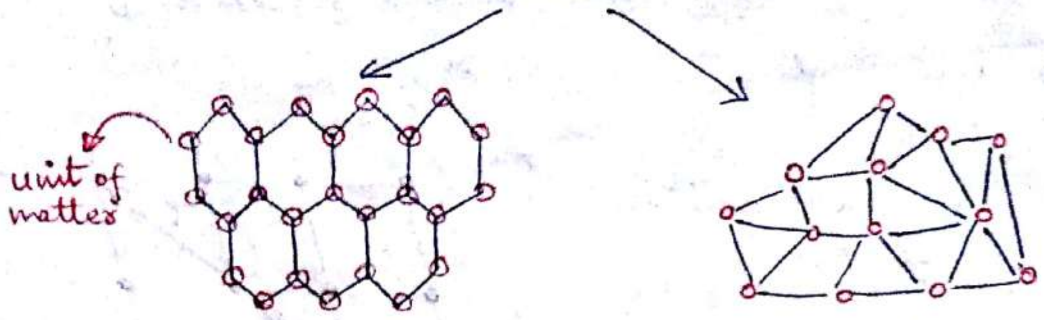
SOLID STATE PHYSICS

Crystal structure, direct lattice & (un)holy grail

solids



crystalline amorphous

(i) Amorphous solid : no order in arrangement of unit of matter (atoms, molecules etc). XRD shows "liquid like" property.

what's "solid"? $\rightarrow$ elasticity

stress $\sigma = K\frac{x}{l}$

x = displacement

l = length of lattice

$$F = -l^2 K \frac{x}{l} = -Klx = -kx,$$

But $\frac{1}{2}k\bar{x}^2 = \frac{1}{2}k_BT$ (equipartition theorem)

$$\therefore \bar{x}^2 = \frac{k_BT}{k} = \frac{k_BT}{Kl}$$

So if $K \rightarrow 0$, $\bar{x}^2 \rightarrow \infty$ $\longrightarrow$ "rigidity"

amorphous solids $\longleftrightarrow$ highly viscous, supercooled liquids.

<u>Example</u> pitch, plastic, silicate glass.

SALIENT FEATURES

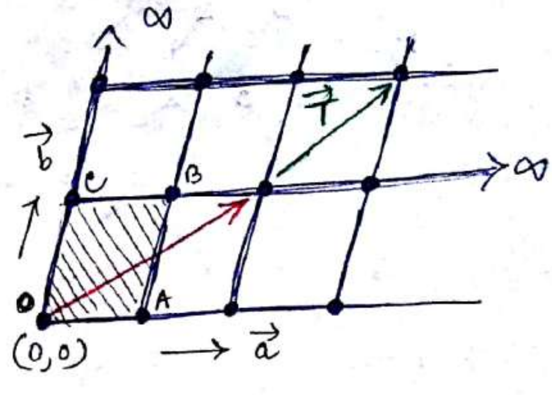
(i) molecular motion is irregular but distance is more or less same with elastic solid.

(ii) no regular shape $\rightarrow$ conductivity, elasticity, tensile strength is isotropic

(iii) no long range order. short range / medium range order possible.

(iv) no sharp melting point.

There are polycrystalline substances which are composed of many small domains/regions of single crystals. Crystalline substances are distinguished from amorphous solids by their anisotropic behaviour (direction dependent).



Ideal crystal : infinite repetition of identical structure in space. Periodic arrangement of unit (atoms, molecules, ions) in a crystal is called the lattice, defined by three fundamental translation vectors $\vec{a}, \vec{b}, \vec{c}$. / basis vectors

Atomic position vector $\vec{r}' = \vec{r} + \vec{T}$

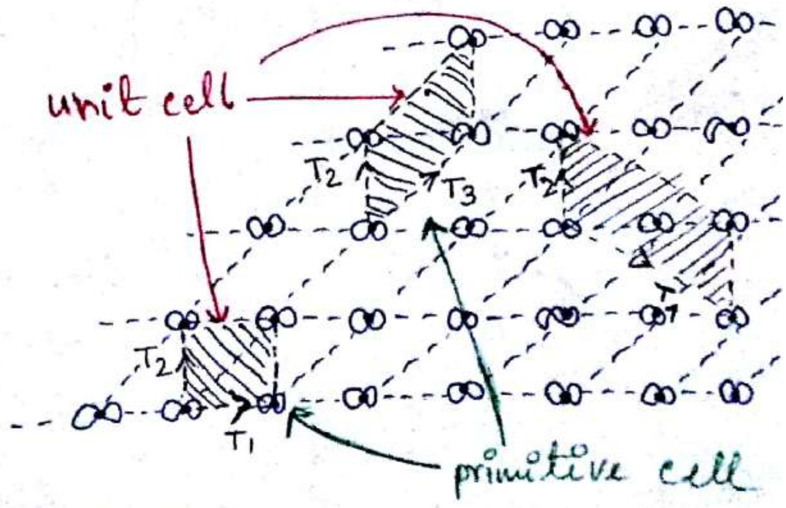
$$= \vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

where n_1, n_2, n_3 are integers.

primitive lattice & Unit cell

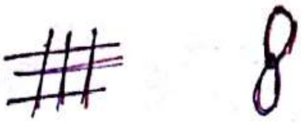
Unit cell is volume from which entire crystal can be constructed by translational repitition. (OABC parallelogram)

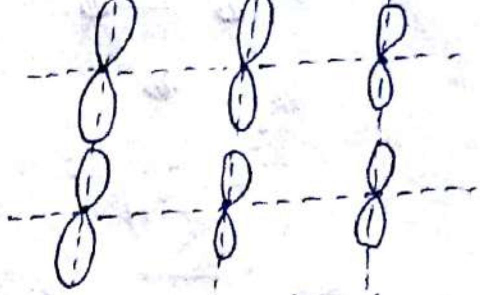
primitive cell is a type of unit cell that contain 1 lattice point at corners & minimum in volume $= |(\vec{a}\times\vec{b})\cdot\vec{c}|$



Basis In crystal structure, every lattice point is associated with an unit assembly of atoms/molecules/ions. This unit is called basis.

crystal structure = lattice + basis





Basis can contain even hundreds & thousands of molecules.

A translation operation leaves the crystal invariant.

$$f(\vec{r}) = f(\vec{r} + \vec{T})$$

physical significance : number density (point mass atom) $n(\vec{r}) = \sum_{\vec{T}} \delta(\vec{r} - \vec{T})$

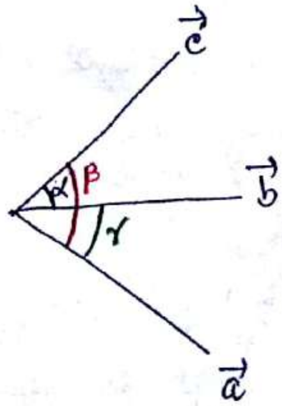
density $\rho(\vec{r}) = \sum_{\vec{T},\alpha} m_\alpha \, \delta(\vec{r} - \vec{T} - \vec{c}_\alpha)$

where m_α is mass of atom at lattice site $\vec{c}_\alpha$.

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{T})$$

For cubic structure $|\vec{a}| = |\vec{b}| = |\vec{c}|$

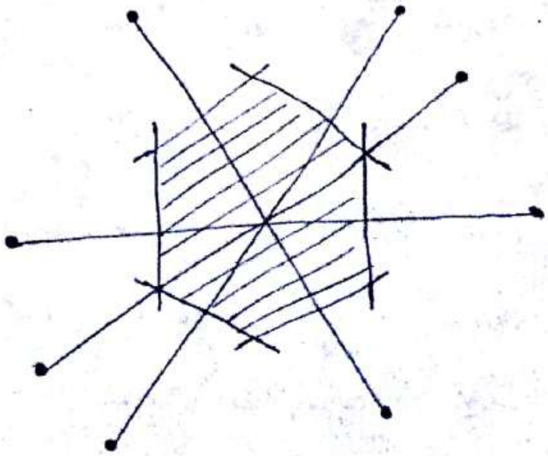
$$\alpha = \beta = \gamma = \frac{\pi}{2}$$



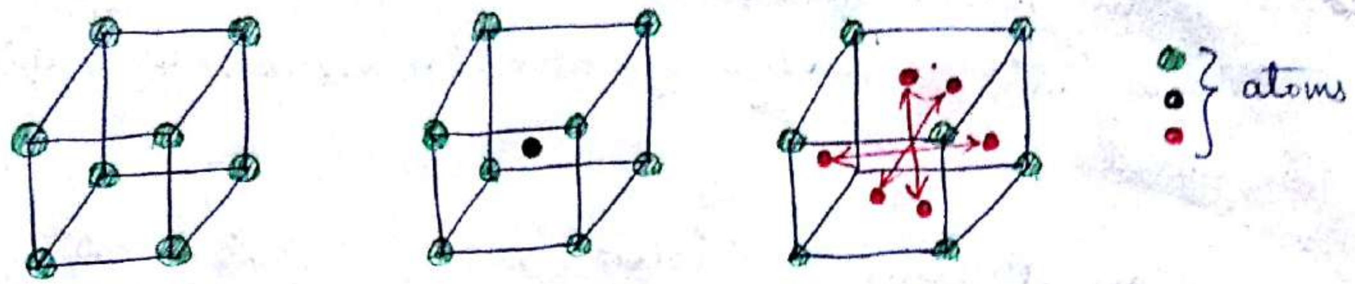
Wigner-Sietz primitive cell

1. Draw lines connecting nearby lattice points.
2. Draw planes/lines at midpoint of line & perpendicular to it.

This is WS primitive cell.



1 atom 2 atom 4 atom



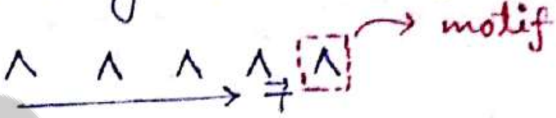
Sc (primitive) bcc fcc

← unit cell →

Elements of symmetry

A symmetry operation transforms the crystal to itself.

(i) Translation $\vec{r}' = \vec{r} + \vec{T}$



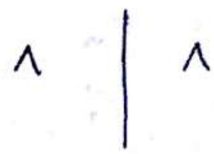
(ii) Rotation $n\phi = 2\pi$

$\phi = 60^\circ = \frac{2\pi}{6}$

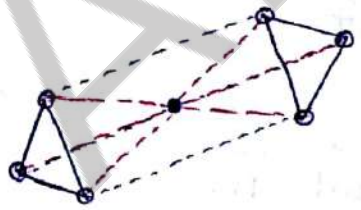
n = multiplicity of rotation axis.

$= 1, 2, 3, 4, \cancel{5}, 6.$ A 2D square lattice has 4-fold rotational symmetry.

(iii) Reflection mirror image



(iv) Inversion
(only for 3D lattice)



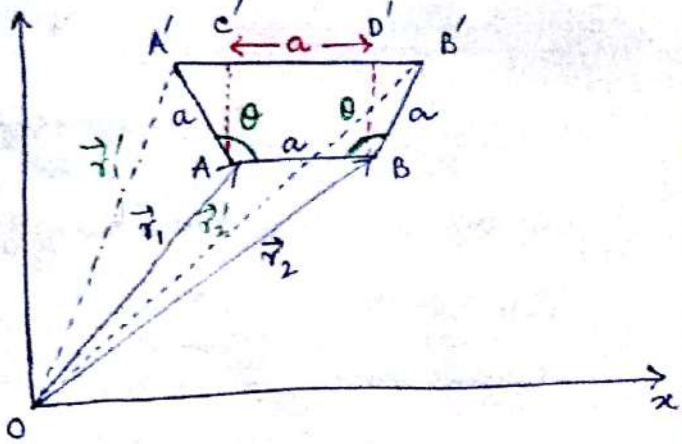
Symmetry operation performed about a point / line are called point group symmetry. 3 type of point group (i) plane of symmetry (reflection), (ii) axis of symmetry (rotation), (iii) centre of symmetry (inversion)

5-fold rotational symmetry : quasicrystals.

But why 5-fold rotational symmetry is not permissible in crystal structure ?

$AB = a = |\vec{a}| = |\vec{r}_1 - \vec{r}_2|$

$= AA' = BB'$



Suppose $A'B' = q|\vec{a}|$ (q = integer)

$\angle A'AC' = \angle D'BB' = \theta - \pi/2$

$A'C' = D'B' = |\vec{a}| \cos\theta$

$\therefore A'B' = |\vec{a}| + |\vec{a}|\cos\theta + |\vec{a}|\cos\theta$

$q|\vec{a}| = |\vec{a}| + 2|\vec{a}|\cos\theta$ or $|\cos\theta| = |\frac{q-1}{2}|$

as $\cos\theta < 1$, allowed values of q are $-1, 0, 1, 2, 3$

$\{q = -1, \theta = \frac{2\pi}{2}\}$, $\{q = 0, \theta = \frac{2\pi}{3}\}$, $\{q = 1, \theta = \frac{2\pi}{4}\}$

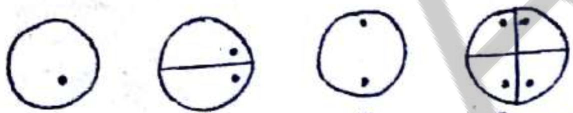
$\{q = 2, \theta = \frac{2\pi}{6}\}$, $\{q = 3, \theta = \frac{2\pi}{1}\}$.

So, $n = 1, 2, 3, 4, 6$ → hexad

2 → diad, 3 → triad, 4 → tetrad

<u>point group</u> <u>& space group</u>

[translation, rotation, reflection] (point) point group.



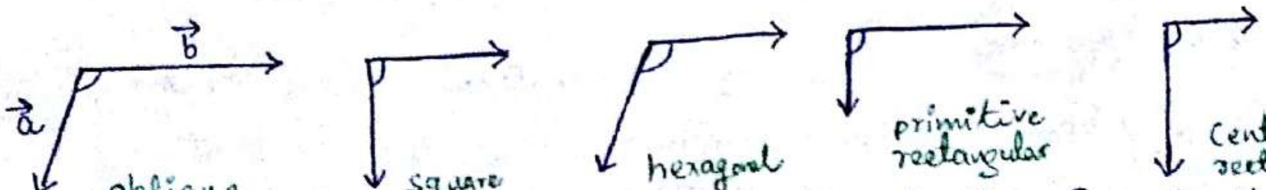
1 1m 2 2mm

Total 32 point groups.

Group of all symmetry elements is space group.

In 2D : 17, 3D : 230.

<u>Bravais lattice :</u> $|\vec{a}|, |\vec{b}|, \phi$ 5combination : symmetry operations are maintained.



oblique
$|\vec{a}| \neq |\vec{b}|, \phi \neq \frac{\pi}{2}$
$\{\frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}\}$
rotation

square
$|\vec{a}| = |\vec{b}|, \phi = \frac{\pi}{2}$
$\{\frac{2\pi}{4}\}$
rotation

hexagonal
$|\vec{a}| = |\vec{b}|, \phi = \frac{2\pi}{3}$
$6\{\frac{2\pi}{[illegible]}\}$
rotation

primitive rectangular
$|\vec{a}| \neq |\vec{b}|, \phi = \frac{\pi}{2}$
$\{\frac{2\pi}{2}\}$
reflection

Centered rectangular
$|\vec{a}| \neq |\vec{b}|, \phi = \frac{\pi}{2}$
$\{\frac{2\pi}{2}\}$
inversion

3D lattice types   14 Bravais lattices

Class	Type & number	Angle	Length of primitive	
Cubic	P, F, I	$\alpha = \beta = \gamma = 90°$	$a = b = c$	isotropic
Tetragonal	P, I	$\alpha = \beta = \gamma = 90°$	$a = b \neq c$	Uniaxial crystal
Hexagonal	P	$\alpha = \beta = 90°, \gamma = 120°$	$a = b \neq c$	
Rhombohedral/ Trigonal	R	$\alpha = \beta = \gamma \neq 90° < 120°$	$a = b = c$	
Orthorhombic	P, F, I, C	$\alpha = \beta = \gamma = 90°$	$a \neq b \neq c$	Biaxial crystal
Monoclinic	P, C	$\alpha = \gamma = 90° \neq \beta$	$a \neq b \neq c$	
Triclinic	P	$\alpha \neq \beta \neq \gamma$	$a \neq b \neq c$	

Atoms per unit cell

(i) Eight corner atoms in cubic unit cell $\frac{1}{8}$th atom

(ii) Six face atoms in unit cell $\frac{1}{2}$th atom.

(iii) If on edge then shared between 4 unit, $\frac{1}{4}$th atom

(iv) If inside cell, then (off course) 1 atom as whole.

Simple cubic cell (sc)

$$\# \text{ of atoms / unit cell} = \frac{8}{8} = 1.$$

Body centered cubic cell (bcc)

$$\# \text{ of atoms / unit cell} = \frac{8}{8} + 1 = 2$$

Face centered cubic cell (fcc)

$$\# \text{ of atoms / unit cell} = \frac{8}{8} + \frac{6}{2} = 4$$

Coordination Number

In crystal lattice, the number of nearest neighbours of an atom is called coordination no.

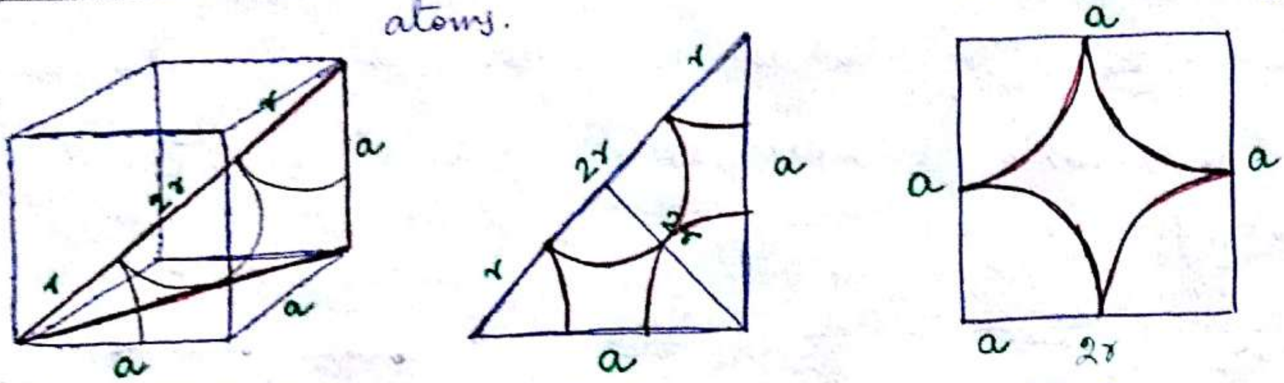
sc cell, coord. no. $= 6$.

bcc cell, coord. no. $= 8$

fcc cell, coord. no. $= 4 \times 3 = 12$

1 plane   ↳ XY, YZ, XZ plane

Atomic radius Distance between centre of two touching atoms.



[bcc] [fcc] [sc]

[bcc]: $(4r)^2 = (\sqrt{2}a)^2 + a^2$ or $r = \frac{\sqrt{3}}{4}a$

[fcc]: $(4r)^2 = 2a^2$ or $r = \frac{a}{2\sqrt{2}}$

[sc]: $2r = a$ or $r = \frac{a}{2}$

Atomic packing fraction/factor/relative packing density

$$P.F.(f) = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}.$$

[bcc] 2 atoms/unit cell, $r = \frac{\sqrt{3}}{4}a$

$\therefore$ vol. of atoms $= 2 \times \frac{4}{3}\pi r^3$, vol. of unit cell $= a^3$.

$$\therefore f = \frac{2 \times \frac{4}{3}\pi \times \left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 68\%.$$

Example: Barium, chromium, sodium, iron, caesium chloride

[fcc] 4 atoms/unit cell, $r = \frac{a}{2\sqrt{2}}$.

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

example: ~~barium~~, nickel, copper, aluminium, lithium, ~~chromium~~, ~~sodium~~, ~~iron~~,

[sc] 1 atom/unit cell, $r = \frac{a}{2}$

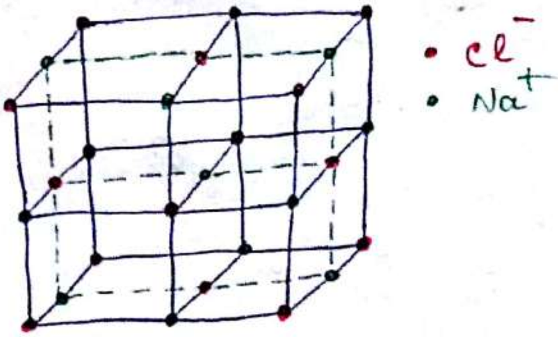
$$\therefore f = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 52\%$$

example: polonium, potassium chloride

HW 1. Primitive translation vector of hcp lattice is $\vec{a} = \frac{\sqrt{3}}{2}a\hat{i} + \frac{a}{2}\hat{j}$, $\vec{b} = -\frac{\sqrt{3}}{2}a\hat{i} + \frac{a}{2}\hat{j}$, $\vec{c} = c\hat{k}$. Compute the volume of the primitive cell.

2. Show that for a fcc crystal structure, lattice constant is $a = \left(\frac{4M}{\rho N}\right)^{1/3}$ where M is the gram molecular weight of molecules at lattice points, ρ is the density & N is Avogadro's number.

<u>NaCl structure</u>



ionic crystal Na^+ & Cl^-, fcc bravais lattice

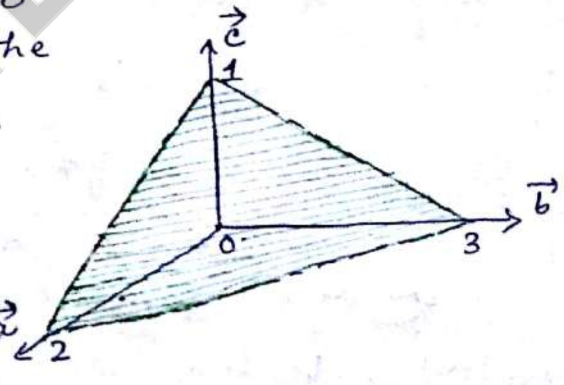
Na $(0,0,0)$ $(\frac{1}{2},\frac{1}{2},0)$ $(\frac{1}{2},0,\frac{1}{2})$ $(0,\frac{1}{2},\frac{1}{2})$.

Cl $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ $(0,0,\frac{1}{2})$ $(0,\frac{1}{2},0)$ $(\frac{1}{2},0,0)$

4 NaCl molecule in unit cube.

Na^+ $(0,0,0)$ & Cl^- $(\frac{a}{2},0,0)$ → 6 nearest neighbour (coordination number).

<u>Miller indices</u> To designate the position & orientation of a crystal plane according to following rule:



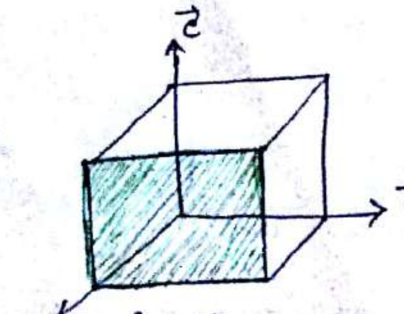
(a) In terms of lattice constant, find the intercept of the plane on crystal axes $\vec{a}, \vec{b}, \vec{c}$ (primitive or nonprimitive)

$(2,0,0)$, $(0,3,0)$, $(0,0,1)$ → $2a, 3b, c$.

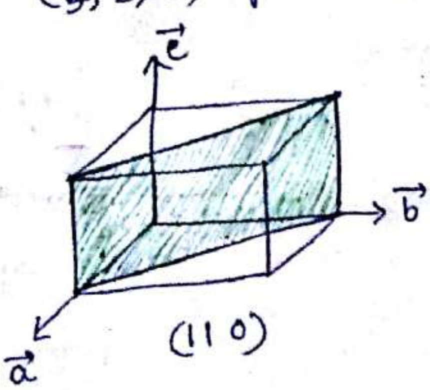
(b) Take reciprocals of them & reduce to smallest 3 integers, Denote with (h, k, l)

So $2a, 3b, c \xrightarrow[\text{reciproc}]{} \frac{1}{2}, \frac{1}{3}, 1 \xrightarrow[\text{smallest}]{} 3, 2, 6$.

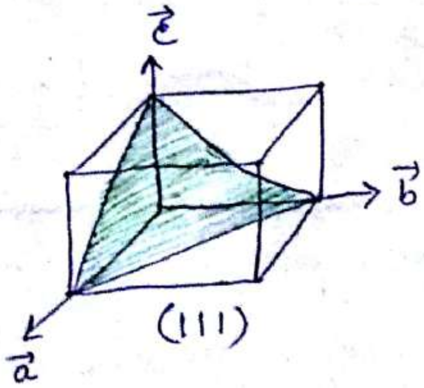
Miller index is $(3,2,6)$ plane.



(100)



(110)



(111)

If plane cuts negative side of axis (say $-\vec{b}$), M-index $(h, \bar{k}, l)$

6-faces of cubic crystal, M-index $(1,0,0), (0,1,0), (0,0,1)$, $(\bar{1},0,0), (0,\bar{1},0), (0,0,\bar{1}) \equiv \{1,0,0\}$

because through rotation, all faces are equivalent & written in $\{\ \}$

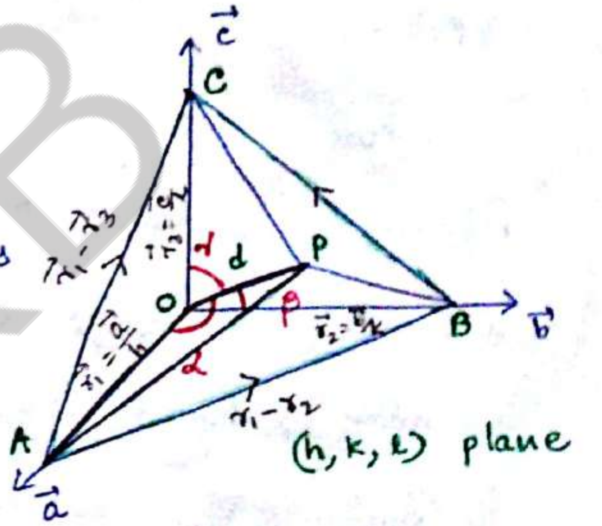
So $(2,0,0)$ plane (M-index) intercepts on $\vec{a}, \vec{b}, \vec{c}$ are $\frac{1}{2}a, \infty, \infty$. & parallel to $(1,0,0)$ & $(\bar{1},0,0)$ plane.

Indices of a direction $[h,k,l]$ & direction is perpendicular to plane (h,k,l). $\vec{a}$ axis $= [1,0,0]$, $-\vec{b}$ axis $= [0,\bar{1},0]$

body diagonal $= [1,1,1]$

(*)

<u>Spacing of planes in sc lattice</u>



simple unit cell $\vec{a} \perp \vec{b} \perp \vec{c}$ &

a plane (h,k,l) (miller index).

Intercepts a/h, b/k, c/l on $\vec{a}, \vec{b}, \vec{c}$ axes

$OP \perp (h,k,l)$ plane & $OP = d$.

& $\angle AOP = \alpha$, $\angle BOP = \beta$, $\angle COP = \gamma$.

& $\angle APO = \angle BPO = \angle CPO = 90^\circ$

$\frac{OP}{OA} = \cos\alpha$ or $OP = OA\cos\alpha$ or $d = \frac{a}{h}\cos\alpha$ or $\cos\alpha = \frac{dh}{a}$

Similarly $\cos\beta = \frac{dk}{b}$, $\cos\gamma = \frac{dl}{c}$.

Law of direction cosines, $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$.

$$\text{or } d^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right) = 1.$$

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

If cubic lattice, $a = b = c$, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

$$d_{100} = \frac{a}{\sqrt{1^2+0+0}} = a, \quad d_{110} = \frac{a}{\sqrt{1^2+1^2+0}} = \frac{a}{\sqrt{2}}, \quad d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$$

Spacing of planes in bcc lattice

One atom at each corner + one atom at cube centre.
(portion) (whole)

$\therefore d_{100} = \frac{a}{2}$ as additional (1,0,0) is there halfway between (100) plane of sc.

$d_{110} = d_{110}^{sc} = \frac{a}{\sqrt{2}}$. but $d_{111} = \frac{1}{2}\frac{a}{\sqrt{3}}$ as (1,1,1) plane lies midway of (111) plane of sc.

Spacing of planes in fcc lattice

one atom at each corner + one atom at each face.
(portion) (portion)

$\therefore d_{100} = \frac{a}{2}$ as additional (1,0,0) is there halfway between (1,0,0) plane of sc.

But $d_{110} = \frac{1}{2}\frac{a}{\sqrt{2}}$ as additional set of (110) is there halfway between (1,1,0) plane.

$d_{111} = \frac{a}{\sqrt{3}}$ as centre of all face plane without new plane.

(*) $\vec{r}_1 = \vec{a}/h$, $\vec{r}_2 = \vec{b}/k$, $\vec{r}_3 = \vec{c}/l$.

$h\vec{a} + k\vec{b} + l\vec{c}$ represents $[h, k, l]$

Now $(\vec{r}_1 - \vec{r}_2)\cdot(h\vec{a} + k\vec{b} + l\vec{c}) = (\frac{\vec{a}}{h} - \frac{\vec{b}}{k})\cdot(h\vec{a} + k\vec{b} + l\vec{c})$

$= \vec{a}\cdot\vec{a} - \vec{b}\cdot\vec{b} = 0$. (as $|a| = |b|$)

Similarly $(\vec{r}_1 - \vec{r}_3)\cdot(h\vec{a} + k\vec{b} + l\vec{c}) = 0$ (as $|a| = |c|$)

As vectors $\vec{r}_1 - \vec{r}_2$ & $\vec{r}_1 - \vec{r}_3$ lie in (h,k,l) plane, so $[h,k,l]$ is perpendicular to plane (h,k,l).

Reciprocal lattice To represent slope & interplanar spacing of crystal plane, each set of parallel plane in a space lattice is represented by normals of planes with length = $\frac{1}{\text{interplanar spacing}}$

points marked at ends.

points form regular arrangement → reciprocal lattice

for $\vec{a}, \vec{b}, \vec{c}$, we describe reciprocal basis vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$ (primitive) such that

$$\vec{a}\cdot\vec{a}^* = 2\pi, \quad \vec{b}\cdot\vec{a}^* = 0, \quad \vec{c}\cdot\vec{a}^* = 0$$
$$\vec{a}\cdot\vec{b}^* = 0, \quad \vec{b}\cdot\vec{b}^* = 2\pi, \quad \vec{c}\cdot\vec{b}^* = 0$$
$$\vec{a}\cdot\vec{c}^* = 0, \quad \vec{b}\cdot\vec{c}^* = 0, \quad \vec{c}\cdot\vec{c}^* = 2\pi.$$

$$\vec{a}^* = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}\cdot\vec{b}\times\vec{c}}, \quad \vec{b}^* = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{a}\cdot\vec{b}\times\vec{c}}, \quad \vec{c}^* = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{a}\cdot\vec{b}\times\vec{c}}$$

reciprocal lattice vector $\vec{r}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

property (i) reciprocal lattice is normal to lattice plane of direct crystal lattice.

$$\vec{r}^*\cdot(\vec{r}_1 - \vec{r}_2) = (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)\cdot\left(\frac{\vec{a}}{h} - \frac{\vec{b}}{k}\right) = 0.$$

Similarly $\vec{r}^*\cdot(\vec{r}_1 - \vec{r}_3) = 0$.

(ii) direct lattice is reciprocal of reciprocal lattice.

sc = self - reciprocal.

bcc ↔ fcc reciprocal of each other.

Definition of R.L. $\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$ direct lattice vector & say $\vec{K}$ constitutes a plane wave $e^{i\vec{K}\cdot\vec{r}}$ which may not have the periodicity of Bravais lattice but $\vec{K}$ has that periodicity.

$$e^{i\vec{K}\cdot(\vec{r}+\vec{T})} = e^{i\vec{K}\cdot r} \quad \text{or} \quad e^{i\vec{K}\cdot\vec{T}} = 1$$

$$\vec{K} = k_1\vec{a}^* + k_2\vec{b}^* + k_3\vec{c}^*$$

$$\therefore \vec{K}\cdot\vec{T} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3)$$

If $e^{i\vec{K}\cdot\vec{T}} = 1$, then $\vec{K}\cdot\vec{T}$ must be $2\pi\times$ integer ⇒ k_1, k_2, k_3 integers

So from $\vec{K}$ only $\vec{K}$ which is linear combination of $\vec{a}^*, \vec{b}^*, \vec{c}^*$ with integral coefficient makes $\vec{K}$ a reciprocal lattice vector.

Reciprocal of reciprocal lattice

As by construction, reciprocal lattice is a "Bravais lattice", reciprocal gives back the direct lattice.

HW Define $\vec{a}^{**} = 2\pi \dfrac{\vec{b}^* \times \vec{c}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$,

$\vec{b}^{**} = 2\pi \dfrac{\vec{c}^* \times \vec{a}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$, $\vec{c}^{**} = 2\pi \dfrac{\vec{a}^* \times \vec{b}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$ as three vectors generated by primitive vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$. Check first, $\vec{a}^* \cdot \vec{b}^* \times \vec{c}^* = \dfrac{(2\pi)^3}{\vec{a} \cdot \vec{b} \times \vec{c}}$ & then show that $\vec{a}^{**} = \vec{a}$, $\vec{b}^{**} = \vec{b}$, $\vec{c}^{**} = \vec{c}$.

Reciprocal of sc lattice $\quad \vec{a} = a\hat{i}$, $\vec{b} = b\hat{j}$, $c = c\hat{k}$.

$$\therefore \vec{a}^* = 2\pi \frac{b\hat{j} \times c\hat{k}}{a\hat{i} \cdot (b\hat{j} \times c\hat{k})} = 2\pi \frac{bc}{abc}\hat{i} = \frac{2\pi}{a}\hat{i}$$

$$\vec{b}^* = 2\pi \frac{c\hat{k} \times a\hat{i}}{a\hat{i} \cdot (b\hat{j} \times c\hat{k})} = \frac{2\pi}{b}\hat{j} = \frac{2\pi}{a}\hat{j} \qquad (a = b = c)$$

$$\vec{c}^* = 2\pi \frac{a\hat{i} \times b\hat{j}}{a\hat{i} \cdot (b\hat{j} \times c\hat{k})} = \frac{2\pi}{c}\hat{k} = \frac{2\pi}{a}\hat{k}.$$

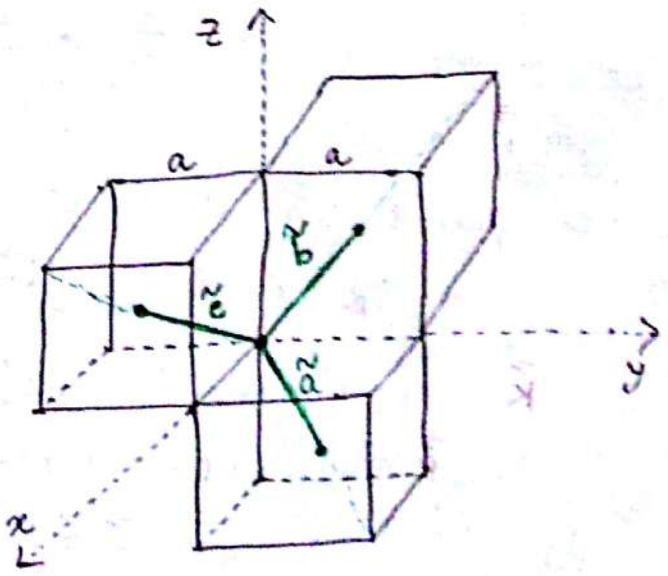
lattice constant $= 2\pi/a$.

Reciprocal of bcc lattice

$$\vec{\tilde{a}} = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k})$$

$$\vec{\tilde{b}} = \frac{a}{2}(-\hat{i} + \hat{j} + \hat{k})$$

$$\vec{\tilde{c}} = \frac{a}{2}(\hat{i} - \hat{j} + \hat{k})$$



volume of primitive cell $= \vec{a} \cdot \vec{b} \times \vec{c} = a^3/2$.

$\therefore \quad \vec{a}^* = 2\pi \dfrac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}} = \dfrac{2\pi}{a}(\hat{i} + \hat{j}),$

$\vec{b}^* = 2\pi \dfrac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}} = \dfrac{2\pi}{a}(\hat{j} + \hat{k})$.

$\vec{c}^* = 2\pi \dfrac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}} = \dfrac{2\pi}{a}(\hat{i} + \hat{k})$.

<u>Reciprocal</u> <u>of fcc lattice</u> $\quad \vec{a} = \dfrac{a}{2}(\hat{i} + \hat{j}), \quad \vec{b} = \dfrac{a}{2}(\hat{j} + \hat{k})$

$\vec{c} = \dfrac{a}{2}(\hat{i} + \hat{k})$

volume of primitive cell $= \vec{a} \cdot \vec{b} \times \vec{c} = a^3/4$.

and $\quad a^* = \dfrac{2\pi}{a}(\hat{i} + \hat{j} - \hat{k}), \quad b^* = \dfrac{2\pi}{a}(-\hat{i} + \hat{j} + \hat{k}), \quad c^* = \dfrac{2\pi}{a}(\hat{i} - \hat{j} + \hat{k})$

$\therefore$ Reciprocal bcc lattice vectors = primitive fcc lattice vectors
Reciprocal fcc lattice vectors = primitive bcc lattice vectors

Crystal diffraction

Why use X-ray for crystollagraphy ?

Atomic spacing (say for NaCl) is 2.8 Å. When X-ray is produced by accelarating electrons through a potential difference V,

$$eV = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{eV} = \frac{6.62\times10^{-34}\times3\times10^{8}}{1.6\times10^{-19}\times10^{4}} \quad (\text{say } V = 10\,kV)$$

$$= 1.24\ \text{Å}.$$

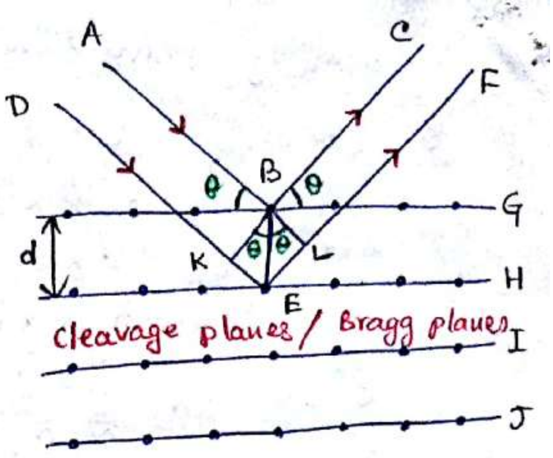
$\lambda_{X\text{-ray}} \approx a$ (elastic scattering without change in λ)

$\lambda_{visible/UV} >> a$ (reflection or refraction)

$\lambda_{\gamma\text{-ray}} << a$ (small angle diffraction)

Bragg's law for crystal diffraction

Maximum intensity from reflected beam (waves) from two different atomic planes (cleavage planes) with path difference equal to integral multiple of $\lambda_{x\text{-ray}}$.



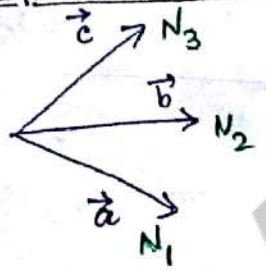
Path difference between ray $[AB, BC]$ & $[DE, EF]$ is $KE + EL$

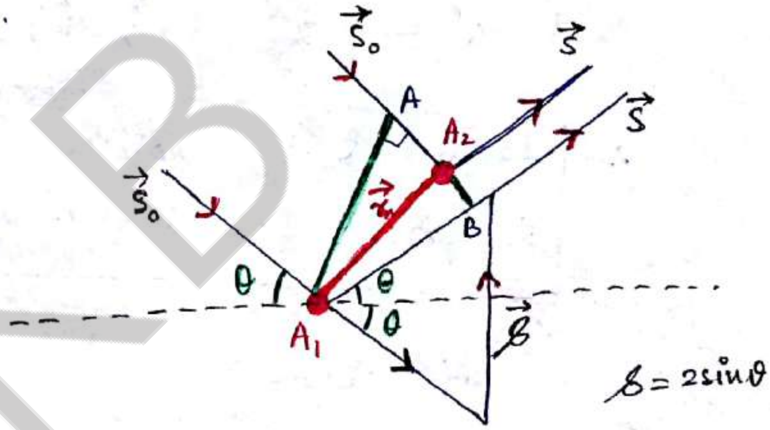
$= d\sin\theta + d\sin\theta = 2d\sin\theta$. So for constructive interference,

$\boxed{2d\sin\theta = n\lambda}$, $n = 1, 2, 3 \ldots \Rightarrow$ "Bragg's law."

$\lambda, \theta =$ Known, $d =$ unknown.

Laue's equation of XRD





Assumptions: (a) The primary X-ray beam travels within the crystal at the speed of light. (b) Each scattered wavelet travels through the crystal without getting rescattered.

Say N_1 number of points along direction $\vec{a}$

N_2 number of points along direction $\vec{b}$

N_3 number of points along direction $\vec{c}$

Total $N = N_1 N_2 N_3$ points in the crystal lattice.

Path difference between two x-rays is $d = \vec{r}_n \cdot \vec{S} - \vec{r}_n \cdot \vec{S}_0 = \vec{r}_n \cdot \vec{\delta}$

$\therefore$ Phase difference is $\frac{2\pi}{\lambda} d = \frac{2\pi}{\lambda} \vec{r}_n \cdot \vec{\delta} = k\, \vec{r}_n \cdot \vec{\delta}$

remember: $\vec{S}, \vec{S}_0$ unit vector, $|\vec{\delta}| = \delta = 2\sin\theta$, $\vec{r}_n = n^{th}$ lattice point from origin $= \vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$.

If y is the displacement of the scattered wave from origin at a distance R at time t with amplitude A_0, then

$$y_0 = \frac{A_0}{R} e^{i\omega t}$$ ∴ displacement from $\vec{r}_n$ is

$$y = \frac{A_0}{R} e^{i\omega t} e^{iK\vec{r}_n \cdot \vec{s}}$$

∴ Total displacement due to the whole Bravais lattice is

$$Y = \sum_{\text{all points}} \frac{A_0}{R} e^{i\omega t} e^{iK\vec{r}_n\cdot\vec{s}}$$

$$= \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} e^{iK[(n_1\vec{a}+n_2\vec{b}+n_3\vec{c})\cdot\vec{s}]} \frac{A_0}{R} e^{i\omega t}$$

$$= \frac{A_0}{R} e^{i\omega t} \sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}} \sum_{n_2=0}^{N_2-1} e^{iKn_2\vec{b}\cdot\vec{s}} \sum_{n_3=0}^{N_3-1} e^{iKn_3\vec{c}\cdot\vec{s}}$$

Now $$\sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}} = 1 + e^{iK\vec{a}\cdot\vec{s}} + e^{i2K\vec{a}\cdot\vec{s}} + \cdots + e^{i(N_1-1)K\vec{a}\cdot\vec{s}}$$

$$= \frac{1-e^{iN_1(\vec{a}\cdot\vec{s})K}}{1-e^{i(\vec{a}\cdot\vec{s})K}}$$

$$\therefore \left(\sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}}\right)\left(\sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}}\right)^*$$

$$= \frac{1-e^{iN_1(\vec{a}\cdot\vec{s})K}}{1-e^{i(\vec{a}\cdot\vec{s})K}} \times \frac{1-e^{-iN_1(\vec{a}\cdot\vec{s})K}}{1-e^{-i(\vec{a}\cdot\vec{s})K}}$$

$$= \frac{1-\cos\{N_1(\vec{a}\cdot\vec{s})K\} + i\sin\{N_1(\vec{a}\cdot\vec{s})K\}}{1-\cos\{(a\cdot\vec{s})K\} - i\sin\{(a\cdot\vec{s})K\}} \times \frac{1-\cos\{N_1(\vec{a}\cdot\vec{s})K\} + i\sin\{N_1(\vec{a}\cdot\vec{s})K\}}{1-\cos\{(\vec{a}\cdot\vec{s})K\} + i\sin\{(\vec{a}\cdot\vec{s})K\}}$$

$$= \frac{(1-\cos\{N_1(\vec{a}\cdot\vec{s})K\})^2 + (\sin\{N_1(\vec{a}\cdot\vec{s})K\})^2}{(1-\cos\{(\vec{a}\cdot\vec{s})K\})^2 + (\sin\{(\vec{a}\cdot\vec{s})K\})^2}$$

$$= \frac{1-\cos\{N_1(\vec{a}\cdot\vec{s})K\}}{1-\cos\{(\vec{a}\cdot\vec{s})K\}} = \frac{\sin^2\{\frac{N_1(\vec{a}\cdot\vec{s})K}{2}\}}{\sin^2\{\frac{(\vec{a}\cdot\vec{s})K}{2}\}} = \frac{\sin^2(N_1\psi_1)}{\sin^2(\psi_1)}$$

where $\psi_1 = \frac{1}{2} K \vec{a} \cdot \vec{s}$.

$\therefore$ Total intensity $I = YY^* = \left(\frac{|A_0|}{R}\right)^2 \frac{\sin^2(N_1\psi_1)}{\sin^2\psi_1} \frac{\sin^2(N_2\psi_2)}{\sin^2\psi_2} \frac{\sin^2(N_3\psi_3)}{\sin^2\psi_3}$

$$\psi_1 = \frac{1}{2} K \vec{a} \cdot \vec{s} = \frac{1}{2} K |\vec{a}| |\vec{s}| \cos\alpha = \frac{1}{2} \frac{2\pi}{\lambda} a \, 2\sin\theta \cos\alpha = \frac{2\pi a \sin\theta \cos\alpha}{\lambda}$$

Similarly $\psi_2 = \frac{1}{2} K \vec{b} \cdot \vec{s} = \frac{2\pi b \sin\theta \cos\beta}{\lambda}$,

$\psi_3 = \frac{1}{2} K \vec{c} \cdot \vec{s} = \frac{2\pi c \sin\theta \cos\gamma}{\lambda}$

[Notice the analogy of $\vec{s}$ with $[h, k, l]$ plane with angles α, γ, β]

In $\lim_{\psi_1 \to h\pi}$, $\frac{\sin^2(N_1\psi_1)}{\sin^2\psi_1}$ is maximum $= N_1^2$

Similarly $\lim_{\psi_2 \to k\pi} \frac{\sin^2(N_2\psi_2)}{\sin^2\psi_1} = N_2^2$, $\lim_{\psi_3 \to l\pi} \frac{\sin^2(N_3\psi_3)}{\sin^2\psi_3} = N_3^2$

Then $I_{max} = \left(\frac{|A_0|}{R}\right)^2 N_1^2 N_2^2 N_3^2 = \frac{|A_0|^2}{R^2} N^2$

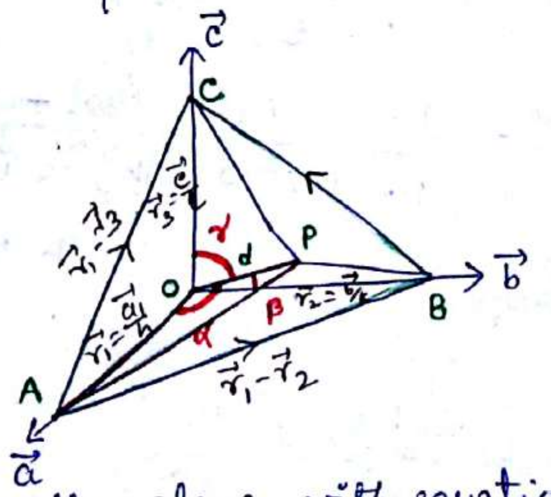
$\therefore$ $\frac{2\pi a \sin\theta \cos\alpha}{\lambda} = h\pi$, $\quad \boxed{2a \sin\theta \cos\alpha = h\lambda}$

$\frac{2\pi b \sin\theta \cos\beta}{\lambda} = k\pi$, $\quad \boxed{2b \sin\theta \cos\beta = k\lambda}$

$\frac{2\pi c \sin\theta \cos\gamma}{\lambda} = l\pi$, $\quad \boxed{2c \sin\theta \cos\gamma = l\lambda}$

"Laue equations".

<u>Bragg's law from Laue equations</u>



From Laue equation, direction cosines of $\vec{s}$ are

$\cos\alpha = \frac{h\lambda}{2a\sin\theta}$, $\cos\beta = \frac{k\lambda}{2b\sin\theta}$,

$\cos\gamma = \frac{l\lambda}{2c\sin\theta}$.

But also see that if (h, k, l) is a miller plane with equation

$\frac{x}{a/h} + \frac{y}{b/k} + \frac{z}{c/l} = 1$ then $\frac{a}{h}\cos\alpha = \frac{b}{k}\cos\beta = \frac{c}{k}\cos\gamma = d$.

$\therefore$ The direction cosines of $\vec{s}$ are also proportional to $h/a, k/b, l/c$, so the X-ray is diffracted from $\vec{s}_0$ to $\vec{s}$ by the miller plane (h, k, l).

$$\therefore d = \frac{a}{h}\cos\alpha = \frac{a}{h}\frac{h\lambda}{2a\sin\theta} = \frac{\lambda}{2\sin\theta}$$

$$= \frac{b}{k}\cos\beta = \frac{b}{k}\frac{k\lambda}{2b\sin\theta} = \frac{\lambda}{2\sin\theta}$$

$$= \frac{c}{l}\cos\gamma = \frac{c}{l}\frac{l\lambda}{2c\sin\theta} = \frac{\lambda}{2\sin\theta}.$$

Note that h, k, l of Laue equation aren't necessarily identical with Miller indices but may contain a common factor n.

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

with d = adjacent interplanar spacing with Miller indices $\frac{h}{n}, \frac{k}{n}$ & $\frac{l}{n}$.

Interpretation of Laue's equation in reciprocal lattice

Reciprocal lattice vector $\vec{r}^* = \vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

magnitude = reciprocal of spacing of (h, k, l) planes of direct lattice.

direction = perpendicular to (h, k, l) plane.

$$\left.\begin{aligned} \vec{G}\cdot\vec{a} &= \vec{r}^*\cdot\vec{a} = 2\pi h \\ \vec{G}\cdot\vec{b} &= \vec{r}^*\cdot\vec{b} = 2\pi k \\ \vec{G}\cdot\vec{c} &= \vec{r}^*\cdot\vec{c} = 2\pi l \end{aligned}\right\}$$

From Laue equation, $\psi_1 = \frac{1}{2}k\,\vec{a}\cdot\vec{s} = h\pi$ or $\frac{1}{\cancel{2}}\frac{2\cancel{\pi}}{\lambda}\vec{s}\cdot\vec{a} = h\cancel{\pi}$

$$\text{or } \frac{2\pi\vec{s}}{\lambda}\cdot\vec{a} = 2\pi h.$$

Similarly from ψ_2 & ψ_3, $\frac{2\pi\vec{s}}{\lambda}\cdot\vec{b} = 2\pi k$, $\frac{2\pi\vec{s}}{\lambda}\cdot\vec{c} = 2\pi l$.

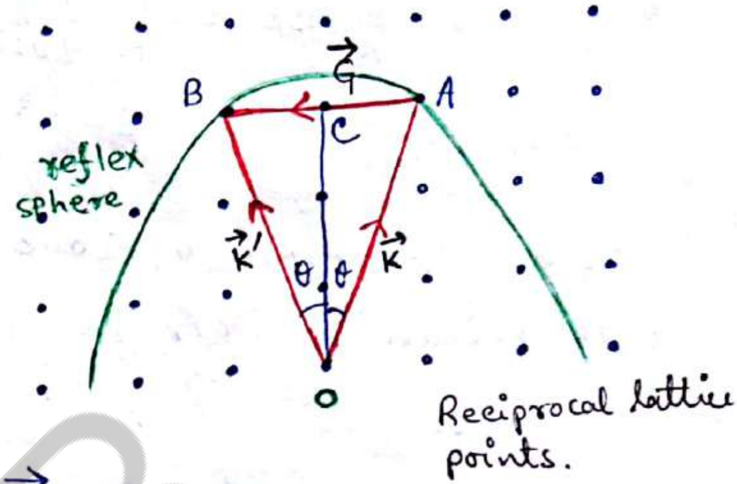
Comparing, $\boxed{\vec{r}^* = \vec{G} = \frac{2\pi\vec{s}}{\lambda}}$

Ewald's construction

Geometrical construction to obtain a relation between wave vector $\vec{K}$ & the direction of incident X-ray using the reciprocal lattice & deducing Bragg's law in vectorial form.

$\vec{K} = \frac{2\pi}{\lambda}$ (magnitude), direction along X-ray beam from O & terminating at point A.

From O with radius $K = \frac{2\pi}{\lambda}$, draw a sphere (reflex sphere).



Suppose it intersects B, then $\vec{AB}$ represents reciprocal vector $\vec{G}$ & $G \perp OC$ (direct lattice plane)

$$G = \frac{2\pi n}{d}.$$

$\vec{K}'$ = diffracted (reflected) wave vector, with $|\vec{K}| = |\vec{K}'|$

So magnitude is same, only direction changes.

$$\vec{K}' = \vec{K} + \vec{G}$$

$$\cancel{|\vec{K}'|^2} = (\vec{K} + \vec{G}) \cdot (\vec{K} + \vec{G}) = \cancel{|\vec{K}|^2} + 2\vec{K} \cdot \vec{G} + \vec{G} \cdot \vec{G}$$

$$\therefore \left(\vec{K} + \frac{\vec{G}}{2}\right) \cdot \vec{G} = 0 \Rightarrow \text{Bragg's law (vectorial form) in reciprocal lattice.}$$

Notice that $AC = OA \sin\theta = CB$.

$$\therefore AB = 2 OA \sin\theta = 2K \sin\theta = 2\frac{2\pi}{\lambda}\sin\theta$$

$$\text{or } G = \frac{4\pi}{\lambda}\sin\theta. \quad \text{or } \frac{2\pi n}{d} = \frac{4\pi}{\lambda}\sin\theta$$

$$\text{or } 2d\sin\theta = n\lambda$$

CW 1. Calculate wavelength & speed of neutron beam, where spacing between successive (100) planes is 3.84 Å, grazing angle is 30° & order of Bragg reflection = 1.

Bragg's law $2d\sin\theta = n\lambda$,

$d = 3.84\times10^{-10}$ m, $\theta = 30°$, $n=1$ $\quad\therefore\ 2\times3.84\times10^{-10}\times\frac{1}{2} = \lambda$

$\therefore\ \lambda = 3.84$ Å.

Using de-Broglie relation $\lambda = \frac{h}{p} = \frac{h}{mv}$

$$v = \frac{h}{m\lambda} = \frac{6.62\times10^{-34}\ \text{Js}}{1.67\times10^{-27}\ \text{Kg}\times3.84\times10^{-10}\ \text{m}} = 1.03\times10^{3}\ \text{m/s}$$

$= 1.03$ Km/s.

2. X-ray of wavelength 1.24 Å is reflected by cubic crystal KCl. Calculate the interplanar distance for (100), (110) & (111) planes. Given density of KCl = 1.98×10^{3} kg/m³, molecular weight 74.5 kg. Avogadro's no. $N = 6.023\times10^{26}$ kg/mole.

for cubic crystal, $a = \left(\frac{nM}{\rho N}\right)^{1/3}$.

for KCl, $n=4$, $a = \left(\frac{4\times74.5}{1.98\times10^{3}\times6.023\times10^{26}}\right)^{1/3} = 6.3\times10^{-10}$ m $= 6.3$ Å

$\therefore\ d_{100} = \frac{1}{2}\frac{a}{\sqrt{1^2+0^2+0^2}} = \frac{6.3\text{ Å}}{2}$, $\quad d_{110} = \frac{1}{2}\frac{a}{\sqrt{1^2+1^2+0^2}} = \frac{1}{2}\frac{a}{\sqrt{2}} = \frac{4.45\text{ Å}}{2}$.

$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}} = 3.63$ Å.

(remember KCl is fcc).

3.(a) Calculate the Bragg angle for X-rays with $\lambda = 1.54$ Å in different orders 1, 2, 3 if interplanar spacing is 2.67 Å. (b) If Brags glancing angle is 15° for 1st order, then calculate glancing angles for 2nd & 3rd order spectrum?

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

$\lambda = 1.54\times10^{-10}$ m, $d = 2.67\times10^{-10}$ m.

$n=1$ (1^{st} order) $\quad 2d\sin\theta_1 = \lambda$

$$\theta_1 = \sin^{-1}\left[\frac{\lambda}{2d}\right] = \sin^{-1}\left[\frac{1.54\times10^{-10}}{2\times2.69\times10^{-10}}\right] = 16.46^\circ.$$

$n=2$ (2^{nd} order) $\quad \theta_2 = \sin^{-1}\left[\frac{2\lambda}{2d}\right] = 35.22^\circ.$

$n=3$ (3^{rd} order) $\quad \theta_3 = \sin^{-1}\left[\frac{3\lambda}{2d}\right] = 59.9^\circ.$

(b) $\quad 2d\sin\theta_1 = \lambda$, $\theta_1 = 15^\circ$ $\quad \therefore$ ~~$\lambda = 1$~~ $\frac{\lambda}{2d} = \sin 15^\circ = 0.2588$

So for 2^{nd} order. $\quad \sin\theta_2 = 2\frac{\lambda}{2d} = 2\times0.2588 = 0.5176$

$\theta_2 = 31.17^\circ$

for 3^{rd} order, $\quad \sin\theta_3 = 3\frac{\lambda}{2d} = 3\times0.2588 = 0.7764$

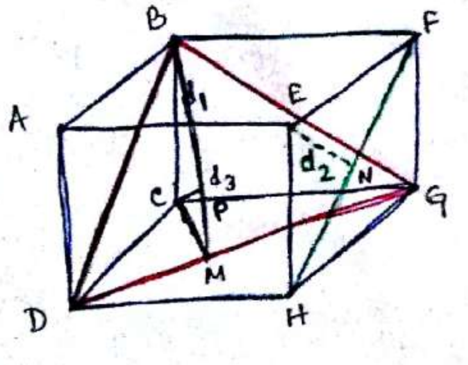
$\theta_3 = 50.93^\circ.$

HW 1. Molecular weight of rock salt (NaCl) crystal is 58.5 Kg/Kilomole & density 2.16×10^3 Kg/m^3. Calculate grating spacing d_{100} of rock salt. Using that, calculate λ of X-rays in 2^{nd} order if angle of diffraction is 26°.

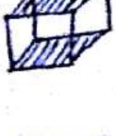
2. If X-rays with $\lambda = 0.5$ Å is diffracted at 5° in 1^{st} order, what is the spacing between adjacent planes of a crystal? At ~~and~~ what angle will 2^{nd} maximum occur?

3. Bragg angle for 1^{st} order reflection from (111) plane of a crystal is 60°, when $\lambda = 1.8$ Å. Calculate interatomic spacing.

Determination of crystal structure



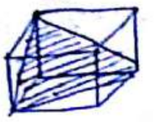
d is to be calculated for given X-ray (λ) by using different plane.



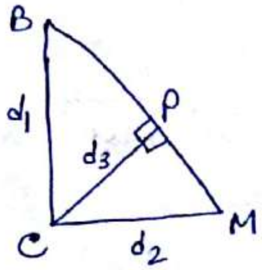
ABFE & CGHD.
d_1 distance apart. → Total 6 faces
(100) plane.

Diagonal plane BFHD inclined at $\pi/4$ to (100) planes

d_2 is interplanar spacing $\frac{d_2}{d_1} = \sin 45^\circ = \frac{1}{\sqrt{2}}$ $\therefore d_2 = \frac{d_1}{\sqrt{2}}$.
(110) plane.



BGD plane. Here $CM \perp DG$ & BM joined to obtain right-angle triangle BCM. $CM = d_2$



$BM = \sqrt{d_1^2 + d_2^2}$ $CP = d_3$,

$$\sin B = \frac{d_3}{d_1} = \frac{d_2}{\sqrt{d_1^2 + d_2^2}}$$

$$\therefore d_3 = \frac{d_1 d_2}{\sqrt{d_1 + d_2^2}} = \frac{d_1}{\sqrt{3}} \quad (\text{substitute } d_2 = \tfrac{d_1}{\sqrt{2}})$$

These are (111) planes.

$$\therefore \frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = 1 : \sqrt{2} : \sqrt{3}$$

Bragg found for KCl crystal for 1^{st} order reflection

θ_1 (from (100) plane) $= 5.22^\circ$ θ_3 (from (111) plane) $= 9.05^\circ$.

θ_2 (from (110) plane) $= 7.30^\circ$

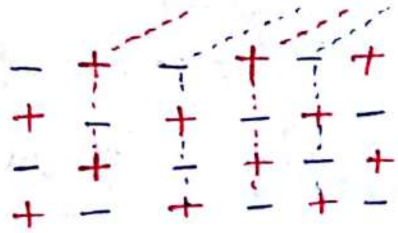
as $\frac{1}{d} = \frac{2\sin\theta}{\lambda}$ $\therefore \frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = \sin 5.22 : \sin 7.30 : \sin 9.05$

$= 0.0910 : 0.1272 : 0.1570$

$= 1 : 1.40 : 1.73 = 1 : \sqrt{2} : \sqrt{3}$.

So KCl has cubic crystal symmetry.

NaCl crystal



8 ions at corner $\rightarrow$ 4 Na^+, 4 Cl^-

$\therefore$ Each ion of NaCl is shared between two adjacent cube & unit cell contain half a molecule of NaCl.

$$\text{mass of unit cell} = \frac{M}{2N} = \frac{23 + 35.5}{2 \times 6.023 \times 10^{26}} \text{ kg}.$$

density of NaCl $= 2.17 \times 10^3$ kg/m^3.

$$\therefore \text{volume } d^3 = \frac{58.5}{2 \times 6.023 \times 10^{26} \times 2.17 \times 10^3} \qquad \therefore d = 2.814 \text{ Å}.$$

Now verify Bragg's law for different order of diffraction.

1^{st} order, $n=1$, $\theta = 11.8^\circ$, $\lambda = 2d\sin\theta = 2\times 2.814\times10^{-10}\times \sin 11.8^\circ$
$= 1.12\,\text{Å}$.

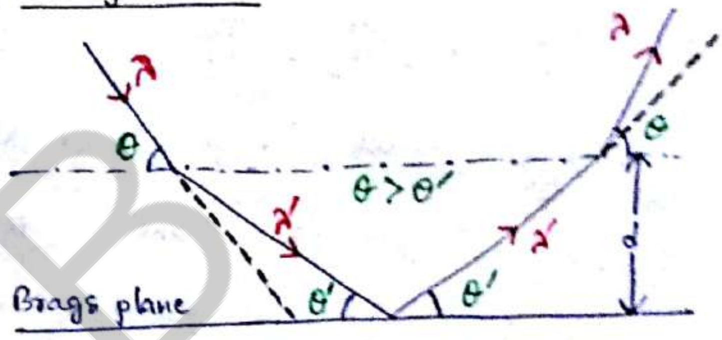
2^{nd} order, $n=2$, $\theta = 23.5^\circ$, $\lambda = \dfrac{2d\sin\theta}{2} = 2.814\times10^{-10}\times\sin 23.5^\circ$
$= 1.12\,\text{Å}$.

3^{rd} order, $n=3$, $\theta = 36^\circ$, $\lambda = \dfrac{2d\sin\theta}{3} = \frac{2}{3}\times 2.814\times10^{-10}\times\sin 36^\circ$
$= 1.12\,\text{Å}$.

$\therefore$ Diffraction from NaCl crystal verifies Bragg's law.

Modification of Bragg's law due to refraction

Refraction of X-rays due to change in wavelength & angle of incidence because of the refractive index of the crystal.



Bragg's equation $n\lambda' = 2d\sin\theta'$

Using Snell's law, the refractive index is $\mu = \dfrac{\lambda}{\lambda'} = \dfrac{\cos\theta}{\cos\theta'}$

$$\therefore\ n\frac{\lambda}{\mu} = 2d\sqrt{1-\frac{\cos^2\theta}{\mu^2}}$$

$$\text{or } n\lambda = 2d\sqrt{\mu^2-\cos^2\theta} = 2d\sqrt{\sin^2\theta-(1-\mu^2)} = 2d\sin\theta\sqrt{1-\frac{1-\mu^2}{\sin^2\theta}}$$

$$\simeq 2d\sin\theta\left(1-\frac{1-\mu^2}{2\sin^2\theta}\right)$$

$$\simeq 2d\sin\theta\left(1-\frac{2(1-\mu)}{2\sin^2\theta}\right)$$

$$\simeq 2d\sin\theta\left(1-(1-\mu)\frac{4d^2}{n^2\lambda^2}\right)$$

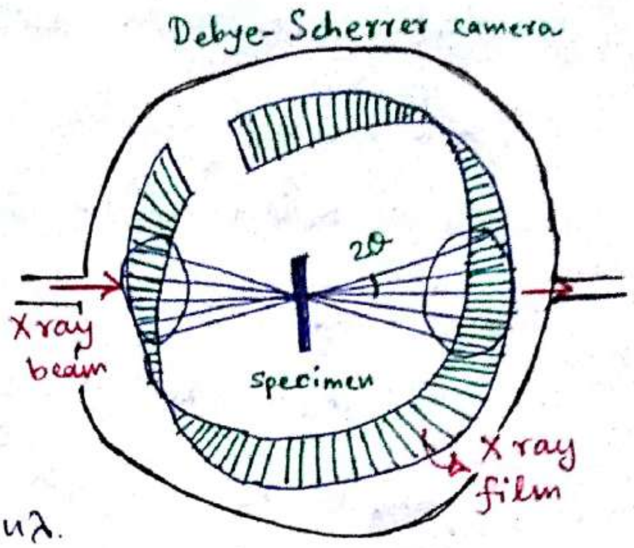
$\left[1-\mu^2 = (1+\mu)(1-\mu) \simeq 2(1-\mu) \text{ as } \mu \simeq 1\right]$

$\left[2d\sin\theta = n\lambda \text{ or } \dfrac{1}{\sin^2\theta} = \dfrac{4d^2}{n^2\lambda^2}\right]$

$$\boxed{n\lambda = 2d\sin\theta\left[1-\frac{4d^2(1-\mu)}{n^2\lambda^2}\right]}$$

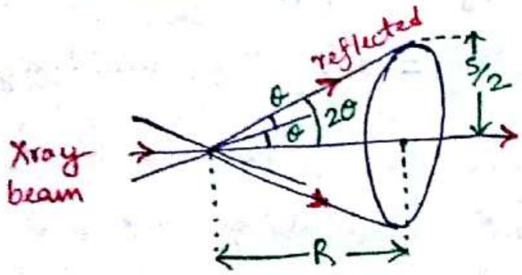
~~Largest~~ The correction term $\dfrac{4d^2(1-\mu)}{n^2\lambda^2}$ is small & becomes more small as "n" increases.

Powder Method of XRD



$2d\sin\theta = n\lambda$, d & θ varies for fixed λ. Powdered specimen is kept in a thin capillary tube on a movable mount at the centre of a cylindrical camera.

For arbitrary orientation, some plane satisfy Bragg reflection $2d\sin\theta = n\lambda$. They lie on a conical section with semi-vertical angle 2θ. Other cones arise due to other set of planes. Cones intersect X-ray film in concentric rings with sharp centre. Specimen is rotated to ensure all possible planes to face the X-rays.



S = distance between diffracted lines

R = radius of the film

$\frac{S}{2R} = 2\theta$ or $\theta = \frac{S}{4R}$ & $\sin\theta \simeq \theta$

so that $2d\sin\theta = \lambda$ (for $n=1$)

$\simeq 2d\theta = \lambda$

or $2d\,\frac{S}{4R} = \lambda. \Rightarrow d = \frac{2R\lambda}{S}$.

From known (measured) R, S, λ, interplanar spacing d is calculated.

Brillouin Zones

We have learned that all k values for which the reciprocal lattice points intersect the Ewald sphere are Bragg reflected. Brillouin zone is the locus of all these k values in the reciprocal lattice which are Bragg reflected.

Brillouin zones for sc lattice in 2D

Primitive translation vectors $\vec{a} = a\hat{i}$, $\vec{b} = a\hat{j}$, $\vec{c} = \hat{k}$ &

corresponding translation vector in reciprocal lattice $\vec{a}^* = \frac{2\pi}{a}\hat{i}$, $\vec{b}^* = \frac{2\pi}{a}\hat{j}$

so that reciprocal lattice vector $\vec{G} = h\vec{a}^* + k\vec{b}^*$
$= \frac{2\pi}{a}(h\hat{i} + k\hat{j})$.

(h, k are integers)

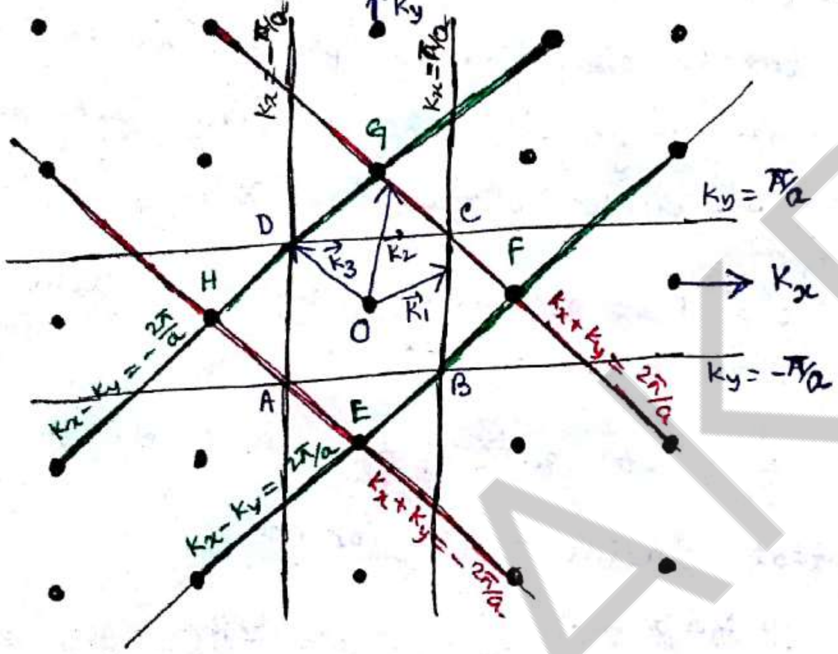
$\vec{k} = k_x\hat{i} + k_y\hat{j}$ $\therefore$ from Bragg's vectorial condition

$2\vec{k}\cdot\vec{G} + G^2 = 0$

or $\frac{4\pi}{a}(hk_x + kk_y) + \frac{4\pi^2}{a^2}(h^2 + k^2) = 0$

or $\boxed{hk_x + kk_y = -\frac{\pi}{a}(h^2 + k^2)}$

For all h, k values, we can obtain k.



If $h = \pm 1, k = 0$ then $k_x = \pm\frac{\pi}{a}$ (k_y arbitrary)

If $h = 0, k = \pm 1$, then $k_y = \pm\frac{\pi}{a}$ (k_x arbitrary)

All $\vec{k}$ (for example $\vec{k}_1, \vec{k}_2$ or $\vec{k}_3$) originating from O & terminating on these parallel lines are Bragg reflected.

If $h = \pm 1, k = \pm 1$ then $\pm k_x \pm k_y = \frac{2\pi}{a}$.

Region enclosed by such lines are the Brillouin zones.
ABCD is the first Brillouin zone & EFGH is the second Brillouin zone.

Brillouin zone boundary represent loci of $\vec{k}$ that obey Bragg's law, meaning they're the reflecting planes. ABCD $\Rightarrow 2d\sin\theta = \lambda$.
EFGH $\Rightarrow 2d\sin\theta = 2\lambda$ & so on.

In 3D, $\boxed{hk_x + kk_y + lk_z = -\frac{\pi}{a}(h^2 + k^2 + l^2)}$

with cubes represent Brillouin zone.

Brillouin zones of the fcc lattice

primitive translation vectors of fcc lattice are

$\vec{a} = \frac{a}{2}(\hat{i}+\hat{j})$, $\vec{b} = \frac{a}{2}(\hat{j}+\hat{k})$, $\vec{c} = \frac{a}{2}(\hat{k}+\hat{i})$ & primitive translation vectors in reciprocal space are

$$\vec{a}^* = \frac{2\pi}{a}(\hat{i}+\hat{j}-\hat{k}),\ \vec{b}^* = \frac{2\pi}{a}(-\hat{i}+\hat{j}+\hat{k}),\ \vec{c}^* = \frac{2\pi}{a}(\hat{i}-\hat{j}+\hat{k})$$

$$\therefore \vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$
$$= \frac{2\pi}{a}\left[(h-k+l)\hat{i} + (h+k-l)\hat{j} + (-h+k+l)\hat{k}\right]$$

To make shortest $\vec{G}$, we can use 8 combinations

$$\vec{G} = \frac{2\pi}{a}(\pm\hat{i}\pm\hat{j}\pm\hat{k})$$

First zone boundary is determined by the 8 planes $\perp$ G at their midpoint. But the corners of the octahedron are truncated by planes which are perpendicular bisector of 6 reciprocal lattice vector $\frac{2\pi}{a}(\pm 2\hat{i})$, $\frac{2\pi}{a}(\pm 2\hat{j})$, $\frac{2\pi}{a}(\pm 2\hat{k})$. So first Brillouin zone is truncated octahedron, which is also the primitive unit cell of **bcc** lattice.

Brillouin zones of bcc lattice

primitive translation vectors of bcc lattice are

$\vec{a} = \frac{a}{2}(\hat{i}+\hat{j}-\hat{k})$, $\vec{b} = \frac{a}{2}(-\hat{i}+\hat{j}+\hat{k})$, $\vec{c} = \frac{a}{2}(\hat{i}-\hat{j}+\hat{k})$ &

primitive translation vectors of reciprocal lattice are

$$\vec{a}^* = \frac{2\pi}{a}(\hat{i}+\hat{j}),\ \vec{b}^* = \frac{2\pi}{a}(\hat{j}+\hat{k}),\ \vec{c}^* = \frac{2\pi}{a}(\hat{k}+\hat{i}).$$

$\vec{G} = \frac{2\pi}{a}\left[(h+l)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}\right]$ & shortest $\vec{G}$ are

the 12 vectors, $\vec{G} = \frac{2\pi}{a}(\pm\hat{i}\pm\hat{j})$

$$= \frac{2\pi}{a}(\pm\hat{j}\pm\hat{k})$$
$$= \frac{2\pi}{a}(\pm\hat{k}\pm\hat{i})$$

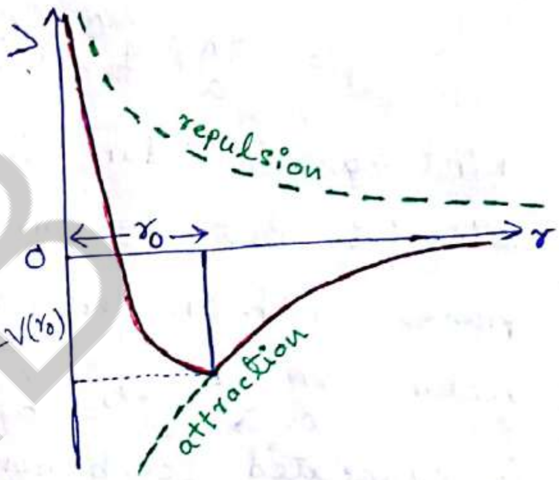
First Brillouin zone is ~~volume~~ by normal bisector of 12 vectors

$\Rightarrow$ rhombic dodecahedron.

Crystal Bonding

The ability to hold the atoms/ions together is called bonding. Atoms vibrate in lattice & nucleus due to heavy mass is almost at rest. So electrostatic interaction happen between electron cloud & distribution of electron leads to 5 types of bonding due to ⓐ "attractive force" of negatively charged electron cloud of one atom with positive nuclear charge of other atom ⓑ "repulsive force" of overlapping negatively charged electron clouds & positively charged nucleus of two atoms.

"spring effect" → attraction → repulsion.



$F = -\dfrac{dV}{dr}$ attractive force = negative potential.

repulsive force = positive potential.

cohesive / binding energy $V(r_0)$ (negative)

dissociation energy $-V(r_0)$ (positive)

Cohesive energy of a solid is the energy that will be given out in forming a crystal by bringing neutral atoms from ∞ to equilibrium separation r_0.

Suppose $V_{attractive} \propto r^{-m}$ & $V_{repulsive} \propto r^{-n}$

$\therefore$ Cohesive energy $V = V_{attractive} + V_{repulsive} = -Ar^{-m} + Br^{-n}$

& force $F = -\dfrac{dV}{dr} = mAr^{-(m+1)} - nBr^{-(n+1)}$

at $r = r_0$, $F = 0 = mAr_0^{-(m+1)} - nBr_0^{-(n+1)}$.

or $r_0^{m-n} = \dfrac{A}{B}\dfrac{m}{n}$

Then equilibrium potential energy $V(r_0) = -Ar_0^{-m} + Br_0^{-n}$

$= -Ar_0^{-m}\left(1 - \dfrac{B}{A}r_0^{m-n}\right) = -Ar_0^{-m}\left(1 - \dfrac{m}{n}\right).$

For V to be minimum, it must be concave upwards curvature,

$$\left.\frac{d^2V}{dr^2}\right|_{r=r_0} > 0 \quad \text{or} \quad \left[-m(m+1)A\,r^{-(m+2)} + n(n+1)B\,r^{-(n+2)}\right]_{r=r_0} > 0$$

$$\text{or} \quad -m(m+1) + n(n+1)\frac{B}{A}\,r_0^{\,m-n} > 0$$

$$\text{or} \quad -\cancel{m}(m+\cancel{1}) + \cancel{n}(n+\cancel{1})\,\frac{\cancel{m}}{\cancel{n}}\,\cancel{\frac{B}{A}}\,\cancel{\frac{A}{B}} > 0$$

$$\text{or} \quad n - m > 0 \quad \text{or} \quad n > m.$$

Thus to form a chemical bond, we always need repulsive force be of shorter range than attractive force.

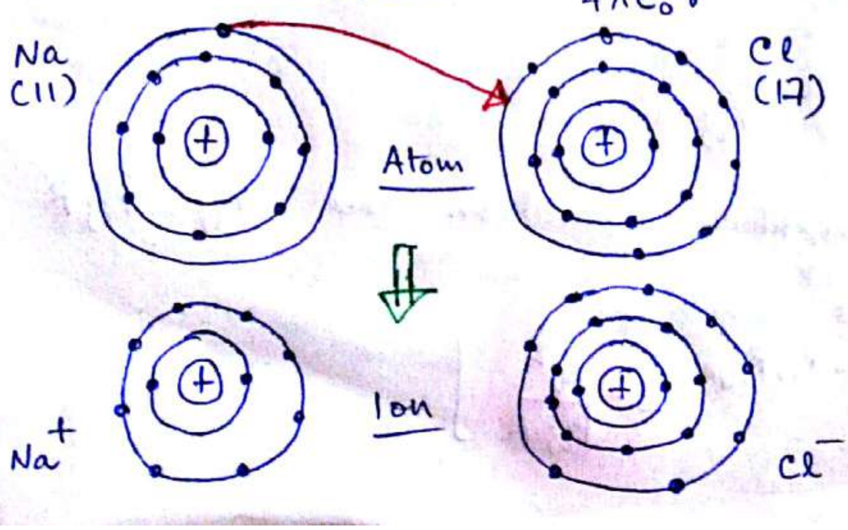
Types of bonding

5 types of bonding exist

(a) Ionic bond (transfer of valence electron) : NaCl, LiF.
(b) Covalent bond (sharing of valence electrons) : Diamond, SiC.
(c) Metallic bond (free nature of valence electron) : Cu, Ag, Fe
(d) Hydrogen bond ($V \propto -r^{-2}$) : Ice
(e) van der Waal's bonding (dipole-dipole interaction)

Ionic / Electrovalent Bonding

Transfer of electrons from an electropositive element to electronegative element, to create $+-$ ion. Electronegative element of large electron affinity accomodate extra added electron to complete outermost valence orbit to stabilize. Oppositely charged ions attract $V_{attraction} = -\dfrac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}$



Na + ionisation energy (5.1 eV) $\rightarrow Na^+ + e^-$

$Cl + e^- \rightarrow Cl^-$ + electron affinity (3.6 eV)

$\therefore Na + Cl + 1.5\,eV \rightarrow Na^+ + Cl^-$

$Z_1 = Z_2 = 1.$

So potential energy $V = -\frac{e^2}{4\pi\epsilon_0 r_0} = \frac{-(1.6\times10^{-19})^2}{4\pi\times 8.85\times10^{-12}\times 2.4\times10^{-10}}$
($r_0 = 2.4$ Å)

$$= -\frac{9.6\times10^{-19}}{1.6\times10^{-19}} \text{ eV} = -6 \text{ eV}.$$

So net energy released $= 5.1 - 3.6 - 6 = -4.5$ eV.

Cohesive energy Binding energy calculated by Born & Madelung in 1910 extended by Mayer.

assumptions : (a) Ionic crystals are formed by positive & negative ions with spherical charge distribution. (b) Force of attraction depends on inter-ionic distance & isotropic (orientation independent), (c) Electrostatic interaction (Madelung energy $V_a = -\frac{\alpha q^2}{4\pi\epsilon_0 r}$, α = Madelung constant) contributes to cohesive energy

According to Born-Madelung theory interaction energy U_i on ion i due to all j other ions, $U_i = \sum_{j\neq i} U_{ij}$

U_i consists of two parts:

1. Short range central field repulsive potential βr_{ij}^{-n} between + & - ions which was modified by $\lambda e^{-r_{ij}/\rho}$, λ = strength, ρ = range of interaction (screened Coulomb)
2. Attractive or repulsive long ranged coulomb force with energy $\pm \frac{q^2}{r_{ij}}$

$$\therefore U_i = \sum_{j\neq i}\left[\lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}\right]$$

If R is the nearest neighbour separation then $r_{ij} = p_{ij}R$ where p_{ij} is a dimensionless quantity.

Then $$U_i = \sum_{j\neq i}\left[\lambda e^{-p_{ij}R/\rho} \pm \frac{q^2}{p_{ij}R}\right]$$

$$= Z\lambda e^{-R/\rho} \pm \sum_{j\neq i} \frac{q^2}{p_{ij}R} = Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}$$

where Z is number of nearest neighbour of i^{th} ion & $\alpha = \pm \sum \frac{1}{p_{ij}}$ is called Madelung constant

If the crystal contain $2N$ ions or N molecules, then

$$U_{total} = NU_i = N\left[Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right]$$

at equilibrium distance $R = R_0$, $\frac{dU_{total}}{dR} = 0$

or $-\frac{Z\lambda}{\rho} e^{-R_0/\rho} + \frac{\alpha q^2}{R_0^2} = 0$ or $\boxed{e^{-R_0/\rho} = \frac{\rho \alpha q^2}{Z\lambda R_0^2}}$

$$\therefore U_{total} = N\left[\cancel{Z\lambda} \frac{\rho\alpha q^2}{\cancel{Z\lambda} R_0^2} - \frac{\alpha q^2}{R_0}\right] = \underbrace{-\frac{N\alpha q^2}{R_0}}_{\text{Madelung energy}} \underbrace{\left(1 - \frac{\rho}{R_0}\right)}_{\text{contribution from short range repulsion}}$$

$$U_i = -\frac{\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right),$$

or in SI units, $\boxed{U_i = -\frac{\alpha q^2}{4\pi\epsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right)}$

as $\frac{\rho}{R_0} \to 0$ repulsive interaction is very short range.

In $\alpha = \sum \pm \frac{1}{p_{ij}}$, $+$ is used for $+$ive ion & $-$ for $-$ive ion if i^{th} ion is $-$ive. & we consider repulsive interaction effective for nearest neighbours only.

Madelung constant for a 1D lattice

$$+ \; - \; + \; - \; + \; \overset{\overset{R}{\longleftrightarrow}}{(-)} \; + \; - \; + \; - \; + \; -$$

reference

$$\alpha = \sum_{j\neq i} \pm \frac{1}{p_{ij}}, \quad \frac{\alpha}{R} = \sum_{j\neq i} \pm \frac{1}{p_{ij}R} = \pm \sum_{j\neq i} \frac{1}{r_{ij}}$$

$$\text{or } \frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \cdots\right]$$

$\therefore \alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right]$

$\uparrow$ due to both side of reference ion

but $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$

if $x=1$, $\ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots$

$\therefore \alpha = 2\ln 2 = 1.38$

Madelung constant for NaCl crystal

Nearest neighbour to $-$ive (reference) ion $= 6$ $+$ive ions with $p_{ij} = p = 1$. 12 $-$ive ions at $p = \sqrt{2}$. 8 $+$ive ions at $p = \sqrt{3}$. 6 $-$ive ions at $p = \sqrt{4}$ & so on

$$\alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \cdots = 1.748$$

Bigger α, more cohesive energy, greater stability of structure

Cohesive energy for repulsive core potential $\propto r^{-n}$

$$V_i = V_{attractive} + V_{repulsive} = -\frac{\alpha q^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

at $r = r_0$, V is minimum, $\left.\frac{dV}{dr}\right|_{r=r_0} = 0 = \frac{\alpha q^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$

$$\therefore B = \frac{\alpha q^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$

$$\therefore V_i = -\frac{\alpha q^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

& for 2N molecules, $V_{tot} = -\frac{N\alpha q^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$

for NaCl, $\alpha = 2\ln 2$, $\boxed{V_{tot} = -\frac{2Nq^2\ln 2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)}$

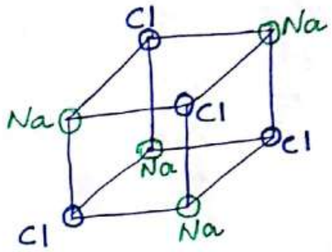
Bulk modulus of Ionic crystals

Volume strain $= \frac{dV}{V}$, change in pressure dp, Bulk modulus

$$B = -\left.\frac{dp}{dV/V}\right|_{R=R_0}$$. Using 1^{st} law of thermodynamics, $dQ = dU + pdV$

$$\text{or } \frac{dU}{dV} = -p \quad (dQ=0) \quad \text{or} \quad \frac{d^2U}{dV^2} = -\frac{dp}{dV}.$$

$$\therefore B = V \left.\frac{d^2U}{dV^2}\right|_{R=R_0}$$



volume occupied by $\frac{1}{2}$ molecule $\rightarrow R_0^3$

volume occupied by 1 molecule $\rightarrow 2R_0^3$ (equilibrium separation)

volume occupied by N molecule $\rightarrow 2NR_0^3$.
(2N ions)

volume of unit cell $\rightarrow (2R_0)^3 = 8R_0^3$ because $a = 2R_0$

$$V = 2NR^3, \quad \frac{dV}{dR} = 6NR^2 \quad \text{and} \quad \left.\frac{dU}{dR}\right|_{R=R_0} = 0$$

$$\therefore \frac{d^2U}{dV^2} = \frac{d}{dV}\left(\frac{dU}{dV}\right) = \frac{d}{dV}\left(\frac{dU}{dR}\cdot\frac{dR}{dV}\right) = \frac{d}{dV}\left(\frac{dU}{dR}\right)\cdot\frac{dR}{dV} + \frac{dU}{dR}\cdot\frac{d^2R}{dV^2}$$

$$= \frac{d}{dR}\left(\frac{dU}{dR}\right)\frac{dR}{dV}\cdot\frac{dR}{dV} + \frac{dU}{dR}\cdot\frac{d^2R}{dV^2} = \frac{d^2U}{dR^2}\cdot\left(\frac{dR}{dV}\right)^2 + \underbrace{\cancel{\frac{dU}{dR}}}_{R=R_0}{}^{\to 0}\cdot\frac{d^2R}{dV^2}$$

$$\therefore \left.\frac{d^2U}{dV^2}\right|_{R=R_0} = \frac{d^2U}{dR^2}\cdot\left(\frac{dR}{dV}\right)^2 = \frac{1}{(6NR_0^2)^2}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}$$

$$\therefore B = V\left.\frac{d^2U}{dV^2}\right|_{R=R_0} = 2NR_0^3\,\frac{1}{36N^2R_0^4}\left.\frac{d^2U}{dR^2}\right|_{R=R_0} = \frac{1}{18NR_0}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}$$

We learned that $U_{total} = N\left[Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right]$

$$\therefore \frac{dU_{total}}{dR} = -\frac{NZ\lambda}{\rho}e^{-R/\rho} + \frac{N\alpha q^2}{R^2}$$

$$\frac{d^2U_{total}}{dR^2} = \frac{NZ\lambda}{\rho^2}\cdot e^{-R/\rho} - \frac{2N\alpha q^3}{R^3}, \quad \text{also } e^{-R_0/\rho} = \frac{\rho\alpha q^2}{Z\lambda R_0^2}$$

$$\therefore B = \frac{1}{18NR_0}\left[\frac{NZ\lambda}{\rho^2}e^{-R_0/\rho} - \frac{2N\alpha q^3}{R_0^3}\right] = \frac{1}{18\cancel{N}R_0}\left[\frac{\cancel{NZ\lambda}}{\cancel{\rho^2}}\frac{\cancel{\rho}\alpha q^2}{\cancel{Z\lambda}R_0^2} - \frac{2\cancel{N}\alpha q^3}{R_0^3}\right]$$

$$\boxed{B = \frac{\alpha q^2}{18R_0^4}\left(\frac{R_0}{\rho} - 2\right)}$$

From B & R_0, range of repulsive interaction can be calculated.

Covalent Bonding

Equal sharing of electrons between neighbouring atom with incomplete outermost shell. Unlike isotropic bonds in ionic, these are directional, due to electron's restricted orbital motion.

Covalent bond can happen due to overlap of s-orbital with opposite spin paired electrons (like H_2) or hybrid bonding due to overlapping S & p orbitals.

For single carbon atom $C_6 = 1s^2\,2s^2\,2p^2$

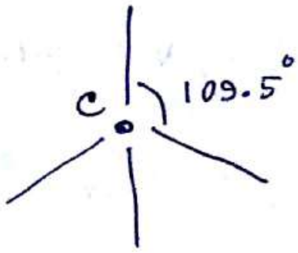
$2p^2$ → unpaired electron

$1s^2$: ↑↓ $2s^2$: ↑↓ $2p_x\,2p_y\,2p_z$: ↑ ↑

But when more carbon atom comes close

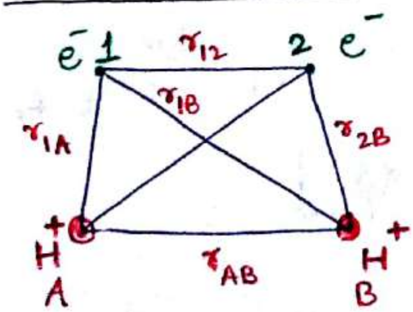
$1s^2$: ↑↓ $2s$: ↑ $2p_x$: ↑ $2p_y$: ↑ $2p_z$: ↑ → unpaired electrons

So 4-bonds can form with bond angle $109.5°$ in a regular tetrahedron using 4 unpaired electrons in 2s, 2p orbital.



(sp^3 hybridization) ⇒ Diamond, Si, Ge etc.

Heitler-London theory



A & B are H^+ nucleus (hydrogen atom) with two electrons 1 & 2 in $1s^1$ orbital.

Ψ_{1A}, Ψ_{2B} are eigenfunction of A, B atoms.

Total Hamiltonian is $$\mathcal{H} = \frac{e^2}{r_{AB}} + \frac{e^2}{r_{12}} - \underbrace{\frac{e^2}{r_{1A}}}_{\mathcal{H}_1} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \underbrace{\frac{e^2}{r_{2B}}}_{\mathcal{H}_2}$$

(the terms $\frac{e^2}{r_{AB}} + \frac{e^2}{r_{12}}$ and $-\frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}}$ together: $\mathcal{H}'$)

$\mathcal{H}_1, \mathcal{H}_2$ = potential energy of electron 1 & 2 (without overlap)

$\mathcal{H}'$ = exchange potential (interaction)

When there is no spin-orbit coupling, A & B are far apart

$$\Psi(\vec{r}_1\vec{s}_1;\vec{r}_2\vec{s}_2) = \underbrace{\psi_{1A}\psi_{2B}}_{\text{space}}\ \underbrace{\phi_{1A}\phi_{2B}}_{\text{spin}}$$ with Pauli exclusion

principle $\Psi(\vec{r}_1\vec{s}_1;\vec{r}_2\vec{s}_2) = -\Psi(\vec{r}_2\vec{s}_2;\vec{r}_1\vec{s}_1)$.

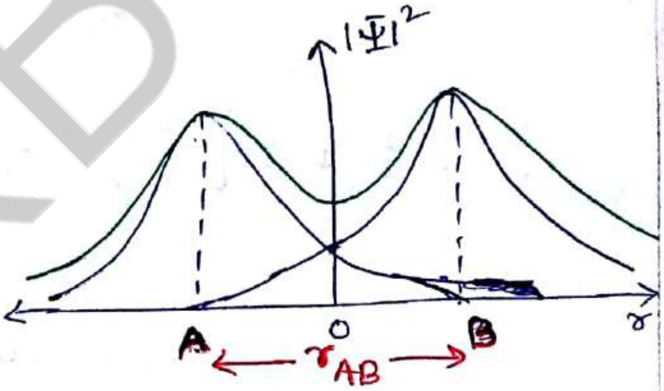
We can write the Schrödinger equation for the two electron system $-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)\Psi + (\mathcal{H}_1+\mathcal{H}_2)\Psi = E\Psi$ (no overlap)

$$\therefore \quad \nabla_1^2\psi_{1A} + \frac{2m}{\hbar^2}(E_1-\mathcal{H}_1)\psi_{1A} = 0$$
$$\nabla_2^2\psi_{2B} + \frac{2m}{\hbar^2}(E_2-\mathcal{H}_2)\psi_{2B} = 0$$

} H-atom solution in radial part, spherical polar & azimuthal part

$$\psi_{1A} \sim \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r_{1A}}{a_0}}, \quad \psi_{2B} \sim \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r_{2A}}{a_0}}, \quad E_1 = E_2 = \frac{e^2}{a_0}$$

[a_0 = Bohr orbit radius]



For 2-H atom $\Psi = \psi_{1A}\psi_{2B}$ is the wave function & $|\Psi|^2$ is probability of finding both electrons.

But they are indistinguishable, so due to exchange degeneracy $\psi_{2A}\psi_{1B}$ is also a wavefunction.

Superpositions are also wavefunction ψ_S (symmetric), ψ_A (antisymmetric)

$$\psi_S = \frac{1}{\sqrt{2+2S}}(\psi_{1A}\psi_{2B} + \psi_{2A}\psi_{1B}), \qquad S = \iint(\psi_{1A}\psi_{2B})^*(\psi_{2A}\psi_{1B})\,dr_1\,dr_2$$

$$\psi_A = \frac{1}{\sqrt{2-2S}}(\psi_{1A}\psi_{2B} - \psi_{2A}\psi_{1B}) \qquad = \iint(\psi_{2A}\psi_{1B})^*(\psi_{1A}\psi_{2B})\,dr_1\,dr_2$$

$=$ overlap integral ≤ 1

$$\therefore \quad H = E_0 + E_0 + \mathcal{H}' = 2E_0 + \mathcal{H}'$$

Exchange interaction is $E' = \frac{\int \psi^*\mathcal{H}'\psi\, d^3r}{\int\psi^*\psi\, d^3r}$

with $\psi = \frac{1}{\sqrt{2\pm 2S}}(\psi_{1A}\psi_{2B} \pm \psi_{2A}\psi_{1B})$.

Remove normalization factors as they cancel from numerator & denominator,

$$\iint (\psi_{1A}\psi_{2B} \pm \psi_{2A}\psi_{1B})^* (\psi_{1A}\psi_{2B} \pm \psi_{2A}\psi_{1B})\, dr_1\, dr_2$$

$$= \iint \psi_{1A}^* \psi_{2B}^* \underbrace{\psi_{1A}\psi_{2B}\, dr_1 dr_2}_{1} + \iint \psi_{2A}^* \psi_{1B}^* \underbrace{\psi_{2A}\psi_{1B}\, dr_1 dr_2}_{1}$$

$$\pm 2\iint \psi_{1A}^* \psi_{2B}^* \psi_{2A}\psi_{1B}\, dr_1 dr_2 \quad = \quad 2 \pm 2S$$

and $\displaystyle\iint (\psi_{1A}\psi_{2B} \pm \psi_{2A}\psi_{1B})^* \mathcal{H}' (\psi_{1A}\psi_{2B} \pm \psi_{2A}\psi_{1B})\, dr_1 dr_2$

$$= \underbrace{\iint \psi_{1A}^* \psi_{2B}^* \mathcal{H}' \psi_{1A}\psi_{2B}\, dr_1 dr_2}_{\text{Coulomb integral}} + \iint \psi_{2A}^* \psi_{1B}^* \mathcal{H}' \psi_{2A}\psi_{1B}\, dr_1 dr_2$$

$$\pm \iint \left[\psi_{1A}^* \psi_{2B}^* \mathcal{H}' \psi_{2A}\psi_{1B} + \psi_{2A}^* \psi_{1B}^* \mathcal{H}' \psi_{1A}\psi_{2B}\right] dr_1 dr_2$$

$2 \Leftrightarrow 1$ interchange

$$= 2\xi \pm 2\eta \quad , \quad \xi = \iint \psi_{1A}^* \psi_{2B}^* \mathcal{H}' \psi_{1A}\psi_{2B}\, dr_1 dr_2$$

= same atom interaction. < 0

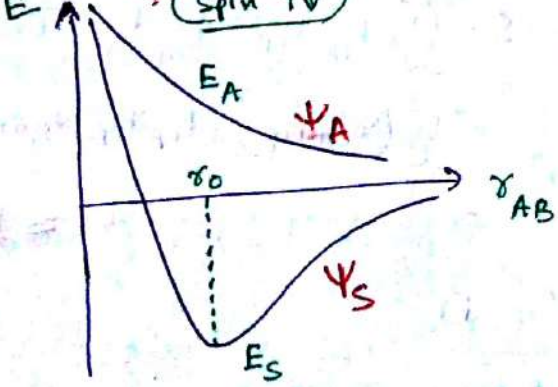
$$\eta = \iint \psi_{1A}^* \psi_{2B}^* \mathcal{H}' \psi_{1B}\psi_{2A}\, dr_1 dr_2$$

= exchange interaction $\lessgtr 0$

$\therefore$ Energy eigenvalues are

$$E_S = 2E_0 + \frac{\xi + \eta}{1 + S} \quad , \quad E_A = 2E_0 + \frac{\xi - \eta}{1 - S}$$

(spin ↑↓) (spin ↑↑)

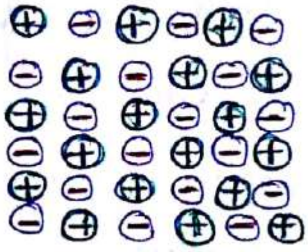


Ψ_A cannot form a bond because $E > 0$

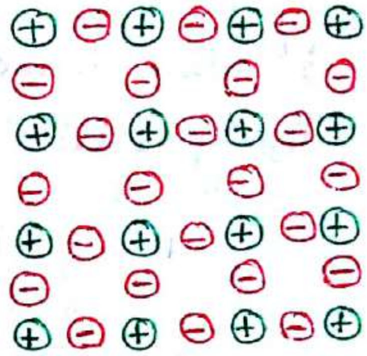
Ψ_S can form the covalent bond.

So two electrons of ↑↓ pair up to form a bond due to "exchange interaction"

Metallic Bonding



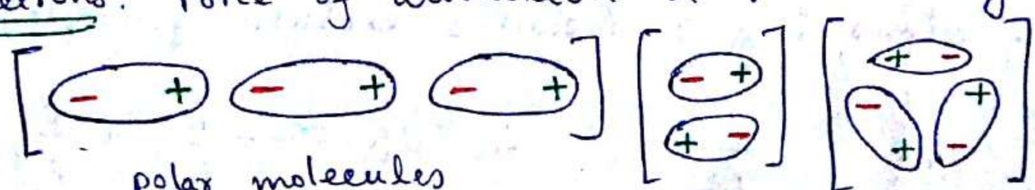
Ionisation energy is low and high electrical conductivity. They have vacant valency orbitals & have very few valency electrons compared to the number of valency orbitals. These electrons in the outermost orbit are loosely bound (conduction/free electrons) & 1 or 2 can be detached from parent atom due to attraction of neighbouring atom cores. These mobile electrons move from one kernel (positively charged atom) to other in metal lattice, & in the process bind two or more kernels together, by electrostatic interaction (partial).



Because electrons are delocalized, do not have directional polarity & weak than covalent bond. They are easy to shear, opaque & lustrous appearance because they radiate light energy of different frequency.

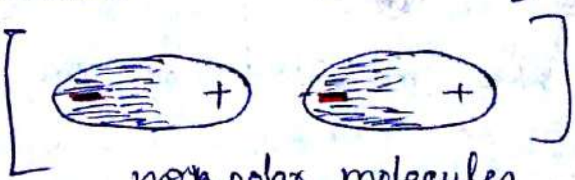
Vander Wall's bonding in molecular crystals

Inert gases attract with weak attractive force, although their outermost electron orbits are completely filled so they have no valence electrons. Force of attraction $\propto r^{-7}$ so very short range.



polar molecules

polar molecules nonpolar



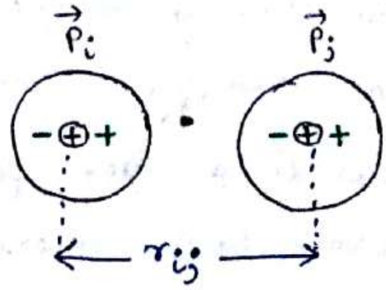
non polar molecules (instantaneous dipole)

dipole-dipole, dipole-induced dipole interaction.

These bonds are around 0.1 eV/bond & break by temperature fluctuations at room temperature. As temperature is reduced, vanderwaal's force dominate & matter transform from gas to liquid or solid.

Binding energy of Inert gas crystals

Dipole-dipole interaction produces a weak attractive force.



Fluctuation of charge distribution on j^{th} atom induces instantaneous dipole moment $\vec{P}_i$ on i^{th} atom. This produces field $\vec{E}$ at centre of the j^{th} atom

$$E_i = \frac{2P_i}{r_{ij}^3}$$

Instantaneous dipole moment $P_j = \alpha E_i = \frac{2\alpha P_i}{r_{ij}^3}$

$\therefore$ Potential energy of the dipole moments is

$$U_{atr} = -\frac{2P_iP_j}{r_{ij}^3} = -\frac{4\alpha P_i^2}{r_{ij}^6}$$

$\propto -\frac{1}{r_{ij}^6} \rightarrow$ short range

$\hookrightarrow$ attractive

$$= -\frac{B}{r_{ij}^6}.$$

Repulsive interaction is due to overlap of electron clouds of atoms i & j (Pauli's exclusion principle)

$$U_{rep} = \frac{C}{r_{ij}^{12}} \qquad \therefore U_{ij} = -\frac{B}{r_{ij}^6} + \frac{C}{r_{ij}^{12}} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right]$$

ϵ is the magnitude of the energy & σ represents extent.

Cohesive energy

$$U_{tot} = NU_i = N\sum_{j\neq i} U_{ij} = \frac{1}{2}N(4\epsilon)\sum_j\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right]$$

substituting $r_{ij} = p_{ij} R$

$$U_{tot} = 2N\epsilon\left[\sum_j \left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j\left(\frac{\sigma}{p_{ij}R}\right)^{6}\right] = 2N\epsilon\left[12.131\left(\frac{\sigma}{R}\right)^{12} - 14.454\left(\frac{\sigma}{R}\right)^{6}\right]$$

for fcc crystal.

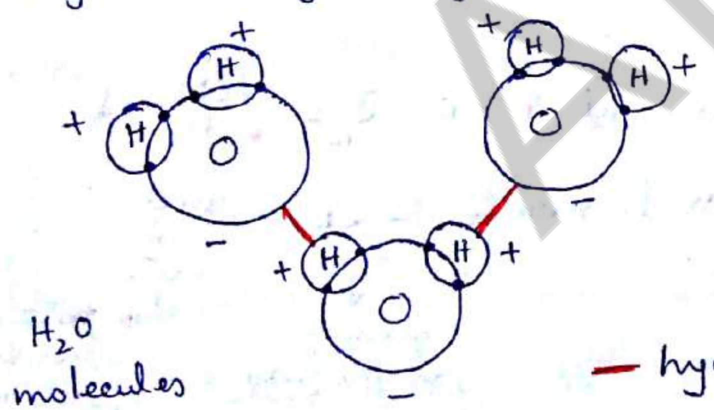
$$\left.\frac{dU_{tot}}{dR}\right|_{R=R_0} = 0 \Rightarrow R_0/\sigma = 1.09.$$

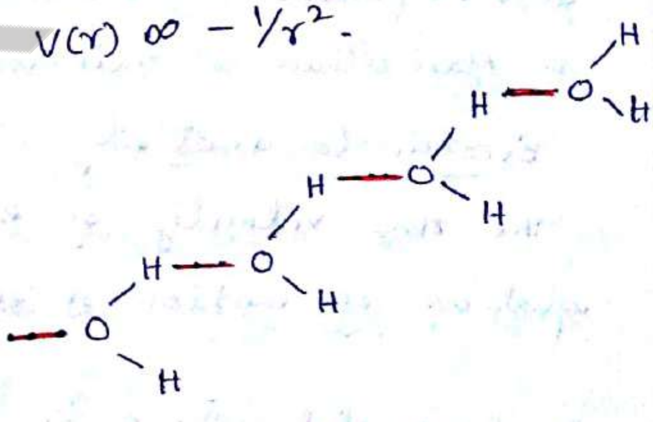
and $$U_{tot} = 2N\epsilon\left[12.131\left(\frac{\sigma}{R_0}\right)^{12} - 14.454\left(\frac{\sigma}{R_0}\right)^{6}\right] = -8.6N\epsilon$$

This is the cohesive energy of the inert gas crystal at absolute zero temperature & zero pressure.

Hydrogen Bonding

A special type of vanderWaal bond happens between hydrogen atom, which has 1 electron loses to other atom leaving behind a poorly shielded proton. The proton (H^+ ion) has two negative ions to attract & its radius is 10^{-15} m, so the VW force is very strong & varies as $V(r) \propto -1/r^2$.

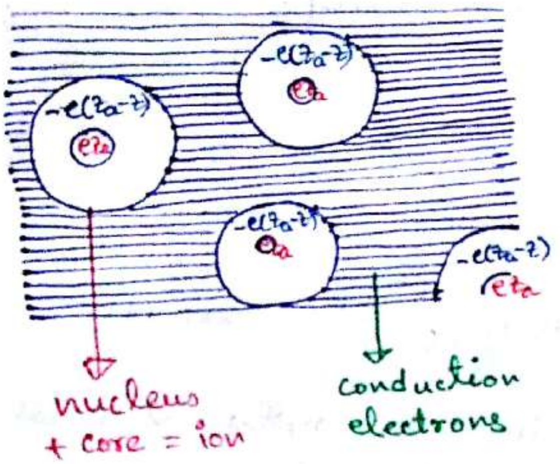


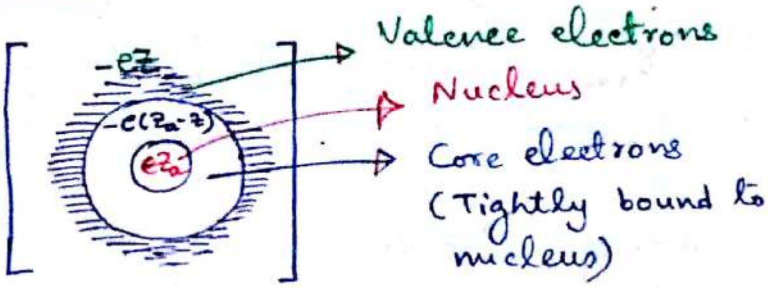


Interaction between oppositely charged ends of permanently polarized molecules with having H-atom is called the Hydrogen bond.

VW ~ 2-7 kJ/mole H-bond ~ 10 kJ/mole	Metallic ~ 20-100 kJ/mole Covalent ~ 170-244 kJ/mole Ionic ~ 184 kJ/mole	Cohesive energy

Free Electron Theory of Metals





Drude - Lorentz theory (Classical free electron theory):

Dense metallic electron gas → kinetic theory of neutral dilute gas. collisions of electron with other electron & ions is neglected, and under external field they move in straight line with Newton's law. Electron-electron interaction is neglected (independent electron approximation), electron-ion interaction is also neglected (free electron approximation). Their speed distribution is Maxwellian & their collisions are elastic.

Electric Conductivity

The rms velocity of electron at T is $\bar{c}_{rms} = \sqrt{\frac{3k_BT}{m}}$ &

equation of motion of electron $m\dot{v} = \underbrace{-eE}_{\text{force by electric field}} - \underbrace{\frac{mv}{\tau}}_{\text{friction force due to collision, } \tau = \text{ collision time}}$

At steady state $\dot{v} = 0 \Rightarrow$

$$v_d = -\frac{e\tau}{m}E = -\mu E$$

v_d = drift velocity, μ = mobility

Current density $J = -nev_d$ ($-ne$ = charge / unit volume, n = no. density of conduction electron)

$$= -ne\left(-\frac{e\tau}{m}E\right)$$

$$= \frac{ne^2\tau}{m}E = \sigma E$$

$\therefore$ Electric conductivity $\sigma = \frac{ne^2\tau}{m} \propto n$

$$= \left(\frac{ne}{m}\right)\left(\frac{e\tau}{m}\right) = ne\mu$$

resistivity $\rho = \sigma^{-1} = \frac{1}{ne\mu} = \frac{m}{ne^2\tau}$

In metals, $n \sim$ constant, μ decreases with temperature, so as σ.
In semiconductor, n exponentially increases with temperature, σ increases
In insulator, $n \sim$ constant, μ increases exponentially $\rightarrow$ dielectric breakdown

Wiedemann-Franz law (metals) $\frac{K}{\sigma} \propto T$, K = thermal conductivity, σ = electrical "

Good conductor of electricity are also good conductors of heat & the ratio $K/\sigma T = \frac{\pi^2 k_B^2}{3e^2}$ = Lorentz number

Although free electron theory explains WF law & validate's ohm's law, low temperature behaviour, $\rho \propto T$ etc cannot be obtained.

Sommerfeld's free electron theory

Despite the success of Drude-Lorentz classical electron theory to explain WF law, difficulties were

(a) Why Debye theory of lattice specific heat that ignores electronic specific heat is accurately "valid" for metals?

(b) Paramagnetism of metals does "not" obey Curie law ($\chi \propto \frac{1}{T}$) & is independent of temperature. But a gas of electrons, each of which are tiny magnet must exhibit large magnetic susceptibility

(c) Hall effect of some divalent metal is positive, meaning that the charge carriers are "positive"!

(d) Electric resistivity has a temperature variation $\rho = \rho_0(1+\alpha T)$ that can't be explained from classical electron gas model.

(e) Certain metals (tin, mercury etc) having poor electrical conductivity becomes superconductor at very low temperature but alkali & noble metals (Ag, Au, Pt etc) do not show superconductivity.

Schrödinger equation for free electron gas in 3D.

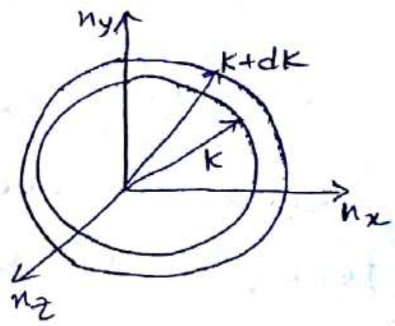
$$-\frac{\hbar^2}{2m}\nabla^2\psi + \underset{\substack{\parallel \\ 0}}{V}\psi = E\psi \quad \Rightarrow \quad \nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0$$

Plane wave solution $\psi(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}}$, $\nabla^2\psi = -k^2\psi$.

$$\text{or} \quad -k^2\psi + \frac{2m}{\hbar^2}E\psi = 0 \quad \Rightarrow \quad E = \frac{\hbar^2k^2}{2m}$$

where $k^2 = \left(\frac{2\pi}{L}\right)^2(n_x^2 + n_y^2 + n_z^2)$, n_x, n_y, n_z integers

because $\psi(\vec{r}) = \psi(\vec{r}+\vec{L})$. Each set of (n_x, n_y, n_z) gives a stationary state of an electron inside the metal. In k-space, number of possible states of integers within k & $k+dk$, each of which gives rise to one state of electron



$$\therefore L^3 D(k) = \frac{4\pi k^2 dk}{(2\pi/L)^3} \qquad E = \frac{\hbar^2k^2}{2m}, \quad dk = \frac{m\,dE\,\hbar}{\hbar^2\sqrt{2mE}}$$

$$= \frac{4\pi L^3}{8\pi^3}\frac{2mE}{\hbar^2}\frac{1}{\hbar}\sqrt{\frac{m}{2}}E^{-1/2}dE \qquad = \frac{1}{\hbar}\sqrt{\frac{m}{2}}E^{-1/2}dE$$

$$= L^3\, 2\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE$$

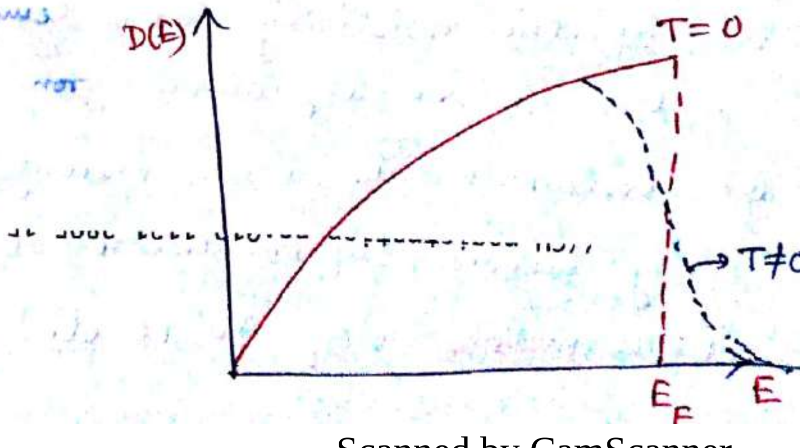
$$\Rightarrow D(E) = 2\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE. \quad [\text{no. of states/unit volume}]$$

Using Pauli's exclusion principle, since electrons are spin $\pm\frac{1}{2}$ so each energy state will have 2-fold degeneracy.

$$\therefore D(E) = 2\times 2\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE.$$

$$D(E) = 4\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE$$

This is valid at T = 0K.

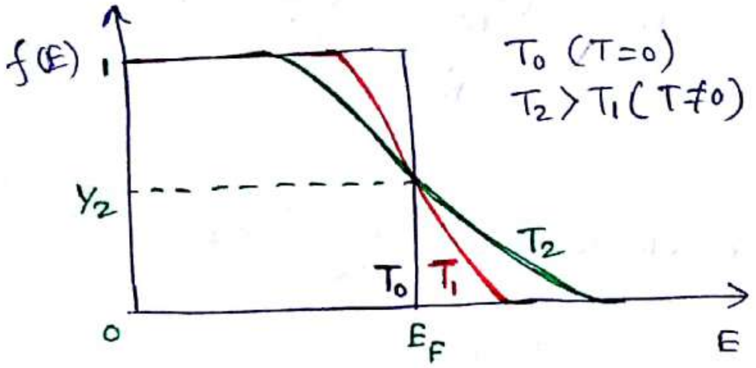


At a finite temperature T, the probability that an electron occupies a state with energy E is given by Fermi-Dirac function

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT}+1} \quad \text{where } E_F = \mu = \frac{\partial G}{\partial N} = \text{chemical potential}$$

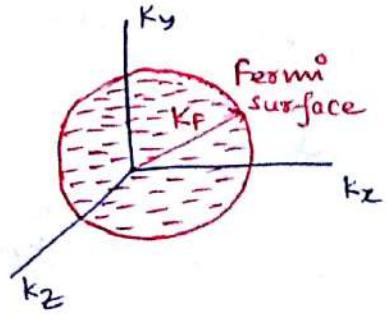
at $T=0$, $f(E) = 0$ if $E > E_f$
$= 1$ if $E < E_f$

at $T \neq 0$, $f(E) = \frac{1}{2}$ if $E = E_f$



at $T=0$, Below fermi energy all states are filled & above states are empty. at $T \neq 0$, at fermi energy half of the states are filled.

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad \text{and in K-space, fermi-sphere } S_F = 4\pi k_F^2$$



Now $\int_0^\infty f(E)\, D(E)\, dE = n$

at $T=0$, $f(E) = 1$ till $E = E_F$

$$\therefore \int_0^{E_F} D(E)\, dE = n.$$

$$\text{or } 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_F} E^{1/2} dE = n. \quad \text{or } \boxed{E_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3}} \propto n^{2/3}$$

at $T \neq 0$ for $E_F \gg k_BT$, $E_F(T)$ is given by Sommerfeld equation

$$E_F(T) = E_F\left[1 - \frac{\pi^2}{12}\frac{(k_BT)^2}{E_F^2}\right]$$

$$\text{from } E_F = \frac{\hbar^2 k_F^2}{2m}, \quad k_F^2 = \frac{2m}{\hbar^2}\frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} = (3n\pi^2)^{2/3}$$

fermi wave vector $\boxed{k_F = (3\pi^2 n)^{1/3}}$

fermi velocity $\boxed{v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}(3\pi^2 n)^{1/3}}$

$E_F = \frac{3}{2} k_B T_F \Rightarrow$ Fermi temperature $T_F = \frac{2E_F}{3k_B} = \frac{2\hbar^2}{6k_B m}(3\pi^2 n)^{2/3}$

Substituting values & $n = 10^{22}/cc$, $T_F \sim 39{,}000\,K$.

Average energy of the electron at $T = 0K$ is

$$\bar{E} = \frac{1}{n}\int_0^{E_F} E\,D(E)\,dE = \frac{1}{n} 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_F} E^{3/2}\,dE$$

$$= \frac{4\pi}{n}\left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{5} E_F^{5/2} = \frac{1}{\cancel{n}} \underbrace{4\pi\left(\frac{2m}{h^2}\right)^{3/2} E_F^{3/2} \frac{2}{3}}_{\cancel{n}} \frac{3}{5} E_F$$

$$\boxed{\bar{E} = \frac{3}{5} E_F}$$

Average speed of electron at $T = 0K$ is $\bar{v} = \frac{1}{n}\int_0^{v_F} v\,dn$

Now $v_F = \frac{\hbar}{m}(3\pi^2 n)^{1/3}$ or $n = \frac{1}{3\pi^2}\left(\frac{m v_F}{\hbar}\right)^3$

If all velocity are below v_F & then $n = \frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 v^3$

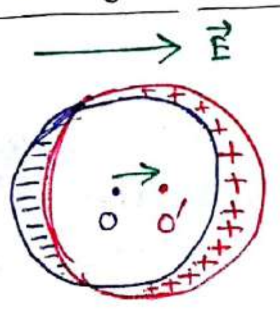
& number density of states between v & $v + dv$ is

$$dn = \frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 3v^2\,dv$$

$$\therefore \bar{v} = \frac{1}{n}\int_0^{v_F} \frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 3v^3\,dv = \frac{1}{n}\frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 \frac{3}{4} v_F^4$$

$$= \frac{1}{\cancel{n}} \underbrace{\frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 v_F^3}_{\cancel{n}} \frac{3}{4} v_F \quad \text{or} \quad \boxed{\bar{v} = \frac{3}{4} v_F}$$

Sommerfeld's free electron theory & conductivity



Concept of Fermi surface $S_F = 4\pi k_F^2$ introduced by Sommerfeld changes the notion of conduction in metals. When an electric field is switched on, movement of the Fermi surface gives a displacement of the centre of Fermi surface. This displacement is equivalent to creation of electrons on one side & positive charges on the other. Like each electron have velocity $\vec{v} = \frac{\hbar \vec{K}}{m}$, then equation of motion of each electron in Fermi surface under steady field is $\frac{d\vec{p}}{dt} = \hbar \frac{d\vec{K}}{dt} = e\vec{E}$, So in the absence of any resistive force, the fermi surface will move at constant rate in K space.

$$\int_{\vec{K}(0)}^{\vec{K}(t)} \hbar \, dK = \int_0^t e\vec{E}\, dt \quad \text{or} \quad \delta \vec{K} = \frac{e\vec{E}}{\hbar} t = \frac{e\vec{E}}{\hbar}\left(\frac{\lambda}{v_F}\right)$$

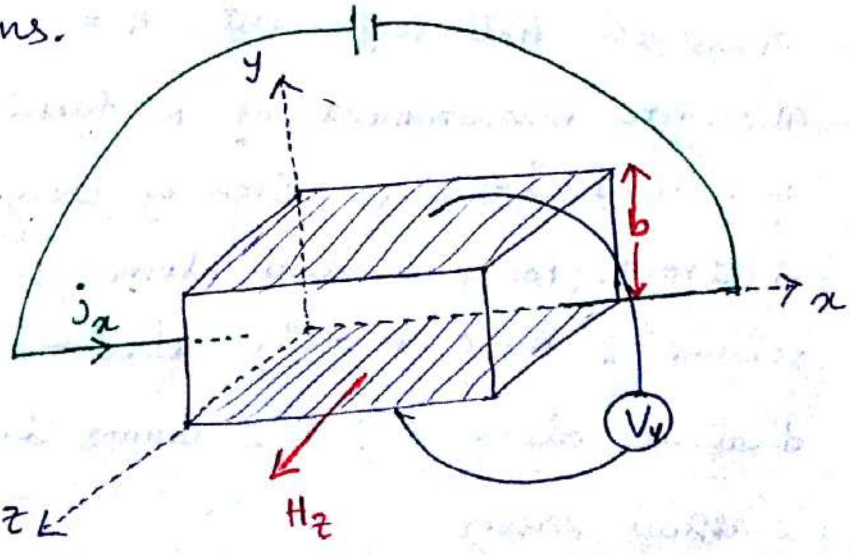
where λ is mean free path or distance between two ions.

But the collision of electron with impurity ions, imperfection & phonons (lattice vibrations) will create a restoring force.

Thus in steady state, $\vec{J} = ne\vec{v}_d$ where $\vec{v}_d = \frac{\hbar \delta \vec{K}}{m}$

$$= \frac{ne\hbar}{m} \delta \vec{K} = \frac{ne\hbar}{m} \frac{e\vec{E}\lambda}{\hbar v_F} = \frac{ne^2\lambda}{mv_F} \vec{E} = \sigma \vec{E}$$

This expression is identical to Drude's free electron theory but it destroys the notion of classical theory that all free electrons are conduction electrons. In Sommerfeld theory only few electrons that lie in the fermi surface are the conduction electrons.



Hall effect

In 1879, Hall discovered that if a uniform magnetic field H_z is applied in z-direction normal to the direction of a steady current flow j_x in a rectangular slab, then a transverse electrical potential difference develops in the y direction

$V_y \propto j_x$

$\quad \propto H_z$

$\quad \propto b$

$$\underbrace{V_y}_{\text{Hall voltage}} = \underbrace{R}_{\text{Hall coefficient}} j_x H_z \underbrace{b}_{\text{Thickness of slab}}$$

Hall effect can be explained by simple classical theory. Current flows in x direction & H_z is applied in z direction. Thus the Lorentz force exerted on an electron in the slab is $F_y = -ev_x H_z$ where v_x is uniform drift velocity, so electrons are deflected in y direction. Because electrons are deposited near the surface, a potential difference in y direction is developed until the Hall electric field E_y stops further deflection of electrons.

$$E_y = \frac{V_y}{b} \text{ and the force } F_y = -eE_y = -\frac{eV_y}{b}.$$

Equating, $\quad -ev_x H_z = -\frac{eV_y}{b} \Rightarrow v_x = \frac{V_y}{bH_z}$

$\therefore$ Current density $\quad j_x = -nev_x = -ne\frac{V_y}{bH_z}$

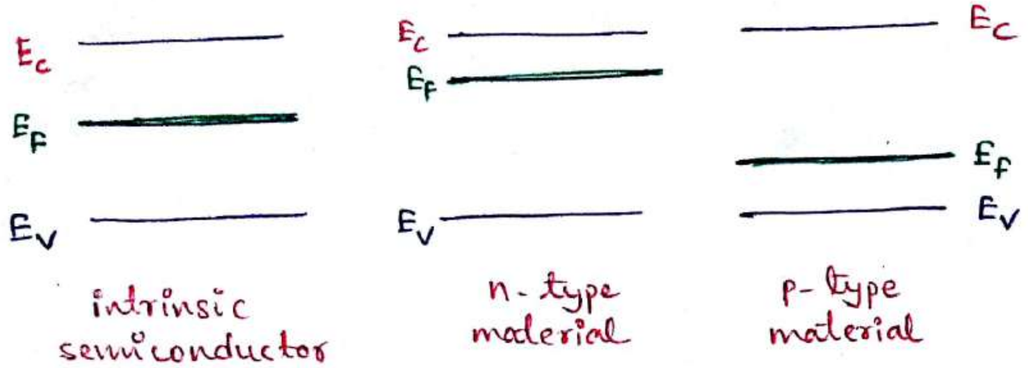
or $\quad V_y = \underbrace{\left(-\frac{1}{ne}\right)}_{R} j_x H_z b.$

Thus the Hall coefficient $R = -\frac{1}{ne}$ is $\propto \frac{1}{n}$ and $-\frac{1}{e}$.

Therefore measurement of R furnishes two important characteristic of a conductor: (1) Sign of charge carrier, (2) density of electrons. For monovalent atoms, n is number of electrons/unit volume & $R < 0$ meaning electrons are carriers. But for certain divalent atom, $R > 0$ & cannot be explained only by the classical theory.

Read about 1D crystal's density of states, $\bar{E} = \frac{1}{3}E_F$ from any standard book.

Position of Fermi level



For intrinsic semiconduct concentration of electrons in conduction band = concentration of holes in valence band & so E_F lies at middle of band gap.

For n-type material concentration of electrons in conduction band > hole concentration in valence band. E_F lies near to E_c. This is opposite in p type material & E_F lies near to E_V. Whenever a PN junction diode is formed, barrier potential V_B is $eV_B = E_{F_n} - E_{F_p}$.

HW 1. In Sodium, free electrons per cubic metre are 2.5×10^{28}. Calculate the Fermi energy & Fermi velocity. You can use $h = 6.625 \times 10^{-34}$ Js, $m = 9.1 \times 10^{-31}$ kg.

2. Consider silver in the metallic state with one free electron per atom. Calculate the Fermi energy. Given density of ~~sti~~ silver is 10.5 gm/cm^3 & atomic weight 108, $N = 6.02 \times 10^{23}$/gm atom

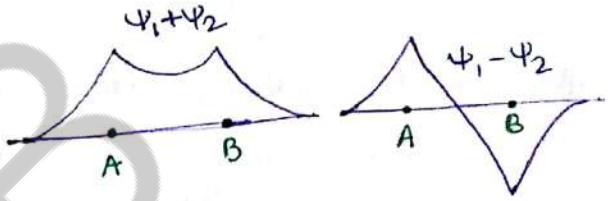
3. Aluminium metal crystallites form fcc structure. If each atom contributes single electron as free electron & lattice constant a is $4\,\mathring{A}$, treating conduction electrons as free electron Fermi gas, calculate Fermi energy E_F, Fermi vector k_F & total K.E. per unit volume at T = 0K.

Band Theory of Solids

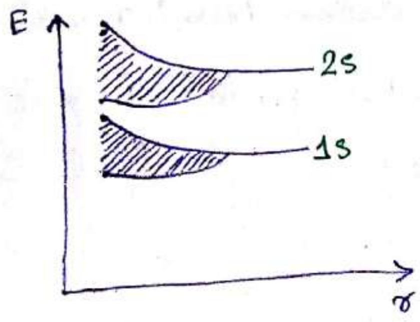
Formation of Energy Bands

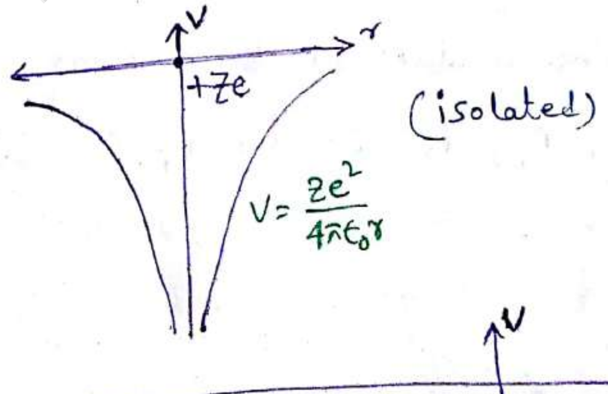
In solids, a periodic potential is formed by the nucleus and other electron cloud. Motion of an electron in periodic potential can be represented by Schrödinger equation, whose solution gives energy states. These states are filled with electrons according to Pauli's exclusion principle & all states are not accessible but bands of energies separated by forbidden energies are possible.

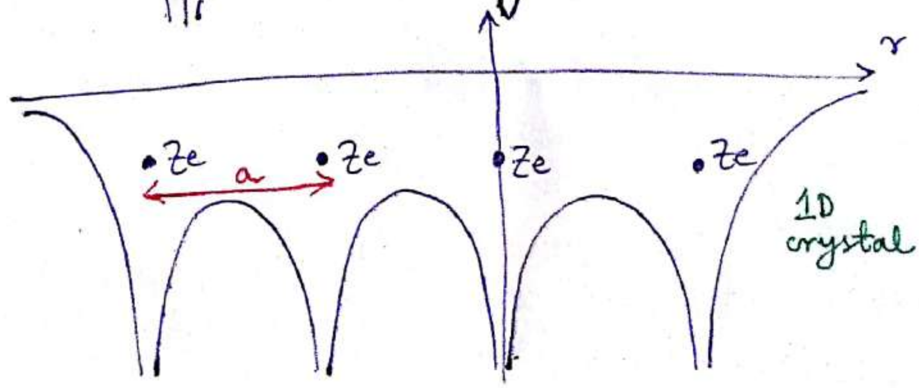
When two atoms are brought close, single energy level splits into a pair of levels. If ψ_1 & ψ_2 are electronic wave functions, then due to overlap, resultant wave function is $(\psi_1 \pm \psi_2)$. For symmetric case, electron can remain midway to A-B but for antisymmetric it cannot, so there is a difference in energy between $(\psi_1+\psi_2)$ & $(\psi_1-\psi_2)$.



Similarly when N no. of atoms are brought together, each energy state splits into N energy states whose separation is very small. These forms quasicontinuous energy band.





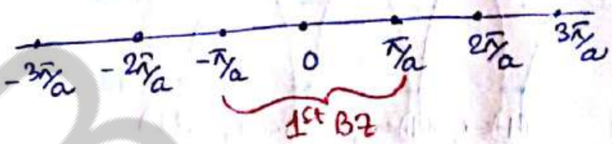


Origin of band structure. This can be understood from nearly free electron model where electrons move in a periodic kernel. in 1D. Energy of a free electron $E_k = \frac{\hbar^2 k^2}{2m}$ & $\psi_k(x) = e^{ikx}$

Low energy electrons can freely travel as their $\lambda >> a$. High energy electrons almost near to fermi energy have $\lambda \sim a$, & suffer diffraction like X-rays in crystal surface. Electron with deBroglie wavelength λ is bragg reflected, $2a\sin\theta = n\lambda$.

or $K = \frac{2\pi}{\lambda}$. after substitution $K = \pm \frac{n\pi}{a\sin\theta}$. For 1D lattice $\theta = \pi/2$ or $K = \pm \frac{n\pi}{a}$.

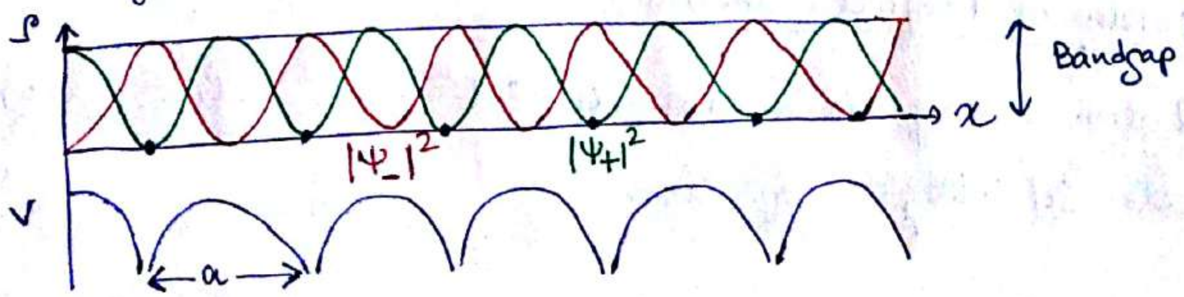
Thus a line representing K values is divided by energy discontinuities into segments of length $\pm \pi/a$ which are the Brillouin zones.



At the boundary $k = \pm\frac{\pi}{a}$, electron wavefunctions are not traveling waves $e^{i\pi x/a}$ & $e^{-i\pi x/a}$ but are standing waves, due to reflection. Two types of standing wave can form

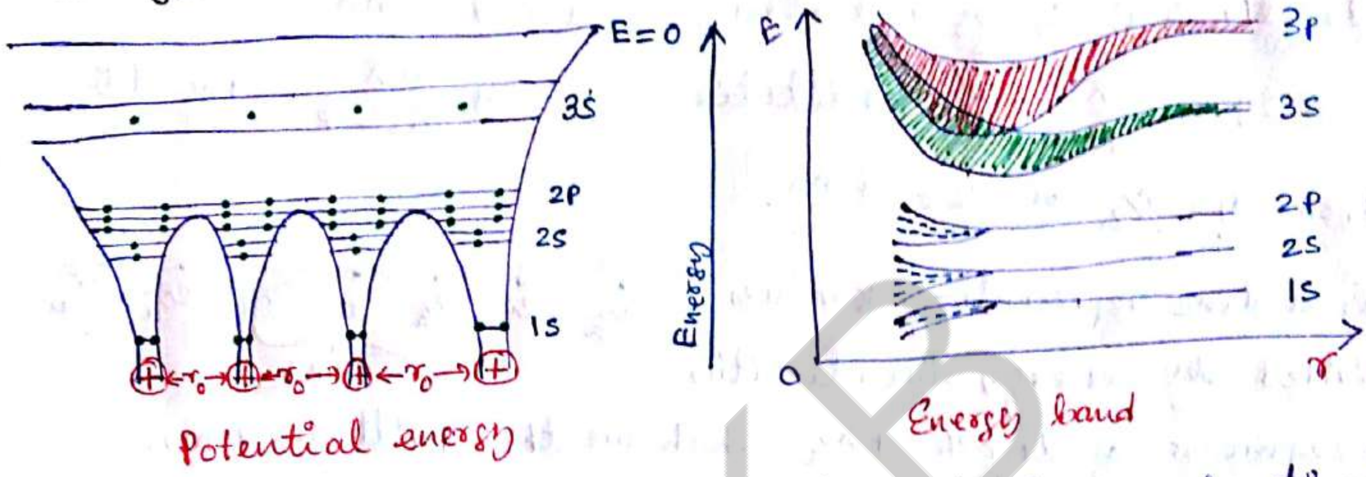
$$\psi_+ = e^{i\pi x/a} + e^{-i\pi x/a} = 2\cos\left(\frac{\pi x}{a}\right) \quad [x \to -x,\ \psi_+ \to \psi_+$$
$$\psi_- = e^{i\pi x/a} - e^{-i\pi x/a} = 2i\sin\left(\frac{\pi x}{a}\right). \quad x \to -x,\ \psi_- \to -\psi_-]$$

In quantum mechanics, probability density of electron is $\rho = \psi^*\psi$ and for traveling wave $\psi = e^{\pm ikx}$, $\rho = 1$ so that electron charge density $e|\psi|^2 =$ constant. However for standing wave, charge density isn't constant but $e|\psi_+|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$, $e|\psi_-|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$



for $x = 0, a, 2a, \ldots$ $\cos^2 \frac{\pi x}{a} = 1$, so its maximum at the kernel core and thus negative electron charge density lowering P.E. of Kernel. for $x = \frac{a}{2}, \frac{3a}{2}, \ldots$, $\sin^2 \frac{\pi x}{a} = 1$, so its maximum in midway between kernel & increasing the P.E. w.r.t. to travelling wave. So E_g is the difference of two energies.

Energy bands in Sodium crystal



Valence orbital overlap for 3s orbital to form quasi continuous energy band. Empty 3p level also spreads, so as 2s & 2p with decrease of r. when $r = r_0 = 0.367$ nm, 3s & 3p states overlap.

In metals, band overlap happens but in other materials they are separated by a band gap E_g & the energy of highest filled level is Fermi energy E_F. At 0K, levels upto E_F is filled & those above are empty. Using Pauli's principle, each s-band having N atoms can accomodate 2N electrons. If highest s-band is fully filled then electron drift using external force is stopped & such solids are called insulators.

Bloch Theorem or Floquet's theorem

for an electron moving in a 1D potential with $V(x) = V(x+a)$ is given by the Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0.$$ Bloch theorem stats that the solution of the Schrödinger equation for a periodic potential is

$\boxed{\psi(x) = e^{\pm ikx} u_K(x)}$ where $u_K(x) = u_K(x+a)$. which are plane waves $e^{\pm ikx}$ modulated by $u_K(x)$ with the periodicity of the lattice. $\psi(x)$ is the Bloch wave or Bloch function.

Proof of Bloch's theorem

If $f(x)$ and $g(x)$ are two real, independent solution of Schrödinger equation $\psi(x) = Af(x) + Bg(x)$. As $V(x) = V(x+a)$, $f(x+a)$ and $g(x+a)$ are also solutions.

$f(x+a) = \alpha_1 f(x) + \alpha_2 g(x)$, $g(x+a) = \beta_1 f(x) + \beta_2 g(x)$.

$$\therefore \; f(x+a) = \alpha_1 f(x) + \alpha_2 g(x)$$

$$\begin{aligned}\psi(x+a) &= Af(x+a) + Bg(x+a)\\ &= (A\alpha_1 + B\beta_1)f(x) + (A\alpha_2 + B\beta_2)g(x)\\ &= \lambda A f(x) + \lambda B g(x) = \lambda\psi(x).\end{aligned}$$ where we have chosen $A\alpha_1 + B\beta_1 = \lambda A$, $A\alpha_2 + B\beta_2 = \lambda B$. with λ a constant.

Now this gives nonzero values of A and B if determinant of coefficient is zero

$$\begin{vmatrix} \alpha_1 - \lambda & \beta_1 \\ \alpha_2 & \beta_2 - \lambda \end{vmatrix} = 0 \text{ or } \lambda^2 - (\alpha_1 + \beta_2)\lambda + \alpha_1\beta_2 - \alpha_2\beta_1 = 0 \quad (1)$$

[[As $f(x)$ & $g(x)$ are solution of Schrödinger equation.

$$\left\{\frac{d^2f(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]f(x) = 0\right\}, \quad \left\{\frac{d^2g(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]g(x)\right\} = 0$$

$g(x) \times$ $\times f(x)$

Substract

$$f(x)\frac{d^2g(x)}{dx^2} - g(x)\frac{d^2f(x)}{dx^2} = 0 \text{ or } \underbrace{f(x)\frac{dg(x)}{dx} - g(x)\frac{df(x)}{dx}}_{\text{wronskian}} = \text{constant} = W(x)$$

$$\begin{aligned}\therefore W(x+a) &= f(x+a)\frac{dg(x+a)}{dx} - g(x+a)\frac{df(x+a)}{dx}\\ &= f(x+a)\left[\beta_1\frac{df(x)}{dx} + \beta_2\frac{dg(x)}{dx}\right] - g(x+a)\left[\alpha_1\frac{df(x)}{dx} + \alpha_2\frac{dg(x)}{dx}\right]\end{aligned}$$

$$= [\alpha_1 f(x) + \alpha_2 g(x)][\beta_1 \frac{df(x)}{dx} + \beta_2 \frac{dg(x)}{dx}] - [\beta_1 f(x) + \beta_2 g(x)][\alpha_1 \frac{df(x)}{dx} + \alpha_2 \frac{dg(x)}{dx}]$$

$$= (\alpha_1\beta_2 - \alpha_2\beta_1)\left[f(x)\frac{dg(x)}{dx} - g(x)\frac{df(x)}{dx}\right] = (\alpha_1\beta_2 - \alpha_2\beta_1) W(x)$$

But $W(x+a) = W(x) =$ constant, $\therefore$ $\underline{\alpha_1\beta_2 - \alpha_2\beta_1 = 1}$]]

Eq. ① becomes, $\underline{\lambda^2 - (\alpha_1 + \beta_2)\lambda + 1 = 0}$. Here $\alpha_1 + \beta_2$ is a function of energy E & we have two roots λ_1 & λ_2 or two functions $\psi_1(x)$ and $\psi_2(x)$ with $\psi_1(x+a) = \lambda\psi(x)$ & $\lambda_1\lambda_2 = 1$.

<u>Special cases</u> $(\alpha_1 + \beta_2)^2 < 4$, $\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0$ have complex roots, & conjugate to each other. $\lambda = e^{\pm ika}$

$$\psi(x+a) = e^{\pm ika}\psi(x)$$ which is of the Bloch form $\psi(x) = e^{\pm ikx} u_k(x)$

$$= e^{\pm ik(x+a)} u_k(x+a) = e^{\pm ika} e^{\pm ikx} u_k(x+a) = e^{\pm ika}\psi(x)$$

$$= \lambda\psi(x)$$ Bloch theorem hence proved.

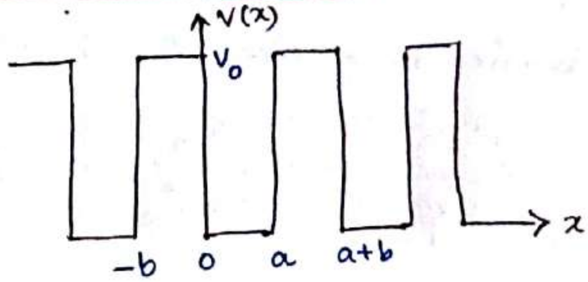
<u>Special cases</u> $(\alpha_1 + \beta_2)^2 > 1$, $\lambda^2 - (\alpha_1 + \beta_2)\lambda + 1 = 0$ have real roots

$\lambda_1 = e^{\mu a}$, $\lambda_2 = e^{-\mu a}$, $\mu =$ real. & corresponding Schrödinger equation, $\psi_1(x) = e^{\mu x} u(x)$, $\psi_2(x) = e^{-\mu x} u(x)$

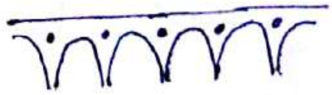
Although mathematically valid, these are forbidden wavefunctions as they're not bounded. at $\pm\infty$, both diverge.

The allowed roots $e^{\pm ika}$ and forbidden roots $e^{\pm \mu a}$ are functions of $(\alpha_1 + \beta_2)$ and hence energy. So energy spectrum of electron moving in periodic potential consists of allowed & forbidden energy regions or bands.

Kronig - Penny Model [Energy spectrum of electron consists of a allowed energy bands separated by forbidden region]



In free electron theory the assumption is valence electrons see zero potential but this isn't true with ionic & covalent bond as electrons are localized near the nuclei, that gives periodically varying potential.



whose solution from Schrödinger equation is very hard.

Instead Kronig & Penny solved it using simpler 1D potential of sharp ~~and~~ edge with periodicity a+b.

$$V = 0, \quad 0 < x < a$$
$$= V_0, \quad -b < x < 0$$

whose Schrödinger equation is

$$\left.\begin{aligned} \frac{d^2\psi}{dx^2} + \underbrace{\frac{2m}{\hbar^2}}_{\alpha^2} E\psi &= 0, \quad 0 < x < a \\ \frac{d^2\psi}{dx^2} + \underbrace{\frac{2m}{\hbar^2}(E - V_0)}_{\beta^2}\psi &= 0, \quad -b < x < 0 \end{aligned}\right\} \text{—} ①, \qquad V(x) = V(x + a + b).$$

According to Bloch theorem, solution of wave equation for periodic potential will be plane wave modulated by the lattice periodicity. $\psi(x) = u_K(x)\, e^{iKx}$ with $u_K(x) = u_K(x+a+b)$.

By substituting $\psi(x)$ in equation ① and substituting the boundary condition: $(u_1)_{x=0} = (u_2)_{x=0}$ $\quad (u_1)_{x=a} = (u_2)_{x=b}$

$$\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0} \qquad \left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=b}$$

one gets four equations & to get nonzero coefficients the 4×4 determinant vanishes. From that K-P obtained,

$$\frac{\beta^2 + \alpha^2}{2\alpha\beta} \sinh\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos K(a+b)$$

To simplify K-P considered when $V_0 \to \infty$ and $b \to 0$, $V_0 b$ is finite or potential barriers become δ-functions. $V_0 b$ is known as barrier strength. As $b \to 0$, $\sinh \beta b \to \beta b$, $\cosh \beta b \to 1$ and

$$\frac{\beta^2 + \alpha^2}{2\alpha\beta} = \frac{mV_0}{\alpha\beta\hbar^2} \quad \therefore \quad \frac{mV_0 b}{\alpha\hbar^2} \sin \alpha a + \cos \alpha a = \cos ka$$

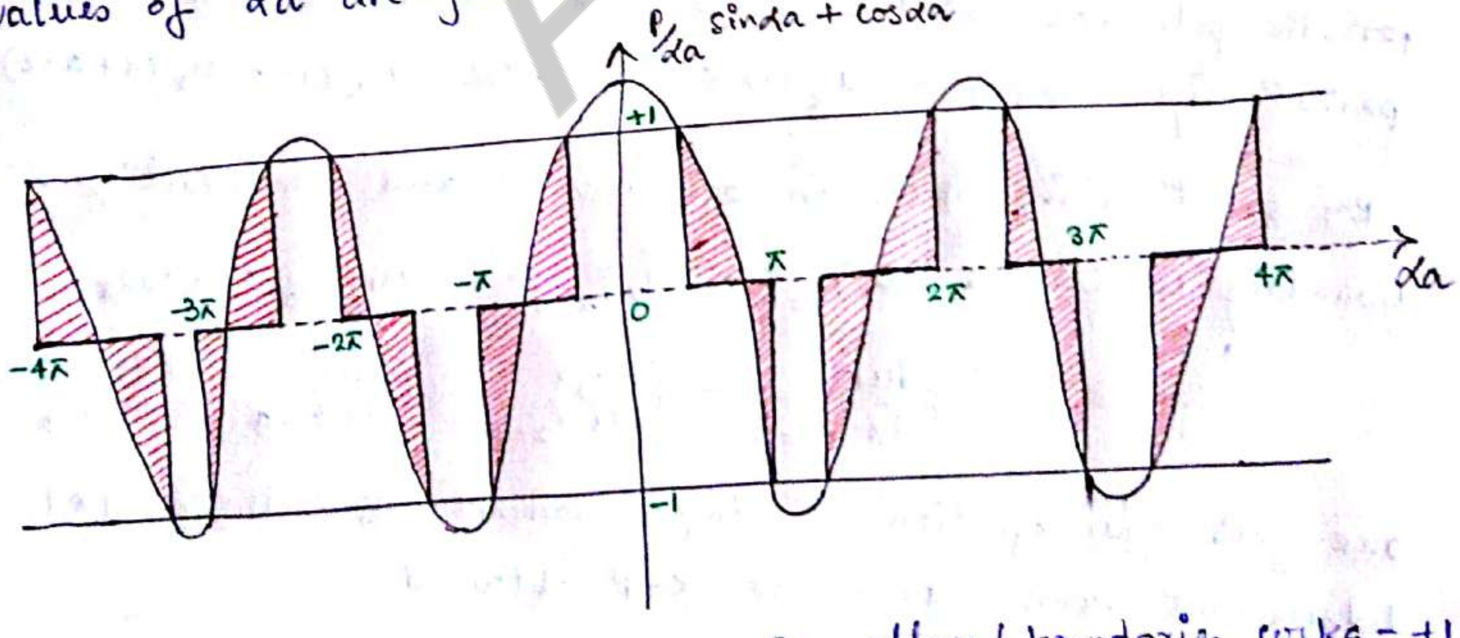
$$\therefore \boxed{P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka} \quad \text{where } P = \frac{mV_0 ab}{\hbar^2}$$

when P is increased, the area of potential barrier is increased and the electron is bound more strongly to a potential well.

$P \to 0$ means barrier is very weak & the electrons become free electron

$$\therefore \lim_{P \to 0}, \quad \alpha a = ka \quad \therefore \alpha^2 = k^2 = \frac{2mE}{\hbar^2} \quad \therefore E = \frac{\hbar^2 k^2}{2m}$$

As $\cos ka$ is bound between $+1$ and -1, LHS should take values of αa for which it lies between $+1$ & -1. $\therefore$ Such αa represent wave like solutions $\psi(x) = e^{ikx} u_k(x)$. Other values of αa are forbidden.



as $ka \to [0, \pi]$, $\cos ka \to [+1, -1]$ allowed boundaries $\cos ka = \pm 1$

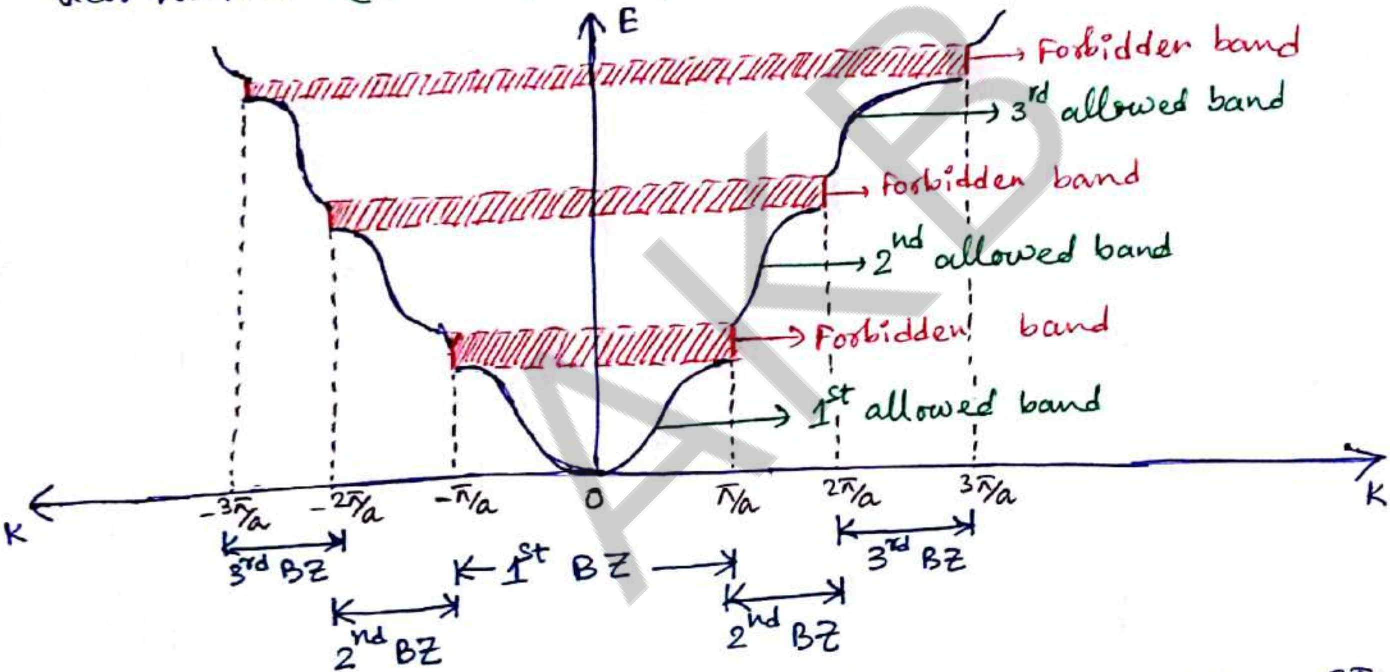
$$\therefore ka = n\pi \quad \text{or} \quad k = \frac{n\pi}{a}.$$

As αa increases, $P\frac{\sin\alpha a}{\alpha a}$ decreases, so the width of allowed energy bands ~~decrease~~ increases & forbidden energy region become narrower. As P increases, width of allowed energy bands decreases and for $P \to \infty$, they are infinitely thin & independent of K.

for $P \to \infty$, allowed αa are points, $\alpha a = \pm n\pi$

$$\text{or } \alpha^2 = \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2} \qquad \therefore E = \frac{n^2\pi^2\hbar^2}{2ma^2} \neq E(K)$$

Energy level is discrete & the electron is completely bound to their nuclei. (line spectrum) for $P = 0$ (quasi-continuous)



$E = \frac{\hbar^2 k^2}{2m}$ will now have discontinuities at $k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm \cdots$

These K values define the 1st, 2nd, 3rd, ... etc Brillouin Zones (BZ)

The curves (bands) are horizontal & at bottom & top, parabolic near top & bottom with curvature in opposite direction, within a band, energy is periodic in K. as $\cos\left(K + \frac{2\pi n}{a}\right)a = \cos Ka$ &

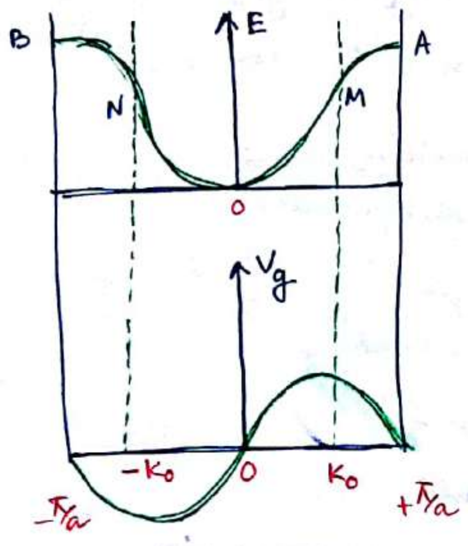
$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos Ka$ eqn. remains same.

Variation of Energy & velocity with wavevector

According to deBroglie an electron moving with a velocity v is equivalent to a wave packet moving with group velocity = particle velocity $v_g = \frac{d\omega}{dK}$. As energy of particle is $E = \hbar\omega$ or $\omega = \frac{E}{\hbar}$

$\therefore v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dK}$. Now we have for free electron $E = \frac{\hbar^2 K^2}{2m}$.

so $\frac{dE}{dK} = \frac{\hbar^2}{m}K$, $\therefore v_g = \frac{1}{\hbar}\frac{dE}{dK} = \frac{\hbar}{m}K = \frac{p}{m}$.



From band theory $E \not\propto K^2$ but varies as shown. Curve is symmetric about OE axis with points of inflexion at M & N where $\frac{dE}{dK}$ = maximum, so as v (as $v = \frac{1}{\hbar}\frac{dE}{dK}$). At points A, O, B slope $\frac{dE}{dK} = 0$. Similarly variation of v shows that at $K = 0, \pm\frac{\pi}{a}$ velocity of electron is zero. So the velocity is zero at bottom & top of Brillouin zone. At ~~of~~ inflexion point $\pm K_0$ velocity is maximum (free electron velocity)

Effective mass of an electron

The electrons in a crystal are not free but interact with the periodic potential of the lattice. So effective mass is introduced so that that can be taken as free carriers of charge (electron or hole) in our calculation.

If electron moves distance dx by electric field $\mathcal{E}$ in dt time,

then $dE = e\mathcal{E}\,dx = e\mathcal{E}\,v\,dt$ where $v = \frac{dx}{dt}$ = velocity

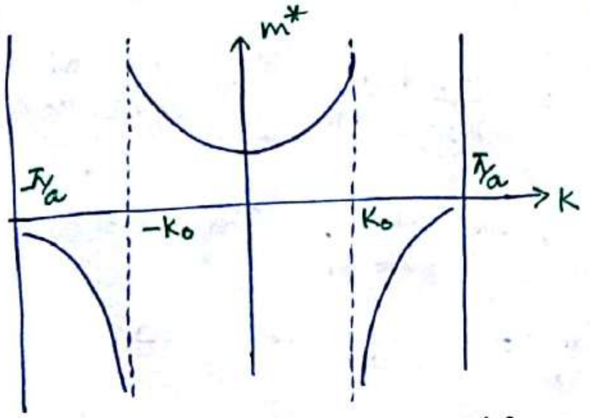
Now $v = \frac{1}{\hbar}\frac{dE}{dK}$ $\therefore dE = \frac{e\mathcal{E}}{\hbar}\frac{dE}{dK}dt$ or $\frac{dK}{dt} = \frac{e\mathcal{E}}{\hbar}$

Now $\hbar K = p$ so $\hbar\frac{dK}{dt} = \frac{dp}{dt} = F = e\mathcal{E}$

Now $a = \frac{dv}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk\,dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{F}{\hbar}$

or $\frac{a}{F} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \frac{1}{m^*}$ (using $F = m^* a$)

$\therefore\ m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$. The ratio of rest mass of free electron m to effective mass in crystal in k-state is $f_k = \frac{m}{m^*} = \frac{m}{\hbar^2}\frac{d^2E}{dk^2}$ which determines the extent to which electron can be thought free. Results of free electron theory can be applied to Band theory with m replaced by m^*.



$$E_F = \frac{\hbar^2}{2m^*}\left(\frac{3N}{8\pi V}\right)^{2/3}$$

Valence & Conduction band ; Forbidden band

The highest filled energy band which includes electrons shared in covalent bonds or electrons transferred in ionic bonds is known as valence band, denoted by E_V. When the number of valence electrons in one atom is less than the number of electrons to fill the outer orbit of other atom in solid, valence electrons are free to move to form free electron gas. A band of energy from 0 to E_F is formed known as conduction band, denoted by E_C. The forbidden energy region where no electron can remain between E_V & E_C is the forbidden band, denoted by E_g.

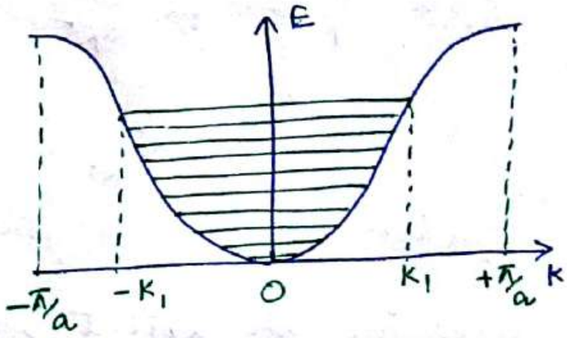
We can distinguish conductors (metals), insulators, semiconductors on the basis of band theory. $f_K = \frac{m}{m^*} = \frac{m}{\hbar^2}\frac{d^2E}{dk^2}$ that measures how much electrons can take part in electric conduction.

Now for a 1-D lattice of periodicity L, $\psi(x+L) = \psi(x)$

$\therefore\ e^{ik(x+L)}u_k(x+L) = e^{ikx}u_k(x)$

Because of periodicity $u_K(x+L) = u_K(x)$

$\therefore e^{iK(x+L)} = e^{iKx}$ or $K = \frac{2\pi n}{L}$ or $dK = \frac{2\pi}{L} dn$, $dn = \frac{L}{2\pi} dK$



dn is the number of possible states between K & $K+dK$. Since two electrons occupy each state, effective no. of free electrons in shaded region is

$$N_{eff} = 2\int_{-K_1}^{K_1} f_K \, dn = 2\int_{-K_1}^{K_1} \frac{m}{\hbar^2} \frac{d^2E}{dK^2} \frac{L}{2\pi} dK$$

$$= \frac{mL}{\pi\hbar^2}\int_{-K_1}^{K_1} \frac{d^2E}{dK^2} dK = \frac{2mL}{\pi\hbar^2}\int_{0}^{K_1} \frac{d^2E}{dK^2} dK = \frac{2mL}{\pi\hbar^2}\left[\frac{dE}{dK}\right]_0^{K_1} = \frac{2mL}{\pi\hbar^2}\left(\frac{dE}{dK}\right)_{K_1}$$

as $\frac{dE}{dK}$ at $K=0 = 0$. So N_{eff} depends on $\left(\frac{dE}{dK}\right)_{K_1}$. When the band is completely full so atop the band $\frac{dE}{dK} = 0$ $\therefore N_{eff} = 0$.

CW Dispersion relation for a 1D crystal of lattice constant a is $E(K) = E_0 - \alpha - 2\beta \cos Ka$ where E_0, α, β constants. Find out the effective mass of the electron at the bottom & top of the band.

We know $m^* = \frac{\hbar^2}{\frac{d^2E}{dK^2}} = \frac{\hbar^2}{2\beta a^2 \cos Ka}$

Atop the band $\cos Ka = \cos\pi = -1$, bottom of band, $\cos Ka = \cos 0 = 1$

$\therefore m^*_{top} = -\frac{\hbar^2}{2\beta a^2}$, $m^*_{bottom} = \frac{\hbar^2}{2\beta a^2}$