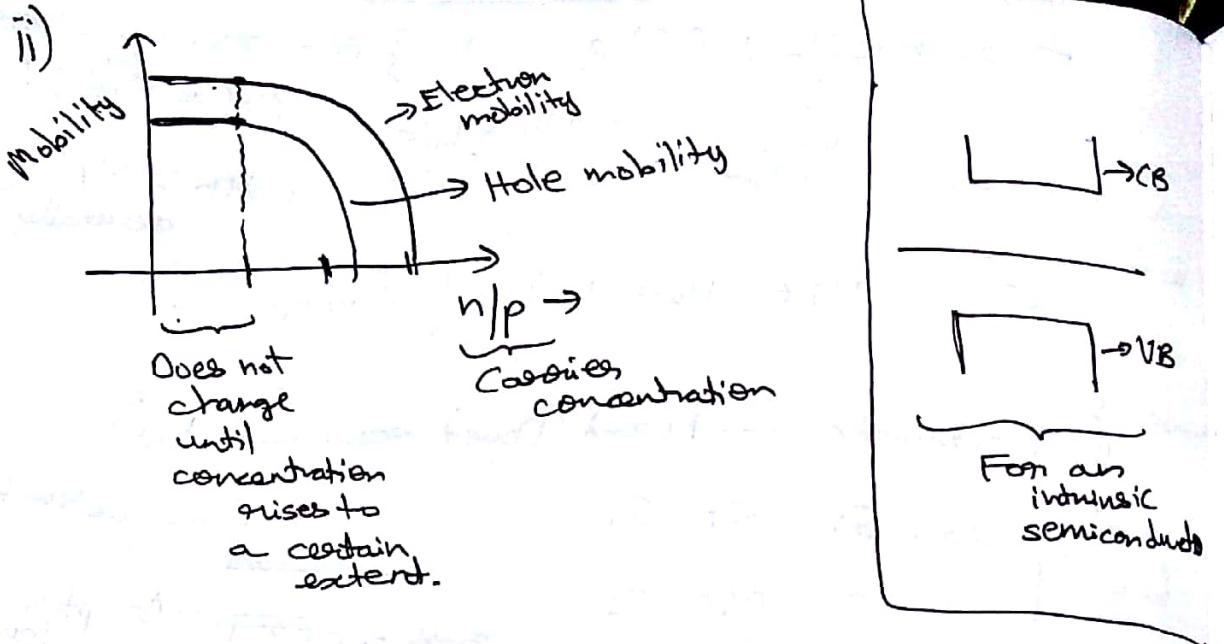
- Electron concentration is large since we have a donor energy level close to C.B.

⇒ Extrinsic semiconductors have large conductivities.



CARRIER CONCENTRATION (n)





$$c_2 = 10^{24} \text{ atoms/m}^3$$

$$(If \quad \cancel{c_1} = 10^{21} \text{ atoms/m}^3)$$

- As  $T \uparrow$ , atoms vibrate more and hence frequency of scattering increases

- Carrier concentration  $c_2 > c_1$  (Mobility drops as carrier conc  $\uparrow$ )

(13)

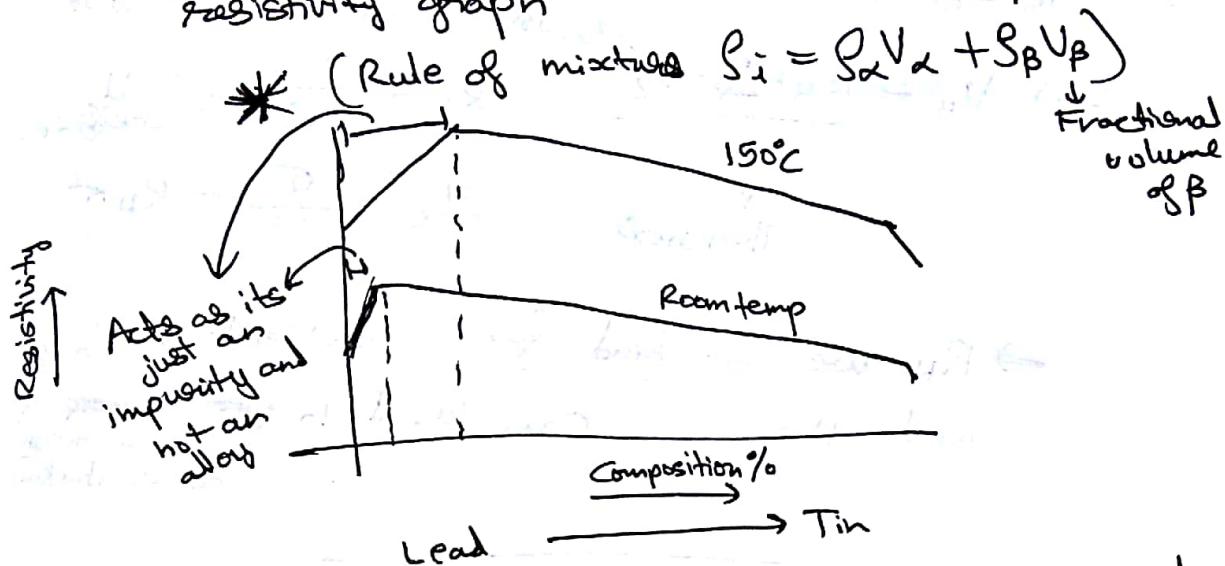
### Energy band structures (in solids)

- As we reduce interatomic distance, splitting of energy bands starts at the topmost level ~~for~~ first and then at other layers. (figure in slides)
  - ⇒ Electrons are distributed across energy levels first and then pairing starts.

Note: Metals don't have a band gap because metallic bonding is weak and hence electrons can be excited easily.

$\Rightarrow$  Electron mobility:  
 o Mobility  $\uparrow$  as crystallinity  $\uparrow \Rightarrow$  Conductivity  $\uparrow$   
 $\rightarrow$  Sudden drop of temperature  $\Rightarrow$  Quenching

$\Rightarrow$  Varying from pure lead to pure tin, plot resistivity graph



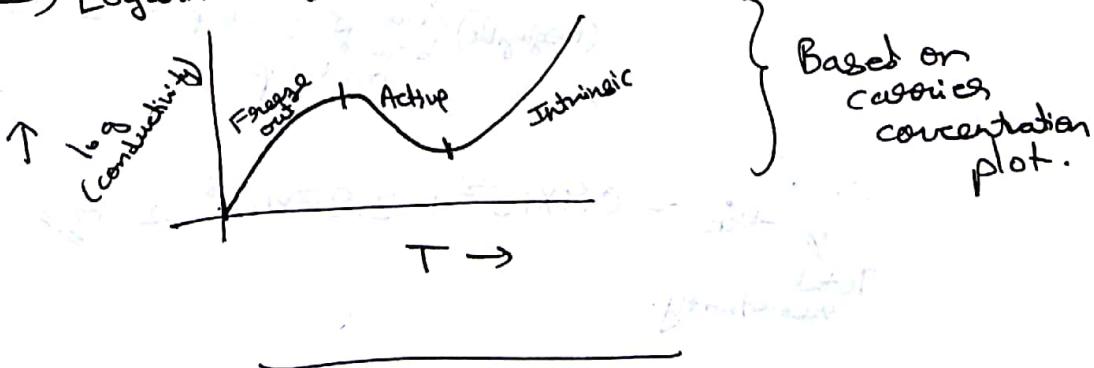
- As  $T \uparrow$ , more amount of Tin can be maintained while staying in the structure of lead (not forming an alloy)

$\Rightarrow$  Which of ZnS and CdSe will have a larger band gap ( $E_g$ )

- ZnS has a larger band gap. As we go up in the periodic table, the band gap increases.

\* (Slides for multiple other plots and graphs)

$\Rightarrow$  Logarithm of conductivity vs Temperature



## \* Hall effect: (Metals & Semiconductors)

- When magnetic field is applied to a current carrying conductor (in L'ies directions), a hall voltage is induced.

$$\Rightarrow V_H = \frac{R_H \cdot I_x \cdot B_z}{d} \quad , \quad R_H = \frac{1}{ne} \quad \left\{ \begin{array}{l} \text{Gauge factor to measure magnetic field} \\ \text{Hall coefficient} \end{array} \right.$$

↓  
Thickness

$$M_e = \frac{\sigma}{ne} = R_H \sigma$$

$\rightarrow R_H$  we can find from gradient of  $V_H$  vs  $B_z$  and then we can find  $n$  ~~carrier concentration~~

(Graphs in slides)

- Q) From graphs of resistivity vs temp & resistivity vs alloy composition at room temp, find conductivity of 85wt% Cu - 15wt% Zn alloy at  $-100^\circ C$ .

$$\rightarrow \rho = \rho_f + \rho_{imp} \quad , \quad \rho_{-100^\circ C} (Cu) = 0.9 \times 10^{-8} \Omega \cdot m$$

At  $-100^\circ C$

$$\text{At room temp} \quad \left\{ \begin{array}{l} \rho_{total} = 4.6 \times 10^{-8} \Omega \cdot m \\ = \rho_{room} + \rho_{imp} \end{array} \right.$$

$$\rho_{room} = 1.75 \times 10^{-8} \Omega \cdot m$$

Does not change based on temp  $\left\{ \rho_{imp} = 2.85 \times 10^{-8} \Omega \cdot m \right.$   
(Negligible)

$$\therefore \rho_{-100^\circ C} = 0.9 \times 10^{-8} + 2.85 \times 10^{-8} \Omega \cdot m$$

Total resistivity.

Q) Is it possible to alloy copper with nickel to achieve a minimum yield strength of 130 MPa and yet maintain an electrical conductivity of  $4.0 \times 10^6 \text{ Ohm}^{-1}\text{m}^{-1}$  (Given Yield strength vs nickel content plot & resistivity vs composition (wt%) of nickel plot)

$\Rightarrow$  Can be done directly based on plots.

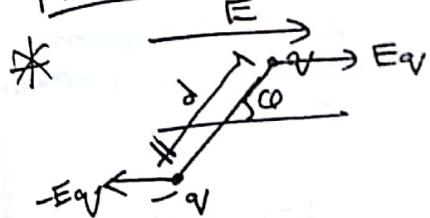
(14)

## Dielectrics & Insulators:

- Dielectric materials : Charge separation is present and a net dipole is present.

(Resultant dipole in symmetric materials is generally zero)

Molecular dipole:



$$\vec{\mu} \rightarrow \text{Dipole moment.}$$

$$\vec{\mu} = q \times d$$

$$\tau = d \sin\theta \cdot (Eq)$$

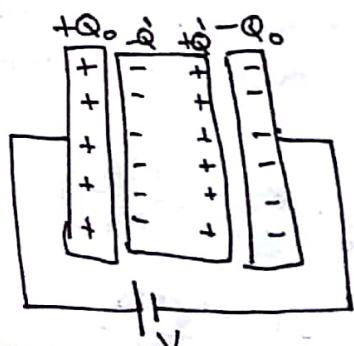
$$= \mu E \sin\theta$$

$$\Rightarrow PE = \omega = \int_{\phi=90}^{90} \tau d\theta = \int_{\phi=90}^{90} \mu E \sin\theta d\theta$$

$$= \mu E [-\cos\theta]_{\phi=90}^{90}$$

$$PE = \mu \cdot \bar{E}_{||}$$

\* Now, consider a ~~dielectric~~ ~~inside~~ a potential,



$$\oint E dS = q / \epsilon_0$$

Without dielectric

$$EA = Q / \epsilon_0$$

$$E = \frac{D}{\epsilon_0}, D = \frac{\epsilon_0}{\epsilon_r} E_{||}$$

With the dielectric, net charge is reduced,

$$\Rightarrow \frac{Q_0 - Q'}{\epsilon_0} = EA$$

$$\frac{Q_0 - Q'}{A} = \epsilon_0 E$$

$$\bar{D} - \bar{P} = \epsilon_0 \bar{E}$$

$$\bar{D} = \epsilon_0 \bar{E} + \bar{P}$$

Permittivity  
of free space

Induced charge  
by surface area.

Medium

Free  
space

$$\Rightarrow \text{We can also write } \bar{D} = \epsilon \bar{E} \rightarrow ②$$

$\Rightarrow$  From ①, ②

$$\epsilon \bar{E} = \epsilon_0 \bar{E} + \bar{P}$$

$$\bar{P} = (\epsilon - \epsilon_0) \bar{E}$$

$$\boxed{\bar{P} = (\epsilon_r - 1) \epsilon_0 E} \rightarrow \text{Polarization of material.}$$

Polarization

$$\bullet \cancel{\text{Polarisability}} = NM$$

$\ast (\because M = \alpha E)$

$$P = NM = N \alpha E$$

$\downarrow$   
Polarisability

$$\bar{P} = (\epsilon_r - 1) \epsilon_0 E \} \text{ From earlier }$$

$$\therefore \epsilon_r - 1 = \frac{N \alpha}{\epsilon_0}$$

$$\boxed{\epsilon_r = 1 + \frac{N \alpha}{\epsilon_0}}$$

This says that every molecule experiences the same field in gases. In solids however we can't treat them as independent.

$$\therefore \epsilon_r = 1 + \frac{N}{\epsilon_0} \cancel{\left( \frac{SNA}{M} \right)}$$

$$P = \frac{NM}{NA}, N = \frac{PA}{M}$$

\* For solid dielectrics we consider a local field at a point due to charge. Assume no medium around dipole

$E_{\text{local}} = E_1 + E_2 + E_3 + E_4$

Due to area of local field  
Field only due to induced dipole moment in dielectric.

Field at a dipole present in the dielectric

$$, \text{we know } \bar{D} = \epsilon_0 \bar{E} + \bar{P}$$

$$\Rightarrow \text{we can say } D = \epsilon_0 E_1$$

$$\therefore \epsilon_0 E_1 = \epsilon_0 E + P$$

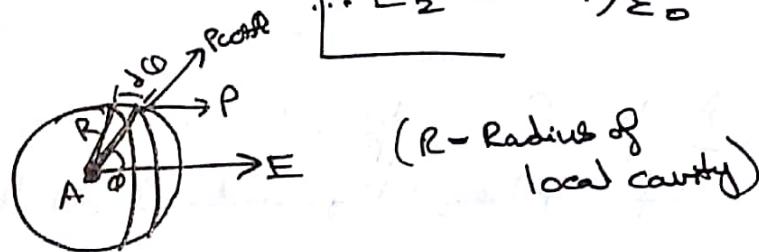
$$\therefore E_1 = E + P/\epsilon_0$$

$$\Rightarrow \bar{D} = 0 \text{ while considering } E_2$$

$$\therefore \bar{D} = \epsilon_0 \bar{E}_2 + \bar{P} = 0$$

$$\therefore E_2 = -P/\epsilon_0$$

$\Rightarrow$  For  $E_3$ ,



$$dq = R \sin \theta$$

$$\begin{aligned} \text{Area of ring} &= (2\pi R \sin \theta) R d\theta \\ &= 2\pi R^2 \sin \theta d\theta \end{aligned}$$

(Polarization = Charge / Area)

$$dq = P \cos \theta \times 2\pi R^2 \sin \theta d\theta$$

$$dE_3 = \frac{1}{4\pi\epsilon_0} \cdot \frac{dq}{R^2} \cdot \cos \theta$$

} Since we want  $E$

$$\int_{\theta=0}^{\theta=\pi} dE_3 = \int_{\theta=0}^{\theta=\pi} \frac{-P \cos^2 \theta d(\cos \theta)}{2\epsilon_0}$$

along applied field direction

$$= \left[ \frac{P}{2\epsilon_0} \cdot \frac{\cos^3 \theta}{3} \right]_{\theta=0}^{\pi}$$

$$E_3 = \frac{P}{3\epsilon_0}$$

Final in direction of external.

, Now  $E_4 = 0$   
(Since net dipole induced moment by elements in locality is 0)

$$\therefore E_{\text{local}} = E + \frac{P}{\epsilon_0} - \frac{P}{\epsilon_0} + \frac{P}{3\epsilon_0} + 0$$

$$E_{\text{local}} = E + \frac{P}{3\epsilon_0}$$

$\Rightarrow$  Now using this  $E_{\text{local}}$ ,

$$P = N \times E_{\text{local}} = N \times \left( E + \frac{P}{3\epsilon_0} \right)$$

$$\rightarrow P = N \times E + \frac{N \times P}{3\epsilon_0}$$

We finally get,

$$\Rightarrow \frac{(\epsilon_r - 1)}{(\epsilon_r + 2)} = \frac{N \times}{3\epsilon_0} //$$

) How?

Note: Polarization: Induced charge  $\frac{(P)}{\text{Surface area}}$

\* Polarizability: Induced dipole moment / Field  $(\alpha)$

Polarizability:

$$\Rightarrow \alpha = \alpha_e + \alpha_i + \alpha_d$$

$\downarrow$  Electronic     $\downarrow$  Ionic     $\uparrow$  Dipole based  
(orientational polarizability)

$\Rightarrow \alpha_e$  is due to actual arrangement of  $e^-$  around atom since electron cloud shifts towards the charged plate. So every atom gains this dipole —  $\text{Electronic polarization}$

(Happens in all materials)

$$\bullet M = \alpha_e \cdot E //$$



$d$  = Shift in center of electron cloud due to external field.

$$\Rightarrow E \cdot (Ze) = \text{External force}$$

• Restoring force is exerted

due to the sphere of radius  $d$ . w.r.t total.

$$\Rightarrow \frac{-Ze}{\frac{4}{3}\pi R^3} \times \frac{4}{3}\pi d^3 = \frac{Zed^3}{R^3} \quad \left. \begin{array}{l} \text{Charge corresponding} \\ \text{to restoring force} \end{array} \right\}$$

∴ Restoring force = External force

$$\therefore (ze) \cdot E = \frac{\left(\frac{ze d^3}{R^3}\right) \times (ze)}{d^2} \cdot \frac{1}{4\pi\epsilon_0}$$

$$\Rightarrow zed = ER^3 \cdot 4\pi\epsilon_0$$

Induced dipole  $\propto M_e = \alpha_e E$

$$4\pi\epsilon_0 \cdot ER^3 = \alpha_e E$$

$$\boxed{\alpha_e = R^3 \cdot 4\pi\epsilon_0} \Rightarrow \alpha_e = R^3 \quad (\text{we ignore constant})$$

Alignment  
in presence  
of field

- $\alpha_i$  corresponds to the polarizability that arises since bond lengths of molecules etc change due to charge at plates.

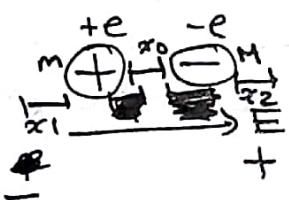
No finite  
dipole in  
material  
if no field

- $\alpha_d$  depends on the temperature.  
■ (Also related to rotation of applied field etc)

(15)

### i) Static field:

\* \* \*  $\alpha_e = R^3$  (from earlier)



- Due to external field the cation moves to the right & anion moves left. ( $x_1, x_2$  displacements)

$$\Rightarrow M = e \cdot x_1 + (+e) \cdot (-x_2)$$
$$= e(x_1 - x_2)$$

- Restoring force developed  $\Rightarrow F_1 \propto -x_1$   
 $F_1 = -\beta_1 x_1$

$$\Rightarrow F_2 \propto -x_2$$
$$F_2 = -\beta_2 x_2$$

$$\Rightarrow x_1 = -\frac{F_1}{\beta_1}$$

$$x_2 = -\frac{F_2}{\beta_2}$$

$$\therefore H = e \left( -\frac{F_1}{\beta_1} - \frac{F_2}{\beta_2} \right)$$

$\Rightarrow F = E \cdot e \}$  Both restoring force

- Cation,  $\omega_0^2 = \frac{\beta_1}{m} \Rightarrow \omega_0^2 \cdot m = \beta_1$

- Anion,  $\omega_0^2 = \frac{\beta_2}{M} \Rightarrow \omega_0^2 \cdot M = \beta_2$

$$\therefore H = -e \left( \frac{eE}{m\omega_0^2} + \frac{eE}{M\omega_0^2} \right)$$

$$\mu_{\text{ionic}} = -\frac{e^2 E}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right)$$

- $\alpha_{\text{ionic}} = \frac{\mu_{\text{ionic}}}{E} \Rightarrow \mu_{\text{ionic}} = \alpha_{\text{ionic}} \cdot E$

$$\therefore \boxed{\alpha_{\text{ionic}} = -\frac{e^2}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right)}$$

$$\Rightarrow \alpha_d = \frac{M_0^2}{3kT} \quad \} \quad \begin{matrix} \text{Dipole} \\ \text{polarizability} \end{matrix}$$

$$*\therefore \boxed{\alpha = R^3 \cdot \frac{e^2}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right) + \frac{M_0^2}{3kT}}$$

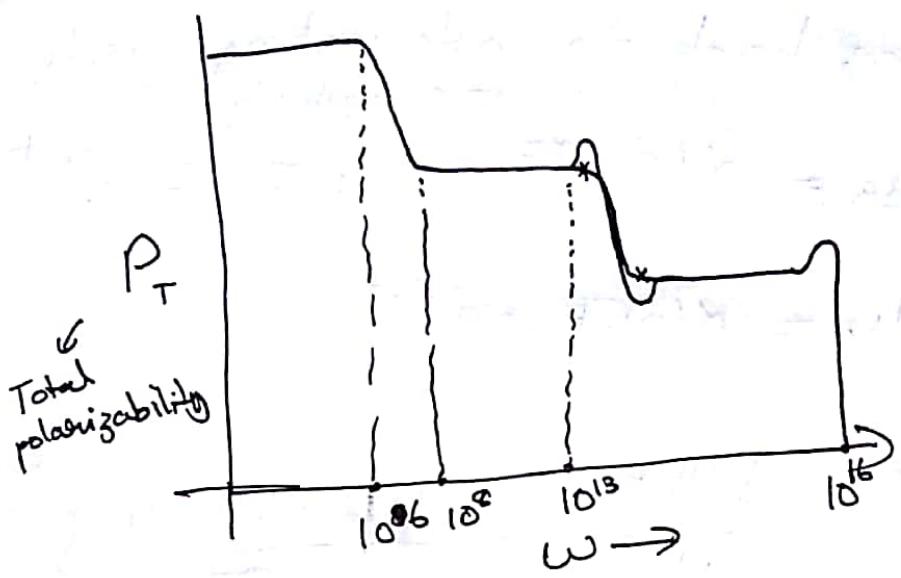
Polarizability of system in a static field.

## \* ii) Alternating field:

- When the field is flipped, molecules take some time to respond and flip to align with the field.

- If reorientation time of molecule  $< \frac{1}{\omega}$

\* where  $\omega = \text{frequency of field flip}$ , then the molecule can follow the field orientation. Else the molecules don't show dipole polarizability.



Dipole polarization (In static field)

$$\frac{dM_d(t)}{dt} = \underbrace{(M_{ds} - M_d(t))}_{\text{Maximum saturated dipole.}} / \tau$$

Minimum reorientation time.

+

(Static field present)

$$\Rightarrow dt = \int \frac{\tau \cdot dM_d(t)}{(M_{ds} - M_d(t))}$$

$$\Rightarrow t = -\tau \log e^{\cancel{(M_{ds} - M_d(t))}} + C$$

$$At t=0, M_d(t)=0$$

$$\Rightarrow 0 = -\tau \log e^{M_{ds}} + C$$

$$\Rightarrow C = \tau \log e^{M_{ds}}$$

$$\therefore M_d(t) = M_{ds} \left( 1 - e^{-\frac{t}{\tau}} \right)$$

For increase to max ( $M_{ds}$ )

$\Rightarrow$  Similarly, for decay from  $M_{ds}$  to zero.

$$M_d(t) = M_{ds} e^{-\frac{t}{\tau}}$$

⇒ Going back to alternating fields,  
static maximum polarizability.

$$*\ast \cdot M_{dB} = \alpha(0) \cdot E, E = E_0 \cdot e^{-i\omega t}$$

$$\Rightarrow M_{dB} = \alpha(0) \cdot E_0 \cdot e^{-i\omega t}$$

- Now,  $\frac{dM_d(t)}{dt} = \frac{M_{dB} - M_d(t)}{\tau}$

From earlier

$$\Rightarrow \frac{dM_d(t)}{dt} + \frac{M_d(t)}{\tau} = \frac{\alpha(0) \cdot E_0 \cdot e^{-i\omega t}}{\tau}$$

- $M_d(t) = \alpha_d(\omega) e^{-i\omega t}$

$$\Rightarrow \frac{dM_d(t)}{dt} = \alpha_d(\omega) (-i\omega) e^{-i\omega t}$$

$$\Rightarrow \cancel{\alpha_d(\omega) (-i\omega) e^{-i\omega t}} + \frac{1}{\tau} \cancel{\alpha_d(\omega) e^{-i\omega t}}$$

$$= \frac{\alpha(0)}{\tau} E_0 \cancel{e^{-i\omega t}}$$

$$\Rightarrow -i\omega \alpha_d(\omega) + \frac{\alpha_d(\omega)}{\tau} = \frac{\alpha(0) \cdot E_0}{\tau}$$

$$\Rightarrow -\alpha_d(\omega) \left[ i\omega - \frac{1}{\tau} \right] = \frac{\alpha(0) \cdot E_0}{\tau}$$

$$\Rightarrow -\alpha_d(\omega) \left[ \frac{i\omega\tau - 1}{\tau} \right] = \frac{\alpha(0) \cdot E_0}{\tau}$$

$$\Rightarrow \alpha_d(\omega) = \frac{\alpha(0) \cdot E_0}{(1 - i\omega\tau)} \rightarrow ①$$

- We know polarization  $P = NH$

$$\chi = P/\epsilon_0 E \quad \} \text{Susceptibility}$$

- $P = NH = N\alpha E$

$$\therefore \chi \cdot \epsilon_0 \cdot E = N\alpha E$$

$$\Rightarrow \chi = \frac{N\alpha}{\epsilon_0}$$

$$\Rightarrow \epsilon_r = 1 + \frac{N\alpha}{\epsilon_0} = 1 + \chi$$

Total  
dielectric  
constant =  $\underbrace{1 + \chi_e}_{\text{Optical}} + \chi_d$

- $D = \epsilon_0 E + P$

$$\epsilon_r \epsilon_0 E = \epsilon_0 E + P$$

$$P = (\epsilon_r - 1) \epsilon_0 E$$

$$= \chi \epsilon_0 E$$

$$\therefore \chi = \epsilon_r - 1$$

$\chi_i = 0$   
considering  
there  
are  
no ions?

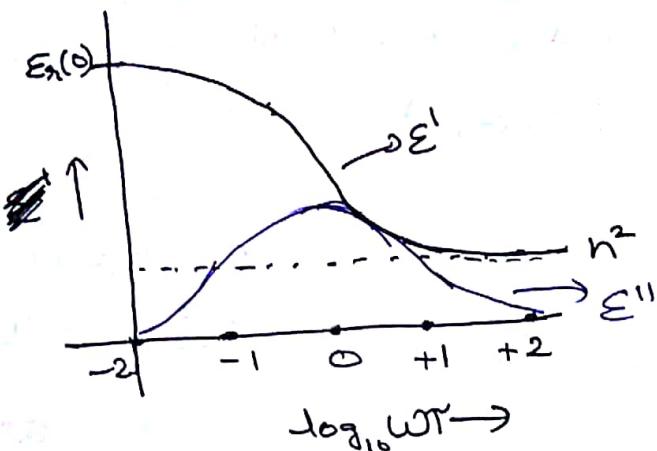
$$\epsilon_r = n^2 + \chi_d \quad \} \begin{matrix} n = \text{Refractive} \\ \text{index} \\ n = \sqrt{\epsilon_r \mu_r} \end{matrix}$$

From ①,  $\chi_d(\omega) = \frac{\chi(0) \cdot E_0}{(1 - i\omega\tau)}$  since both  $\chi_d$  &  $\alpha_d$  behave in a similar way.

$$\Rightarrow \epsilon_r = n^2 + \frac{\chi(0) \cdot E_0}{(1 - i\omega\tau)}$$

$$\begin{aligned} \Rightarrow \epsilon_r &= \epsilon' + i\epsilon'' \\ &= \left( n^2 + \frac{\epsilon_r(0) - n^2}{1 + \omega^2\tau^2} \right) \\ &\quad + i \left( \frac{\omega\tau(\epsilon_r(0) - n^2)}{1 + \omega^2\tau^2} \right) \end{aligned}$$

- We can then plot these terms w.r.t  $\omega$ .



(Plotting the real values terms & imaginary terms individually)

⑯

Ionic polarizability:

$$\epsilon_r(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 - \left(\frac{\omega^2}{\omega_{\pm}^2}\right)}$$

static dielectric constant due to ionic polarizability

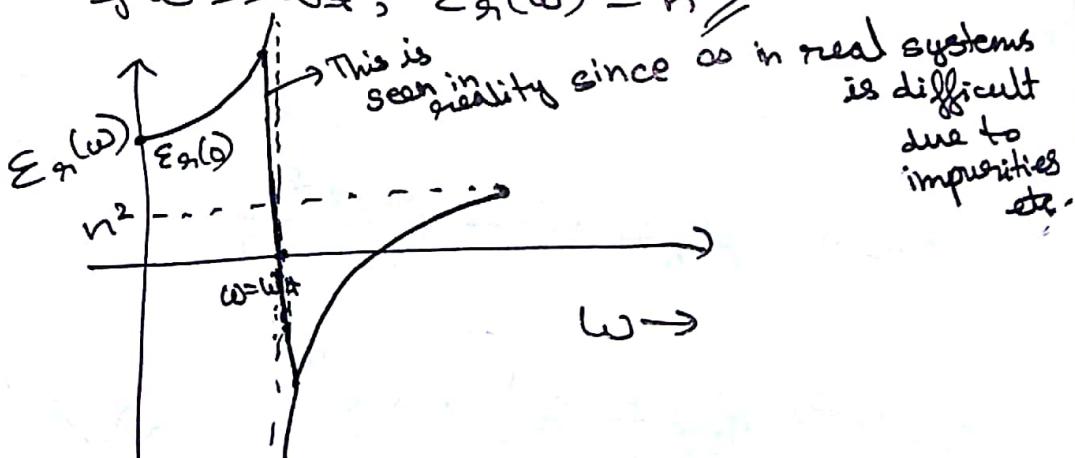
(Proof not needed)

• If  $\omega \ll \omega_{\pm}$ ,  $\epsilon_r(\omega) = \epsilon_r(0)$

Applied field  $\uparrow$  Natural frequency of ions  $\uparrow$

frequency.

• If  $\omega \gg \omega_{\pm}$ ,  $\epsilon_r(\omega) = n^2$



Note: ∞ dielectric constant means vibrations are not restricted at all and bonds can be extended to any length.

## \* Electronic polarizability:

↪ Electron cloud oscillates to and fro in field.

$$-eE = -m\omega_0^2 x = m \cdot \frac{d^2x}{dt^2}$$

→ On solving,  $x = x_0 e^{-\omega t}$

→  $E = E_0 \cdot e^{-\omega t}$  } Applied field

•  ~~$m\alpha_0(\omega^2 - \omega_0^2)$~~  =  $-eE_0$

$$\Rightarrow m\alpha_0(\omega^2 - \omega_0^2) = -e^2 E_0$$

$$\alpha_e = \frac{ex_0}{E_0} = -\frac{e^2/m}{(\omega - \omega_0^2)}$$

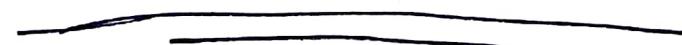
$$\chi(\omega) = \frac{N\alpha_e^2}{\epsilon_0} \quad , \quad \underbrace{\epsilon_g = 1 + \chi}_{\epsilon_g(\omega) = 1 + \frac{Nze^2/\epsilon_0 m}{\omega_0^2 - \omega^2}}$$

$Nz$  is  
total charge  
units

\*  $\Rightarrow \epsilon_g(\omega) = 1 + \frac{Nze^2}{\epsilon_0 m (\omega_0^2 - \omega^2)}$

• If  $\omega \gg \omega_0$ ,  $\epsilon_g(\omega) = 1$

If  $\omega \ll \omega_0$ ,  $\epsilon_g(\omega) = 1 + \frac{Nze^2}{\epsilon_0 m (\omega_0^2)}$



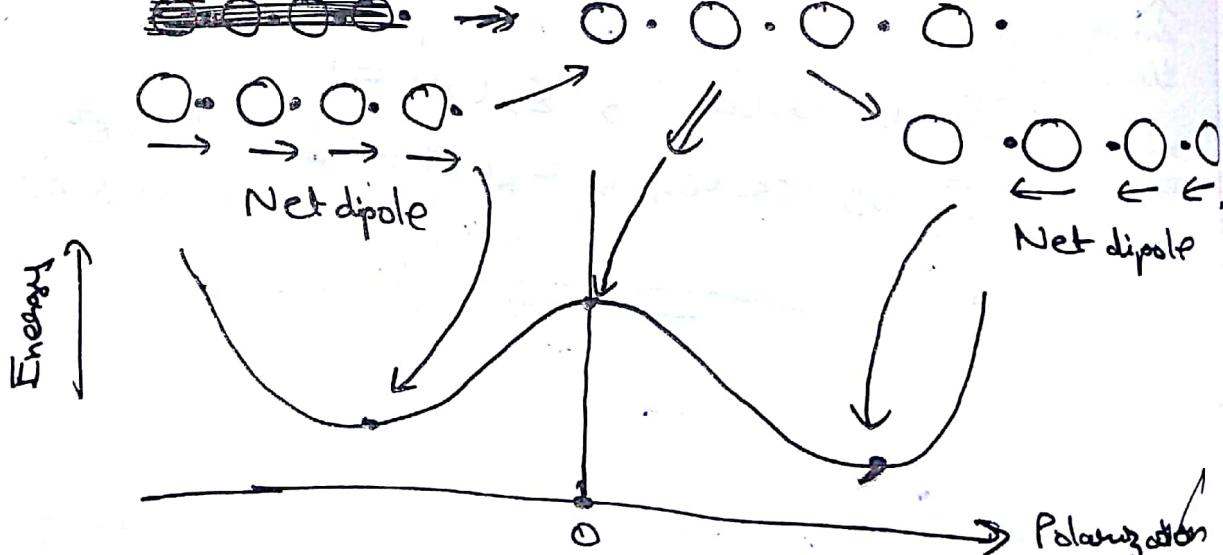
## \* Ferro Electricity: (Acts as memory device)

- Polarization reversed
- No center of inversion symmetry } Required to ensure material is ferro electric
- Temperature dependent.  $\rightarrow$  At large temperatures, loss polarizability

ex:  $\text{BaTiO}_3$  } This has an FCC structure  
with Ti at ~~near~~ body center.  
↑  
Ferro electric material ( $\text{O}^{2-}$  ions are not present at the face centers exactly but are present with a little offset)

- This exhibits spontaneous polarization since there is a net dipole present per unit cell.

### Polarization reversal:



### \* (Hysteresis in ferroelectrics $\rightarrow$ Graph in slides)

?  
Polarization Reversal  $\rightarrow$  Allows for memory storage.

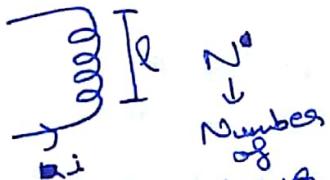
## \* Piezoelectricity:

- No stress  $\rightarrow$  Neutral
- Extension  $\rightarrow$  One orientation of field  
Compression  $\rightarrow$  Opposite orientation of field  
(example in slides)

— END of Mid2 —

17

## Magnetism:

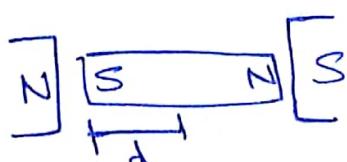

$$H = \frac{NI}{l} \quad , \quad B = \frac{\Phi}{A}$$

Field strength                                      Flux

$\uparrow$

$$\bullet B = \mu_0 H, \mu_0 = 4\pi \times 10^{-7}$$

- Diamagnetism is a universal property, in some materials ferro or para magnetism dominates this.
- $M_s = \frac{M}{\mu_0}$  } Based on this we can determine the magnetic type of the material.



$$\bullet M = m \times 2d$$

$\downarrow$   
Magnetic moment

$$\bullet I = \frac{M}{V} \quad \} \text{amp/m}$$

Intensity  
of magnetisation

$$\bullet B = MH = \mu_0 H + \mu_0 M - \mu_0 M$$

Total magnetic field

$$= \mu_0 M H + \mu_0 M - \mu_0 M$$
$$= \mu_0 M H + \mu_0 M (M_s - 1)$$

$$B = H_0H + H_0H\left(\frac{\mu}{H_0} - 1\right)$$

$$= H_0H + H_0\left(\frac{H - H_0}{H_0}\right)$$

Magnetic flux  
due to induced  
magnetism

$$= H_0H \xrightarrow{\text{Field strength}} + H_0I \xrightarrow{\text{Intensity of magnetization}}$$

$$\boxed{B = H_0(H + I)}$$

$$\Rightarrow I \propto H, I = \chi H$$

$$\therefore \chi = \frac{I}{H}, \quad \chi = \begin{cases} -ve & \rightarrow \text{Diamagnetic} \\ +ve & \rightarrow \text{Paramagnetic} \\ \text{close to } 1 & \rightarrow \text{Ferromagnetic} \end{cases}$$

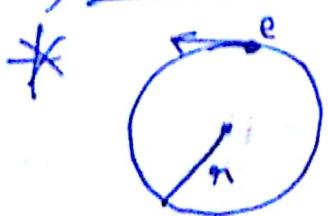
$$\Rightarrow M_r = \frac{\mu}{H_0} = \frac{B/H}{B/(H+I)} = \frac{H+I}{H} = 1+\chi$$

$$\therefore \boxed{M_r = 1 + \chi} \rightarrow \text{Similar to electricity.}$$

Causes of magnetism:

- Orbital motion of  $e^-$
- Spin motion of  $e^-$
- Spin motion of nucleus

i) Orbital motion of  $e^-$ :



$\bullet H = IA$

$$= \frac{e \cdot v}{2\pi r} \cdot \pi r^2 = \frac{e \cdot \pi r v}{2} = \frac{e \cdot \pi r \omega}{2}$$

( $v$  = Velocity of  $e^-$ )

For  
more  
details  
 $\pi r / v$

$$\therefore \mu = \frac{e}{2m} q^2 \omega \cdot m = \frac{eL}{2m} \rightarrow \begin{array}{l} \text{Angular} \\ \text{momentum} \end{array}$$

$$\mu = \frac{e \cdot nh}{2m \cdot 2\pi} \quad (\because \text{Angular momentum is quantized})$$

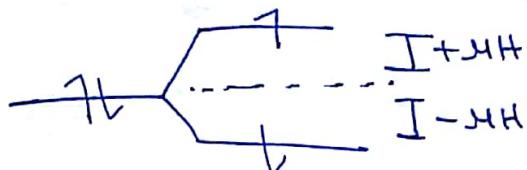
$$\therefore \mu = n \left( \frac{eh}{4\pi m} \right) \rightarrow \text{Bohr magneton } (\mu_B)$$

$$\therefore \boxed{\mu = n \cdot \mu_B} \quad \mu_B = 9.24 \times 10^{-24} \text{ Am}^2$$

### i) Spin motion of $e^-$ :

\*  $\mu_{\text{spin}} = g \cdot \frac{e}{2m} \times \cancel{\text{Spectroscopic splitting factor}}$  Spin angular momentum

- Spectroscopic splitting factor ( $g$ )



• Since

$$\gamma = \ln H \sin \theta$$

- Energy change by  $4H$ .

(For a pair of  $e^-$ ,  $g=2$  (theoretically))  
(Typically  $g=2$ )

$$\therefore \mu_{\text{spin}} = \frac{Z \times e}{2m} \times \frac{\hbar}{2\pi} = \frac{e\hbar}{2m} = \frac{eh}{4\pi m}$$

$$\therefore \boxed{\mu_{\text{spin}} = \pm \mu_B} \quad = \mu_B$$

### iii) Spin motion of nucleus:

- Generally ignored since proton mass is much higher than  $e^-$ .

Note: Total angular momentum

For more than half filled shells  
 $J = L + S$   
 $J = L - S$   
Sum of all orbital numbers  
For less than half filled shells

$$g = 1 + \frac{(J(J+1) + S(S+1) - L(L+1))}{2J(J+1)}$$

(Per  $e^-$ , spin is  $\pm 1/2$ )

ex: For  $Z=24 \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

$\boxed{h\boxed{h\boxed{h}}$
-2 -1 0 1 2

Since  $t$  is less than half filled.

$$\left. \begin{array}{l} J = L - S \rightarrow \frac{1}{2} \times 4 = 2 \\ \downarrow \\ -2 - 1 + 0 + 1 = -2 \end{array} \right\} \quad \dots J = -4$$

Now, we can calculate  $g$  and then use it.

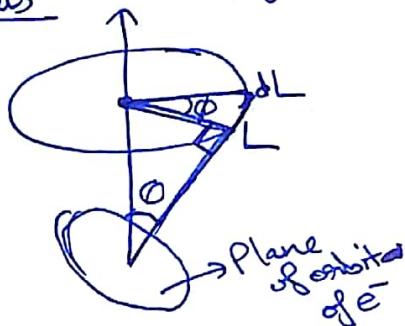


### Diamagnetic



### Materials

$H$  (External field applied)



(Diamagnetism arises due to this precession motion)

$$\frac{d\phi}{dt} = \text{Precessional motion}$$

$$M_{\text{orb}} = \frac{e}{2m} \cdot L$$

$$\tau = \frac{dL}{dt}$$

$$\Rightarrow \tau = \bar{M} \times \bar{H} = \frac{e \cdot \bar{L}}{2m} \times \bar{H}$$

$$\therefore \frac{dL}{dt} = \frac{e}{2m} \cdot \bar{L} \times \bar{H} = \frac{e}{2m} \cdot L H \sin \theta$$

$$\omega_L = \frac{d\phi}{dt}$$

Frequency of precessional motion  $\leftarrow$  Larmour frequency

$$dL = d\phi \cdot \underbrace{L \sin \theta}_{\text{radius}}$$

$$\therefore d\phi = \frac{dL}{L \sin \theta}$$

$$\therefore \omega_L = \frac{1}{L \sin \theta} \cdot \frac{dL}{dt} = \frac{1}{L \sin \theta} \cdot \frac{e}{2m} \cdot L H \sin \theta$$

Larmour frequency  $\leftarrow$

$$\boxed{\omega_L = \frac{eH}{2m}}$$

Due to  $\mu_{\text{ind}} = -\frac{e}{2m} \times \omega_L \times m r^2 \approx \frac{-e}{2m} \times m r^2 \cdot \frac{eH}{2m}$

$\downarrow$   
Induced magnetic moment due to  $\frac{1}{2}$  orbital motion

$$\therefore H_{\text{ind}} = \frac{-e^2 \mu_{\text{m}} r^2}{4m^2} \cdot H$$

$$= \frac{-e^2 \mu_{\text{m}} r^2}{4m} \cdot H$$

//

o Considering all  $e_i$ ,

$$M = N \cdot z \cdot \mu_{ind} = -\frac{Nz e^2 \sigma^2}{4\pi} \cdot H$$

$$\chi = \frac{M}{H} = -\frac{N e^2 g^2}{4m} // \quad \left. \begin{array}{l} \text{-ve} \\ \text{indicates} \\ \text{diamag} \\ \text{relaxm} \end{array} \right\}$$

18

- Point defects
  - Line defects
  - Surface defects
  - Volume defects
- Vacancy defect  
Impurity defect  
Interstitial  
Substitutional
- Edge dislocations, Burgers vector is  $\perp$  to dislocation line  
 $T = \text{Stress} = c \exp\left(-\frac{kT}{E}\right)$  Take plane spacing Step size
- Screw dislocations, volume is shifted, Burgers vector is parallel to dislocation line  
Mixed dislocations
- $\rightarrow$  FCC:  $a = 0.414R$  (octahedral site)  $\rightarrow$  12 interstitial sites contributing to 4 unit cells  
BCC:  $a = 0.291R$  (radius of atom)  $\rightarrow$  24 interstitial sites contributing to 2 unit cells (tetrahedral site)

- Size of interstitial site,
  - Frenkel & Schottky defects
- Cation is displaced Anion removed to balance charge due to Frenkel.

### Burgers vectors

$$\begin{aligned} \hookrightarrow \text{FCC: } & \frac{a}{2} \langle 110 \rangle \\ \hookrightarrow \text{BCC: } & \frac{a}{2} \langle 111 \rangle \\ \hookrightarrow \text{Primitive: } & a \langle 100 \rangle \\ \hookrightarrow \text{HCP: } & \frac{a}{3} \langle 1\bar{1}0 \rangle \end{aligned}$$

## Electric properties

- 1) Drude: Indep of Free  $e^-$   
Mean free path, mean collision time
- $\bullet V = iR$
- $\bullet E = J \cdot \sigma \rightarrow$  Resistivity  
 $\uparrow$   
Current density
- $\bullet J = -neV_d$

$$\begin{aligned} \bullet F &= -Ee \\ \frac{mV_d}{\tau} &= -Ee \\ \tau &= \frac{ne^2 \tau}{m} E = \sigma E \quad \text{Conductivity} \\ \sigma &= \frac{ne^2 \tau}{m} \end{aligned}$$

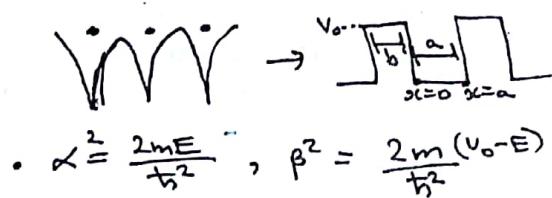
2) Sommerfeld:  $\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0$  (continuity boundary conditions)

$$\psi(x) = \frac{1}{\sqrt{V}} \cdot e^{ikx}, \quad E = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (nx + ny^2 + nz^2)$$

Highest energy level  $\rightarrow$  Fermi energy level.

$$f(E) = \frac{1}{1 + e^{\frac{E - Ef}{kT}}} \quad \begin{array}{l} \text{Prob of} \\ \text{finding } e^- \\ \text{with energy } E. \end{array}$$

### Kronig-penney model:



$$\alpha^2 = \frac{2mE}{\hbar^2}, \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0, \quad 0 < x < a$$

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left[ \frac{E}{V_0} - \frac{1}{a} \right] \psi = 0, \quad -b < x < 0$$

$$\begin{aligned} \psi_1 &= A e^{i(\alpha - k)x} + B e^{-i(\alpha + k)x} \\ \psi_2 &= C e^{i(\beta - ik)x} + D e^{-i(\beta + ik)x} \end{aligned}$$

$$\rightarrow \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \underbrace{\cos ka}_{\pm 1 \text{ limits}} \quad \begin{array}{l} \text{Regions satisfying are allowed} \\ \text{on } \alpha a \text{ vs LHS graph.} \end{array}$$

$$\downarrow \alpha = \frac{3\pi}{2}$$

$$\hookrightarrow \text{If } p = 0, \quad \alpha = k, \quad \alpha^2 = \frac{2mE}{\hbar^2} = k^2 \rightarrow E = \frac{\hbar^2 k^2}{2m} \quad \begin{array}{l} \text{Drude} \\ \parallel \end{array}$$

$$\hookrightarrow \text{If } p = \infty, \quad \sin \alpha a = 0, \quad \alpha^2 = \frac{\hbar^2 \pi^2}{a^2} \rightarrow E = \frac{\hbar^2 \pi^2}{8ma^2}$$

$$\Rightarrow \sigma = \frac{I}{E} = n e M \quad \text{Mobility of } e^-$$

### Mattheissen's rule:

$$\text{Resistivity } S = S_T + S_{\text{imp}} + S_{\text{defects}}$$

$$\underbrace{S_{\text{tot}}}_{\text{Sat}} \quad \underbrace{A_{ci}(1 - ci)}_{\text{core of imp in atoms to}}$$

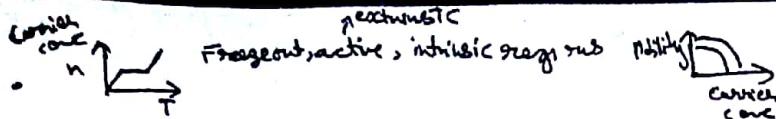
### Semiconductors

Intrinsic: Small band gap (pure materials), as  $T \uparrow$  conductivity  $\uparrow$

$$\sigma = n_i e (4n + 4p) \quad \begin{array}{l} \text{Electrons + Holes} \\ \parallel \end{array}$$

Extrinsic: P type:  $\frac{[CB]}{[VB]}$  Accepter level

N type:  $\frac{[CB]}{[VB]}$  ... Donor level.



Hall effect:  

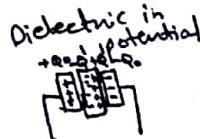
$$V_H = \frac{R_H \cdot I \times B_2}{d} \quad \text{Magnetic field}$$

- Quenching: Sudden drop in temp.
- As we move up in periodic table, band gap increases

Molecular dipole:

$$\Rightarrow \vec{D} = q/d, \gamma = d \sin \theta \cdot E_0 \\ = \mu E \sin \theta$$

$$\Delta PE = \int T d\theta = \mu E$$



$$\oint E dS = \sigma / \epsilon_0, E = \frac{\bar{D}}{\epsilon_0}$$

$$\text{Due to dielectric, } \frac{Q - Q'}{\epsilon_0} = EA, \bar{D} - \bar{P} = \epsilon_0 \bar{E}, \bar{D} = \epsilon_0 \bar{E} + \bar{P}, E_d = \frac{\bar{E}}{\epsilon_0}$$

$$\Rightarrow E \bar{E} = \epsilon_0 \bar{E} + \bar{P}, \\ \bar{P} = (\epsilon_d - 1) \epsilon_0 \bar{E}$$

$$\rho = NH = N \alpha E, \epsilon_d = 1 + \frac{N \alpha}{\epsilon_0}$$

$$E_{\text{local}} = E_1 + E_2 + E_3 + E_4, \epsilon_0 E_1 = \epsilon_0 E + P, E_1 = E + P/\epsilon_0$$

$$= E + P/3\epsilon_0$$

$$0 = \epsilon_0 E_2 + P, E_2 = -P/\epsilon_0$$

$$\Delta E_3 = \frac{1}{4\pi\epsilon_0 R^2} \cos \theta, \Delta Q = \rho \cos \theta \cdot 2\pi R^2 \sin \theta d\theta$$

$$E_3 = P/3\epsilon_0, E_4 = 0$$

Polarization  
of net  
dipole

Hartree-Fock graph.  
(Field vs Polarization)

Piezoelectricity

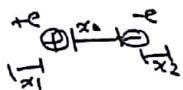
↓  
Extension  
compression  
↓  
Different  
orientation  
of fields

Polarization:  $P = \text{Charge} / \text{Area}$   
Polarizability:  $\alpha = \text{Dipole moment} / \text{Field}$

$$\alpha = \alpha_e + \alpha_i + \alpha_d$$



$$E \cdot Z_e = \frac{(Z e d^3)}{R^3} \times Z_e \quad \begin{cases} \text{restoring force} \\ \text{Electrostatic force} \end{cases}$$



$$M = ex_1 + eox_2, F_1 = -\beta_1 x_1, F_2 = -\beta_2 x_2$$

$$F = Ee, \omega_0^2 = \frac{\beta_1}{m}$$

$$\omega_0^2 = \frac{\beta_2}{M}$$

$$\mu_i = -\frac{e^2 E}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right)$$

$$\alpha_i = \mu_i / E = -\frac{e^2}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right)$$

$$\alpha_d = \mu_0^2 / 3RT$$

$$\alpha = R^3 - \frac{e^2}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right) + \frac{\mu_0^2}{3KT}$$

$$\frac{dM_d(t)}{dt} = (M_{ds} - M_d(t)) / \tau \Rightarrow M_d(t) = M_{ds} (1 - e^{-t/\tau}) \quad \begin{cases} \text{Increase} \\ \text{Decay} \end{cases}$$

Alternating field:  $E = E_0 e^{-i\omega t}$

$$M_{ds} = \alpha(0) \cdot E$$

$$\frac{dM_d(t)}{dt} = \frac{M_{ds} - M_d(t)}{\tau}, M_d(t) = \alpha_d(\omega) e^{-i\omega t}$$

$$\Rightarrow -i\omega \alpha_d(\omega) + \frac{\alpha_d(\omega)}{\tau} = \frac{\alpha(0) \cdot E_0}{\tau}$$

$$\Rightarrow \alpha_d(\omega) = \alpha(0) \cdot \frac{E_0}{(1 - i\omega\tau)}$$

$$\epsilon_g(\omega) = \hbar^2 + \frac{\epsilon_g(0) - \hbar^2}{1 - (\omega^2/\omega_g^2)}$$

$\epsilon_g(\omega)$  vs  $\omega$  graph  
Electronic polarization  
 $\Rightarrow E = E_0 e^{-i\omega t}, -\omega E = m \frac{d^2 x}{dt^2}$

$$\alpha_e = -\frac{\omega^2 / m}{(\omega^2 - \omega_g^2)}, \epsilon_g(\omega) = 1 + \frac{N \omega^2}{\omega_g^2 (1 - \omega^2/\omega_g^2)}$$

$$\alpha_e = \frac{\omega^2 / m}{(\omega^2 - \omega_g^2)}, \epsilon_g(\omega) = \frac{\chi(0) \cdot E_0}{(1 - i\omega\tau)}$$

( $\lambda$  = shift in  
center of  
electron  
cloud  
due to  
external  
field)

Polarizability  
in a static field

$$\alpha_d = \mu_0^2 / 3RT$$

$$\alpha = R^3 - \frac{e^2}{\omega_0^2} \left( \frac{1}{m} + \frac{1}{M} \right) + \frac{\mu_0^2}{3KT}$$

$$\frac{dM_d(t)}{dt} = (M_{ds} - M_d(t)) / \tau \Rightarrow M_d(t) = M_{ds} (1 - e^{-t/\tau}) \quad \begin{cases} \text{Increase} \\ \text{Decay} \end{cases}$$

Susceptibility

$$\chi = P / \epsilon_0 E$$

$$\epsilon_g = 1 + \chi_e + \chi_d \\ = \hbar^2 + \chi_d$$

$$\epsilon_g = \hbar^2 + \frac{\chi(0) \cdot E_0}{(1 - i\omega\tau)}$$