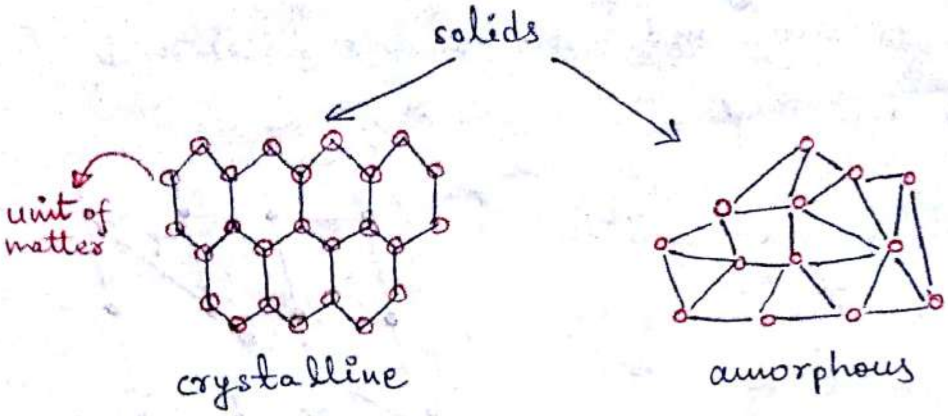
SOLID STATE PHYSICS

Crystal structure, direct lattice & (un)holy grail



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

what's "solid"? → elasticity

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

$x =$ displacement

$l =$ length of lattic

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

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 $K \to 0$, $\bar{x}^2 \to \infty \longrightarrow$ "rigidity"

amorphous solids ⟷ highly viscous, supercooled liquids.

Example pitch, plastic, silicate glass.

SALIENT FEATURES

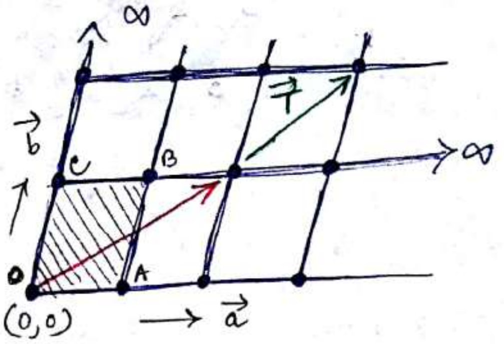
(i) molecular motion is irregular but distance is more or less same with elastic solid.

(ii) no regular shape → 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 $\vec{r}' = \vec{r} + \vec{T}$

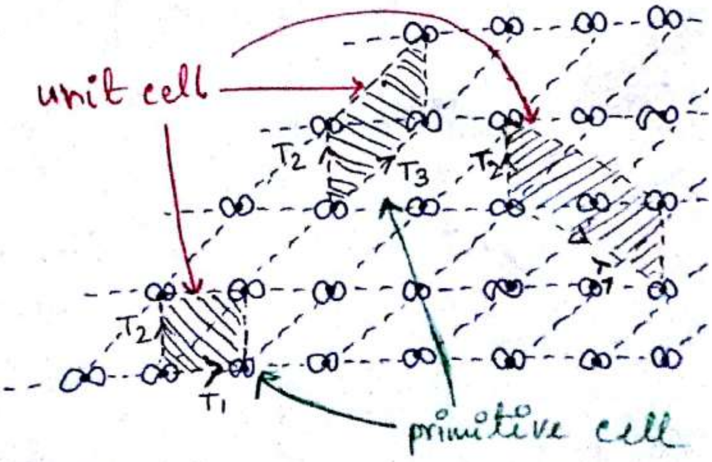
$$= \vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

where n_1, n_2, n_3 are integers.

primitive lattice & Unit cell

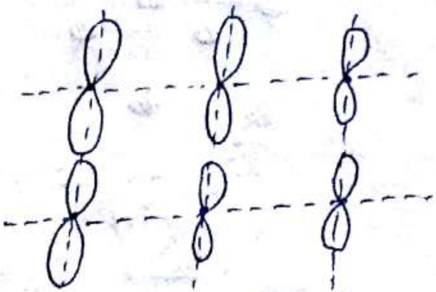
Unit cell is volume from which entire crystal can be constructed by translational repitition. (OABC parallelogram)

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.

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

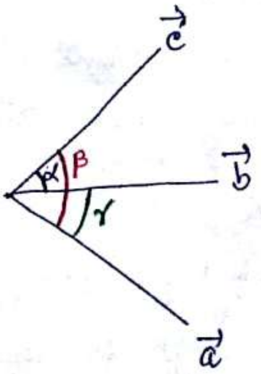
physical significance : number density $n(\vec r) = \sum_{\vec T} \delta(\vec r - \vec T)$

(point mass atom)

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 $\vec c_\alpha$.

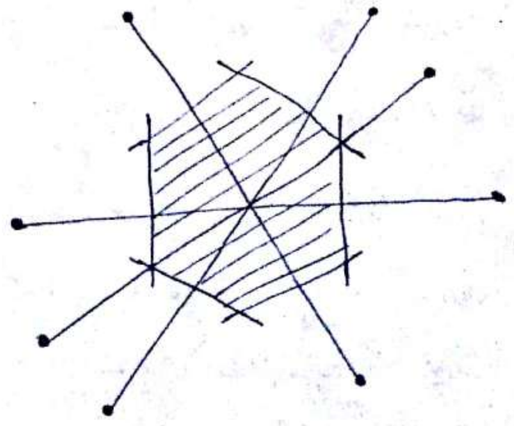
$$\rho(\vec r) = \rho(\vec r + \vec T)$$



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

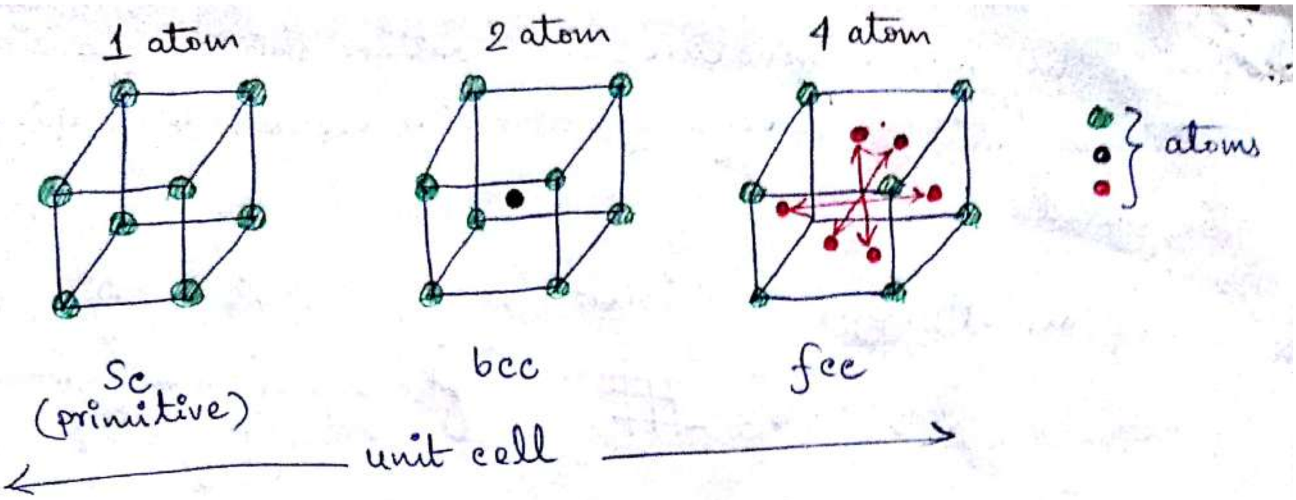
$$\alpha = \beta = \gamma = \frac{\pi}{2}$$

Wigner-Sietz primitive cell



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

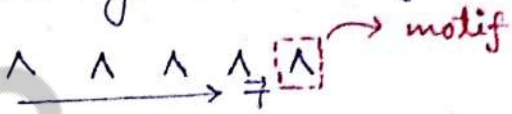
This is WS primitive cell.



Elements of symmetry

A symmetry operation transforms the crystal to itself.

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



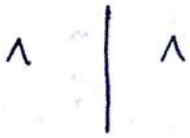
(ii) Rotation $n\phi = 2\pi$

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

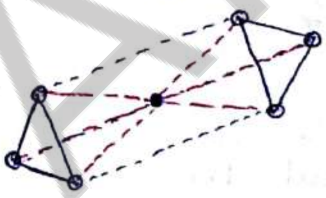
n = multiplicity of rotation axis.

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

(iii) Reflection mirror image



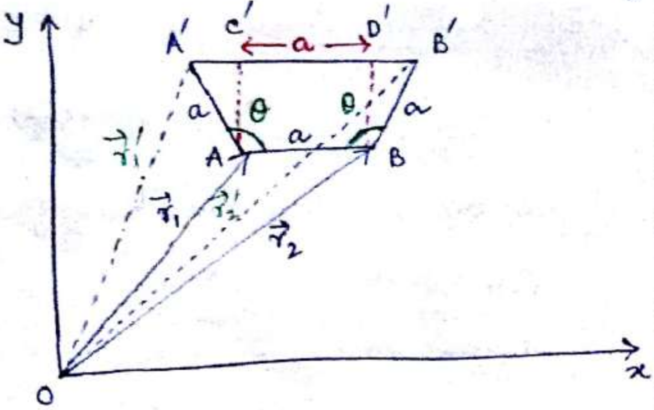
(iv) Inversion
(only for 3D lattice)



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 $|\cos\theta| = \left|\frac{q-1}{2}\right|$

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

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

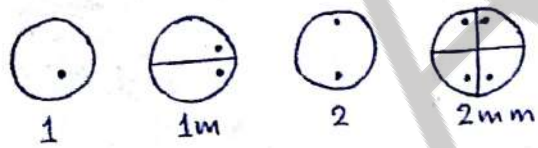
$\{q = 2, \theta = \frac{2\pi}{6}\}$, $\{q = 3, \theta = \frac{2\pi}{1}\}$.

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.

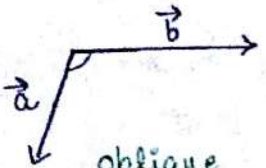


Total 32 point groups.

Group of all symmetry elements is space group.

In 2D : 17, 3D : 230.

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

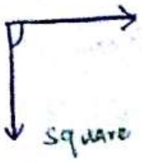


oblique

$|\vec{a}| \neq |\vec{b}|, \phi \neq \frac{\pi}{2}$

$\{\frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}\}$

rotation



square

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

$\{\frac{2\pi}{4}\}$

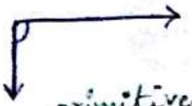
rotation

hexagonal

$|\vec{a}| = |\vec{b}|, \phi = \frac{2\pi}{3}$

$6\{\frac{2\pi}{[illegible]}\}$

rotation

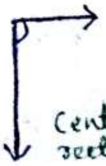


primitive rectangular

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

$\{\frac{2\pi}{2}\}$

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	Uniaxial crystal
Tetragonal	P, I	$\alpha = \beta = \gamma = 90°$	$a = b \neq c$	
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)

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

Body centered cubic cell (bcc)

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

Face centered cubic cell (fcc)

# 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.

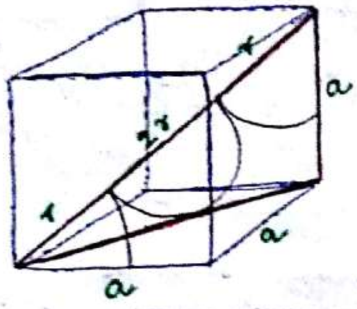
sc cell, coord. no. = 6.

bcc cell, coord. no. = 8

fcc cell, coord. no. = 4 × 3 = 12

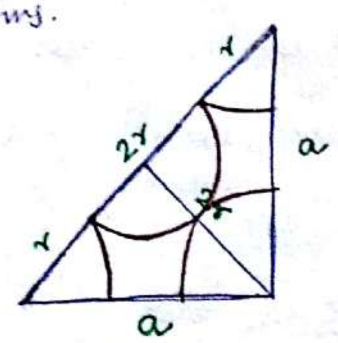
1 plane ↳ xy, yz, xz plane

Atomic radius Distance between centre of two touching atoms.



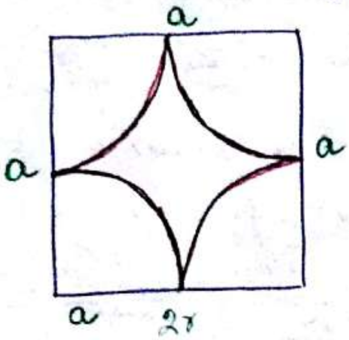
[bcc]

$$(4r)^2 = (\sqrt{2}a)^2 + a^2$$
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

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

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

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

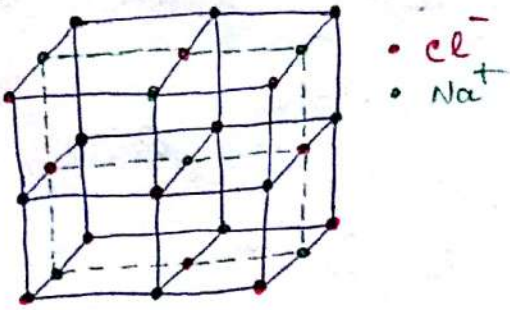
$$\therefore f = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 52\%$$

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.

NaCl structure



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

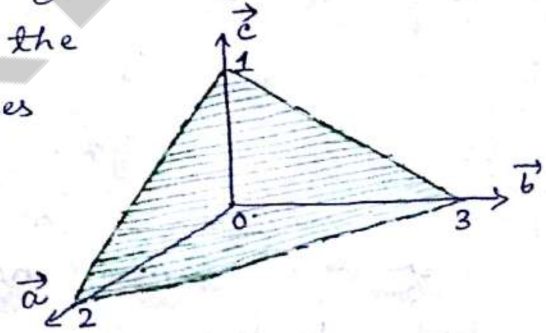
Na $(0,0,0)$ $(\frac{1}{2},\frac{1}{2},0)$ $(\frac{1}{2},0,\frac{1}{2})$ $(0,\frac{1}{2},\frac{1}{2})$

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).

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



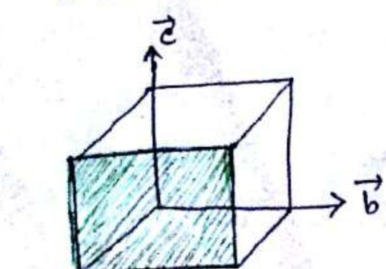
(a) In terms of lattice constant, find the intercept of the plane on crystal axes $\vec{a}, \vec{b}, \vec{c}$ (primitive or nonprimitive)

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

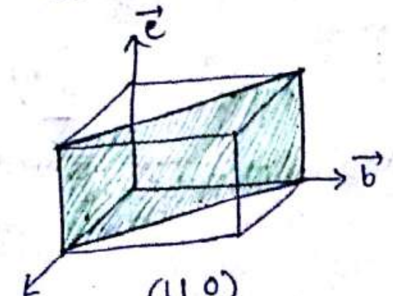
(b) Take reciprocals of them & reduce to smallest 3 integers, Denote with (h, k, l)

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

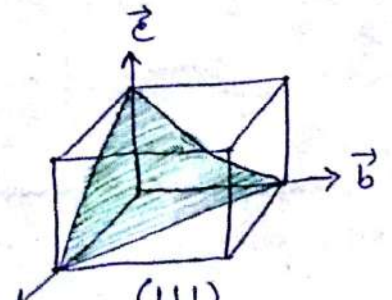
Miller index is $(3,2,6)$ plane.



(100)



(110)



(111)

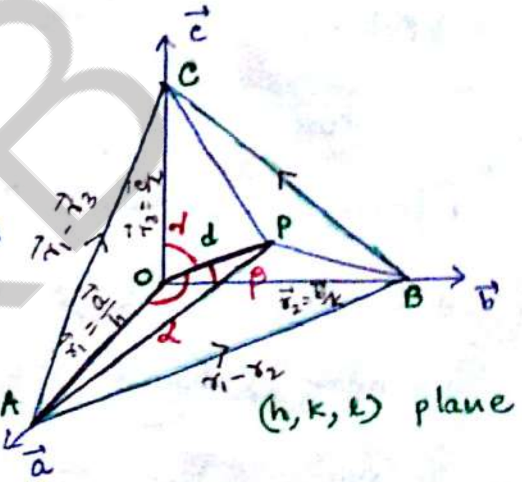
If plane cuts negative side of axis, M-index $(h, \bar{k}, l)$
(say $-\vec{b}$)

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

$= \vec{a}\cdot\vec{a} - \vec{b}\cdot\vec{b} = 0$. (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 $\Rightarrow k_1, k_2, k_3$ 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 $\vec{a}^{**} = 2\pi \frac{\vec{b}^* \times \vec{c}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$,

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

Reciprocal of sc lattice

$\vec{a} = a\hat{i}$, $\vec{b} = b\hat{j}$, $c = c\hat{k}$.

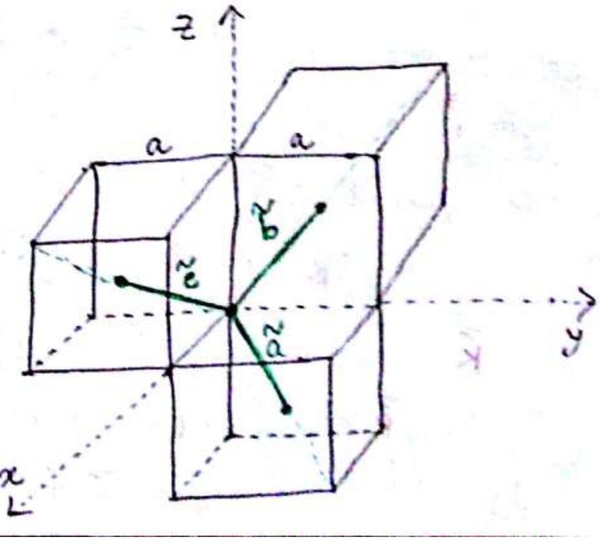
$$\therefore \vec{a}^* = 2\pi \frac{b\hat{j} \times c\hat{k}}{a\hat{i} \cdot (b\hat{j} \times c\hat{k})} = 2\pi \frac{bc}{abc}\hat{i} = \frac{2\pi}{a}\hat{i}$$

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

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

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

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

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

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

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

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

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

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

∴ 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,

$$eV = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{eV} = \frac{6.62\times10^{-34} \times 3\times10^{8}}{1.6\times10^{-19} \times 10^{4}} \quad (\text{say } V = 10\,\text{kV})$$

$$= 1.24\ \text{Å}.$$

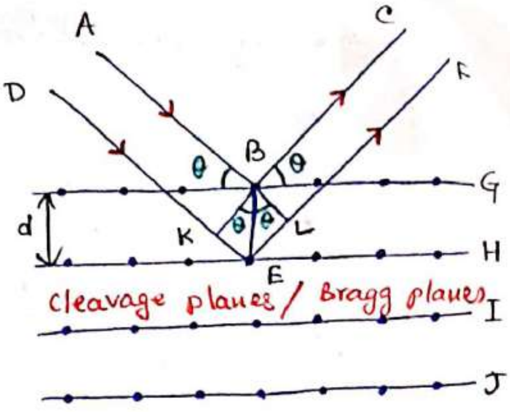
$\lambda_{\text{X-ray}} \approx a$ (elastic scattering without change in λ)

$\lambda_{\text{visible/UV}} >> a$ (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 $\lambda_{x\text{-ray}}$.



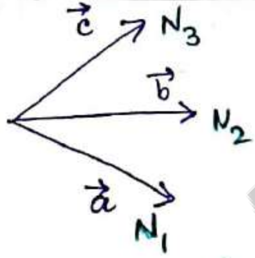
Path difference between ray [AB, BC] & [DE, EF] is KE + EL

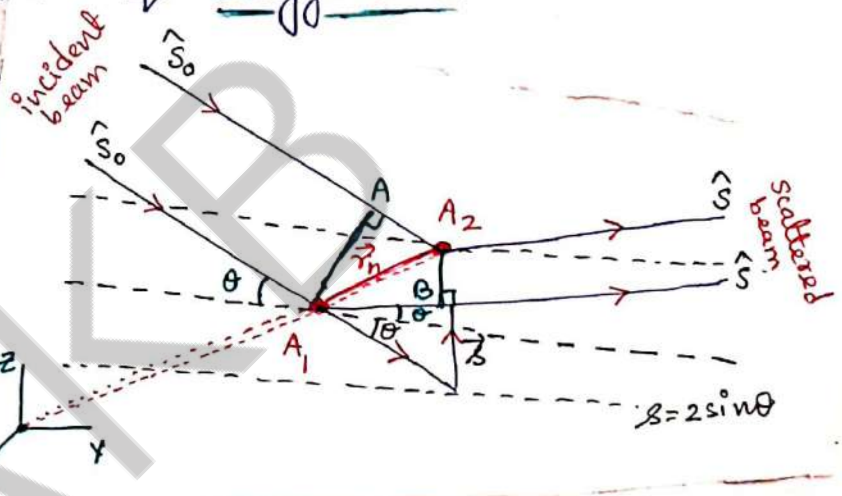
$= d\sin\theta + d\sin\theta = 2d\sin\theta$. So for constructive interference,

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

λ, θ = Known, d = ~~unk~~ 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 $d = \vec{r}_n \cdot \vec{S} - \vec{r}_n \cdot \vec{S}_0 = \vec{r}_n \cdot \vec{s}$

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

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

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

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

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

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

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

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

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

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

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

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

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

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 $= N_1^2$

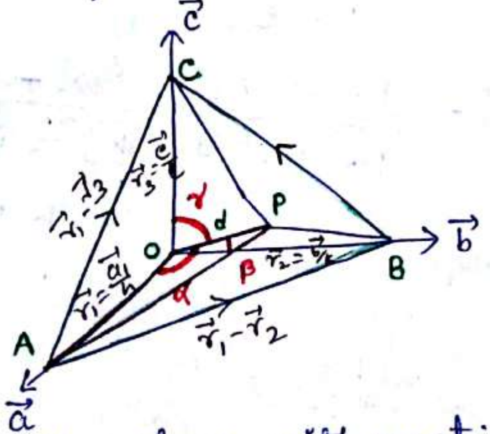
Similarly $\lim_{\psi_2 \to K\pi} \frac{\sin^2(N_2\psi_2)}{\sin^2\psi_1} = N_2^2$, $\lim_{\psi_3 \to l\pi} \frac{\sin^2(N_3\psi_3)}{\sin^2\psi_3} = N_3^2$

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

$\therefore$ $\frac{2\pi a \sin\theta \cos\alpha}{\lambda} = h\pi$, $\frac{2\pi b \sin\theta \cos\beta}{\lambda} = K\pi$, $\frac{2\pi c \sin\theta \cos\gamma}{\lambda} = l\pi$,

$$\boxed{\begin{aligned} 2a \sin\theta \cos\alpha &= h\lambda \\ 2b \sin\theta \cos\beta &= K\lambda \\ 2c \sin\theta \cos\gamma &= l\lambda \end{aligned}}$$

"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 $\frac{a}{h}\cos\alpha = \frac{b}{K}\cos\beta = \frac{c}{K}\cos\gamma = d$.

∴ 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 Laués 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 $\frac{1}{\cancel{2}}\frac{\cancel{2\pi}}{\lambda}\vec{s}\cdot\vec{a} = h\cancel{\pi}$

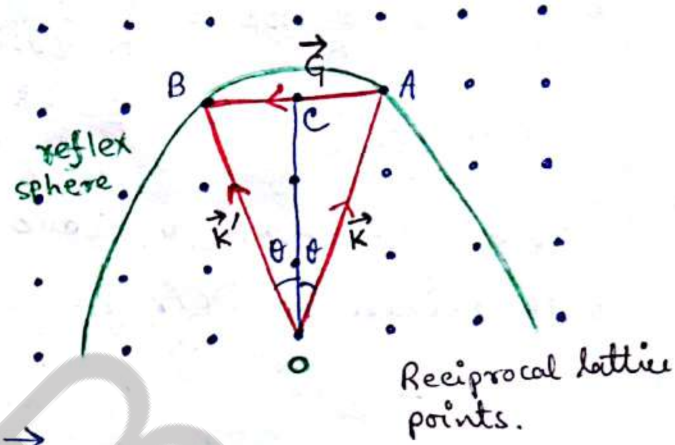
or $\frac{2\pi\vec{s}}{\lambda}\cdot\vec{a} = 2\pi h$.

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.

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

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

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

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

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

∴ $\lambda = 3.84$ 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/m^3, molecular weight 74.5 kg. Avogadro's no. N = 6.023×10^{26} kg/mole.

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

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

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

$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}} = 3.63$ 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 Braggs glancing angle is 15° for 1st order, then calculate glancing angles for 2nd & 3rd order spectrum?

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

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

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

$$\theta_1 = \sin^{-1}\left[\frac{\lambda}{2d}\right] = \sin^{-1}\left[\frac{1.54\times10^{-10}}{2\times2.67\times10^{-10}}\right] = 16.76^\circ.$$

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

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

(b) $2d\sin\theta_1 = \lambda$, $\theta_1 = 15^\circ$ $\therefore$ ~~$\lambda = 0.1$~~ $\frac{\lambda}{2d} = \sin 15^\circ = 0.2588$

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

$\theta_2 = 31.17^\circ$

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

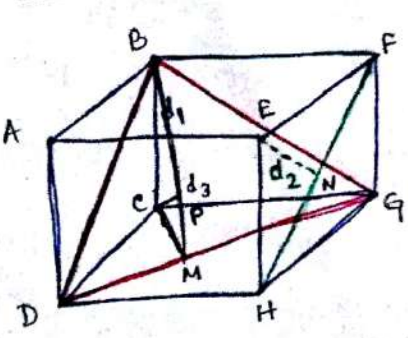
$\theta_3 = 50.93^\circ.$

HW 1. Molecular weight of rock salt (NaCl) crystal is 58.5 Kg/Kilomole & density 2.16×10^3 Kg/m³. 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°.

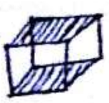
2. If X-rays with $\lambda = 0.5$ Å is diffracted at 5° in 1^{st} order, what is the spacing between adjacent planes of a crystal? At ~~what~~ what angle will 2^{nd} maximum occur?

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



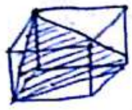
d is to be calculated for given X-ray (λ) by using different plane.



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

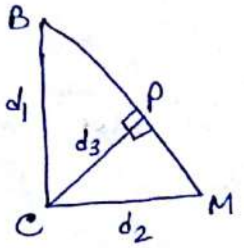
Diagonal plane BFHD inclined at $\pi/4$ to (100) planes

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



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

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



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

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

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 1st order reflection

θ_1 (from (100) plane) = 5.22° θ_3 (from (111) plane) = 9.05°.

θ_2 (from (110) plane) = 7.30°

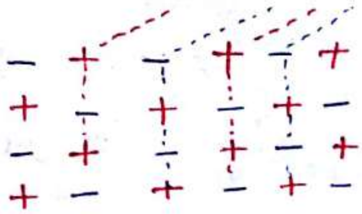
as $\frac{1}{d} = \frac{2\sin\theta}{\lambda}$ ∴ $\frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = \sin 5.22 : \sin 7.30 : \sin 9.05$

$= 0.0910 : 0.1272 : 0.1570$

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

So KCl has cubic crystal symmetry.

NaCl crystal



8 ions at corner → 4 Na^+, 4 Cl^-

∴ 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 = 2.17×10^3 kg/m^3.

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

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

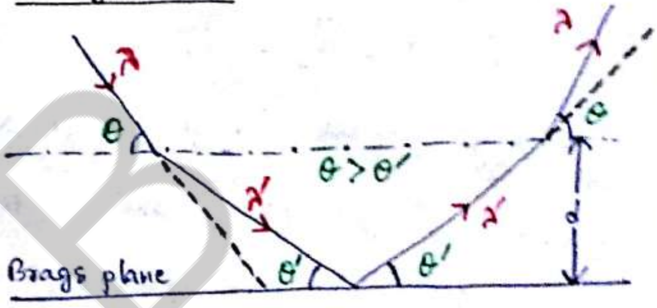
1^{st} order, $n=1$, $\theta = 11.8^\circ$ $\quad \lambda = 2d\sin\theta = 2\times 2.814\times 10^{-10} \times \sin 11.8^\circ$
$= 1.12\ \mathring{A}$.

2^{nd} order, $n=2$, $\theta = 23.5^\circ$, $\quad \lambda = \frac{2d\sin\theta}{2} = 2.814\times 10^{-10}\times \sin 23.5^\circ$
$= 1.12\ \mathring{A}$.

3^{rd} order, $n=3$, $\theta = 36^\circ$, $\quad \lambda = \frac{2d\sin\theta}{3} = \frac{2}{3}\times 2.814\times 10^{-10}\times \sin 36^\circ$
$= 1.12\ \mathring{A}$.

∴ 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, therefractive index is $\mu = \frac{\lambda}{\lambda'} = \frac{\cos\theta}{\cos\theta'}$

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

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

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

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

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

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

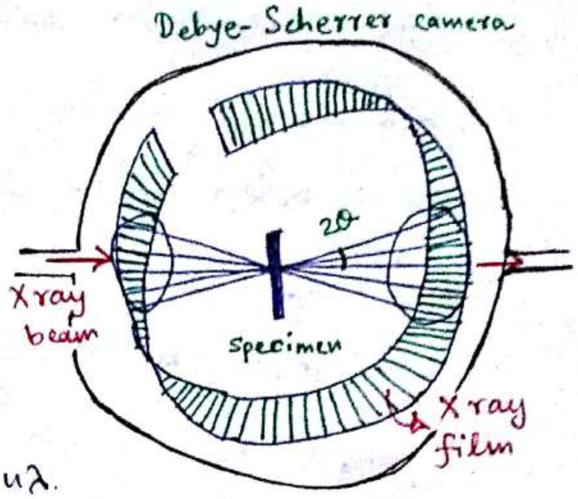
$$\left[2d\sin\theta = n\lambda \text{ or } \frac{1}{\sin^2\theta} = \frac{4d^2}{n^2\lambda^2}\right]$$

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

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

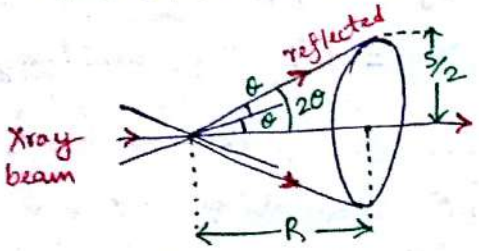
Powder Method of XRD

Debye-Scherrer camera



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

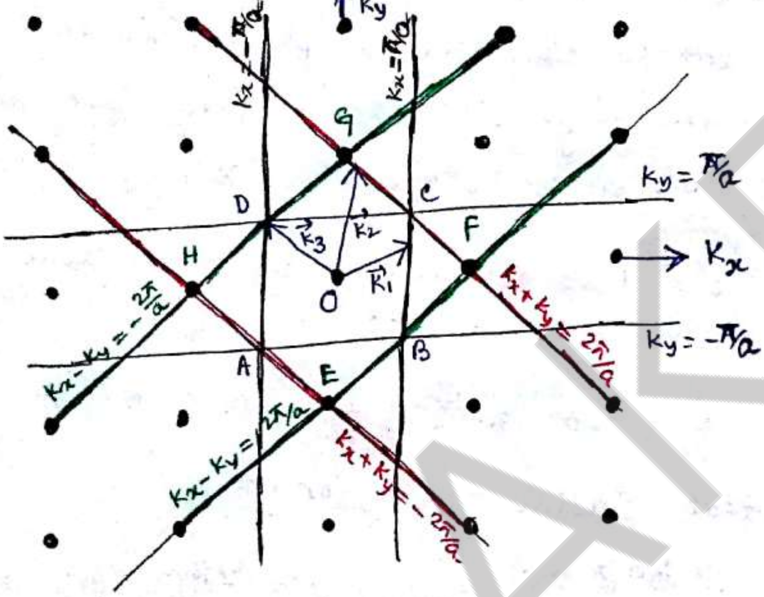
$\vec{k} = k_x\hat{i} + k_y\hat{j}$. ∴ from Bragg's vectorial condition

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

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

If h = 0, k = ±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 = ±1, k = ±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 ⇒ $2d\sin\theta = \lambda$. EFGH ⇒ $2d\sin\theta = 2\lambda$ & 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

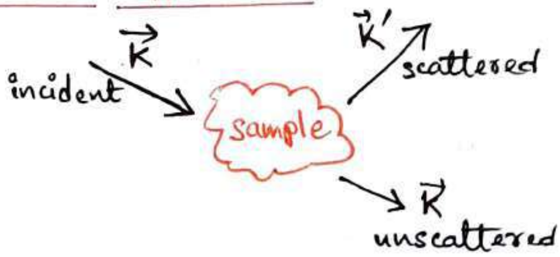
$$\vec{a}^* = \frac{2\pi}{a}(\hat{i}+\hat{j}),\ \vec{b}^* = \frac{2\pi}{a}(\hat{j}+\hat{k}),\ \vec{c}^* = \frac{2\pi}{a}(\hat{k}+\hat{i}).$$

$$\vec{G} = \frac{2\pi}{a}\left[(h+l)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}\right]$$ & 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 ~~dodaeme~~ by normal bisector of 12 vectors $\Rightarrow$ rhombic dodecahedron.

Structure of Solids – Fermi's Golden Rule approach



In scattering experiment, transition rate between incident plane wave state $|\vec{K}\rangle$ with momenta $\hbar\vec{K}$ to outgoing (scattered) plane wave state $|\vec{K}'\rangle$ with momenta $\hbar\vec{K}'$ is measured. If the scattering medium interaction potential is $U(\vec{x})$, then from Fermi's golden rule, the transition rate per unit time is

$$\Gamma_{\vec{K}\vec{K}'} = \langle\vec{K}|U|\vec{K}'\rangle = \int d^d x' \, e^{-i\vec{K}\cdot\vec{x}'} U(\vec{x}') \, e^{i\vec{K}'\cdot\vec{x}'} , \qquad d = 1,2,3$$

so that differential cross-section per unit solid angle is

$$\frac{d^2\sigma}{d\Omega} \sim \frac{2\pi}{\hbar} |\langle K|U|K'\rangle|^2 \, \delta(E_{\vec{K}} - E_{\vec{K}'}).$$

This is true for any arbitrary arrangement of atoms/lattice points (periodic/aperiodic). But for a periodic crystal $\vec{x}' = \vec{x} + \vec{T}$ and $U(\vec{x}+\vec{T}) = U(\vec{x})$

so that

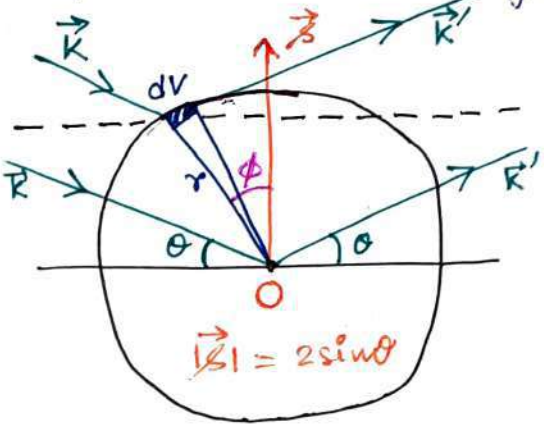
$$\begin{aligned}
\Gamma_{KK'} &= \int d^d\vec{x}' \, e^{-i(\vec{K}-\vec{K}')\cdot\vec{x}'} U(\vec{x}') \\
&= \sum_{\vec{T}} \int_{\text{unit cell}} d^d\vec{x} \, e^{-i(\vec{K}-\vec{K}')\cdot(\vec{x}+\vec{T})} U(\vec{x}+\vec{T}) \\
&= \overset{= 0 \text{ if } \vec{K}-\vec{K}' \neq \vec{G}}{\left[\sum_{\vec{T}} e^{-i(\vec{K}-\vec{K}')\cdot\vec{T}}\right]} \left[\int_{\text{unit cell}} d^d\vec{x} \, e^{-i(\vec{K}-\vec{K}')\cdot\vec{x}} U(\vec{x})\right] \\
&= \left[\sum_{\vec{T}} e^{-i\vec{G}\cdot\vec{T}}\right] \int_{\text{unit cell}} d^d x \, e^{-i\vec{G}\cdot\vec{x}} U(\vec{x}) \qquad \left(\because \vec{K}-\vec{K}' = \vec{G}\right) \\
&= N_c S_{\vec{G}} \qquad \text{where } N_c = \#\text{ of cells in lattice}
\end{aligned}$$

and $S_{\vec{G}}$ is known as the structure factor (Geometrical). This is the scattering amplitude and square of this is the scattering intensity.

The atomic scattering factor (form factor) is defined as the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by a single electron at a point.

$$f = \frac{\text{Amplitude of radiation scattered from an atom}}{\text{Amplitude of radiation scattered from an electron}} \leq Z$$

where Z = atomic number = # of electrons present in the atom. Due to weak interaction with X-rays with atomic nuclei, the scattering due to nuclei is neglected compared with scattering due to electrons.



Let us consider spherically symmetric electron distribution of atom and we want to calculate scattering from charge $\rho(\vec{r})\,dV$ at a distance $\vec{r}$ from origin and electron at origin O. We know that the phase difference between incident & scattered X-ray is $\frac{2\pi}{\lambda}\vec{r}\cdot\vec{s}$. So if the X-ray scattering along $\vec{K}'$ from the electron at O is $A e^{i(kx-\omega t)}$ then the scattered intensity from $\rho(r)\,dV$ will be

$$A e^{i\left[(kx-\omega t)+\underbrace{\frac{2\pi}{\lambda}\vec{r}\cdot\vec{s}}_{\text{''}\phi_r}\right]}\rho(\vec{r})\,dV$$

$$\therefore df = \frac{\text{Amplitude of radiation scattered by } \rho(\vec{r})\,dV}{\text{Amplitude of radiation scattered by electron at O}}$$

$$= \frac{A e^{i[(kx-\omega t)+\phi_r]}\rho(\vec{r})\,dV}{A e^{i(kx-\omega t)}} = e^{i\frac{2\pi}{\lambda}(\vec{r}\cdot\vec{s})}\rho(\vec{r})\,dV$$

Now $dV = 2\pi r^2 \sin\phi\, d\phi\, dr$, $\frac{2\pi}{\lambda}(\vec{r}\cdot\vec{s})\cancel{\rho(\vec{r})dr} = \frac{2\pi}{\lambda} r|\vec{s}|\cos\phi$

$$= \frac{2\pi}{\lambda} r\, 2\sin\theta\cos\phi = \frac{4\pi}{\lambda} r\sin\theta\cos\phi = \mu r\cos\phi$$

$$\therefore \text{Atomic form factor } f = \int df = \int_{r=0}^{\infty}\int_{\phi=0}^{\pi} e^{i\mu r\cos\phi}\rho(r)\,2\pi r^2\sin\phi\,d\phi\,dr$$

Now $\int_{\phi=0}^{\pi} e^{i\mu r\cos\phi}\sin\phi\,d\phi = \frac{2\sin\mu r}{\mu r}$; $\lim_{\theta\to 0} \mu\to 0$ & $\frac{\sin\mu r}{\mu r}\to 1$.

$$\therefore f = \int_{r=0}^{\infty} 4\pi r^2\rho(r)\frac{\sin\mu r}{\mu r}\,dr \underset{\mu\to 0}{\overset{\lim}{=}} \int_{r=0}^{\infty} 4\pi r^2\rho(r)\,dr = Z = \#\text{ of electrons in ato}$$

For atoms containing large number of electrons (beyond Rubidium) using Hartree-Fock approximation or from Thomas-Fermi model $\rho(\vec{r})$ can be obtained that match experiments fairly well.

Geometrical Structure Factor

$$\text{Geometrical Structure factor} = \frac{\text{Amplitude of radiation scattered by unit cell}}{\text{Amplitude of radiation scattered by electron at origin.}}$$

The position of j^{th} atom in unit cell is

$$\vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c}\,, \quad 0 \le [x_j, y_j, z_j] \le 1.$$

For a given (hkl) reflection the scattering amplitude is

$$F_{hkl} = \sum_j f_j e^{i\phi_j} = \sum_j f_j e^{i\left(\frac{2\pi}{\lambda}\right)(\vec{r}_j\cdot\vec{S})},$$

Here f_j is the atomic form factor, ϕ_j is the phase differance between scattering from scattering from origin and j^{th} atom of the unit cell to the scattering from origin and j^{th} atom of the unit cell.

$\sum$ is over all the atoms in the unit cell.

from $\vec{a}\cdot\vec{S} = 2a\sin\theta\cos\alpha = h\lambda$, $\vec{b}\cdot\vec{S} = 2b\sin\theta\cos\beta = k\lambda$

and $\vec{c}\cdot\vec{S} = 2c\sin\theta\cos\gamma = l\lambda$ (Laue equations)

$$F_{hkl} = \sum_j f_j e^{i\frac{2\pi}{\lambda}[(x_j\vec{a}+y_j\vec{b}+z_j\vec{c})\cdot\vec{S}]}$$

$$= \sum_j f_j e^{i\frac{2\pi}{\lambda}[x_j(h\lambda)+y_j(k\lambda)+z_j(l\lambda)]}$$

$$= \sum_j f_j e^{i2\pi(hx_j+ky_j+lz_j)} \underset{\substack{\text{identical}\\\text{atom}}}{=} f\sum_j e^{i2\pi(hx_j+ky_j+lz_j)}$$

$\therefore$ Geometrical structure factor $= \dfrac{F_{hkl}}{f} = \sum_j e^{i2\pi(hx_j+ky_j+lz_j)}$

Scattering intensity $I = F^*_{hkl}F_{hkl} = \left[\sum_j f_j\cos 2\pi(hx_j+ky_j+lz_j)\right]^2 + \left[\sum_j f_j\sin 2\pi(hx_j+ky_j+lz_j)\right]^2.$

GSF for sc lattice There is only 1 atom per unit cell which can be assumed to be at origin ($x_j = y_j = z_j = 0$)

∴ $F_{hkl} = f$. & $I = f^2$. So all lines satisfying Bragg's law will be visible provided the atomic form factor f is large enough.

GSF for bcc lattice There are two atoms per unit cell, one at origin ($x_1 = y_1 = z_1 = 0$) & other at body diagonal ($x_2 = y_2 = z_2 = \frac{1}{2}$), so that

$$F_{hkl} = f \sum_j e^{i2\pi(hx_j + ky_j + lz_j)}$$
$$= f[1 + e^{i\pi(h+k+l)}].$$

So for a reflection where $h+k+l = 2n$ (even) we have $F^{even}_{hkl} = f(1+1) = 2f$, $I = 4f^2$. for $h+k+l = 2n+1$ (odd), $F^{odd}_{hkl} = f(1-1) = 0$ & $I = 0$. Therefore (100), (111), (210) etc reflections will be missing in first order, but (200) will be present. This is the case with Metallic Sodium.

GSF for fcc lattice There are 4 atoms per unit cell at $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, $(0,\frac{1}{2},\frac{1}{2})$, so that

$$F_{hkl} = f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)}].$$

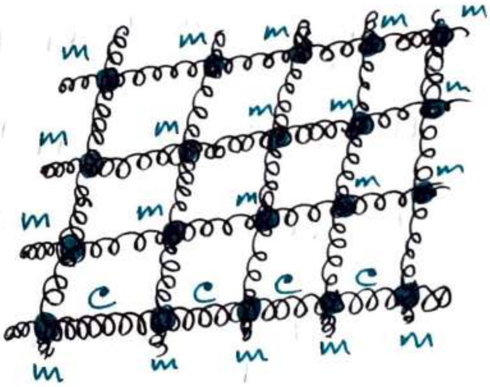
If $h,k,l \overset{all}{=}$ even/odd, $F_{hkl} = 4f$, $I = 16f^2$, while if h,k,l = mix of even & add, $F_{hkl} = 0$, $I = 0$. So no reflecti can occur for which (h,k,l) are partly even & partly odd.

systematic absences of scattering

sc	all (h,k,l) allowed
bcc	h+k+l must be even
fcc	h,k,l must be all odd or all even

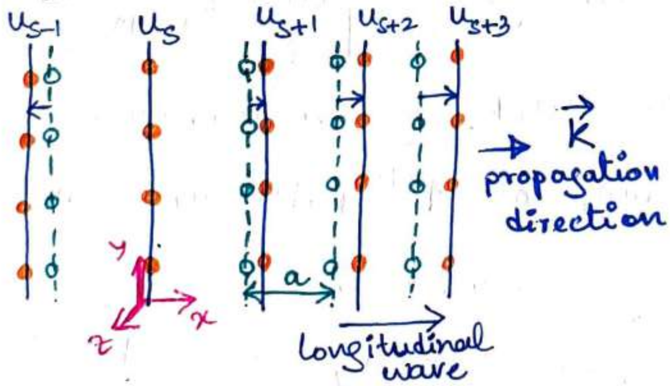
Crystal Vibrations

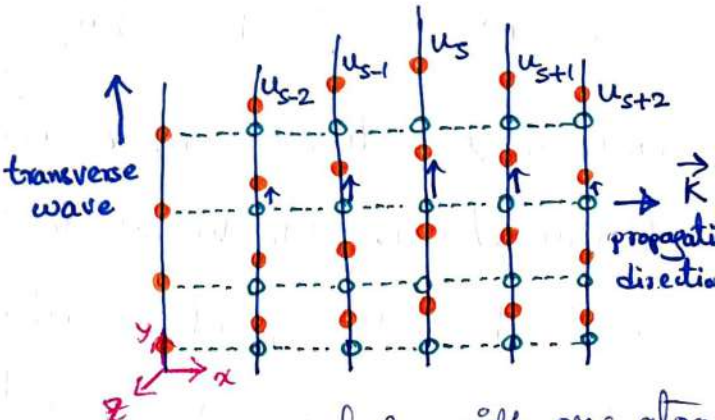
A solid is comprised of atoms/molecules that are closely packed & there is a competition between attractive long-ranged electrostatic force & short-ranged repulsive (mostly steric or soft) force, due to which atoms/molecules remain fixed to their equilibrium position, yet due to interatomic vibration, vibrate about their mean position. These are known as lattice vibrations. There exists various elementary excitations in solids, e.g. EM wave (photon), elastic wave (phonon), collective electron wave (plasmon), magnetization wave (magnon), electron interacting with elastic deformation (polaron), polarization wave (exciton) & so on.



To closest representation, crystals are periodic atoms connected with elastic springs. Dynamics of one atom/molecule is coupled to other atoms/molecules & the lattice will freely vibrate in normal mode. Thermal properties of solids (e.g. thermal conductivity, specific heat) are attributed to this kind of vibration.

Vibrations of a 1D monoatomic chain





Let us consider the elastic vibrations of a crystal with one atom in the primitive unit cell. We want to find the frequency of an elastic wave as a function of $\vec{K}$ & elastic constants. When an elastic wave propagates along cube edge ([100]), face diagonal ([110]) and body diagonal ([111]), then entire plane of atoms move in phase with displacements in ∥ & ⊥ direction of $\vec{K}$. The problem becomes 1D as we can define displacement of s-plane from its equilibrium position as u_s & for every $\vec{K}$ there will be 3 modes, 1 for longitudinal polarization & 2 for transverse polarization

At low temperature, elastic energy is harmonic in displacement so that force exerted on s-plane by $s \pm p$ plane ($p=1$ corresponds to nearest neighbour plane only) is proportional to $u_{s\pm p} - u_s$, i.e.

$$F_s = c(u_{s+1} - u_s) + c(u_{s-1} - u_s) = m\frac{d^2u_s}{dt^2}, \quad c = \text{force constant}$$

$$m\ddot{u}_s = c(u_{s+1} + u_{s-1} - 2u_s) \quad m = \text{mass of atom}$$

The periodic travelling wave solution of the displacement is

$$u_{s\pm1} = u e^{i(\omega t + (s\pm1)Ka)}, \quad a = \text{interplanar spacing},$$

$$K = \text{wave vector}.$$

$$u_s = u e^{i(\omega t + sKa)} \quad Ka = x \text{ is the displacement}.$$

$$\therefore -\omega^2 m u \cancel{e^{i(\omega t + sKa)}} = c u \cancel{e^{i\omega t}}\left[e^{i(\cancel{s}+1)Ka} + e^{i(\cancel{s}-1)Ka} - 2e^{i\cancel{s}K}\right]$$

$$\text{or } \omega^2 m = -c\left[e^{iKa} + e^{-iKa} - 2\right] = c\left[2 - 2\cos Ka\right]$$

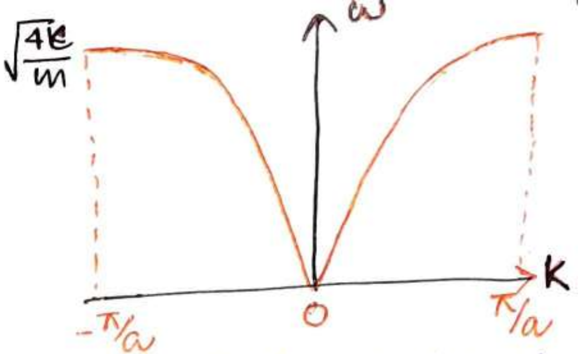
$$\text{or } \omega^2 = \frac{2c}{m}(1-\cos Ka) = \frac{4c}{m}\sin^2\frac{Ka}{2} \Rightarrow \boxed{\omega = \pm\sqrt{\frac{4c}{m}}\sin\frac{Ka}{2}}$$

This is the dispersion relation $\omega = \omega(K)$ for a monoatomic linear chain. We know that boundary of 1st Brillouin zone is at $K = \pm\frac{\pi}{a}$, at which slope of ω vs. K is

$$\left.\frac{d\omega}{dK}\right|_{K=\pm\pi/a} = \pm\sqrt{\frac{4c}{m}}\,\frac{a}{2}\cos\left.\frac{Ka}{2}\right|_{K=\pm\pi/a} \sim \cos\frac{\pi}{2} = 0, \text{ means } K = \pm\frac{\pi}{a}$$

is an inflection point (change of direction of curvature)

Energy of elastic wave is quantised & the quantum of energy is known as "phonon". Phonon wave propagates in crystal at speed of sound.



To find out the range of K that are physically significant notice that $\frac{u_{s+1}}{u_s} = \frac{u e^{i[\omega t+(s+1)Ka]}}{u e^{i[\omega t + sKa]}} = e^{iKa}$ that defines the range of K as $-\pi \leq Ka \leq \pi$ or $-\pi/a \leq K \leq \pi/a$ (1^{st} BZ) & by a linear transformation, any other value of $K' = K \pm \frac{2\pi n}{a}$, that lie outside the 1^{st} BZ can be mapped back to 1^{st} BZ as $\frac{u_{s+1}}{u_s} = e^{iK'a} = e^{iKa} e^{\pm i 2\pi n} = e^{iKa}$. So the displacement can always be described by K within 1^{st} BZ by adding/substracting $\frac{2\pi n}{a}$ which is the reciprocal lattice vector G (where d = a the interplanar spacing for [100] plane). At 1^{st} BZ boundary, u_s represent a standing wave. This can be realized as follows.

Dispersion relation $\omega = \pm\sqrt{\frac{4C}{m}} \sin\frac{Ka}{2}$. If instead of individual atoms, we consider an entire plane, then linear density along line is $\rho = \frac{m}{a}$, so $\omega = \pm\sqrt{\frac{4C}{a\rho}} \sin\frac{Ka}{2}$

If E = elastic stiffnes = Ca, then $\omega = \pm\sqrt{\frac{4E}{a^2\rho}} \sin\frac{Ka}{2} = \pm\frac{2v_0}{a}\sin\frac{Ka}{2}$ where $v_0 = \sqrt{\frac{E}{\rho}}$ is the longitudinal velocity of wave along line.

(i) Low-frequency, long wavelength limit :

$\lim_{K\to 0} \sin\frac{Ka}{2} = \frac{Ka}{2}$, so $\omega = \pm\frac{2v_0}{a}\frac{Ka}{2} = \pm v_0 K$

So phase velocity $v_p = \frac{\omega}{K} = \pm v_0$ which is same as group velocity $v_g = \frac{d\omega}{dK} = \pm v_0$.

This is true for a homogeneous line for which the atomic nature of linear chain has no importance.

(ii) High-frequency, short-wavelength limit :

From dispersion relation $v_g = \frac{d\omega}{dK} = \pm v_0 \cos\frac{Ka}{2}$ and $v_p = \frac{\omega}{K} = \frac{2v_0}{Ka}\sin\frac{Ka}{2}$. While both group & phase velocity is function of K, the crystal medium is "dispersive", as in dispersion of light the refractive index of medium is a function of frequency.

(iii) Frequency maxima $\omega = \sqrt{\frac{4C}{m}}$:

$\sin\frac{Ka}{2} = \pm 1$ or $\frac{Ka}{2} = \pm\frac{\pi}{2}$ (or $K = \pm\pi/a$)

or $\frac{2\cancel{\pi}}{\lambda}\frac{a}{\cancel{2}} = \pm\frac{\cancel{\pi}}{\cancel{2}}$ or $\underline{\underline{\lambda = 2a}}$.

$$\therefore v_p = \frac{\omega}{K} = \frac{2v_0}{aK}\sin\frac{Ka}{2} = \pm\frac{2v_0}{\cancel{a}\frac{\pi}{\cancel{a}}}\sin\frac{\pi}{2} = \pm\frac{2v_0}{\pi} \text{ and}$$

$$v_g = \frac{d\omega}{dK} = \pm v_0\cos\frac{Ka}{2} = \pm v_0\cos\frac{\pi}{2} = 0.$$

So the group velocity, that represents the velocity of wave, energy transmission is zero represents a standing wave.

This is similar to 1st order Bragg reflection at normal incidence ($\theta = \pi/2, n=1$) so that Bragg's low $2d\sin\theta = n\lambda$ becomes $\underline{\underline{2d = \lambda}}$.* Moreover, the linear chain can propagate waves $\omega \leq \frac{2v_0}{a}$ (cutoff frequency), so the monoatomic lattice acts as a "low pass filter." For typical crystal with $a = 3$ Å, $\omega = 2\times10^{13}$ Hz.

[* When Bragg condition is satisfied, a travelling wave cannot propagate in a lattice but through successive reflections sets up a standing wave.]

(iv) Calculation of force constant (C) :

Long range interaction between ion to ion through the conduction electron sea happen in metals, where planes of atoms separate by nearly 20 planes are found to interact. In such case to derive dispersion relation, one has to consider displacement $u_{s\pm p}$ of the pth plane from the reference u_s plane displacement, so that

$$\omega^2 = \frac{2}{m}\sum_{p>0} C_p(1-\cos pKa) \quad \text{or} \quad m\omega^2\cos rKa = 2\sum_{p>0} C_p(1-\cos pKa)\cos rKa$$

$$\therefore\ m\int_{-\pi/a}^{\pi/a}\omega^2\cos rKa = 2\sum_{p>0} C_p\int_{-\pi/a}^{\pi/a}\cos rKa(1-\cos pKa)\,dK$$

$$= 2\sum_{p>0} C_p\left[\int_{-\pi/a}^{\pi/a}\cos rKa\,dK - \int_{-\pi/a}^{\pi/a}\cos rKa\cos pKa\,dK\right]$$

Now $\displaystyle\int_{-\pi/a}^{\pi/a}\cos rKa\,dK = \frac{1}{ra}\sin rKa\Big|_{-\pi/a}^{\pi/a} = \frac{2}{ra}\cancelto{0}{\sin r\pi} = 0$ (r = integer)

& $\displaystyle -2\int_{-\pi/a}^{\pi/a}\cos rKa\cos pKa\,dK = -\int_{-\pi/a}^{\pi/a}[\cos(r-p)Ka + \cos(r+p)Ka]\,dK$

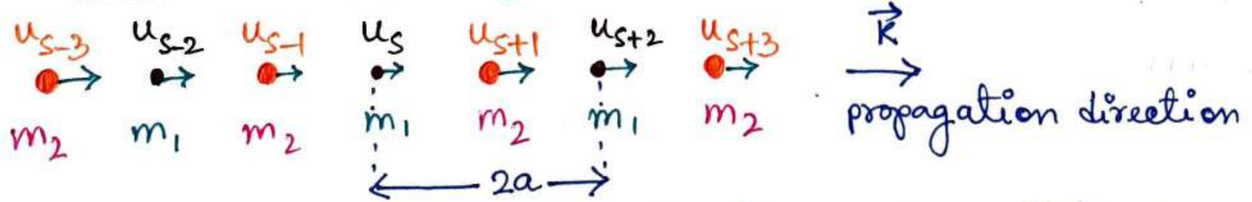
$$= -\frac{1}{a(r-p)}\sin(r-p)Ka\Big|_{-\pi/a}^{\pi/a} + \frac{1}{a(r+p)}\sin(r+p)Ka\Big|_{-\pi/a}^{\pi/a}$$

$$= -\frac{2}{a(r-p)}\sin(r-p)\pi + \frac{2}{a(r+p)}\cancelto{0}{\sin(r+p)\pi} \quad (r+p = \text{integer})$$

$$\overset{r=p}{=} -\frac{2\pi}{a}\delta_{r,p} \quad (\text{Using L'Hospital rule})$$

$$\therefore\ m\int_{-\pi/a}^{\pi/a}\omega^2\cos rKa = -\frac{2\pi}{a}C_p\delta_{r,p} \qquad \therefore\ \boxed{C_p = -\frac{ma}{2\pi}\int_{-\pi/a}^{\pi/a}\omega^2\cos pKa\,dK}$$

Vibrations of a 1D linear diatomic Chain



Let us consider the elastic vibrations of a diatomic crystal (two atoms per primitive basis), e.g. NaCl, KBr, Diamond etc, for which the atomic arrangements are shown above. For ideal arrangement, force constant C is same. Let $u_{s\pm p}$ with p = even is the displacement of m_1 atoms with amplitude u and for p = odd is the displacement of m_2 atoms with amplitude v with p atoms in the primitive cell. Suppose $m_2 > m_1$ & distance between nearest neighbours is a so that the repeat distance is $2a$. Elastic waves propagate along body diagonal ([111]) in NaCl & cube edge ([100]) in CsCl, so that single plane of vibration contains only one type of atom & each plane interacts only with nearest-neighbour plane.

The equation of motion is $m_1 \frac{d^2u_s}{dt^2} = c(u_{s+1} + u_{s-1} - 2u_s)$ &

$$m_2 \frac{d^2u_{s+1}}{dt^2} = c(u_{s+2} + u_s - 2u_{s+1})$$

The travelling wave solution on alternate planes are

$u_s = u e^{i(\omega t - ska)} \Rightarrow u_{s+2} = u e^{i(\omega t - (s+2)ka)}$ &

$u_{s\pm1} = v e^{i(\omega t - (s\pm1)ka)}$, with k = wavevector of that particular mode of vibration - same for m_1 & m_2 as they both participate in wave motion. Substituting in E.O.M. we have

$$-\omega^2 m_1 u = cv(e^{ika} + e^{-ika}) - 2cu \ \&$$

$$-\omega^2 m_2 v = cu(e^{ika} + e^{-ika}) - 2cv$$

or $\left.\begin{array}{l}(2c - m_1\omega^2)u - 2c\cos ka\, v = 0 \ \& \\ (2c - m_2\omega^2)v - 2c\cos ka\, u = 0.\end{array}\right\}$ — ① This pair of homogeneous equations will have a solution provided that determinant of the coefficient vanishes, or $\begin{vmatrix} (2c - m_1\omega^2) & -2c\cos ka \\ -2c\cos ka & (2c - m_2\omega^2) \end{vmatrix} = 0$

or $(2c - m_1\omega^2)(2c - m_2\omega^2) - 4c^2\cos^2 ka = 0$

or $m_1 m_2 \omega^4 - 2c(m_1 + m_2)\omega^2 + 4c^2(1 - \cos^2 ka) = 0$

or $\omega^4 - 2c\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\omega^2 + \frac{4c^2}{m_1 m_2}\sin^2 ka = 0$

This equation is true for two positive values of ω^2 as

$$\boxed{\omega_\pm^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm c\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\sin^2 ka\right]^{1/2}}$$ so that

for a given K, there are two ω (namely ω_+ & ω_-). To remind, dispersion relation for 1D linear monoatomic lattice was $\omega^2 = \frac{4c}{m}\sin^2\frac{ka}{2}$, so for a given K, only one positive ω was possible. Here, instead, for each polarization mode in a given propagation direction, dispersion relation develops 2 branches, known as the "acoustical" (longitudinal (LA) & transverse (TA)) and "optical" (longitudinal (LO) & transverse (TO) modes) branches. With p atoms in primitive cell, 3p branches to the dispersion relation, there are 3 acoustical branch (1 LA, 2TA) and 3p−3 optical branches (1 LO, 2 TO for Germanium/KBr with total 6 branches to dispersion relation as $p=2$).

Analysis of different branches of the dispersion relation curve

$$\omega_+^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + c\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\sin^2 ka\right]^{1/2} \rightarrow \text{Optical branch}$$

$$\omega_-^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - c\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\sin^2 ka\right]^{1/2} \rightarrow \text{Acoustical branch}$$

(i) Optical branch (ω_+): $\lim\limits_{K\to 0} \sin ka \to 0$ so that

$$\omega_+^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \quad \text{or} \quad \boxed{\omega_+ = \left[c\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right]^{1/2}}$$

$\lim\limits_{K\to \pi/2a} \sin ka \to 1$, so $\omega_+^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + c\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\right]^{1/2}$

$$= c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + c\left(\frac{1}{m_1}-\frac{1}{m_2}\right) = \frac{2c}{m_1}$$

$$\therefore \boxed{\omega_+ = \sqrt{\frac{2c}{m_1}}}$$

(ii) Acoustical branch (ω_-): $\lim\limits_{K\to 0} \sin ka \to ka$ otherwise $\omega_- = 0$

So that $$\omega_-^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - c\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\left[1 - \frac{4K^2a^2}{m_1 m_2}\left(\frac{m_1 m_2}{m_1+m_2}\right)^2\right]^{1/2}$$

$$= c\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\left[1 - \left\{1 - \frac{m_1 m_2}{(m_1+m_2)^2}4K^2a^2\right\}^{1/2}\right]$$

$$\simeq c\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\left[\cancel{1}-\cancel{1}+\frac{m_1 m_2}{(m_1+m_2)^2}\,2k^2a^2+\cdots\right]$$ neglecting higher powers

$$= \frac{2c}{m_1+m_2}k^2a^2 \qquad \therefore \boxed{\omega_- = ka\sqrt{\frac{2c}{m_1+m_2}}}$$

for $\lim\limits_{k\to \pi/2a} \sin ka \to 1$, $\omega_-^2 = c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - c\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2-\frac{4}{m_1m_2}\right]^{1/2}$

$$= c\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - c\left(\frac{1}{m_1}-\frac{1}{m_2}\right) = \frac{2c}{m_2}$$

$$\therefore \boxed{\omega_- = \sqrt{\frac{2c}{m_2}}}$$

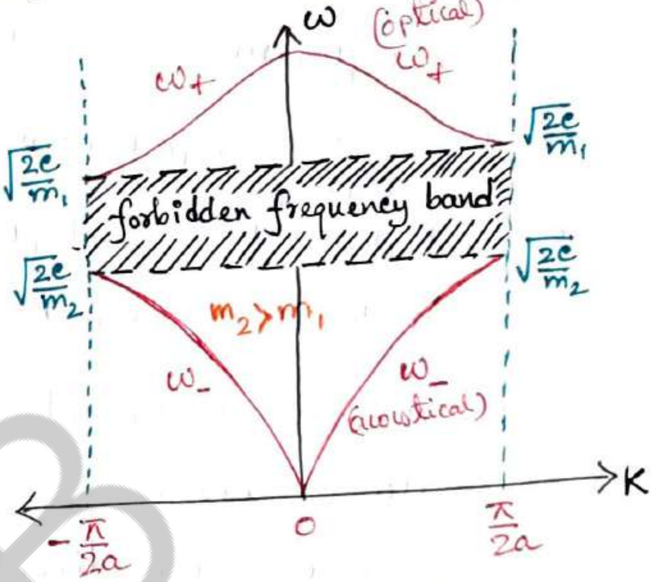


Figure beside displays the dispersion relation alongwith the two frequency branches. We note the following features:

(i) The frequency range of propagation is split into two branches – acoustic branch ω_- (lower) & optical branch ω_+ (upper).

We recall the equation of motion ①

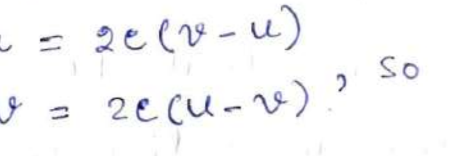
$$(2c - m_1\omega^2)u - 2c\cos ka\, v = 0, \quad (2c - m_2\omega^2)v - 2c\cos ka\, u = 0$$

For ω_+, $\lim\limits_{k\to 0}\cos ka \to 1$, so $(2c - m_1\omega_+^2)u - 2cv = 0$ &

$(2c - m_2\omega_+^2)v - 2cu = 0$.

$$\therefore \frac{u}{v} = \frac{2c}{2c - m_1\omega_+^2} = \frac{2c - m_2\omega_+^2}{2c} \quad \Bigg| \quad \begin{aligned} -m_1\omega_+^2 u &= 2c(v-u) \\ -m_2\omega_+^2 v &= 2c(u-v) \end{aligned}, \text{ so}$$

$$\frac{u}{v} = \frac{(v-u)/m_1}{(u-v)/m_2} = -\frac{m_2}{m_1}.$$ This means that the two atoms move in opposite directions & their amplitudes are inversely proportional to their masses so that the center of mass of the unit cell does not move. For equal masses too they move in opposite direction & for unequal masses as $m_2 > m_1$, $u > v$.



For ω_-, $\lim\limits_{k\to 0}\cos ka = 1 - \frac{k^2a^2}{2}$ and then the equation of motion ① is

$(2c - m_1\omega_-^2)u - 2c(1-\frac{k^2a^2}{2})v = 0$, $(2c - m_2\omega_-^2)v - 2c(1-\frac{k^2a^2}{2})u = 0$

$\therefore -m_1\omega_-^2 u = 2c(1-\frac{k^2a^2}{2})v - 2cu$

$+m_2\omega_-^2 v = 2c(1-\frac{k^2a^2}{2})u - 2cv$. Adding and substituting

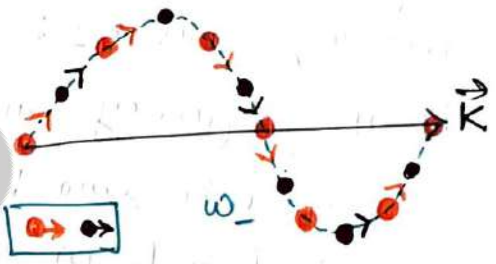
$\omega_- = ka\sqrt{\frac{2c}{m_1+m_2}}$ (as obtained earlier), we get,

$\cancel{-}\omega_-^2(m_1u+m_2v) = \cancel{-}k^2a^2(u+v)c$

or $\cancel{k^2a^2}\frac{2\cancel{c}}{m_1+m_2}(m_1u+m_2v) = \cancel{k^2a^2}(u+v)\cancel{c}$

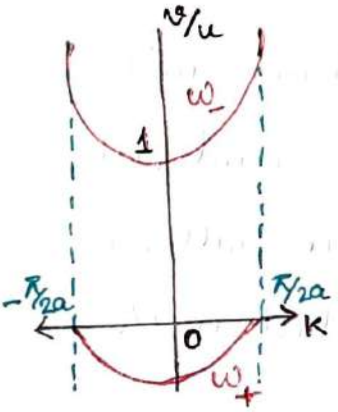
or $2m_1u+2m_2v = (m_1+m_2)(u+v)$ or $m_1u+m_2v = m_1v+m_2u$

or $(m_1-m_2)u = (m_1-m_2)v$ or $\frac{u}{v} = +1$. This signifies that in the acoustical branch even if the masses are different then also two atoms move in same direction with equal amplitude. Because of this, the center of mass moves just like pressure wave (sound). Monoatomic crystal subjected to a force makes the atoms to move in same direction, by the vibrations of the acoustical branch. On the other hand, movement of neighbouring atoms can be achieved using a light source that due to its EM nature will vibrate the optical branch. Hence these names are justified. Diamond & hcp lattices exhibit optical branch.



(ii) As drawn in dispersion curve, that wave like solutions do not exist for $\sqrt{\frac{2c}{m_2}} \leq \omega \leq \sqrt{\frac{2c}{m_1}}$, so there is a forbidden frequency band for unequal mass atoms $(m_1 \neq m_2)$ for which frequencies cannot propagate. As the atomic masses are larger $(\frac{m_2}{m_1} >>)$, the wider the forbidden frequency band between acoustical & optical branch. Only for ~~monoatomic~~ equal mass atoms $(m_1 = m_2)$, the band vanishes. The 1st Brillouin Zone is with wavevector $-\frac{\pi}{2a} \leq K \leq \frac{\pi}{2a}$. So the

Smallest possible wavelength of this zone is 4a corresponding to the largest wavevector $K = \frac{\pi}{2a}$ at the zone boundary. As m_2 increases more, the optical branch flattens & acoustical branch goes downward. At $m_2 \to \infty$, optical branch becomes parallel to K-axis (flat) & acoustical branch disappears. As m_1 decreases, optical branch moves upward (acoustical branch is unaffected). At $m_1 \to 0$, optical branch disappears as in monoatomic lattice vibration, with lattice constant 2a.



For all wave vector K, the amplitude variation for both branches is shown beside. For $K = \pm\frac{\pi}{2a}$ we know $\omega_+ = \sqrt{\frac{2c}{m_1}}$, from equation ①, $\frac{v}{u} = 0$ and for $\omega_- = \sqrt{\frac{2c}{m_2}}$ $\frac{v}{u} = \infty$. So in optical branch, $v = 0$ means all the heavier atoms m_2 are at rest, while in acoustical branch $u = 0$ means all the lighter atoms m_1 are at rest. So only one of the sublattices, lighter atoms of optical branch & heavier atoms in acoustical branch oscillates at the BZ boundary. They both represent standing wave with $\frac{\pi}{2}$ phase difference. Both the sublattices vibrate for $K < \pi/2a$.

Phonons - quantised lattice vibrations

According to quantum mechanics, energy of an elastic wave with angular frequency of vibration ω with the mode is excited to a quantum number n is $E = (n + \frac{1}{2})\hbar\omega$ or the mode is occupied with n phonons. The zero point energy of the mode is $\frac{1}{2}\hbar\omega$. Due to equivalence of photons (EM wave quanta) and phonons (elastic wave quanta) to harmonic oscillator, energy of phonon is quantised with each phonon having energy $\hbar\omega$. and velocity of propagation of sound. Vibration spectrum of phonon is $10^4 - 10^{12}$ Hz, with the lower frequency side is in the acoustic region (sound waves in crystal lattice) and higher side in the infra-red region (similar to thermally excited photons in blackbody radiation). Like photons, phonons are spin-zero wave satisfying Bose-Einstein statistics $\bar{n} = \frac{1}{e^{h\nu/k_BT} - 1}$ (indistinguishable)

Despite no direct evidence of quantization of phonons, the following experimental inferences predict the existence :

(a) Lattice heat capacity is zero at the zero temperature limit which can be explained only if lattice vibrations is quantized &

(b) The change of momentum / energy during inelastic scattering of x-ray or neutron beam on crystal is associated with gain/loss of phonons.

phonon amplitude : To compute the quantized mean square phonon amplitude, consider the standing wave mode

$u = u_0 \cos kx \cos \omega t$ where u is the displacement of a volume element from its equilibrium position x in the crystal. The time-averaged energy $\bar{E} = (n + \frac{1}{2})\hbar\omega = \frac{1}{2}(n+\frac{1}{2})\hbar\omega + \frac{1}{2}(n+\frac{1}{2}\hbar\omega) = \bar{E}_{KE} + \bar{E}_{PE}$. KE density with mass density ρ is $\frac{1}{2}\rho\left(\frac{\partial u}{\partial t}\right)^2$

$\therefore$ Total KE of crystal at volume V $= \frac{1}{4}\rho V \omega^2 u_0^2 \sin^2 \omega t$

$\therefore \bar{E}_{KE} = \frac{1}{8}\rho V \omega^2 u_0^2 = \frac{1}{2}(n+\frac{1}{2})\hbar\omega$ or $u_0^2 = 4(n+\frac{1}{2})\frac{\hbar}{\rho V \omega}$

$$\therefore \boxed{u_0 = \sqrt{\frac{4(n+1/2)\hbar}{\rho V \omega}}}$$

phonon momentum: A phonon of wavevector $\vec{K}$ due to its particle nature as well interacts / collides with photons, neutrons, electrons as if it had a momentum $\hbar\vec{K}$. This momentum is called "crystal momentum", while a phonon on a lattice really has no momentum in the physical sense. This is because a phonon coordinate (except for K=0) involves relative atomic coordinates, e.g. in H_2 molecule, internuclear vibrational coordinate $\vec{r}_1 - \vec{r}_2$ doesn't carry linear momentum, while the CM coordinate $\frac{\vec{r}_1 + \vec{r}_2}{2}$ carries linear momentum although this corresponds to $K=0$.

Normal Process: From Fermi's golden rule we know that in crystals there is wavevector selection rule for allowed transitio between quantum states. Bragg's law define the elastic scattering of an x-ray photon by a crystal with wavevector selection rule

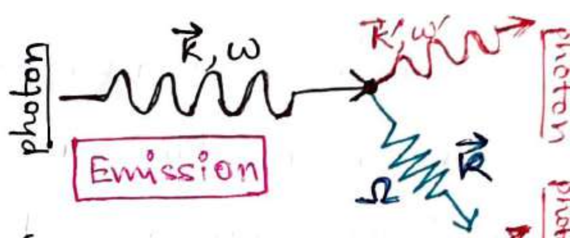
$\vec{K}' = \vec{K} + \vec{G}$, $\vec{K}'$ = wavevector of scattered photon,
or $\hbar\vec{K}' = \hbar\vec{K} + \hbar\vec{G}$ $\vec{K}$ = wavevector of incident photon &
$\vec{G}$ = reciprocal lattice vector.

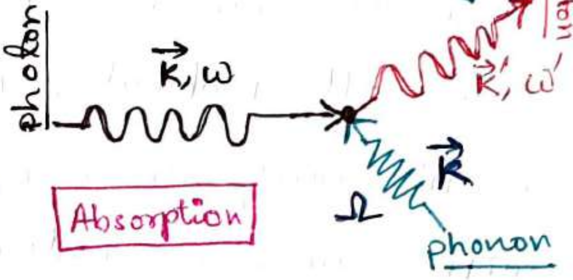
In this process the crystal recoils with a momentum $\hbar\vec{G}$ without changing the wavelength of the incident photon i.e. $|\vec{K}'| = |\vec{K}|$. This is called a "Normal process" (N-process) where no phonon is created or absorbed.

Umklapp Process: In N-process total wavevector of interacting waves is conserved, or crystal momentum is conserved which is the momentum modulo the reciprocal lattice vector. Note that this is not strictly due to Noether's theorem that deals with conservation of momentum due to translational invariance of space. Crystal momentum conservation results from space being invariant under translations of lattice constant a, giving momentum conserved modulo $\frac{2\pi}{a}$.

In an inelastic scattering of a photon by a crystal, frequenc of the incident photon changes & a new photon is emitted alongwith a phonon of wavevector K, so that according to wavevector conservatio law, $\vec{K}' + \vec{\mathbf{K}} = \vec{K} + \vec{G}$ (emission)

$\vec{K}' = \vec{K} + \vec{\mathbf{K}} + \vec{G}$ (absorption)

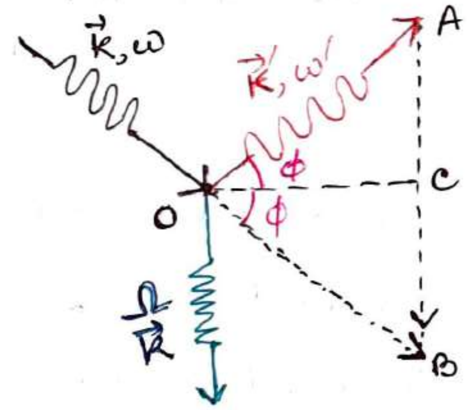




Such processes in which wavelength of the photon changes is called "umklapp process" (U-process). The energy conservation yields $\hbar\omega' + \hbar\Omega = \hbar\omega$ (emission)

$\hbar\omega' = \hbar\omega + \hbar\Omega$ (absorption). To note, emission/absorption of photon by scattering of a phonon is not possible, although they have mechanical similarity with photons (wave-particle duality, energy quanta, indistinguishable particle nature obeying BE statistics). Due to sound wave nature of phonons, they're very different than EM natured photons.

Inelastic Scattering of photons by phonons



Let us consider a photon with wavevector K and angular frequency ω is incident on a crystal with refractive index n. The velocity of the photon then is $\frac{c}{n}$ and from $v = \nu\lambda$ we have $\frac{c}{n} = \frac{\omega}{2\pi}\lambda = \frac{\omega}{K}$, so $K = \frac{\omega n}{c}$.

As the refractive index of the crystal changes due to change in concentration of atoms by the elastic strain field of the sound waves, the photon interacts with phonon to get inelastically scattered. Suppose the magnitude of phonon wave vector $\mathbf{K}$ is comparable to incident photon wavevector K and the phonon velocity v is constant, then

$$v = \nu\lambda = \frac{\Omega}{2\pi}\frac{2\pi}{\mathbf{K}} = \frac{\Omega}{\mathbf{K}}, \quad \text{or} \quad \Omega = v\mathbf{K}$$

while c/n (light velocity in medium) $>>$ v (velocity of sound)

so $\frac{c}{n}K >> v\mathbf{K}$ (as $K \simeq \mathbf{K}$) or $\omega >> \Omega$

Using this in energy conservation $\hbar\omega' \simeq \hbar\omega$ or $\omega' \simeq \omega$ and $K' = \frac{\omega' n}{c} \simeq \frac{\omega n}{c} = K$. In the isosceles triangle OAB, we have $OA = OB$ and $AB = |\vec{K}| = 2K\sin\phi = \frac{2\omega n}{c}\sin\phi$. So $\Omega = vK = \frac{2v\omega n}{c}\sin\phi$. This is the wavevector & angular frequency of the emitted phonon, that matches the experiment on quartz/sapphire crystal directed to a visible laser light source to produce phonons in the microwave range.

Thermal properties of Phonons

Next we discuss on the heat capacity of a phonon gas. When defining 1st law of TD we have already discussed the definition of Molar specific heat at constant volume $C_V = \left(\frac{dQ}{dT}\right)_V$ and at constant pressure $C_p = \left(\frac{dQ}{dT}\right)_p$. In solids, the increase in internal energy takes place due to rigorous vibrations of (nearly) free atoms about their equilibrium positions and due to thermal excitation of electrons to higher energy states (metals & semiconductors).

$\therefore U = U_{lattice} + U_{electron}$ and we have heat capacity

$$C_V = \left(\frac{dU}{dT}\right)_V = \frac{dU_{lattice}}{dT} + \frac{dU_{electron}}{dT} = \underbrace{C_{lattice}}_{\text{Lattice heat capacity}} + C_{electron}$$

$$\simeq C_{lattice}$$

while the basic assumption is no free electrons are present, so that the main contribution to specific heat is due to the excitations of thermal vibrations of the lattice. At room temperature, the heat capacity is $\sim 3R$ where $R = Nk_B$ = # of atoms in solid × Boltzmann's constant ~ 6 cal/mole-K. As one approaches $\lim_{T\to 0K}$, $C_{lattice}$ sharply decreases by following T^3 law (insulators), T-law (metals) for superconductor the decrement is faster. In magnetic solids, $C_{lattice}$ increases near the Curie temperature when the magnetic momen are ordered.

Classical Theory : A crystal can be considered as a 3D harmonic oscillator where due to strong cohesive energy atoms are arranged in periodic manner, freely vibrate about equilibrium position. Thermal energy increases the vibrational energy (internal energy) & so they can be termed as N independent oscillators with 3 d.o.f. or 3N 1D harmonic oscillators. with natural frequency ω_0, so that

$$\mathcal{E} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2$$ is the total energy.

While the energy distribution of the oscillators obey Gibbs distributi the average energy of each harmonic oscillator is

$$\bar{\mathcal{E}} = \frac{\int \epsilon e^{-\beta\epsilon} d\epsilon}{\int e^{-\beta\epsilon} d\epsilon} = \frac{\iint \left(\frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) e^{-\frac{\beta p^2}{2m}} e^{-\frac{m\omega_0^2 x^2 \beta}{2}} dp\,dx}{\iint e^{-\beta p^2/2m} e^{-\frac{m\omega_0^2 x^2 \beta}{2}} dp\,dx}$$

$$= \frac{\int \frac{p^2}{2m} e^{-\beta p^2/2m} dp}{\int e^{-\beta p^2/2m} dp} + \frac{\int \frac{1}{2}m\omega_0^2 x^2 e^{-m\omega_0^2 x^2 \beta/2} dx}{\int e^{-m\omega_0^2 x^2 \beta/2} dx}$$

$$\beta = \frac{1}{K_B T}$$

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$= \frac{1}{2m} \frac{\frac{1}{4}\sqrt{\pi (2mK_BT)^3}}{\frac{1}{2}\sqrt{\pi(2mK_BT)}} + \frac{1}{2}m\omega_0^2 \frac{\frac{1}{4}\sqrt{\pi\left(\frac{2K_BT}{m\omega_0^2}\right)^3}}{\frac{1}{2}\sqrt{\pi\left(\frac{2K_BT}{m\omega_0^2}\right)}}$$

$$= \frac{1}{2}K_BT + \frac{1}{2}K_BT = K_BT$$

So total vibrational energy $E = 3N\bar{\mathcal{E}} = 3NK_BT$ & heat capacity $C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3NK_B = 3R = 5.96$ cal/moleK. So the molar specific heat of all solids is constant & independent of temperature & frequency. This is called Dulong & Petit's law which fails at the low temperature limit. due to classical nature (energy ranging continuously from 0 to ∞).

Discrepancy removal in Einstein's Theory

In 1911 using Planck's quantum theory by replacing classical harmonic oscillators with quantum harmonic oscillators, so that discrete energy values are feasible, resolved the low temperature discrepancy of Dulong-Petit's law. The basic assuptions were

(i) atoms are identical independent quantum harmonic oscillators with discrete energy levels $\varepsilon_n = (n+\frac{1}{2})\hbar\omega_0$, $n = 0,1,2,3$ quantum numbers. There are 3N quantum oscillators.

(ii) The atomic oscillators are distinguishable & obey Gibb's distributio in energies, all atoms vibrate in identical environments & have the same natural frequency.

So average energy of an oscillator $\bar{\varepsilon} = \dfrac{\sum_{n=0}^{\infty} \varepsilon_n e^{-\beta\varepsilon_n}}{\sum_{n=0}^{\infty} e^{-\beta\varepsilon_n}}$

$$\boxed{\begin{aligned} x &= -\frac{\hbar\omega_0}{k_BT} \\ &= -\beta\hbar\omega_0 \end{aligned}}$$

$$= \frac{\sum_{n=0}^{\infty}(n+\frac{1}{2})\hbar\omega_0 \exp[-(n+\frac{1}{2})\beta\hbar\omega_0]}{\sum_{n=0}^{\infty}\exp[-(n+\frac{1}{2})\beta\hbar\omega_0]}$$

$$= \hbar\omega_0 \frac{\sum_{n=0}^{\infty}(n+\frac{1}{2})\exp[(n+\frac{1}{2})x]}{\sum_{n=0}^{\infty}\exp[(n+\frac{1}{2})x]} = \hbar\omega_0 \frac{[\frac{1}{2}e^{x/2} + \frac{3}{2}e^{3x/2} + \frac{5}{2}e^{5x/2} + \dots]}{[e^{x/2} + e^{3x/2} + e^{5x/2} + \dots]}$$

$$= \hbar\omega_0 \frac{d}{dx}\ln(e^{x/2} + e^{3x/2} + e^{5x/2} + \dots)$$

$$= \hbar\omega_0 \frac{d}{dx}\ln[e^{x/2}(1 + e^{x} + e^{2x} + \dots)]$$

$$= \hbar\omega_0 \frac{d}{dx}[\frac{x}{2} + \ln(1 + e^{x} + e^{2x} + \dots)] = \hbar\omega_0[\frac{1}{2} - \frac{d}{dx}\ln(1-e^{x})]$$

$$= \hbar\omega_0[\frac{1}{2} + \frac{e^{x}}{1-e^{x}}] = \hbar\omega_0[\frac{1}{2} + \frac{1}{e^{\hbar\omega_0\beta}-1}]$$

$$= \underbrace{\frac{1}{2}\hbar\omega_0}_{\text{zero point energy}} + \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0}-1}$$

Note that at T = 0K, $\bar{\varepsilon} = \frac{1}{2}\hbar\omega_0$ so each atom possesses vibrational energy that isn't zero but contribution to C_V is zero. Also $\bar{\varepsilon}$ is a function of ω_0 and β. So the energy (total internal) of the crystal is

$E = 3N\bar{E} = \frac{3}{2}N\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\beta\hbar\omega_0}-1}$ so that heat capacity is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{e^{\hbar\omega_0/k_BT}}{\left(e^{\hbar\omega_0/k_BT}-1\right)^2} = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}$$

where $\boxed{\theta_E = \frac{\hbar\omega_0}{k_B}}$ is the characteristic Einstein temperature. The frequency ν of the atomic oscillator corresponding to the Einstein temperature θ_E is known as Einstein frequency $\nu = \frac{k_B\theta_E}{h}$.

predictions and comparison with experimental results :

(i) High temperature Limit $(k_BT >> \hbar\omega_0)$ $(T >> \theta_E)$:

At large temperature $\bar{E} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT}-1} \simeq \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{\cancel{1}+\frac{\hbar\omega_0}{k_BT}-\cancel{1}}$

$= \frac{1}{2}\hbar\omega_0 + k_BT \simeq k_BT$ which agrees with the classical picture.

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2} \simeq 3R\left(\frac{\theta_E}{T}\right)^2 \frac{1}{\left(1+\frac{\theta_E}{T}-1\right)^2} = 3R\left(\frac{\theta_E}{T}\right)^2\left(\frac{T}{\theta_E}\right)^2$$

$= 3R$ which is the Dulong-Petit's law.

(ii) Low temperature limit $(k_BT << \hbar\omega_0)$ $(T << \theta_E)$:

At low temperature $\bar{E} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT}-1} \simeq \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT}}$

$= \frac{1}{2}\hbar\omega_0 + \hbar\omega_0 e^{-\hbar\omega_0/k_BT}$. So the average vibrational energy decreases exponentially with decreasing temperature.

$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2} \simeq 3R\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$. A plot of C_V vs $\frac{T}{\theta_E}$ for Diamond at $\theta_E = 1320K$ fits the experimental results over a wide range of temperature except at very-low liquid Helium temperature where $C_V \propto e^{-\theta_E/T}$ breaks down and follows $C_V \propto T^3$. Experimentally, Einstein temperature can be easily measured using ω_0 (for monoatomic basis $\omega_0 = \sqrt{\frac{4C}{m}}$) by substituting the elastic constant. for most metals, $100K \leq \theta_E \leq 200K$.

Discrepancy removal in Debye's theory

In 1912, Debye noticed the factual oversimplification in Einstein's theory of the independence of quantum oscillators. The basic flaw was that the vibrational motion of the crystal was taken to be same as natural vibrational frequency of a single atom ω_0. Debye proposed that the crystals can propagate from low frequency (sound waves) to high frequency (infrared absorption) elastic waves having a number of modes of vibration. The number of vibrational modes per unit frequency range is called the density of modes $D(\nu)$ that we determine next.

In 1D if we have a continuous string of length L with two ends fixed, then the solution of wave equation $u'' = \frac{1}{v^2}\ddot{u}$ corresponds to a standing wave $u(x,t) = A\sin\left(\frac{n\pi x}{L}\right)\cos 2\pi\nu_n t$. Substituting this back, we get $\frac{n^2\pi^2}{L^2} = \frac{1}{v^2}4\pi^2\nu_n^2$ or $\nu_n = \frac{nv}{2L} = \frac{v}{2L/n} = \frac{v}{\lambda_n}$ where $\lambda_n = \frac{2L}{n}$. This means that frequency of the string have integral multiple of $\frac{v}{2L}$. While $n = \frac{2L}{v}\nu_n$ we have $dn = \frac{2L}{v}d\nu = D(\nu)d\nu$. This is the number of vibrational modes. In 3D, the wave equation is $\nabla^2 u = \frac{1}{v^2}\ddot{u}$ that corresponds to a fixed-face cube of size L. The standing wave solutions are $u(\vec{r},t) = A\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)\cos 2\pi\nu$

with $n_x, n_y, n_z \geq 1$. Substituting back we have

$$\frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2) = \frac{4\pi^2\nu^2}{v^2} \quad \text{or} \quad n_x^2 + n_y^2 + n_z^2 = \frac{4L^2\nu^2}{v^2}.$$

To determine the possible modes of vibration $D(\nu)d\nu$ we consider a network of points whose coordinates are (n_x, n_y, n_z). The radius vector R_n from origin to any point is $R_n^2 = n_x^2 + n_y^2 + n_z^2$

So $R_n = \frac{2L}{v}\nu_n$ or $dR = \frac{2L}{v}d\nu$. As each point occupies on an average a unit volume in the integer space, so the number of points in the spherical shell between R & R+dR is equal to the volume of one octant of a spherical shell,

So Volume of one octant of spherical shell $= \frac{1}{8}4\pi R^2 dR$

$= D(\nu)\,d\nu$

Substituting R & dR, we obtain

$$D(\nu)\,d\nu = \frac{4\pi}{8}\,\frac{4L^2\nu^2}{v^2}\,\frac{2L}{v}\,d\nu = \frac{4\pi L^3}{v^3}\nu^2 d\nu = \frac{4\pi V}{v^3}\nu^2 d\nu$$

While there are one longitudinal wave & two transverse waves (having two ⊥ direction of polarisation) in an elastic solid, we have the total number of vibrational modes as

$$D(\nu)\,d\nu = 4\pi V\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\nu^2 d\nu$$

Debye Approximation

Debye assumed that the crystal can be regarded as a continuum as long as wavelength of elastic wave is large compared to interatomic spacing. Also while the total number of vibrational modes are limited to 3N, so there is an upper cutoff to the frequency ν_D (Debye frequency) of the elastic wave. Therefore

$$\int_0^{\nu_D} D(\nu)\,d\nu = 3N \quad \text{or} \quad \int_0^{\nu_D} 4\pi V\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\nu^2 d\nu = 3N$$

$$\text{or} \quad \boxed{\nu_D^3 = \frac{9N}{4\pi V}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)^{-1}}$$

This is not a good approximation because taking $v_l \simeq v_t \sim 10^3$ m/s & $\frac{N}{V} = 10^{28}/m^3$, $\nu_D \sim 10^{13}\,s^{-1}$ that corresponds to wavelength ~ 1 Å = interatomic spacing, so the validity of continuum theory is doubtable. Also v_l & v_t is not always independent of the wavelength.

Neglecting the zero point energy that doesn't contribute to C_V, we know that the average vibrational energy of an oscillator with frequency ν at T is known from Planck's theory

$\bar{\varepsilon} = \dfrac{h\nu}{e^{h\nu/k_BT}-1}$. We can associate with each vibrational mode a quantum oscillator so that the vibrational energy of the crystal is $E = \int_0^{\nu_D} \bar{\varepsilon}\, D(\nu)\, d\nu$

$$= \int_0^{\nu_D} 4\pi V\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)\frac{h\nu^3}{e^{h\nu/k_BT}-1}\, d\nu = 4\pi hV\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)\int_0^{\nu_D}\frac{\nu^3 d\nu}{e^{h\nu/k_BT}-1}$$

$$= \frac{9Nh}{\nu_D^3}\int_0^{\nu_D}\frac{\nu^3 d\nu}{e^{h\nu/k_BT}-1} = \frac{9Nh}{\nu_D^3}\left(\frac{k_BT}{h}\right)^4\int_0^{x_m}\frac{x^3dx}{e^x-1} \qquad \left[\frac{h\nu}{k_BT}=x,\ \frac{h\nu_D}{k_BT}=x_m = \theta_D/T\right]$$

$$= 9N\left(\frac{k_BT}{h\nu_D}\right)^3 k_BT\int_0^{x_m}\frac{x^3dx}{e^x-1} = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3dx}{e^x-1}$$

So the specific heat is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{e^x x^4}{(e^x-1)^2}dx = 3R\left(\frac{\theta_D}{T}\right)F_D$$

where F_D is called the Debye function $= 3\left(\frac{T}{\theta_D}\right)^4\int_0^{\theta_D/T}\frac{e^x x^4}{(e^x-1)^2}dx$

and $\theta_D = \dfrac{h\nu_D}{k_B}$ is the Debye temperature.

Predictions and comparison with experimental results:

(i) High temperature limit ($k_BT \gg h\nu$) ($T \gg \theta_D$):

At high temperature $e^x - 1 \simeq 1+x-1 = x$ so that

$E = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T} x^2 dx = 3Nk_BT = 3RT$ so that the specific heat $C_V = \dfrac{\partial E}{\partial T} = 3R$ (Dulong-Petit's law). So the quantum considerations are insignificant at high temperatures.

(ii) Low temperature limit ($k_BT \ll h\nu$) ($T \ll \theta_D$):

while $\theta_D >> T$, $x_m = \frac{\theta_D}{T} \to \infty$. So that mean vibrational energy

$$E = 9RT\left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{x^3 dx}{e^x - 1} = 9RT\left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5} R \frac{T^4}{\theta_D^3}.$$

The noticeable similarity is $E \propto T^4$ (Stefan's law in Blackbody radiation of photons) which is only true for phonons at small temperatures only. Now the heat capacity becomes

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{12\pi^4}{5} R \left(\frac{T}{\theta_D}\right)^3.$$ So $\boxed{C_V \propto T^3}$ (Debye-T^3 law)

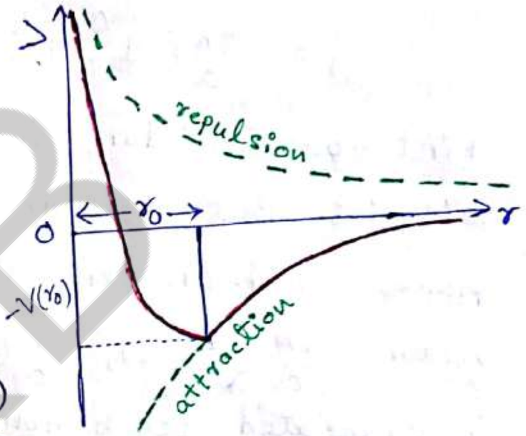
and it holds for $T \leq 0.1\theta_D$. For Silver with $\theta_D = 225K$, Debye model remarkably matches with experiment. The Debye model yields a larger specific heat compared to Einstein's model as Debye model considers the low frequency modes which at low temperature have higher vibrational energy (or more C_V). At very low temperature, C_V is relatively insensitive to the variations of the density of modes.

Limitations of the Debye Model

1. Because it's a continuum model valid for long-wavelength, low frequencies only in the solid, it neglects the dispersion of waves.
2. While solid is treated as elastic continuum, it can have infinite number of frequencies but Debye's theory restricts to 3N modes.
3. ν_D is assumed equal for v_l and v_t which is very unlikely.
4. At $< 0.1\theta_D$ the theory breaks down & not only that $\theta_D = \frac{h\nu_D}{k_B}$ varies upto 10% with temperature.
5. Debye theory is inapplicable to not-identical atoms crystals, e.g. NaCl, CsCl etc.
6. Debye theory completely neglects interatomic interaction & electronic contribution to heat capacity.

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.

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

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

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

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

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

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

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

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

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

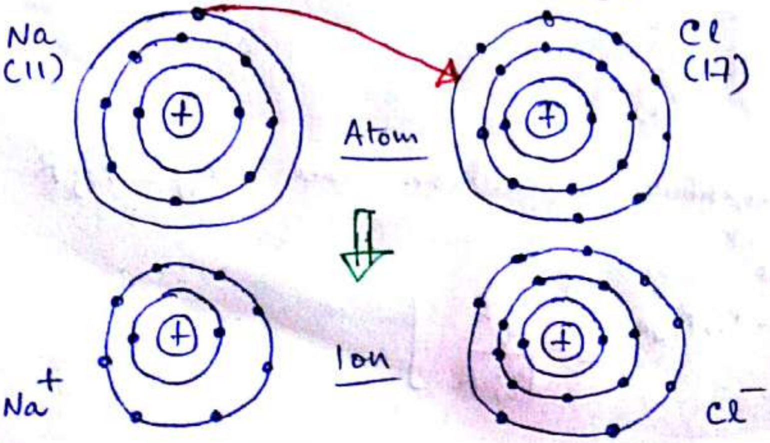
or $n-m > 0$ or $n > m$. Thus to form a chemical bond, we always need repulsive force be of shorter range than attractive force.

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 $V_{attraction} = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}$



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

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

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

$Z_1 = Z_2 = 1$.

So potential energy $V = -\frac{e^2}{4\pi\epsilon_0 r_0} = \frac{-(1.6\times10^{-19})^2}{4\pi\times8.85\times10^{-12}\times2.4\times10^{-10}}$
$(r_0 = 2.4\ \text{Å})$

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

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

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

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

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

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

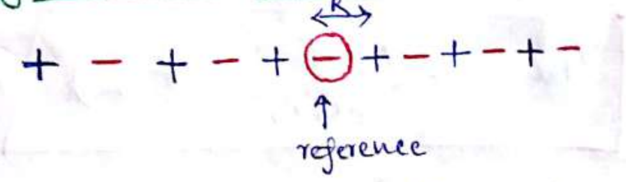
$$U_i = -\frac{\alpha q^2}{R_0}\left(1-\frac{\rho}{R_0}\right),$$

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



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

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

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

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

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

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

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

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

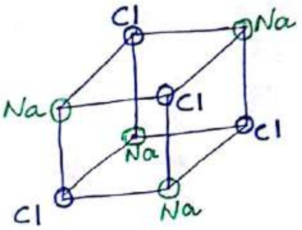
Bulk modulus of Ionic crystals

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

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

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

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



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

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

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

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

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

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

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

$R=R_0$

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

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

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

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

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

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

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

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.

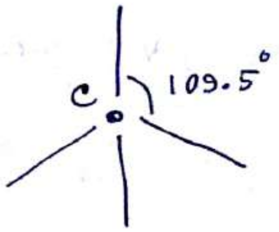
$\uparrow\uparrow$ $2p_x\ 2p_y\ 2p_z$

$\uparrow\downarrow$ $2s^2$

$\uparrow\downarrow$ $1s^2$

For single carbon atom $C_6 = 1s^2 2s^2 2p^{②}$ → unpaired electron

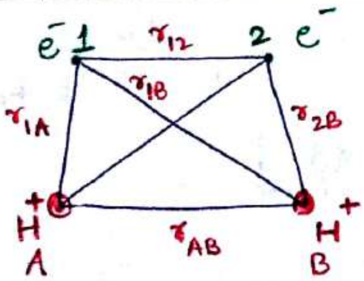
But when more carbon atom comes close $\underset{1s^2}{\uparrow\downarrow}$ $\underset{2s}{\uparrow}$ $\underset{2p_x}{\uparrow}$ $\underset{2p_y}{\uparrow}$ $\underset{2p_z}{\uparrow}$ → unpaired electrons



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^+ neucleus (hydrogen atom) with two electrons 1 & 2 in $1s^1$ orbital. Ψ_{1A}, Ψ_{2B} are eigenfunction of A, B atoms.

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

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

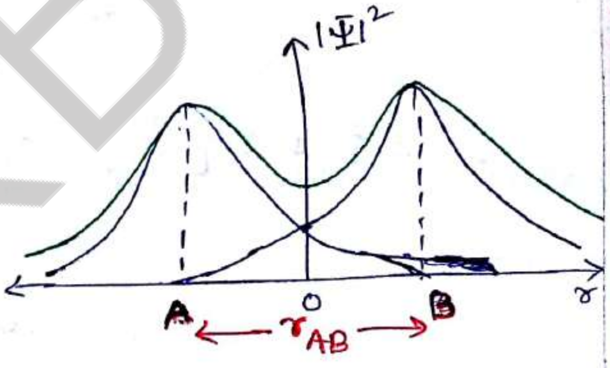
We can write the Schrödinger equation for the two electron system $-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)\Psi + (\mathcal{H}_1+\mathcal{H}_2)\Psi = E\Psi$ (no overlap)

$$\therefore \left.\begin{aligned} \nabla_1^2\psi_{1A} + \frac{2m}{\hbar^2}(E_1-\mathcal{H}_1)\psi_{1A} &= 0 \\ \nabla_2^2\psi_{2B} + \frac{2m}{\hbar^2}(E_2-\mathcal{H}_2)\psi_{2B} &= 0 \end{aligned}\right\} \text{H-atom solution in radial part, spherical polar \& azimuthal part}$$

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

[a_0 = Bohr orbit radius]

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



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

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

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

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,

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

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

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

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

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

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

2 ⟺ 1 interchange

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

= same atom interaction, < 0

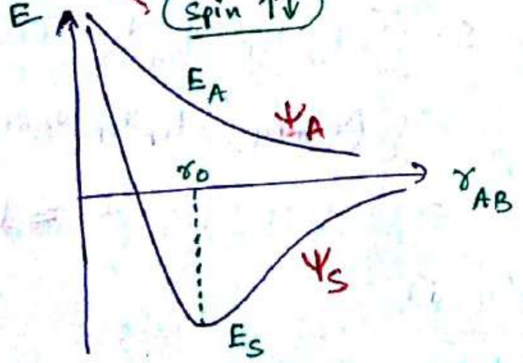
$$\eta = \iint \psi_{1A}^* \psi_{2B}^* \mathcal{H}' \psi_{1B}\psi_{2A}\, dr_1 dr_2$$

= exchange interaction < 0

∴ Energy eigenvalues are

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

E_S (spin ↑↓) $\quad$ E_A (spin ↑↑)

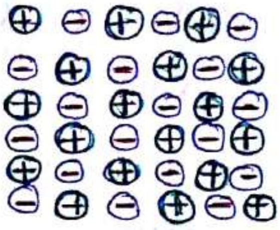


ψ_A cannot form a bond because $E > 0$

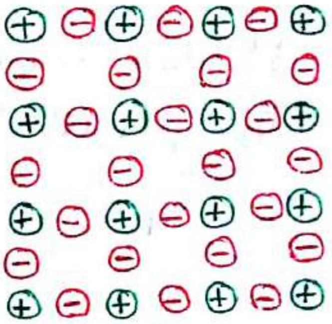
ψ_S can form the covalent bond.

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

Metallic Bonding



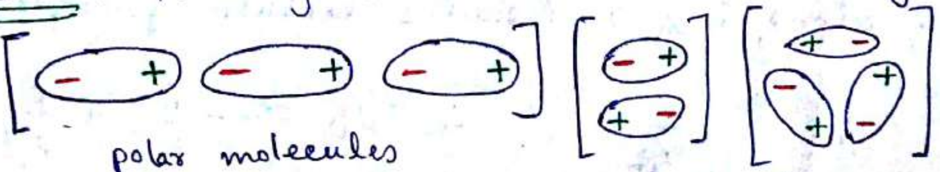
Ionisation energy is low and high electrical conductivity. They have vacant valency orbitals & have very few valency electrons compared to the number of valency orbitals. These electrons in the outermost orbit are loosely bound (conduction/free electrons) & 1 or 2 can be detached from parent atom due 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.



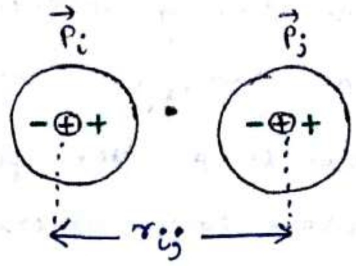
polar molecules

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 free.

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

∴ Potential energy of the dipole moments is

$$U_{atr} = -\frac{2P_iP_j}{r_{ij}^3} = -\frac{4\alpha P_i^2}{r_{ij}^6} \qquad \alpha - \frac{1}{r_{ij}^6} \rightarrow \text{short range}$$

↳ 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.

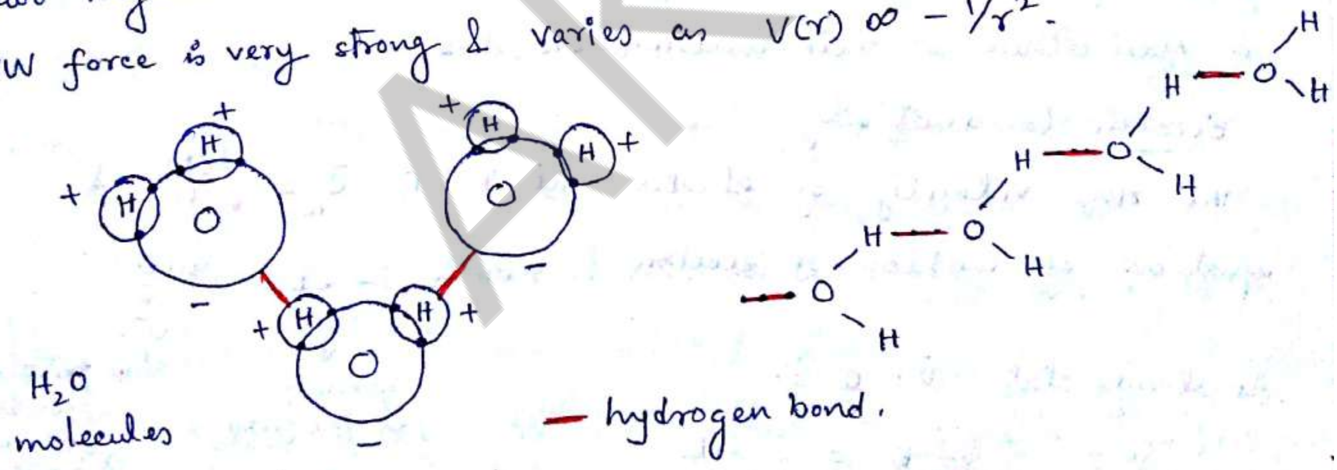
$$\left.\frac{dU_{tot}}{dR}\right|_{R=R_0} = 0 \Rightarrow R_0/\sigma = 1.09.$$

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 $V(r) \propto -1/r^2$.

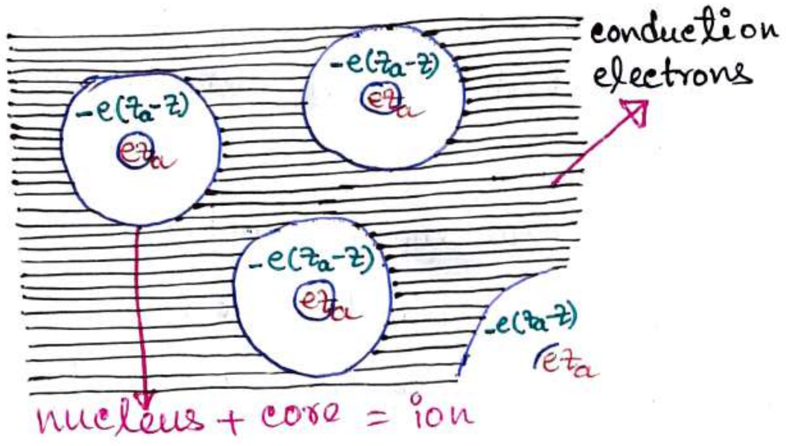


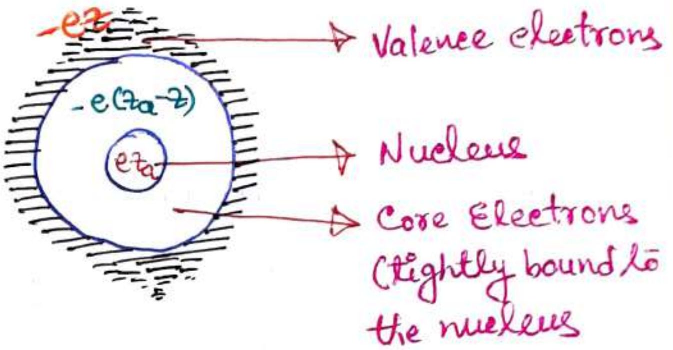
Interaction between oppositely charged ends of permanently polarized molecules with having H-atom is called the Hydrogen bond.

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

Cohesive energy

Free Electron Theory (of Metals)





The modern theory of solids initiated in more than a century back, especially metals due to their striking properties, e.g. good conductor of heat & electricity, malleable & ductile, lucrative lustre & sharp melting points. Agriculture & weaponry got renovated after human's usage of Copper (8000 BC), Bronze (3000 BC), iron (1200 BC). After the proposition of Kinetic Theory of Gases by Ludwig Boltzmann in 1872 and the discovery of electrons by JJ Thomson in 1896 (corpuscle of charge), it was a natural question to ask why electrons are immobile in some materials but very much mobile in other, although every material have electrons. Graphite is a conductor, but Diamond is an insulator although both are made of Carbon. In 1900 Paul Drude applied the Kinetic Theory to electrons to understand metallic conduction.

Drude-Lorentz theory (Gellium Model):

In the classical free electron theory, the kinetic theory of neutral dilute gas is applied to the dense metallic electron gas with certain assumptions: (a) Independent Electron Approximation, where collisions between different electrons is neglected, (b) Free Electron Approximation, where electron-ion interaction is also neglected, (c) Relaxation time Approximation, electrons under external field move in straight line following Newton's law, having Maxwellian speed distribution, elastic collissions with a relaxation time τ whose origin is unknown. The scattering probability in time interval dt is $\frac{dt}{\tau}$, and after collission, the momentum of electron resets instantaneously to $p = 0$.

To justify the assumptions, let us note that typical number density of conduction electrons is $\sim \underline{10^{22}/cm^3}$. The atomic distance is measured in terms of the "Bohr radius" (Hydrogen atom in ground state) $= \frac{\hbar^2}{me^2} = 0.529 \times 10^{-8}\,cm = \underline{0.529\,\mathring{A}}$. If $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$ is radius of a sphere whose volume is equal to the volume per conduction electron, then typically in metals, $2a_0 \leq r_s \leq 6a_0$. In the **classical** picture at room temperature $\underline{\tau \sim 10^{-14} - 10^{-15}\,s}$. From the equipartition theorem $\frac{1}{2}mv_0^2 = \frac{3}{2}k_BT$ we have average electronic speed $\underline{v_0 \sim 10^7\,cm/s}$, so that the average distance traversed by electron between collissions $\underline{l} = v_0\tau \sim 1\text{–}10\,\mathring{A}$ $\underline{\sim a_0}$. This justifies assumption ⓐ but in the **quantum** picture at ~~room~~ low temperature $\underline{\tau \sim 10^{-13} - 10^{-14}\,s}$ and $v_0 \neq v_0(T)$ so that the mean free path at low temperature $\underline{l} \sim 10^3 - 10^8\,\mathring{A} \sim \underline{1\,cm}$ which is roughly the size of the sample. So assumption ⓑ isn't justified!

The equation of motion of the electron is found from the temporal history of momentum $\vec{p}$ as

$$\underbrace{\langle \vec{p}(t+dt)\rangle}_{\text{thermal averaged momentum at } t+dt} = \underbrace{\left(1-\frac{dt}{\tau}\right)}_{\text{probability of no collission}}[\underbrace{\vec{p}(t) + \vec{F}dt}_{\text{acceleration due to } \frac{d\vec{p}}{dt} = \vec{F}}] + \overset{\text{scattering to zero momentum}}{\vec{0}}\underbrace{\frac{dt}{\tau}}_{\text{probability of collission}}$$

$$\text{or} \quad \frac{d\vec{p}}{dt} = \vec{F} - \underbrace{\frac{\vec{p}}{\tau}}_{\text{drag force}} \quad \text{or} \quad m\dot{\vec{v}} = \underbrace{-e(\vec{E} + v\times\vec{B})}_{\text{Lorentz force}} - \frac{m\vec{v}}{\tau}$$

DC Electric Conductivity: For this purpose, let us suppose that we have $\vec{E} \neq 0, \vec{B} = 0$ so that $m\dot{\vec{v}} = -e\vec{E} - \frac{m\vec{v}}{\tau}$. At steady state $\dot{\vec{v}} = 0$ yields Drift velocity $\vec{v}_d = -\frac{e\tau}{m}\vec{E} = -\mu\vec{E}$ where $\mu = \frac{e\tau}{m}$ is the mobility. If n is the number density of electrons then the electrical current is $\vec{J} = -ne\vec{v}_d = -ne\left(-\frac{e\tau}{m}\vec{E}\right) = \frac{ne^2\tau}{m}\vec{E} = \sigma\vec{E}$ which is the Ohm's law with dc electrical conductivity $\sigma = \frac{ne^2\tau}{m} = \left(\frac{ne}{m}\right)\left(\frac{e\tau}{m}\right) = ne\mu$.

In metals, $n \sim$ constant, μ decreases with temperature, so as σ.

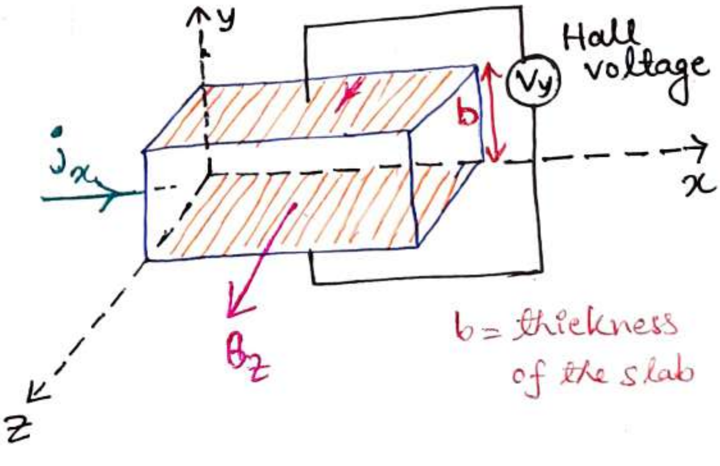
In semiconductor, n exponentially increases with temperature, σ increases.

In insulator, $n \sim$ constant, μ increases exponentially → dielectric breakdown.

Thermal transport property: from Fourier's law of heat conduction, heat current density $\vec{J}_q = K\vec{\nabla}T$ where thermal conductivity K is $K = \frac{1}{3}nc_v\langle v\rangle\lambda$ with $c_v = \frac{3}{2}k_B$ is the heat capacity per particle for a monoatomic gas, $\langle v\rangle$ average thermal velocity & $\lambda = \langle v\rangle\tau$ is the scattering length. In Metals, "**Wiedemann-Franz law**" states that good conductor of electricity are also good conductor of heat and the ratio (Lorenz number) $L = \frac{K}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 \sim 1.11 \times 10^{-8}$ Watt Ω/K^2 the experimental value was 2.22×10^{-8} Watt Ω/K^2, twice that of Drude's theory. The falacy of the theory & striking correctness of WF law lies in the fact that $C_V \neq \frac{3}{2}k_B$ because c_V is mostly contributed by the vibrational (Debye) specific heat (phonons) and linear T dependence at low temperature, instead of electronic specific heat. In Drude's theory C_v is way too large & velocity is way too small that cancels out in the ratio of L.

Hall Effect:

Edwin Hall in 1879 discovered that if a uniform magnetic field B_z is applied in $\hat{z}$-direction normal to the direction of a steady current flow j_x in a rectangular slab, then



a transverse electric potential difference develops in the $\hat{y}$ direction such as $V_y \propto j_x$ $\therefore$ $V_y = R_H j_x B_z b$.

$\propto B_z$ $\qquad$ $\overset{\downarrow}{\text{Hall coefficient.}}$

$\propto b$

Due to the magnetic field, the electrons moving in the $-x$ direction experiences a Lorentz force $F_y = -e v_x B_z$ where v_x is the uniform drift velocity. While the electrons are deflected in the y direction and are deposited near the surface of the slab, a potential differance in y direction is developed until the Hall electric field E_y stops further deflection of electrons.

$\therefore$ $F_y = -eE_y = -\dfrac{eV_y}{b} = -e v_x B_z$. Equating we have

$$e v_x B_z = \frac{eV_y}{b} \quad \therefore \quad v_x = \frac{V_y}{b B_z}$$

So the current density $j_x = -n e v_x = -ne\dfrac{V_y}{bB_z}$

or $V_y = -\dfrac{1}{ne} j_x B_z b = R_H j_x B_z b$ where $\boxed{R_H = -\dfrac{1}{ne}}$

We could've obtained the same expression from the equation of motion in the steady state $\dfrac{d\vec{p}}{dt} = -e(\vec{E} + \vec{v}\times\vec{B}) - \dfrac{\vec{p}}{\tau} = \vec{0}$

or $-e\vec{E} + \dfrac{\vec{j}\times\vec{B}}{n} + \dfrac{m}{ne\tau}\vec{j} = \vec{0}$ $\quad$ $[\because \vec{p} = m\vec{v},\ \vec{j} = -ne\vec{v}]$

$[\vec{j} = \overline{\overline{\sigma}}\vec{E}$

or $\vec{E} = \dfrac{1}{ne}(\vec{j}\times\vec{B}) + \dfrac{m}{ne^2\tau}\vec{j} = \overline{\overline{\rho}}\,\vec{j}$ $\qquad$ $\vec{E} = \overline{\overline{\rho}}\,\vec{j}\,]$

$$\overline{\overline{\rho}} = \begin{pmatrix} \frac{m}{ne^2\tau} & \frac{B}{ne} & 0 \\ -\frac{B}{ne} & \frac{m}{ne^2\tau} & 0 \\ 0 & 0 & \frac{m}{ne^2\tau} \end{pmatrix}$$

$\dfrac{E_y}{j_x} = \rho_{xy} = -\rho_{yx} = \dfrac{B}{ne} =$ "Hall resistivity"

and $R_H = \dfrac{\rho_{yx}}{B} = -\dfrac{1}{ne}$. $\quad$ $\left[\dfrac{E_x}{j_x} = \rho_{ii} = \dfrac{m}{ne^2\tau}\right.$ magnetoresistance$]$

While $R_H \propto n^{-1}$ and $R_H \propto -e^{-1}$, therefore the measurement of Hall coefficient furnishes two important characteristic of a conductor : ⓐ density of conduction electrons, ⓑ sign of the charge carrier. For monovalent atoms (Li, Na, K), $R < 0$ means electrons are the carriers. However for certain divalent (Be, Mg) atom, $R > 0$ which cannot be explained by the Drude's classical picture. Nevertheless the Hall-probe experiment on metals can successfully measure the #density of electrons n or viceversa, for a given n one can determine the strength of the magnetic field (Hall sensor). Drude's theory works well where n is low so that R_H, V_y etc are large (such as semiconductors)

#Read about AC electrical conductivity $\sigma(\omega) = \frac{ne^2\tau/m}{1 - i\omega\tau}$ and plasma oscillations (plasmons) from any standard book.

Sommerfeld's Free electron Theory of Metals:

Despite the success of Drude-Lorenz classical electron theory that upto reasonable success explained WF law, difficulties were

ⓐ Why Debye theory of lattice specific heat that ignores electronic specific heat is accurately valid for metals? $\frac{3}{2}k_B$ heat capacity is non-existent in metals for which Seebeck & Peltier coefficients comes out to be wrong by a factor of 100.

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

ⓒ Hall effect of some divalent metal (Be, Mg, Ca) is positive, meaning that the charge carriers are positive.

ⓓ Electric resistivity has a temperature dependence $\rho = \rho_0(1+\alpha T)$ that cannot be explained from the classical electron gas model.

ⓔ Certain metals (Tin, Mercury), having poor electrical conductivity, becomes superconductor at very low temperature but alkali & noble metals (Ag, Au, Pt) do not exhibit superconductivity.

Quantum Properties of Fermions :

In the independent-electron approximation, we represent confinement of N electrons to a volume V due to ion-electron attraction. To that end, we have to treat electrons as fermions and find out the 1-electron quantum states from time-independent Schrödinger equations with Born-von Karmann boundary condition (periodic) to restrict to bulk properties (rather than surface) as well as plane progressive wave solutions instead of standing wave. Then we will populate N-electron quantum states using Pauli's exclusion principle.

Schrödinger equation for free electron in 3D

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \overset{=0}{V}\psi = E\psi \;\Rightarrow\; \nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0.$$

Applying the boundary condition $\psi(\vec{r}) = \psi(\vec{r}+\vec{L}) = Ae^{i\vec{K}\cdot\vec{r}}$ with $e^{iK_xL} = e^{iK_yL} = e^{iK_zL} = 1$ giving $K_x = \frac{2\pi n_x}{L}$, $K_y = \frac{2\pi n_y}{L}$, $K_z = \frac{2\pi n_z}{L}$ (n_x, n_y, n_z integers), we have (quantization condition)

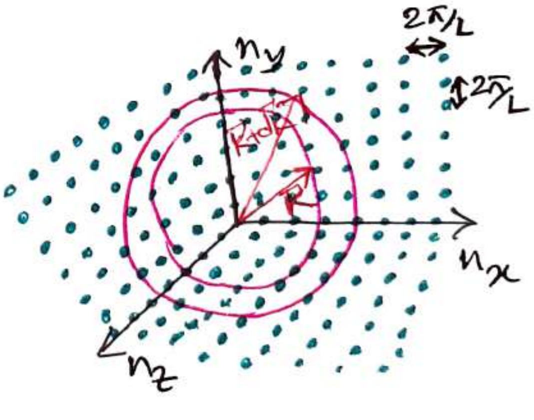
$$\nabla^2\psi = -K^2\psi \quad \text{so that} \quad -K^2\psi + \frac{2m}{\hbar^2}E\psi = 0$$

$$\text{or } E = \frac{\hbar^2K^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2).$$

Each set of (n_x, n_y, n_z) gives a stationary state of an electron inside the metal. In K-space, however we need to calculate the number of possible states of integers within $\vec{K}$ & $\vec{K}+d\vec{K}$, each of which gives rise to one electronic state, which is

$$L^3 D(K) \simeq \frac{4\pi K^2 dK}{(2\pi/L)^3}$$

or # of allowed points $\simeq \dfrac{\text{volume of space contained within } K \text{ \& } K+dK}{\text{volume of K-space per point}}$



Now $E = \frac{\hbar^2 K^2}{2m}$, $dK = \frac{m\,dE\,\hbar}{\hbar^2\sqrt{2mE}} = \frac{1}{\hbar}\sqrt{\frac{m}{2}}\,E^{-1/2}dE$. Substituting back,

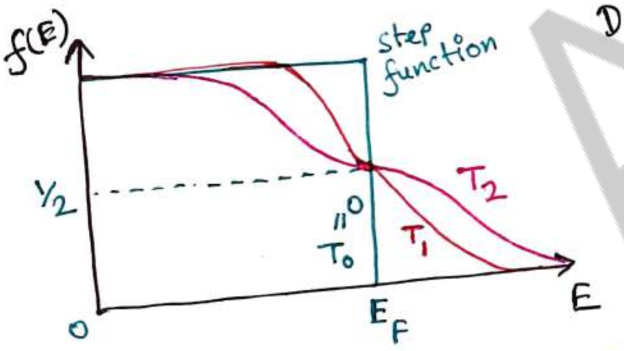
$$L^3 D(E) = \frac{4\pi L^3}{8\pi^3}\,\frac{2mE}{\hbar^2}\,\frac{1}{\hbar}\sqrt{\frac{m}{2}}\,E^{-1/2}dE = L^3\,2\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE$$

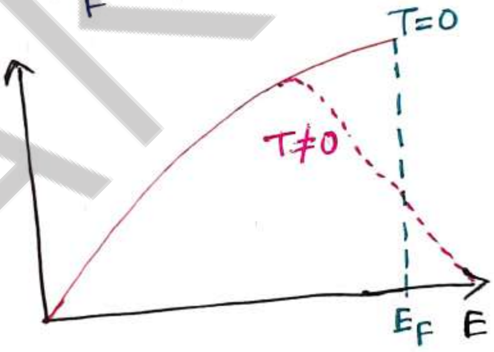
or $D(E) = 2\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE$. Since electrons have spin $\pm\frac{1}{2}$, so each energy state will have 2-fold degeneracy, so using Pauli's Exclusion principle, the total number of states per unit volume at $T=0K$ is $D(E) = 2\times 2\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE = 4\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE$.

At a finite temperature for a system of fermions with chemical potential μ, the probability that an electron occupies a state with energy E is given by Fermi-Dirac distribution function

$$f(E) = \frac{1}{e^{(E-\mu)/k_BT}+1} = \frac{1}{e^{\beta(E-\mu)}+1}$$ where $\beta = \frac{1}{k_BT}$ and $\mu = \frac{\partial G}{\partial N}$

is the chemical potential. $= E_F$ (Fermi Energy at $T=0$).

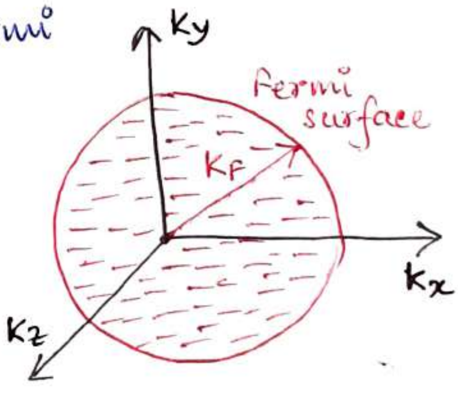




At $T=0$, $f(E)=0$ if $E > E_F$ and $f(E)=1$ if $E < E_F$. At $T\neq 0$, $f(E)=\frac{1}{2}$ if $E=E_F$.

$\therefore$ At $T=0$, $f(E) = \textcircled{H}(E_F - E)$ is a step-function. Below Fermi energy E_F, all states are filled & above E_F, all states are empty. At finite temperature at E_F, only half of the states are filled. In K-space, the sphere of radius K_F (Fermi wave vector) containing the occupied 1-electron levels is called the Fermi Sphere with Fermi Surface energy $E_F = \frac{\hbar^2 K_F^2}{2m}$ with Fermi momentum $p_F = \hbar K_F$.

$S_F = 4\pi K_F^2$,



To calculate the expression of these quantities in terms of number density of electrons, we know that

$$\int_0^{\infty} f(E)\, D(E)\, dE = n \Rightarrow \int_0^{\infty} D(E)\, \textcircled{H}(E_F - E)\, dE = n$$

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

or $\boxed{E_F = \dfrac{h^2}{2m}\left(\dfrac{3n}{8\pi}\right)^{2/3}}$. This is true at $T=0$, but at finite temperature $f(E) \neq \textcircled{H}(E_f - E)$ & in the vicinity of $\mu = E_F$ in the neighbourhood $\Delta E \sim K_B T$, one can Taylor expand $D(E)$ about $E = \mu$ to obtain

$$\int_{-\infty}^{\infty} D(E) f(E)\, dE = \int_{-\infty}^{\mu} D(E)\, dE + \frac{\pi^2}{6}(K_B T)^2 D'(\mu) + O(K_B T)^4$$

that yields $\displaystyle \mu = E_F - \frac{\pi^2}{6}(K_B T)^2 \frac{D'(E_F)}{D(E_F)} = E_F - \frac{E_F}{3}\left(\frac{\pi K_B T}{2E_F}\right)^2$. So the shift in chemical potential is $O(T^2) \sim 0.01\%$ at room temperat

Again at $T=0$, from $\displaystyle E_F = \frac{\hbar^2 k_F^2}{2m}$ we have $\displaystyle k_F^2 = \frac{2m}{\hbar^2}\frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3}$
$= (3n\pi^2)^{2/3}$

∴ Fermi wave vector $\boxed{k_F = (3\pi^2 n)^{1/3}}$ and Fermi velocity $\displaystyle v_F = \frac{\hbar k_F}{m}$

$\boxed{v_F = \dfrac{\hbar}{m}(3\pi^2 n)^{1/3}}$. We can also estimate Fermi Temperature from $E_F = \frac{3}{2} K_B T_F$ as $\boxed{T_F = \dfrac{2E_F}{3K_B} = \dfrac{2\hbar^2}{6K_B m}(3\pi^2 n)^{1/3}.}$ $\sim 39000\text{K}$ For $n \sim 10^{22}/\text{cm}^3$ we have Fermi wave vector $\displaystyle k_F = \frac{3.63}{r_s/a_0}\,\text{Å}^{-1} \sim \underline{\underline{\text{Å}^{-1}}}$ so that $\lambda_F \sim 1\text{Å}$

Fermi velocity $\displaystyle v_F = \frac{4.2}{r_s/a_0} \times 10^8\ \text{cm/s} \sim \underline{\underline{10^8\ \text{cm/s}}}$. Fermi energy $\displaystyle \varepsilon_F = \frac{e^2}{2a_0}(k_F a_0)^2$
$\displaystyle \sim \frac{e^2}{2a_0}\ \underline{(\text{Rydberg's constant})}_{= 13.6\ \text{eV}} = \frac{50.1}{(r_s/a_0)^2}\,\text{eV} \sim \underline{\underline{[1.5 - 15]\,\text{eV}}}$ and Fermi temperature
$\displaystyle T_F = \frac{58.2}{(r_s/a_0)^2} \times 10^4\,\text{K} \sim \underline{\underline{10^4\,\text{K}}}.$

AT $T = 0K$, the average energy of the electron is

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

$$= \frac{4\pi}{n}\left(\frac{2m}{h^2}\right)^{3/2}\frac{2}{5}E_F^{5/2} = \cancel{\frac{1}{n}}\,\underbrace{4\pi\left(\frac{2m}{h^2}\right)^{3/2} E_F^{3/2}\frac{2}{3}}_{\cancel{n}}\,\frac{3}{5}E_F = \frac{3}{5}E_F \qquad \boxed{\bar{E} = 0.6E_F}$$

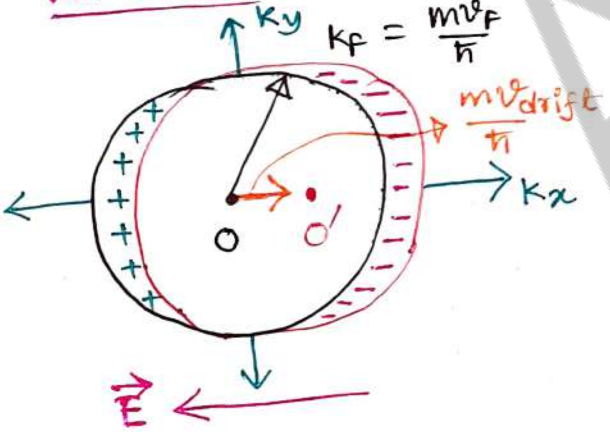
Average speed of electron at $T = 0K$ is $\bar{v} = \frac{1}{n}\int_0^{v_F} v\,dn$

Now $v_F = \frac{\hbar}{m}(3\pi^2 n)^{1/3}$ or $n = \frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 v_F^3$. If all electronic velocity are below v_F then from $n = \frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 v^3$, the differential number density of states between v & $v + dv$ is $dn = \frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 3v^2 dv$

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

$$= \cancel{\frac{1}{n}}\,\underbrace{\frac{1}{3\pi^2}\left(\frac{m}{\hbar}\right)^3 v_F^3}_{\cancel{n}}\,\frac{3}{4}v_F, \quad \therefore \boxed{\bar{v} = \frac{3}{4}v_F = 0.75v_F}$$

Sommerfeld's Free electron theory ; DC electrical conductivity revisited :



In 1925 Pauli discovered the exclusion principle & in 1926 Fermi-Dirac derived the FD statistics. Sommerfeld incorporated this into Drude's classical electron theory, and corrected the overestimated heat capacity per particle & underestimated velocity of electrons, whose compensating ratio gave Wiedemann-Franz somewhat correct estimate. Despite all this, Drude's theory gives correct estimate of transport properties (DC electrical conductivity, Hall coefficient). This is surprising, but the concept of Fermi Surface introduced by Sommerfeld changes the notion of conduction in metals. Firstly to realize that $\frac{\hbar^2}{2m} = 6.11 \times 10^{-39}$ m kg/s and for $L = 0.01m$, $k = \frac{2\pi}{L} = 628\ m^{-1}$, $E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 = 2.41 \times 10^{-33}$ J. So the 1 electron states with $E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2(n_x^2 + n_y^2 + n_z^2)$

are "quasi-continuous", $n_x = 0 = n_y = n_z$, $E = 0$, $n_x = 1, n_y = n_z = 0$, $E = 2.41 \times 10^{-33}$ J, $n_x = 1, n_y = 1, n_z = 0$, $E = 8.42 \times 10^{-33}$ J, ...

When an electric field is switched on, movement of the Fermi surface gives a displacement of the centre of Fermi sphere. This displacement is equivalent to creation of electrons on one side & positive charges on the other side. Shifted Fermi sea has an average drift velocity $\vec{v}_d$ due to the electric field. Since the kinetic energy of the shifted Fermi sphere is higher than the energy of zero average velocity fermi sphere, electrons will scatter back with scattering time τ to lower the KE & bring the Fermi-sea back to its original position.

So if each electron have velocity $\vec{v} = \frac{\hbar \vec{K}}{m}$, then the 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 a constant rate in K-space,

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

where λ is the mean freepath of electrons or distance between two ions? But the collission of electron with impurity ions, imperfections & phonons will create a restoring force. Thus in steady state, $\vec{J} = ne\vec{v}_d$

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

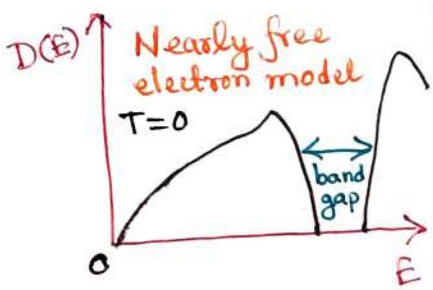
which is the "Ohm's law."

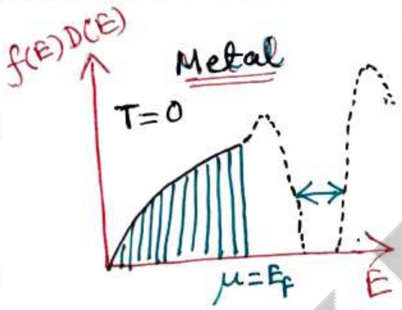
This expression is identical to Drude's free electron theory, but it destroys the notion of classical theory that all free electrons are conduction electrons, rather in the Sommerfeld's theory, only few electrons that lie in the vicinity of the fermi surface are the conduction electrons. Not all shortcomings are removed, eg. $\lambda = v_F t$ ~ 100 Å at room temperature but interionic spacing ~ 1-2 Å, so why no electron scattering from ions? Band theory solved these problems.

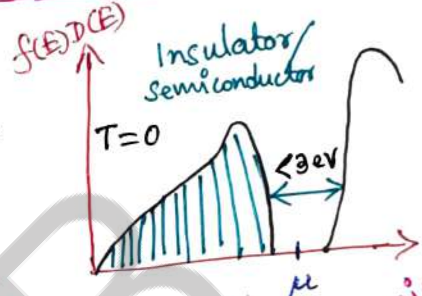
The Wiedemann-Franz law (revisited)

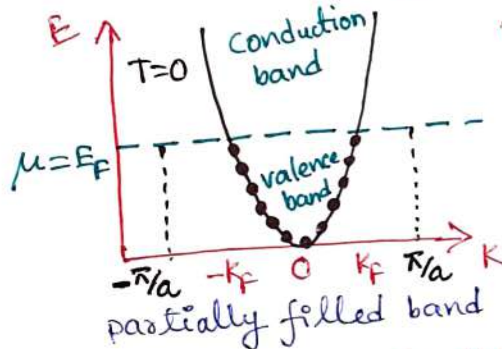
The estimate of Lorenz number $\frac{K}{\sigma T} = L$ is correct in Sommerfeld's theory $= \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.45 \times 10^{-8}\ W\Omega/K^2$ for many metals. Although we have the same expression for electrical & thermal conductivity, velocity is appropriately modified with Fermi velocity & the heat capacity as well. Thermopower also got resolved in Sommerfeld's theory.

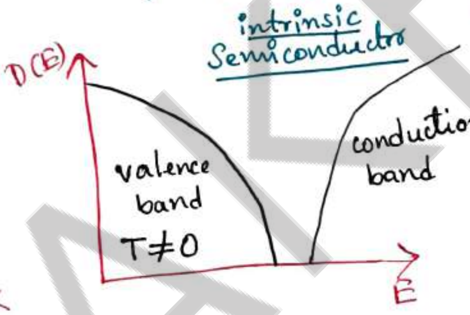
Position of Fermi level for Metals, Insulator & Semiconductor:

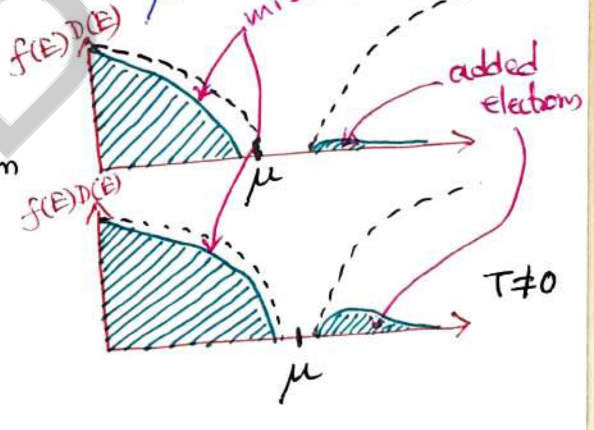


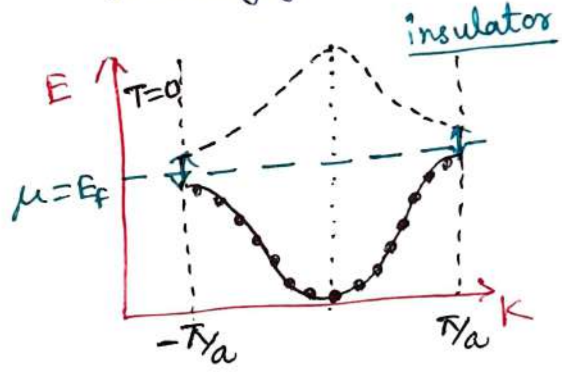


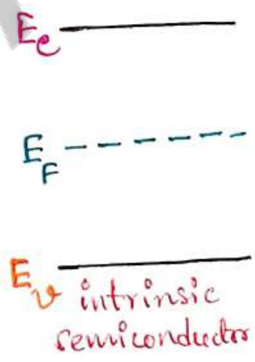


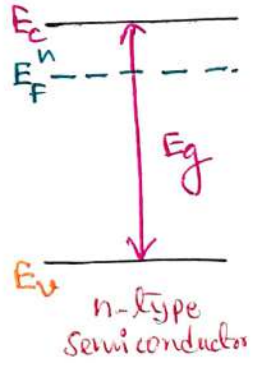


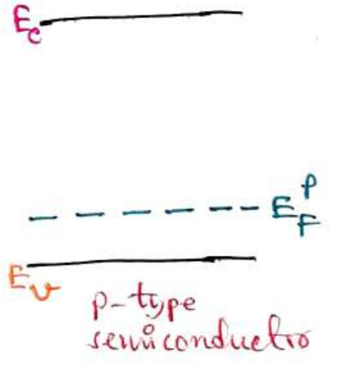












For intrinsic semiconductors, concentration of electrons in Conduction band (CB) is equal to the concentration of holes in the Valence band (VB). So $\lim_{T \to 0} \mu = E_F$ lies at the middle of the band gap E_g. For n-type material, concentration of electrons in the CB is greater than hole concentration in VB. Here, E_F lies near to E_C. This is opposite in p-type material where F_F lies near to E_V. Whenever a PN junction diode is formed, Barrier potential is

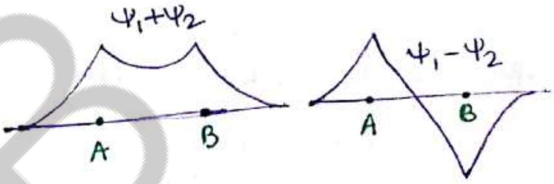
$$eV_B = E_F^n - E_F^p$$

Band Theory of Solids

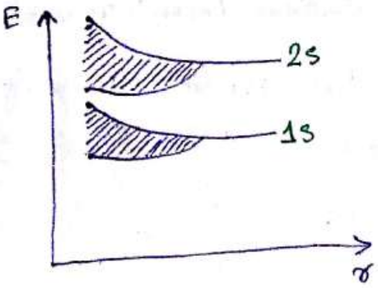
Formation of Energy Bands

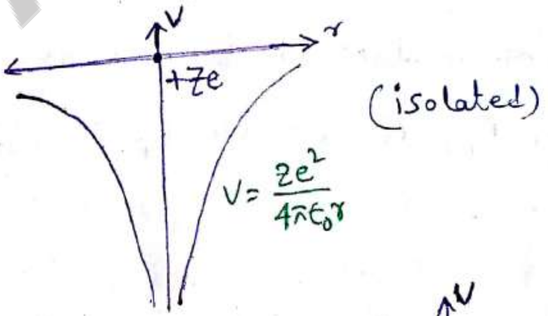
In solids, a periodic potential is formed by the nucleus and other electron cloud. Motion of an electron in periodic potential can be represented by Schrödinger equation, whose solution gives energy states. These states are filled with electrons according to Pauli's exclusion principle & all states are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

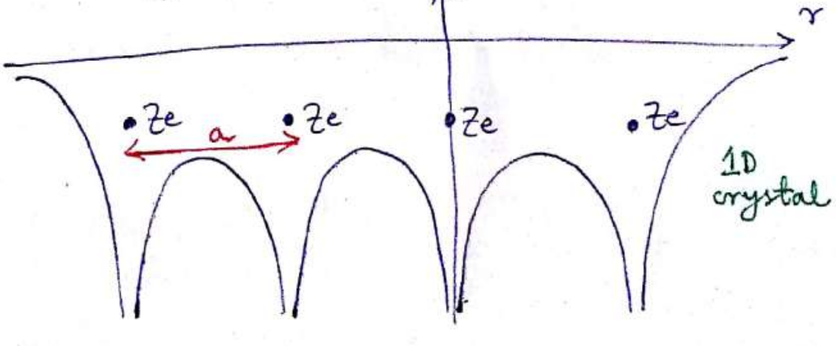
When two atoms are brought close, single energy level splits into a pair of levels. If ψ_1 & ψ_2 are electronic wave functions, then due to overlap, resultant wave function is $(\psi_1 \pm \psi_2)$. For symmetric case, electron can remain midway to A-B but for antisymmetric it cannot, so there is a difference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





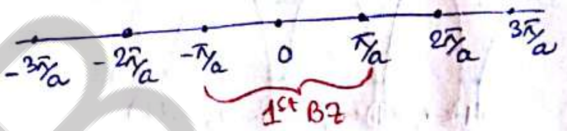


Origin of band structure This can be understood from nearly free electron model where electrons move in a periodic kernel in 1D. Energy of a free electron $E_K = \frac{\hbar^2 k^2}{2m}$ & $\psi_K(x) = e^{ikx}$

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 $K = \pm \frac{n\pi}{a}$.

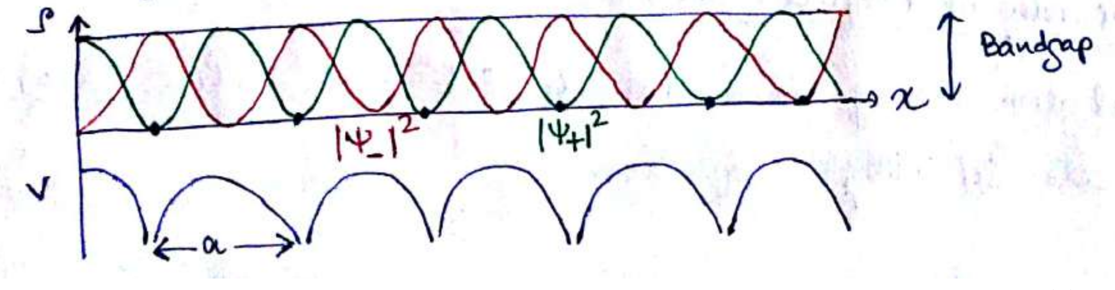
Thus a line representing K values is divided by energy discontinuities into segments of length $\pm \pi/a$ which are the Brillouin zones.



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

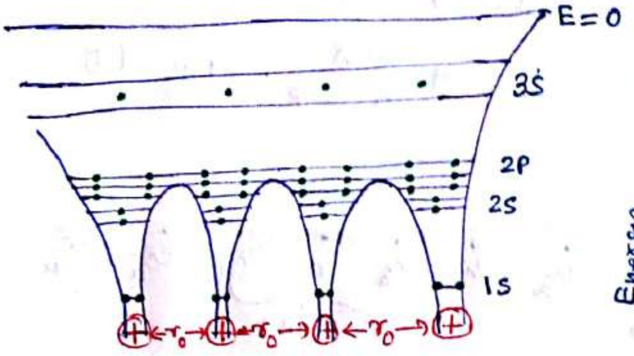
$$\psi_+ = e^{i\pi x/a} + e^{-i\pi x/a} = 2\cos\left(\frac{\pi x}{a}\right) \quad [x \to -x,\ \psi_+ \to \psi_+$$
$$\psi_- = e^{i\pi x/a} - e^{-i\pi x/a} = 2i\sin\left(\frac{\pi x}{a}\right). \quad x \to -x,\ \psi_- \to -\psi_-]$$

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 $e|\psi_+|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$, $e|\psi_-|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$

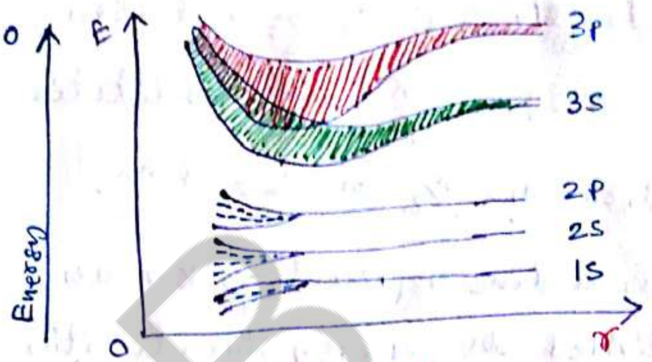


For $x = 0, a, 2a, \dots$ $\cos^2 \frac{\pi x}{a} = 1$, so its maximum at the kernel core and thus negative electron charge density lowering P.E. of Kernel. For $x = \frac{a}{2}, \frac{3a}{2}, \dots$, $\sin^2 \frac{\pi x}{a} = 1$, so its maximum in midway between kernel & increasing the P.E. w.r.t. to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

Energy bands in Sodium crystal



Potential energy



Energy band

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 states 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.

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

$$\begin{aligned}\psi(x+a) &= Af(x+a) + Bg(x+a)\\ &= (A\alpha_1 + B\beta_1) f(x) + (A\alpha_2 + B\beta_2) g(x)\\ &= \lambda A f(x) + \lambda B g(x) = \lambda \psi(x).\end{aligned}$$

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

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

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

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

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

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

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

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

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

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

Eq. ① becomes, $\lambda^2 - (\alpha_1 + \beta_2)\lambda + 1 = 0$. 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 $\psi_1(x+a) = \lambda\psi(x)$ & $\lambda_1\lambda_2 = 1$.

Special cases $(\alpha_1 + \beta_2)^2 < 4$, $\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0$ 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.

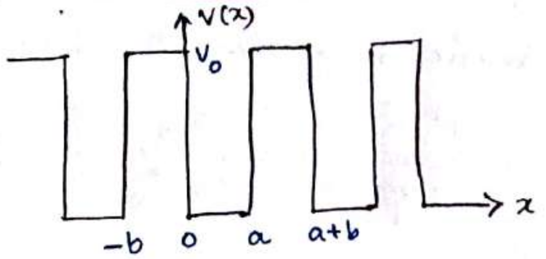
Special cases $(\alpha_1 + \beta_2)^2 > 1$, $\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0$ have real roots

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

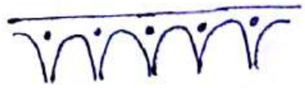
Although mathematically valid, these are forbidden wavefunctions as they're not bounded. at $\pm\infty$, both diverge.

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 orbands.

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~~ edgewith periodicity a+b. whose Schrödinger equation is

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

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

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 vanish. 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

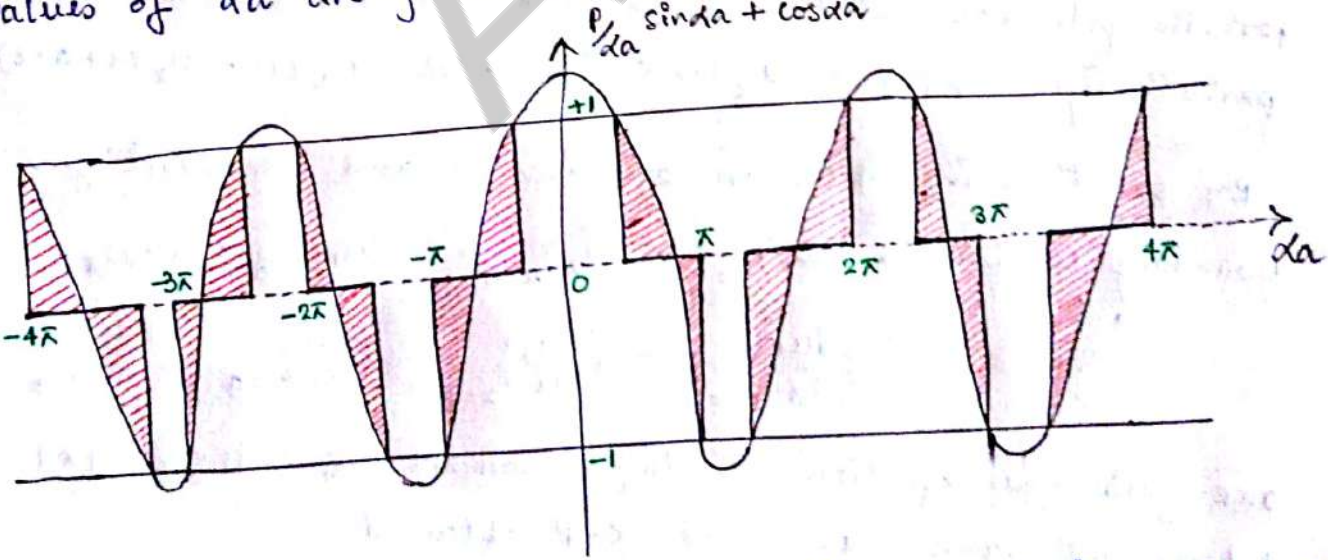
$$\frac{\beta^2+\alpha^2}{2\alpha\beta} = \frac{mV_0}{\alpha\beta\hbar^2} \qquad \therefore \quad \frac{mV_0 b}{\alpha\hbar^2}\sin\alpha a + \cos\alpha a = \cos ka$$

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

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. ∴ 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 $\cos ka = \pm 1$

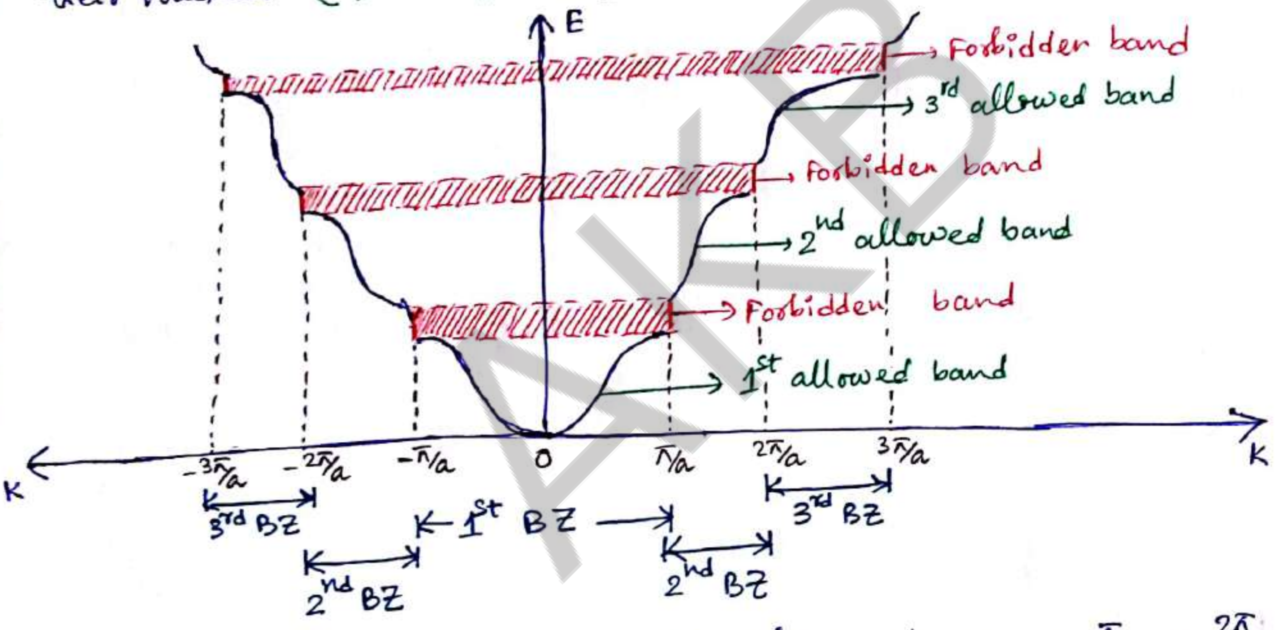
or $ka = n\pi$ or $k = \frac{n\pi}{a}$.

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, $\alpha a = \pm n\pi$

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

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



$E = \frac{\hbar^2k^2}{2m}$ 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 $\cos(k+\frac{2\pi n}{a})a = \cos ka$ &

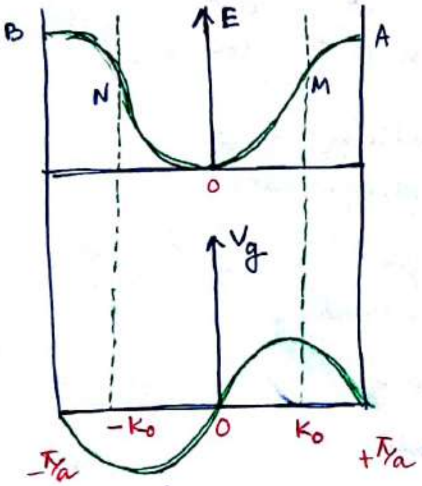
$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$ eqn. remains same.

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 ~~at~~ 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

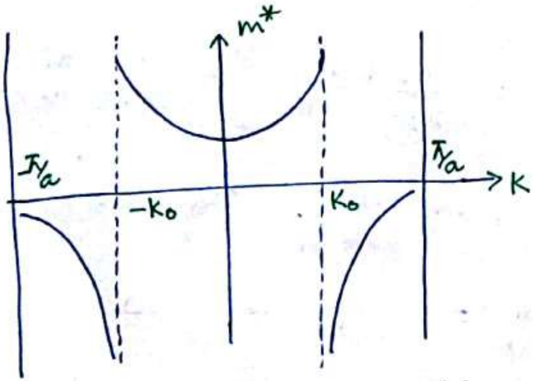
Now $v = \frac{1}{\hbar}\frac{dE}{dK}$ $\therefore dE = \frac{e\mathcal{E}}{\hbar}\frac{dE}{dK}dt$ or $\frac{dK}{dt} = \frac{e\mathcal{E}}{\hbar}$

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 $F = m^*a$)

∴ $m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$. 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.

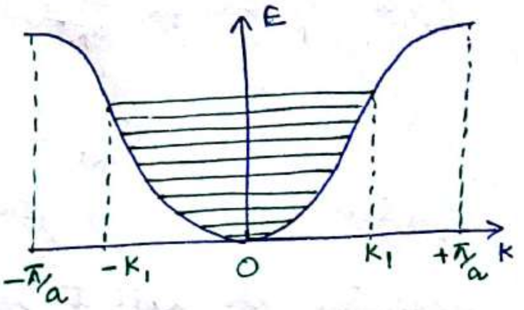
We can distinguish conductors (metals), insulators, semiconductors on the basis of band theory. $f_k = \frac{m}{m^*} = \frac{m}{\hbar^2}\frac{d^2E}{dk^2}$ that measures how much electrons can take part in electric conduction.

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

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

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

∴ $e^{iK(x+L)} = e^{iKx}$ 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 $\frac{dE}{dK} = 0$ ∴ $N_{eff} = 0$.

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, $\cos Ka = \cos 0 = 1$

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