

SECTION - A

Q.1.

(i) b

(ii) b

(iii) e

(iv) d

(v) d

(vi) b

(vii) e

(viii) d

(ix) d

(x) a

SECTION - B

Q.2 (a) There are only fourteen ways of arranging points in space lattices such that all the points have exactly the same environment. These fourteen lattice type are grouped into seven crystal systems according to seven types of conventional unit cells. These are triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, and Hexagonal. They are collectively known as Bravais lattice.

<u>Crystal system</u>	<u>Restrictions on cell axes</u>	<u>Restrictions on cell angle</u>	<u>Lattice symmetry</u>
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	Primitive
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	Primitive Base Centered
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive Body Centered Face Cent. Base Cent.
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive Body cent.
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive Body Center Face Center
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$ $< 120^\circ$	Primitive
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Primitive

2(b)

Given that

$$a = 1.2 \text{ \AA}$$

$$b = 1.8 \text{ \AA}$$

$$c = 2.0 \text{ \AA}$$

$$h = 2$$

$$k = 3$$

$$l = 1$$

therefore; intercepts on X =  $\frac{a}{h} = p$ " on Y =  $\frac{b}{k} = q$ " on Z =  $\frac{c}{l} = r$ 

$$\therefore p:q:r = \frac{1.2}{2} : \frac{1.8}{3} : \frac{2.0}{1}$$

$$= 0.6 : 0.6 : 2.0$$

Since  $p = 1.2 \text{ \AA}$ 

$$\therefore 1.2 : q = 0.6 : 0.6$$

$$\therefore q = \frac{1.2 \times 0.6}{0.6} = 1.2 \text{ \AA}$$

Similarly  $1.2 : r = 0.6 : 2.0$ 

$$r = \frac{1.2 \times 2.0}{0.6} = 4.0 \text{ \AA}$$

therefore intercepts along Y and Z are  $1.2 \text{ \AA}$  and  $4.0 \text{ \AA}$  respectively.

Q.3. Geometrical Structure factor

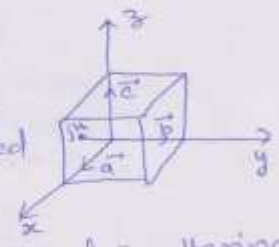
The relative intensities of various reflections depend upon the contents of unit cell i.e.

- number of atoms in unit cell
- position of atom
- electronic distribution of atoms in unit cell

If more atoms are present, then the phase differences of the scattered wave from different atoms must be taken into consideration. Let  $N$  atoms in a unit cell. Let us consider  $j$ th atom of the cell and atom is specified by

$$\vec{r}_j = u_j \vec{a} + v_j \vec{b} + w_j \vec{c}$$

Assume that all the electrons of the  $j$ th atom are concentrated at position  $r_j$ . Let  $f_j$  (form factor) represents a measure of scattering power of  $j$ th atom.



Total scattered amplitude is defined as the ratio of the amplitude of radiation scattered by the entire unit cell to the amplitude of radiation scattered by a single point electron placed at origin for same wavelength.

$$F(h'k'l') = \sum_j f_j e^{i\phi_j}$$

$$= \sum_j f_j e^{i \left(\frac{2\pi}{\lambda}\right) (\vec{r}_j \cdot \vec{N})}$$

$\phi_j \rightarrow$  phase difference between radiation scattered from  $j$ th atom of unit cell and that electron placed at origin.

(5)

$$\phi_j = \frac{2\pi}{\lambda} (\vec{r}_j \cdot \vec{N})$$

$(u_j, v_j, w_j)$  is coordinate of  $j^{\text{th}}$  atom

$$\vec{r}_j \cdot \vec{N} = \lambda (u_j e + v_j f + w_j g)$$

$$\therefore \vec{a} \cdot \vec{N} = e\lambda \quad \text{and} \quad \vec{N} = (\vec{s} - \vec{s}_0)$$

for identical atoms;  $f_j$  have same value  $f$   
then

$$F(efg) = fS$$

where  $S = \sum_j e^{\frac{2\pi i}{\lambda} (\vec{r}_j \cdot \vec{N})}$

$$S = \sum_j e^{2\pi i (u_j e + v_j f + w_j g)}$$

Geometrical Structure factor depends on geometrical arrangement of atoms within unit cell.

$$S = \frac{F}{f} = \frac{\text{Total scattering amplitude}}{\text{Atomic scattering factor}}$$

Intensity of radiation  $\propto (\text{Amp.})^2$

then  $I = |F|^2 = F^* F$

therefore,

$$I = \left[ \sum_j f_j \cos 2\pi (u_j e + v_j f + w_j g) \right]^2 + \left[ \sum_j f_j \sin 2\pi (u_j e + v_j f + w_j g) \right]^2$$

where  $F^*$  is complex conjugate of  $F$ .

For bcc

$n=2$ ; let  $(0,0,0) + (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

then  $F(h'k'l') = f \sum_j e^{2\pi i (u_j h' + v_j k' + w_j l')}$

$$= f \left[ 1 + e^{2\pi i \left( \frac{1}{2} (h'+k'+l') \right)} \right]$$

$$= f \left[ 1 + e^{\pi i (h'+k'+l')} \right]$$

$\therefore$  Structure factor for bcc;  $S = 1 + e^{\pi i (h'+k'+l')}$



$$S = 1 + e^{n\pi i(h'+k'+l')}$$

$$\text{Let } e^{n\pi i} = \cos n\pi + i \sin n\pi$$

$$\text{if } n=1 \text{ then } e^{i\pi} = \cos\pi + i\sin\pi = -1$$

$$n=2 \text{ then } e^{2\pi i} = \cos 2\pi + i\sin 2\pi = 1$$

Hence if  $n = \text{odd}$  then  $S = 0$ ;  $F = 0 \Rightarrow I = 0$

if  $n = \text{even}$  then  $S = 2$ ;  $F \neq 0 \Rightarrow I \neq 0$

$$n = h' + k' + l'$$

presence or absence of a reflection is considered only in terms of the first order reflection. So when the sum of miller indices are even then we get intensity but for odd numbers of  $n$  there will be no reflection. Such as

$h'$	$k'$	$l'$	$n = h' + k' + l'$	$S$	$F$	$I$
1	0	0	1	0	0	0
1	1	1	3	0	0	0
2	1	0	3	0	0	0

and so on

Q.4. (a)

Consider infinitesimal parallelepiped having dimensions  $dx, dy$  and  $dz$ .  
 work done by tension component  $(T_{xx}, T_{yy}, T_{zz})$   
 = force  $\times$  distance

$$= T_{xx} dy dz \times \delta e_{xx} dx$$

$$= T_{xx} \delta e_{xx} dx dy dz$$

$e_{xx}$  = unit elongation due to force including other components also

$$\text{work done} = [T_{xx} \delta e_{xx} + T_{yy} \delta e_{yy} + T_{zz} \delta e_{zz}] dx dy dz \quad \text{--- (1)}$$

work done by tangential component  $(T_{xy}, T_{yz}, T_{zx})$

Consider face normal to  $x$ -axis then  $T_{zx} dy dz$  constitute a couple whose moment is  $T_{zx} dy dz dx$ . Due to this couple, body is

sheared by angle  $e_{zx}$  and  $\delta e_{zx}$  represents the change in shear angle then

$$\text{work done} = T_{zx} dy dz dx \delta e_{zx}$$

$$= T_{zx} \delta e_{zx} dx dy dz$$

Similarly work done by  $T_{yz}$  and  $T_{xy}$  are added

$$\text{work done} = [T_{yz} \delta e_{yz} + T_{zx} \delta e_{zx} + T_{xy} \delta e_{xy}] dx dy dz \quad \text{--- (2)}$$

From eq<sup>n</sup> (1) & (2);

$$\text{work done} = [T_{xx} \delta e_{xx} + T_{yy} \delta e_{yy} + T_{zz} \delta e_{zz} + T_{yz} \delta e_{yz} + T_{zx} \delta e_{zx} + T_{xy} \delta e_{xy}] dx dy dz$$

So work done per unit volume

$$dW = [T_{xx} \delta e_{xx} + T_{yy} \delta e_{yy} + T_{zz} \delta e_{zz} + T_{yz} \delta e_{yz} + T_{zx} \delta e_{zx} + T_{xy} \delta e_{xy}] \quad \text{--- (3)}$$

(8)

when body undergoes elastic deformation, the work done by elastic forces is transformed into potential energy and some amount of work done is given by the body when deformation disappears  $dU = dW$

elastic energy density of body

$$U = F(e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx}, e_{xy})$$

$$\delta U = \left(\frac{\partial U}{\partial e_{xx}}\right) \delta e_{xx} + \left(\frac{\partial U}{\partial e_{yy}}\right) \delta e_{yy} + \left(\frac{\partial U}{\partial e_{zz}}\right) \delta e_{zz} \\ + \left(\frac{\partial U}{\partial e_{yz}}\right) \delta e_{yz} + \left(\frac{\partial U}{\partial e_{zx}}\right) \delta e_{zx} + \left(\frac{\partial U}{\partial e_{xy}}\right) \delta e_{xy}$$

From eq<sup>n</sup> (3) & (4),

$$T_{xx} = \left(\frac{\partial U}{\partial e_{xx}}\right) ; \quad T_{yz} = \left(\frac{\partial U}{\partial e_{yz}}\right)$$

$$T_{yy} = \left(\frac{\partial U}{\partial e_{yy}}\right) ; \quad T_{zx} = \left(\frac{\partial U}{\partial e_{zx}}\right)$$

$$T_{zz} = \left(\frac{\partial U}{\partial e_{zz}}\right) ; \quad T_{xy} = \left(\frac{\partial U}{\partial e_{xy}}\right)$$

Now;  $\frac{\partial U}{\partial e_{xx}} = T_{xx} = C_{11}e_{xx} + C_{12}e_{yy} + C_{13}e_{zz} \\ + C_{14}e_{yz} + C_{15}e_{zx} + C_{16}e_{xy}$

let  $\frac{\partial T_{xx}}{\partial e_{zx}} = \frac{\partial^2 U}{\partial e_{xx} \partial e_{zx}} = C_{15}$  — (5)

since  $\frac{\partial U}{\partial e_{zx}} = T_{zx} = C_{51}e_{xx} + C_{52}e_{yy} + C_{53}e_{zz} \\ + C_{54}e_{yz} + C_{55}e_{yz} + C_{56}e_{xy}$

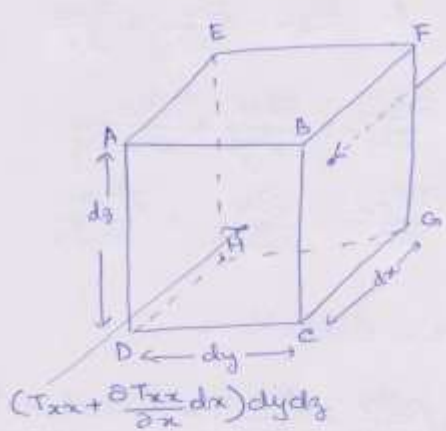
$$\frac{\partial^2 U}{\partial e_{zx} \partial e_{xx}} = \left(\frac{\partial T}{\partial e_{xx}}\right) = C_{51}$$
 — (6)

from (5) + (6)  $C_{15} = C_{51}$

In general form  $C_{ij} = C_{ji}$



Q.4 (b) Elastic waves in cubic crystals



Forces on the faces ABCD, EFGH are  $-T_{xx}dydz$  and  $(T_{xx} + \frac{\partial T_{xx}}{\partial x} dx)dydz$ . Net force along x-axis will be

$$= \frac{\partial T_{xx}}{\partial x} dx dy dz$$

the net x-component of force

on the cube is

$$F_x = \left( \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} \right) dx dy dz$$

$$= \text{mass} \times \text{acceleration}$$

$$= \text{volume} \times \text{density} \times \text{acceleration}$$

$$= \rho \frac{d^2 u}{dt^2} dx dy dz$$

where  $\rho$  = density and  $u$  = displacement along x-axis

$$\rho \frac{d^2 u}{dt^2} dx dy dz = \left( \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} \right) dx dy dz$$

$$\rho \frac{d^2 u}{dt^2} = \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z}$$

$$\text{Since } T_{xx} = C_{11}e_{xx} + C_{12}e_{yy} + C_{12}e_{zz}$$

$$T_{xy} = C_{44}e_{xy}$$

$$T_{xz} = C_{44}e_{xz}$$

$$\text{therefore } \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z}$$

$$= C_{11} \left( \frac{\partial e_{xx}}{\partial x} \right) + C_{12} \left( \frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x} \right) + C_{44} \left( \frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{xz}}{\partial z} \right)$$

$$\therefore \rho \frac{d^2 u}{dt^2} = C_{11} \left( \frac{\partial e_{xx}}{\partial x} \right) + C_{12} \left( \frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x} \right) + C_{44} \left( \frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{xz}}{\partial z} \right)$$

since  $e_{xx} = \frac{\partial u}{\partial x}$  ;  $e_{yy} = \frac{\partial v}{\partial y}$  ;  $e_{zz} = \frac{\partial w}{\partial z}$

$e_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}$  &  $e_{zx} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}$

$$\therefore \frac{\partial e_{xy}}{\partial x} = \frac{\partial^2 u}{\partial x^2} ; \quad \frac{\partial e_{xy}}{\partial y} = \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 v}{\partial x \partial y}$$

$$\frac{\partial e_{xy}}{\partial x} = \frac{\partial^2 v}{\partial x \partial y} ; \quad \frac{\partial e_{zx}}{\partial z} = \frac{\partial^2 u}{\partial z^2} + \frac{\partial^2 w}{\partial z \partial x}$$

$$\frac{\partial e_{zz}}{\partial x} = \frac{\partial^2 w}{\partial x \partial z}$$

therefore we get for x-direction

$$\rho \frac{d^2 u}{dt^2} = C_{11} \frac{d^2 u}{dx^2} + C_{44} \left( \frac{d^2 u}{dy^2} + \frac{d^2 u}{dz^2} \right) + (C_{12} + C_{44}) \left( \frac{d^2 v}{dx dy} + \frac{d^2 w}{dx dz} \right)$$

Equation of elastic wave in x-direction.

for [100] direction:-

Since longitudinal waves in 100 direction

$$u = u_0 e^{i(kx - \omega t)} \quad \text{--- (1)}$$

$$\frac{d^2 u}{dt^2} = -\omega^2 u_0 e^{i(kx - \omega t)}$$

$$\frac{d^2 u}{dx^2} = -k^2 u_0 e^{i(kx - \omega t)}$$

substituting we get

$$-\rho \omega^2 u_0 e^{i(kx - \omega t)} = -C_{11} k^2 u_0 e^{i(kx - \omega t)}$$

$$\text{then } \omega^2 \rho = C_{11} k^2$$

therefore longitudinal wave

$$v_l = \left( \frac{C_{11}}{\rho} \right)^{1/2}$$

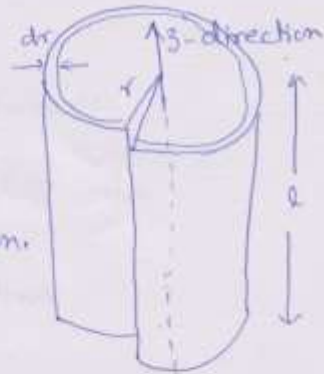
& Shear waves in [100] direction produce

$$v = v_0 e^{i(kx - \omega t)}$$

$$\text{so } v_s = \left( \frac{C_{44}}{\rho} \right)^{1/2} \quad \text{in y- & z- direction.}$$

Q.5. (a) Elastic strain energy of screw dislocation

Consider a cylindrical crystal of length  $l$ . Let a cut be made along the axis and the two sides of cut be displaced w.r.t. each other with a shear ' $b$ ' in  $z$ -direction.



$$\text{Elastic shear strain} = \gamma = \frac{b}{2\pi r}$$

Let  $G$  = shear modulus

$$\text{Stress required } T = G\gamma = G\left(\frac{b}{2\pi r}\right) \quad \text{--- (1)}$$

As the force build up from zero to its maximum value during the displacement  $b$

$$\text{So } T_{av} = \frac{1}{2}T = \frac{Gb}{4\pi r} \quad \text{--- (2)}$$

therefore, energy of dislocation

$$E = \int T_{av} b dA \quad \text{--- (3)}$$

$$\therefore dA = l dr$$

$$\therefore E = \int \left(\frac{Gb}{4\pi r}\right) b l dr \quad \text{--- (4)}$$

Let lower limit is  $r_0$  to upper limit  $R$ .

$$\begin{aligned} \text{then } E(R, r_0) &= \int_{r_0}^R \frac{Gb^2 l}{4\pi r} dr \\ &= \frac{Gb^2 l}{4\pi} \ln\left(\frac{R}{r_0}\right) \end{aligned}$$

$$\frac{E(R, r_0)}{l} = \frac{Gb^2}{4\pi} \ln\left(\frac{R}{r_0}\right) = \text{energy per unit length}$$

Energy is relatively insensitive to  $\frac{R}{r_0}$  term as it occurs in logarithmic term.

Q.5 (b)

(12)

Given

energy required for Frenkel defect  $E_F = 1.4 \text{ eV}$

$$T_1 = 300 \text{ K}$$

$$T_2 = 600 \text{ K}$$

$$\text{therefore } n = (N_{\text{Ni}})^{1/2} \exp\left(-\frac{E_F}{2k_B T}\right)$$

$$\text{we get } n_{300} = (N_{\text{Ni}})^{1/2} \exp\left(-\frac{1.4}{600 k_B}\right)$$

$$\text{and } n_{600} = (N_{\text{Ni}})^{1/2} \exp\left(-\frac{1.4}{1200 k_B}\right)$$

$$\begin{aligned} \text{So that } \frac{n_{300}}{n_{600}} &= \exp\left(-\frac{1.4}{k_B}\right) \left(\frac{1}{600} - \frac{1}{1200}\right) \\ &= \exp\left(-\frac{1.4}{8.614 \times 10^{-5}}\right) \times \frac{1}{1200} \end{aligned}$$

$$\frac{n_{300}}{n_{600}} = 1.316 \times 10^{-6}$$

= Ratio of frenkel defect

Q. (6)

De-Haas - Van Alphen effect

(15)

The cyclotron motion should be quantised because it is a periodic motion. The quantisation of electron orbit in a magnetic field give rise to a non-zero diamagnetism. This effect is connected with the oscillation in the magnetic moment as a function of magnetic field.

If a magnetic field  $\vec{H}$  is applied normal to x-y plane, then the energy levels of free electrons are

$$E_l = \frac{e\hbar H}{2mc} (2l+1) \quad \text{--- (1)}$$

where;  $l$  is quantum number. Applying the selection rule  $\Delta l = \pm 1$ , the standard result of cyclotron resonance frequency is

$$\hbar \omega_c = E_{l+1} - E_l = \frac{2e\hbar H}{2mc} = \frac{e\hbar H}{mc} \quad \text{--- (2)}$$

the energy of electron on a FS is written as

$$E_l = \hbar \omega_c \left( l + \frac{1}{2} \right) \quad \text{--- (3)}$$

where  $\frac{1}{2}$  is the phase factor.

Since cyclotron resonance frequency

$$\omega_c = \frac{2\pi eH}{\hbar^2 c} \frac{dE}{dA} \quad \text{--- (4)}$$

$$\& \int dA = \frac{2\pi eH}{\hbar^2 c \omega_c} \int dE = \frac{2\pi eH}{\hbar^2 c \omega_c} \times \hbar \omega_c \left( l + \frac{1}{2} \right)$$

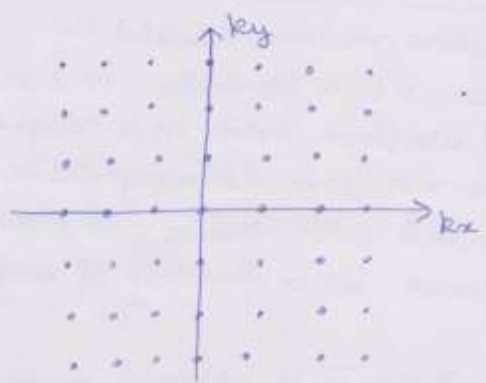
then

$$A = \frac{2\pi eH}{\hbar c} \left( l + \frac{1}{2} \right) \quad \text{--- (5)}$$

It shows that in a magnetic field, the area of orbit in k-space is quantised.

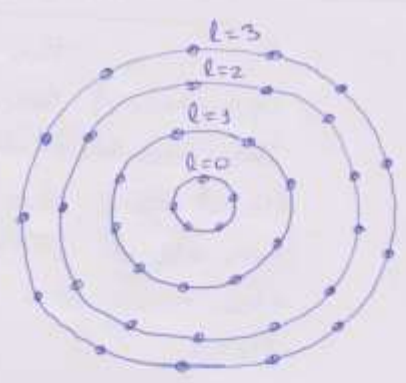


Effect of magnetic field :-



(a)

Allowed energy states for electrons in absence of magnetic field



(b)

Allowed electron states in a strong magnetic field

For a square specimen of side  $L$ , there are  $(\frac{L}{2\pi})^2 (\frac{2\pi eH}{c\hbar})$  states for each value of  $l$ .

The degeneracy of a level  $l$  is

$$= g_H = (\frac{L}{2\pi})^2 \frac{2\pi eH}{c\hbar}$$

The energy of electron in fully occupied level is

$$E = \sum_{l=0}^{\infty} (g_H) \hbar \omega_c (l + \frac{1}{2})$$

the magnetic moment at absolute zero is

$$\mu = -\frac{\partial E}{\partial H} = \frac{e}{2cT} (\frac{c\hbar}{eH})^2 A \quad ; \quad A = \text{Area bounded by cyclotron orbit}$$

$$\text{So } \Delta E = \mu \Delta H = \frac{e}{2cT} (\frac{c\hbar}{e})^2 A \Delta(\frac{1}{H}) \quad \text{--- (1)}$$

if only one type of cyclotron orbit, then

$$\Delta E = \hbar \omega_c = \frac{2\pi \hbar}{T} \quad \text{--- (2)}$$

From eq (1) & (2)

$$\Delta(\frac{1}{H}) = \frac{2\pi e}{\hbar c A}$$

By measuring the period of oscillation area  $A$ , the shape of Fermi surface can be determined.

### Q.7 (a) Orthogonalised Plane-wave method

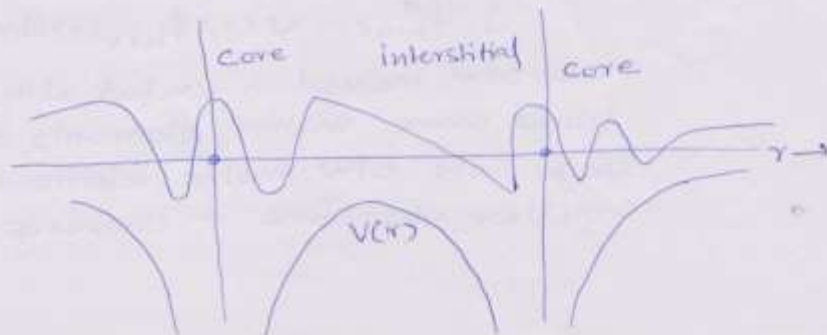
An alternative method of combining rapid oscillations in the ion-core region with plane-wavelike in interstitial region is orthogonalised plane-wave method. It does not require a muffin-tin potential.

The core wave-functions are well localised at lattice sites. The valence electrons can be found with appreciable probability in interstitial regions where their wave functions will be approximated by a very small number of plane waves. The approximating a valence wave function by a few plane waves everywhere in space fails to produce the rapid oscillatory behaviour required in core region. Herring suggested that plane wave orthogonalised to core levels may be used instead of simple plane waves. Thus, we define the orthogonalised plane wave (OPW)  $\phi_k$  by

$$\phi_k = e^{i\vec{k}\cdot\vec{r}} + \sum_c b_c \psi_c^e(r) \quad \text{--- (1)}$$

where

sum is over all core levels with Bloch wave vector  $k$ .



The core wave functions are assumed to be known, and the constants  $b_c$  are determined by requiring that  $\phi_k$  be orthogonal to every core level

$$\int dr \psi_k^{c*}(r) \phi_k(r) = 0 \quad \text{--- (2)}$$

$$\int \psi_k^{c*}(r) \left( e^{ikr} + \sum_c b_c \psi_k^c(r) \right) dr = 0$$

gives 
$$b_c = - \int \psi_k^{c*}(r) e^{ikr} dr$$

both plane wave  $e^{ikr}$  and core wave function  $\psi_k^c(r)$  separately satisfy the Bloch condition with wave vector  $k$ , therefore OPW  $\phi_k$  will also satisfy Bloch condition.

Now, actual electronic eigenstates of Schrödinger equation as a linear combination of OPWs

$$\psi_k = \sum_K c_K \phi_{k+K} \quad \text{--- (3)}$$

It is possible to determine the coefficients  $c_K$  and energies  $E(k)$  by using variational principle and with the condition that derivatives of resulting expression vanishes w.r.t. all  $c_K$ . The crystal potential  $V(r)$  may consider as in secular problem

$$\int \phi_{k+K}^*(r) V(r) \phi_{k+K}(r) dr$$

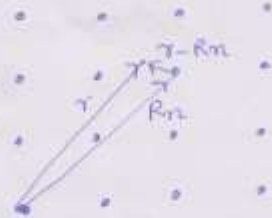
The OPW method is useful although the plane wave matrix elements of  $V$  are large; its OPW matrix elements are smaller therefore it converges very fast.

Q7(b)

Tight-Binding Approximation

Bloch suggested that crystal wave function with correct symmetry could be constructed by linear combination of atomic orbitals (LCAO).

If we take an electron in free atom and then suppose that such atoms are brought together to form a crystal.



$r \rightarrow$  position vector of  $e^-$

$R_n \rightarrow$  " " "  $n^{\text{th}}$  atom in crystal

$V(r - R_n) \rightarrow$  Potential of an  $e^-$  in free atom which is independent of other atoms

$V(r) \rightarrow$  crystal potential

The wavefunction of an  $e^-$  for a free atom is then approximated as  $\psi_0(r - R_n)$  so that crystal wave function may be written as an linear chain of the form

$$\psi_k(r) = \sum_n e^{i\vec{k} \cdot \vec{R}_n} \psi_0(r - R_n) \quad \text{--- (1)}$$

since electrons are in a periodic potential,

$\psi_k(r)$  must be a Bloch function

$$\begin{aligned} \psi_k(r + R_m) &= \sum_n e^{i\vec{k} \cdot \vec{R}_n} \psi_0(r - R_n + R_m) \\ &= e^{i\vec{k} \cdot \vec{R}_m} \sum_n e^{i\vec{k} \cdot (\vec{R}_n - \vec{R}_m)} \psi_0[r - (\vec{R}_n - \vec{R}_m)] \\ &= e^{i\vec{k} \cdot \vec{R}_m} \psi_k(r) \end{aligned}$$

this satisfies the Bloch condition.

$\psi_k(r)$  should be a solution of Schrödinger equation

$$H\psi_k(r) = E\psi_k(r)$$



The wavefunction of an  $e^-$  for a free atom is approximated as  $\psi_0(r-R_n)$  so that crystal wave function may be written as linear comb. Now, crystal Hamiltonian

$$H = H_0 + H_1$$

where  $H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V_0(r-R_n)$

$$\& H_1 = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$$

$$H_1 = V(r) - V_0(r-R_n)$$

$V_0(r-R_n) \rightarrow$  Potential due to  $n^{\text{th}}$  ground state atom on the electron at  $r$ .

The energy of the electron in the crystal  $E(k)$  can be found by evaluating

$$E(k) = \frac{\int \psi_k^*(r) (H_0 + H_1) \psi_k(r) dr}{\int \psi_k^*(r) \psi_k(r) dr} \quad \text{--- (2)}$$

Denominator

$$\int \psi_k^*(r) \psi_k(r) dr = \sum_m \sum_n e^{ik(R_n - R_m)} \int \psi_0^*(r-R_m) \psi_0(r-R_n) dr$$

neglecting overlap between atoms such that  $\text{--- (3)}$

$$\int \psi_0^*(r-R_m) \psi_0(r-R_m) dr = \delta_{nm}$$

$$\text{and } \int \psi_k^*(r) \psi_k(r) dr = N = \text{total atom}$$

Hence eq<sup>n</sup> (2) becomes

$$\begin{aligned} E(k) &= \frac{1}{N} \int \psi_k^*(r) [H_0 + H_1] \psi_k(r) dr \\ &= \frac{1}{N} \int \psi_k^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 + V_0(r-R_n) \right) \psi_k(r) dr \\ &\quad + \frac{1}{N} \int \psi_k^*(r) (V(r) - V_0(r-R_n)) \psi_k(r) dr \end{aligned}$$



$$E(k) = E_0 + \frac{1}{N} \sum_m \sum_n e^{ik(R_m - R_n)} \int \frac{\psi_0^*(r - R_m) (V(r) - V_0(r - R_n)) \psi_0(r - R_n) dr}{\psi_0^*(r - R_m) \psi_0(r - R_n)}$$

for  $n=0$  to  $n=N-1$  contains  $N$  identical terms.

$$E(k) = E_0 + \frac{1}{N} \sum_m e^{-ik \cdot R_m} \int \psi_0^*(r - R_m) (V(r) - V_0(r)) \psi_0(r) dr$$

Sum is taken over all the atoms of the crystal. — (3)

Further, if we make an approximation that  $\psi_0$  is spherically symmetric so that the contributions due to all nearest neighbours may be assumed to be identical.

for  $m=0$ ; eq<sup>n</sup> (3) becomes

$$\int \psi_0^*(r) [V(r) - V_0(r)] \psi_0(r) d\tau = -\alpha$$

and

$$\int \psi_0^*(r - R_m) (V(r) - V_0(r)) \psi_0(r) d\tau = -\beta$$

$R_m$  is a vector connecting the atom at the origin with nearest neighbour atom. So we get

$$E = E_0 - \alpha - \beta \sum_m e^{-ik \cdot R_m} \quad \text{--- (4)}$$

For fcc :-  $R_m = \pm \frac{a}{2}(\hat{i} + \hat{j})$  ;  $\pm \frac{a}{2}(\hat{j} + \hat{k})$  ;  $\pm \frac{a}{2}(\hat{k} + \hat{i})$

$$\text{therefore } \sum_m e^{-ik \cdot R_m} = e^{-i(k_x \frac{a}{2} + k_y \frac{a}{2})} + e^{-i(k_y \frac{a}{2} + k_z \frac{a}{2})} + e^{-i(\frac{a}{2} k_z + \frac{a}{2} k_x)} + e^{i(k_x \frac{a}{2} + k_y \frac{a}{2})} + e^{i(k_y \frac{a}{2} + k_z \frac{a}{2})} + e^{i(k_z \frac{a}{2} + k_x \frac{a}{2})}$$

Solving & substituting in eq<sup>n</sup> (4); it gives

$$E(k) = E_0 - \alpha - 4\beta (\cos k_x \frac{a}{2} + \cos k_y \frac{a}{2} + \cos k_z \frac{a}{2})$$

$$\text{for } \cos k_x \frac{a}{2} = +1 = \cos k_y \frac{a}{2} = \cos k_z \frac{a}{2}$$

$$E(k)_{\min} = E_0 - \alpha - 12\beta$$

$$\text{for } \cos k_x \frac{a}{2} = -1 = \cos k_y \frac{a}{2} = \cos k_z \frac{a}{2}$$

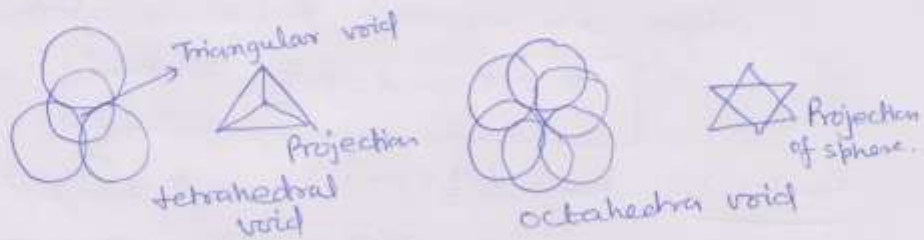
$$E(k)_{\max} = E_0 - \alpha + 12\beta$$

$$\text{Difference } = E(k)_{\max} - E(k)_{\min} = 24\beta$$

Q.8. (a) Voids in closed packed structures

Two kinds of voids that occur in close packing. If a triangular void in a close packed layer has a sphere directly above it, the resulting void will have four spheres around it. These spheres are arranged on the corners of a regular tetrahedron, such a void is called tetrahedral void.

If a triangular void pointing up in one close packed layer is covered by a triangular void pointing down in next layer. The resulting void will be surrounded by six spheres. These spheres are arranged on the corners of an octahedron. Such a void is known as an octahedral void.



In stacking, around one sphere 3B voids & 3C voids. The first three becomes tetrahedral void and other three becomes octahedral void.



Each octahedral void is surrounded by six spheres. & each sphere is surrounded by six voids. In tetrahedral void, each void is surrounded by four spheres and each sphere is surrounded by 8 voids.

### 8(b) Ewald's sphere

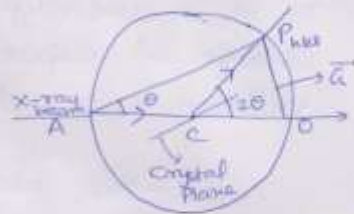
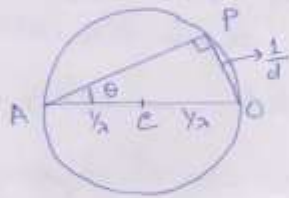
Bragg's diffraction condition gives

$$2d \sin \theta = n\lambda \quad \text{--- (1)}$$

$$\text{or } \lambda = 2 \left( \frac{d}{n} \right) \sin \theta = 2d_{hkl} \sin \theta_{hkl} \quad \text{--- (2)}$$

$$\sin \theta_{hkl} = \frac{(n/2)}{d_{hkl}} = \frac{1/d_{hkl}}{2/\lambda} \quad \text{--- (3)}$$

Triangle inscribed inside a circle is a right-angled triangle when the diameter of the circle is taken as hypotenuse of the triangle.



AO is direction of incident beam. AP makes an angle  $\theta$  with respect to incident beam. Since OP is normal to crystal plane and length  $\frac{1}{d_{hkl}} = \sigma_{hkl} = a$  is called reciprocal lattice vector. CP is direction of diffracted beam. The crystal to be at the center of a circle of radius  $\frac{1}{2}$ . The origin O is origin of reciprocal lattice net. Whenever a reciprocal lattice vector intersect the circle, the Bragg's condition is satisfied, then the diffracted beam passes through the point of intersection. The locus of point where the diffracted beam and reciprocal lattice point intersect a circle of radius  $\frac{1}{2}$  is called Ewald sphere or sphere of reflection.



### 8(c) London's Equations

At any temperature, the total sum of superelectrons and normal electrons is equal to the conduction electron density in the material in normal state. The conduction electrons  $n$  become

$$n = n_n + n_s \quad \text{--- (1)}$$

Let us suppose that a small transient electric field  $E$  arises within a superconductor which freely accelerates the superelectrons. If  $v_s$  is average velocity,  $m$  is mass and  $e$  is charge of superelectron, then equation of motion is  $m \frac{dv_s}{dt} = -eE$  --- (2)

and the current density of superelectron is  $J_s = -en_s v_s$  --- (3)

$$\Rightarrow \boxed{\frac{dJ_s}{dt} = \frac{n_s e^2}{m} E} \quad \text{--- (4)}$$

This is called London first equation. This shows that it is possible to have steady state current in a superconductor in the absence of an electric field.

$$\text{since } J_n = \sigma E \quad \text{--- (5)}$$

from Maxwell's eq<sup>n</sup>  $\nabla \times E = -(\frac{dB}{dt}) \Rightarrow E=0 \Rightarrow B = \text{const.}$

$$\text{Let } \nabla \times (\frac{dJ_s}{dt}) = -\frac{n_s e^2}{m} \frac{dB}{dt}$$

Integrating above w.r.t. time we get

$$\boxed{\nabla \times J_s = -\frac{n_s e^2}{m} B} \quad \text{--- (6)}$$

This is London second equation.