

## COURSE OUTLINE

⇒ Crystal Structure, X-ray Crystallography, Amorphous Solids, Packing of atoms, Miller Indexes, Important types of Crystal Structure, Lattice structures.

⇒ X-ray Crystallography, Crystallographic Symmetry, Point group, Structure determination, Braggs Law and Laue diffraction equations, Reciprocal lattice and Construction of Brillouin's zones.

⇒ Atomic Scattering factor, Geometrical Structure factor And structure Amplitude factor, Crystal binding, Lattice Vibration of monoatomic And diatomic chains, Elastic waves In Cubic Crystals, Elastic Properties, Specific heat from Lattice Vibrations, Free Electron model, Free Electron gas heat Capacity, Electrical And thermal Conductivities

## REFERENCES

⇒ SOLID STATE PHYSICS By : Kittle (Best)

⇒ " " " By : Dekker

⇒ " " " By : Hart Jaures.

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Textbook

- \* M.A. Omar: Elementary Solid State Physics  
Addison Wesley 1993
- \* Charles Kittel: Introduction to Solid State Physics.  
8<sup>th</sup> Edition, Wiley 2004 - (major)
- \* N.W. Ashcroft And N.D. Mermin Solid State Physics.
- \* J.S. Blakemore: Solid State Physics, 3<sup>rd</sup> Edition Cambridge University Press, 1995
- \* H.-J. Bach, H. Luth: Solid State Physics. An Introduction to Principles of material Science, Springer 2003.

COURSE GOAL

- ⇒ Solid state Physics - Condensed matter Physics - largest branch of Physics - rubber/plastic - glasses - liquids - metal - Semiconductor - Ceramics/powders. - Applications.
- ⇒ MRI (magnetic resonance imaging) - SuperConductor
- ⇒ Chip Implementation.
- ⇒ Rechargeable lithium ion battery - New Physics.

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## BRANCHES OF SOLID STATE PHYSICS

1  $\Rightarrow$  Mechanical Properties

mass density.

Cohesive Energy.

Elastic Properties.

2  $\Rightarrow$  Thermal Properties.

Heat Capacity.

Thermal Conductivity

3  $\Rightarrow$  Electrical Properties.

Conductivity.

4  $\Rightarrow$  Magnetic Properties

magnetic Susceptibility

Pera

5  $\Rightarrow$  Optical Properties

## CRYSTALS

Material that have a periodic And regular repeated pattern.

CRYSTALS

Crystalline.

CRYSTALS  $\rightarrow$  Non Crystalline (Amorphous)

A Crystal Is Defined As a Periodic Array of Atoms Or molecules. This regular Array Or Arrangement may or may not result In External Symmetry. X-ray Diffraction, Scanning Electron Microscopy etc Can reveal The Structure.

Crystals Are Associated with Defects Such As Given Boundaries, Valencies, Impurities E.t.c  
Example of Crystals Are Quartz, NaCl.

### Amorphous Material

An Amorphous Solid has Short range Order In It's nearest neighbour bonds but not Long range Order of Periodic Atoms Structure. Examples Are Polymerized Plastic, Carbon black, graphites, glass

### Stacking of Atoms

The Atom of materials Can be Considered As hard spheres, Which Can be Stacked As closely As Possible. Atom Can be Stacked In the following ways:

- i - AB AB - Hexagonal close Packing (HCP)
- ii - ABC ABC - Face Centred Cubic (FCC)

### Periodic Structure

An Ideal Crystal Is Constructed by Placing An Infinite number of Structural Units together. In the Case of Cubic Crystals These Units will be Cubes. In general Case they Are Parallelopipeds Solids with Six faces All Parallelograms

Crystals Are Describes In terms of a Single Periodic lattice. The Outline of the Units Are Drawn from What Is called Lattice. A Lattice

Is a grid which has translational Symmetry - if we move from one point of the lattice to an equidistant point in another lattice in the neighbour around this point will look identical.

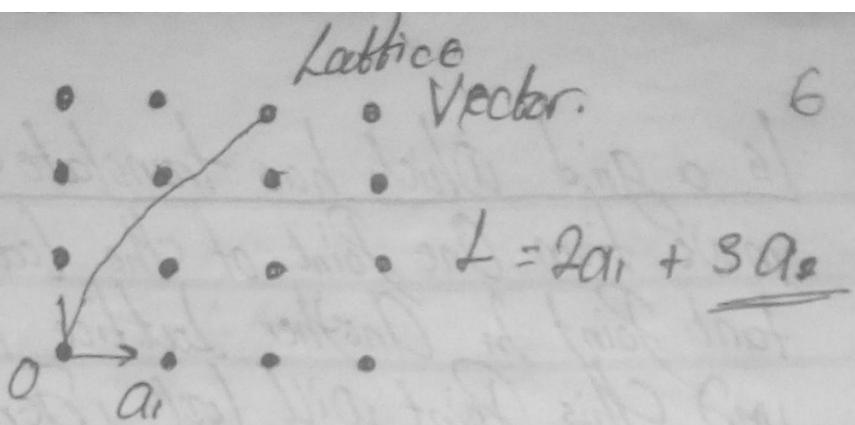
### Bravais Lattice.

Bravais lattice is a mathematical array of points in space such that the arrangement of the points about a given point is exactly the same as the arrangement of points about any other points. There are 14 Bravais lattices mathematically.

Structure	Cell Axis's	Lattice types
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$

### Lattice Vector / Unit Cell

Consider a two dimensional space lattice. To move from point O to any point of a rectangular lattice, for example we use TRANSLATION (i.e motion).



$$L = u a_1 + v a_2 \quad (2\text{-Dimension})$$

$a_1 + a_2$  = basis Vector

$L$  is lattice Vector

In 3-Dimension.

Where  $u, v$  and  $w$  are Integer.

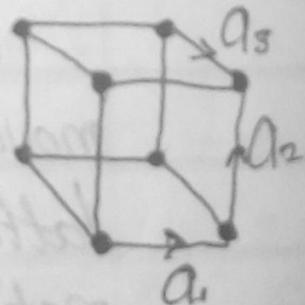
The basis Vector  $a_1, a_2$  and  $a_3$ , are Primitive if we can get from  $O$  to any other point of the lattice by using the lattice Vector  $L = u a_1 + v a_2 + w a_3$ . The Unit cell formed by the outline of the primitive basis vector is called the primitive unit cell. The Criteria for determining a primitive or non-primitive unit cell. If primitive cell will contain only one atom while the non primitive cell contain more than one atom. Non primitive.

### Examples of Primitive Cells (finding a single atom)

1) Simple Cubic (Sc) Each Atom

In

$$\text{Total no. of Atom} = \frac{1}{8} \times 8 = 1 \text{ atom}$$



1. C = Contribution of atoms + Contribution of corner atoms  
 Gives the Total No. atoms

## 2) Body Centred Cubic (B.C.C)

- Contribution of Corner

$$\text{Atom} = \frac{1}{8} \times 8 = 1$$

- Contribution of Centered Atom = 1  
Total =  $1+1=2$  Atoms.

$\Rightarrow$  Not Primitive  $\rightarrow$  more than 1 Atom.

## 3) Face Centered Cubic (F.C.C)

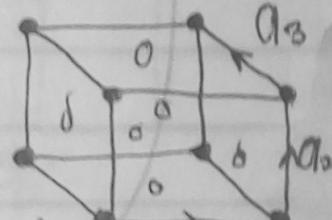
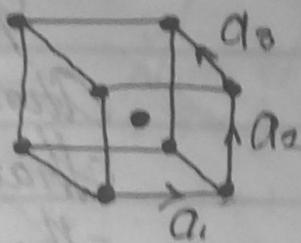
- Contribution from Eight Corner Atom =  $\frac{1}{8} \times 8 = 1$

- Contribution from Face Atom =  $\frac{1}{2} \times 6 = 3$

Six face Atom Contribute 3 Atom in the cell.

$$\therefore \text{Total number of Atom} = 1+3=4 \text{ Atom}$$

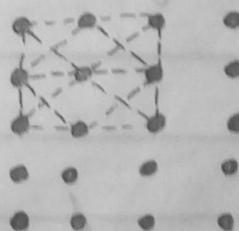
+ Was  $\Rightarrow$  The cell is non-Primitive.



Some of the Unit Cells as calculated have more than One Atom therefore we use technique such as wigner-seitz Cell to get a Primitive Cell.

The Principle.

- \* 1) Draw Perpendicular bisectors of line On the lattice Using a chosen Atom As the Origin.
- \* 2) The Volume Enclosed by the Perpendicular bisectors Is a Unit Primitive Cell.



(0,0,0)

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## The Wegner Seitz Primitive Cell.

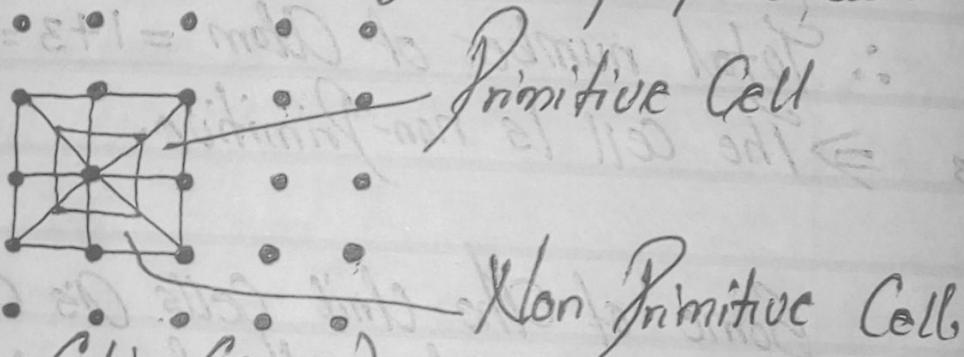
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The wegner Seitz primitive cell about an atom i.e If region of space that is closer to that point than to any other point that has the full system symmetry of the crystal. It has → a unique unit primitive cells.

### Co-Ordinate of Atoms In Cubic Crystals.

To obtain wegner Seitz.

- 1) Draw a line perpendicular Using a chosen Point
- 2) The volume Enclosed by the Perpendicular.



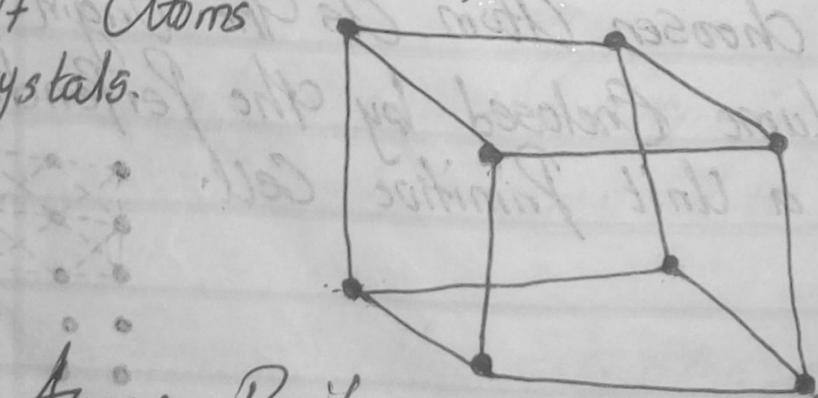
\* Simple Cubic (0,0,0)

\* Body Centred Cubic

\* Face-Centred Cubic

Co-ordinate of Atoms  
In Cubic Crystals.

### Simple Cubic.

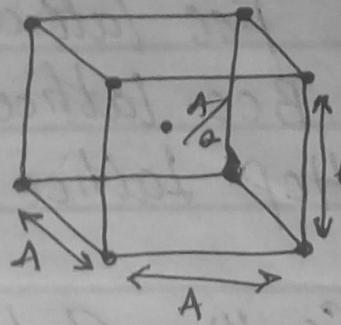
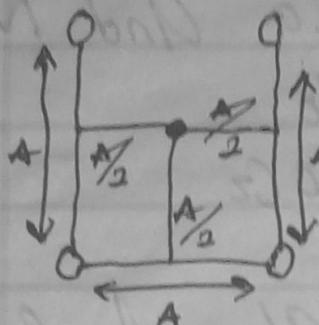


Atoms Position Uniquely Describe by Simple Cubic Is (0,0,0)

2)

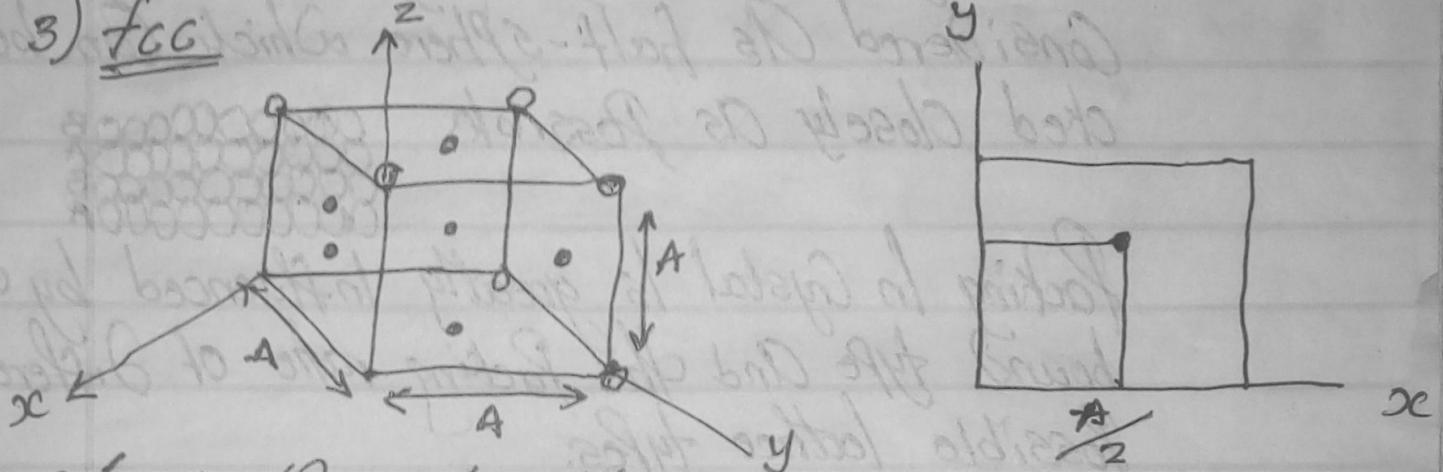
## Body Centered Cubic (BCC)

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$$\begin{aligned} \text{Num. of Atoms} &= 8 \times \frac{1}{8} + 1 \\ 1 + 1 &= 2 \end{aligned}$$

Coordinate  $(0,0,0)$  And  $\left(\frac{A}{2}, \frac{A}{2}, \frac{A}{2}\right)$

3) fcc

- 1)  $x$ -Plane  $y=0$
- 2)  $x-y$  Plane  $z=0$
- 3)  $y$ -Plane  $x=0$

 $x, y, z$ 

$x, z$  Axis,  $y$  Is not Active.  $(0, 0, 0)$

$(\frac{A}{2}, 0, \frac{A}{2})$

$x, y$  Axis,  $z$  Is not Active

$(\frac{A}{2}, \frac{A}{2}, 0)$

$y, z$  Axis  $x$  Is not Active.

$(0, \frac{A}{2}, \frac{A}{2})$

## Examples

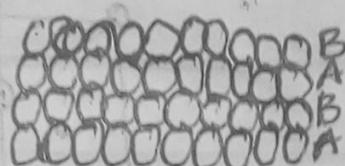
Fcc lattice  $\Rightarrow$  Al, Ag, Ca And NaCl

Bcc lattice  $\Rightarrow$  Cr, Na, Fe

Hcp Lattice  $\Rightarrow$  Be, Zn, Co, Cr

## Stacking And Packing of Atoms In Crystals

Many atoms especially in metal can be considered as half-sphere which can be stacked closely as possible.



Packing in Crystal is greatly influenced by the bond type and the packing ratio of different possible lattice types.

{ Bonding is the strongest if each atom of the solid has many closed neighbours as possible. }

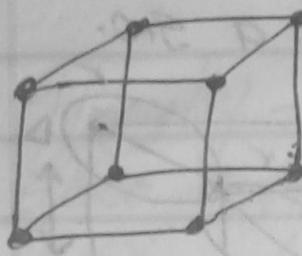
- To determine which lattice type is more closely packed, we apply the following procedure.
- 1) Work out the number of atoms per unit volume in different lattices.
  - 2) Work out the volume of the unit cell of the lattices.
  - 3) Determine a dimensionless number called the filling factor.

Filling factor also know as  
Packing factor.

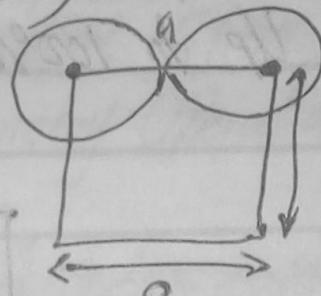
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Filling factor (ff) = Vol. Occupied by the Atom In  
a Unit cell.

total Vol of the Unit cell.



Simple Cubic



Edge length

$$a = r + r$$

$$a = 2r$$

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

$$ff = \frac{\text{Vol. Occupied by Atom}}{\text{Vol. of Unit cell}} \times 100$$

- Num. of Atoms In a Unit cell S.C = 1
- Vol. of Atom In. Unit cell =  $\frac{4}{3} \pi r^3$
- Vol. of Unit cell =  $A^3$

For Simple Cubic, S.C the ff formula is

$$ff = \frac{Z \cdot \text{Vol. Occupied by Atom}}{\text{Vol. of Unit cell}} \times 100 \quad \left\{ \begin{array}{l} Z = r \\ A = a \end{array} \right.$$

$Z = \text{Num. of Atom In Unit cell}$

$$ff = \frac{1 \times \frac{4}{3} \pi r^3}{A^3} \times 100$$

$$= \frac{1 \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

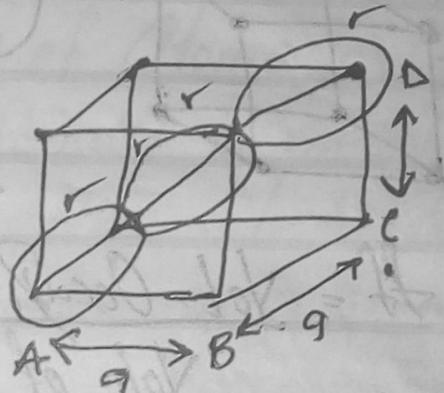
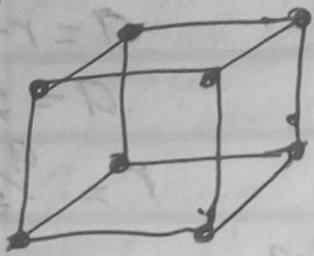
$$= \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} \times 100$$

$$\frac{\frac{4}{3} \pi a^3 / 2^3}{a^3} \times 100$$

$$= \frac{4}{3} \pi \left(\frac{1}{8}\right) \times 100$$

$$= \frac{\pi}{6} \times 100 = 52.36\%$$

It's now noted that in a S.C., the lattice are closely packed upto 52.3% but are not perfectly packed up to 100% in a S.C.



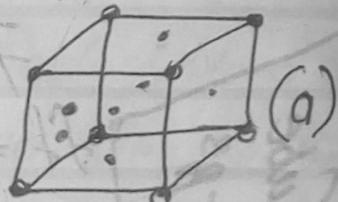
$AD = r + r/2$  is of equal to null

$AD = 4r$  (no fails of model to Jov)

$AD^2 = AC^2 + DC^2$  (no fails to Jov)

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### PACKING IN CRYSTALS



3) Face Centered Cubic Structure (FCC)

$\Rightarrow$  The number of Atoms in a Unit Cell = 4

$\Rightarrow$  Volume of Atoms in a Unit Cell =  $4 \times \frac{4\pi R^3}{3}$

$\Rightarrow$  Volume of the Unit Cell =  $A^3$

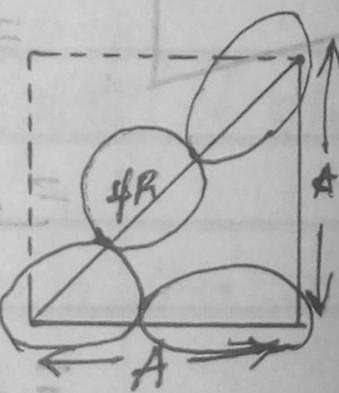
From the geometry diagram i.e. of the diagram in (b)

Using Pythagoras therefore in  $\triangle ABC$

$$(4R)^2 = 2A^2$$

$$A = \frac{4R}{\sqrt{2}} = 2\sqrt{2} \cdot R$$

$$\therefore \text{Volume of Unit Cell} = A^3 = 8 \cdot (\sqrt{2} \cdot R)^3$$



B: Diagram B As {Atoms touch faces of Diagram}

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$$\therefore \text{Filling factor} = \frac{4 \times 4\pi R^3}{16 \times \sqrt{2} \cdot R^3 \times 3} \approx \frac{\pi}{3\sqrt{2}} = \frac{\sqrt{2} \cdot \pi}{6} = 74\%$$

Only About 26% of the Volume is free (High Density).  
\* Found for HCP, Hexagonal.

### CRYSTAL SYMMETRY

⇒ Symmetry - Symmetry Operation, - Point graphs, - Space graphs.

Symmetry: A certain Pattern Or Arrangement of a body. It is symmetrical when it is produced by a certain operations.

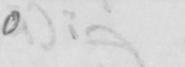
### Symmetry Operations

A Symmetry Axis rotation Axis represents An Imaginary line through the Center of a Crystal Selected so that the rotation of the Crystal about this line results in the arrangement of the forward angle being identical with that of the starting position.

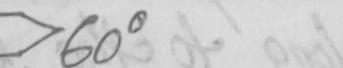
Thus if the angle of rotation is  $\theta$ , the Order of the Axis is given by  $n = \frac{360}{\theta}$ . An Axis may be:

1- One fold  $\Rightarrow$    $360^\circ$

2- Two fold  $\Rightarrow$    $180^\circ$

3- Three fold  $\Rightarrow$    $120^\circ$

4- Four fold  $\Rightarrow$    $90^\circ$

5- Six fold  $\Rightarrow$    $60^\circ$

NB  $n=1 \Rightarrow$  no Symmetry. Get

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Symmetry Operations consists of: (Elements of Symmetry)

\* 1 - Translation

\* 2 - Rotation.

\* 3 - Reflection (mirror)

\* 4 - Inversion

## Reciprocal Lattice:

The Crystal lattice is a lattice in the real space (space defined by Co-ordinate) whereas the reciprocal lattice is the lattice in the associated reciprocal state or associated  $\vec{k}$  space or associated Fourier state, the reciprocal lattice is an infinite, periodic, three dimensions array of point whose spacing is inversely proportional to the distance between the plane of the direct lattice, mathematically we consider a set of point  $\vec{R}_i$  of the direct lattice at a plane wave  $e^{i(\vec{k} \cdot \vec{R}_i)}$  for general  $\vec{k}$  this will real have the periodicity of the bravais lattice but for special cases for  $\vec{k}$  they yield the plane wave  $e^{i(\vec{k} \cdot \vec{R})}$  with the periodicity of the bravais lattice of point  $\vec{R}$  is called the reciprocal lattice.  $\vec{k}$  belong to the bravais lattice of point  $\vec{R}$  provided that  $e^{i(\vec{k} \cdot (\vec{R} + \vec{r}))} = e^{i\vec{k} \cdot \vec{r}} \rightarrow$  These

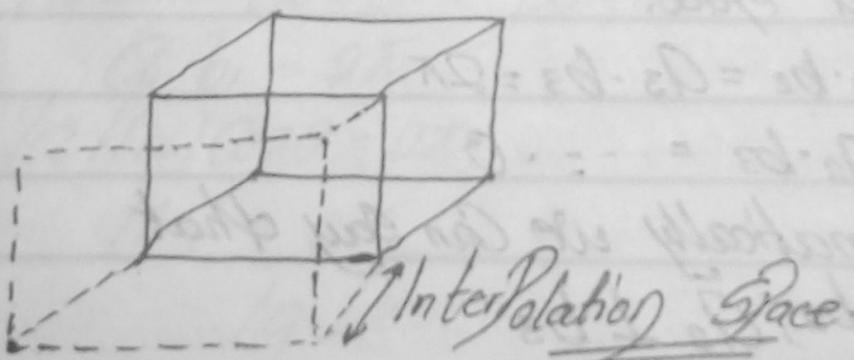
Expression Assume that we have a periodic lattice for all  $\vec{r}$  And  $a_{\vec{R}+\vec{r}}$  is in the Direct lattice.

$$\begin{aligned} e^{i\vec{R}(\vec{R}+\vec{r})} &= e^{i(\vec{R} \cdot \vec{r})} \\ e^{i\vec{R} \cdot \vec{R}} \cdot e^{i\vec{R} \cdot \vec{r}} &= e^{i\vec{R} \cdot \vec{r}} \\ e^{i\vec{R} \cdot \vec{R}} &= 1 \end{aligned} \quad \left. \right\} \text{No}$$

Constructing a reciprocal lattice.

- ① Pick up some point as Origin.
- ② From the Origin, layout the normal to every set of planes in the real O. Direct lattice.
- ③ Set the length of each normal equal to the reciprocal of the InterPlaner Spacing of a particular set of plane.
- ④ Put a point at end of each normal, the assembly of these point represent the tabulation of
  - The normal to all the Direct lattice plane.
  - The InterPlaner Spacing.

The collection of point layed out gives a new lattice array in which is the reciprocal lattice.



The basic set of the reciprocal lattice are define by  $a_i \cdot b_j = 2\pi \delta_{ij}$   
 $i = 1, 2, 3$

Where  $i = 1, 2, 3, \dots$

$j = 1, 2, 3, \dots$

$\delta_{ij}$  is called KROHECHER DELTA

Where

$\delta_{ij} = 0$  It mean  $i \neq j$

$\delta_{ij} = 1$  It means  $i = j$

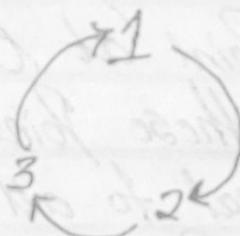
$a_i = (a_1, a_2, a_3, \dots)$  are been vector of real lattices

$b_i = (b_1, b_2, b_3, \dots)$  are been vector of real reciprocal lattices.

$$\bar{b}_1 = \frac{2\pi(\bar{a}_2 \times \bar{a}_3)}{\bar{a}_1(\bar{a}_2 \times \bar{a}_3)}$$

$$\bar{b}_2 = \frac{2\pi(\bar{a}_3 \times \bar{a}_1)}{\bar{a}_1(\bar{a}_2 \times \bar{a}_3)}$$

$$\bar{b}_3 = \frac{2\pi(\bar{a}_1 \times \bar{a}_2)}{\bar{a}_1(\bar{a}_2 \times \bar{a}_3)}$$



Where  $\bar{a}_1(\bar{a}_2 \times \bar{a}_3)$  is simple the volume of the unit cell in the real space.

$$a_1 \cdot b_1 = a_2 \cdot b_2 = a_3 \cdot b_3 = 2\pi$$

$$a_1 \cdot b_2 = a_2 \cdot b_3 = \dots = Q$$

mathematically we can say that

$$a_1 \perp b_2, a_2 \perp b_3$$

$$a_1 \perp b_1$$

$$a_1 \cdot b_2 = 0$$

In the Direct lattice/real lattice

$$\vec{r} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$$

In the reciprocal lattice.

$$\vec{g} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$\vec{g} \cdot \vec{r} = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)(u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3)$$

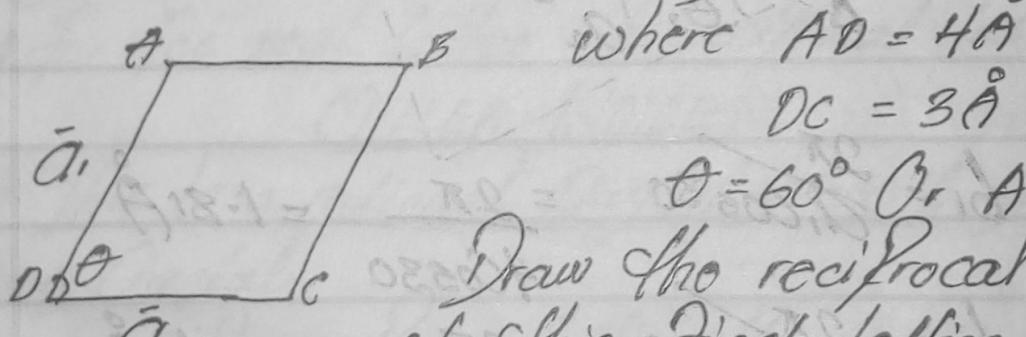
Since we know that

$$a_1 \cdot b_1 = a_2 \cdot b_2 = a_3 \cdot b_3 = 2\pi$$

$$\vec{g} \cdot \vec{r} = 2\pi(hu + kv + lw) = 2\pi N$$

where  $N = (hu + kv + lw)$  and it can be any integer

Example: Consider a 2-dimensional lattice ABCD



Draw the reciprocal lattice  
of this direct lattice Recall that  
Solution

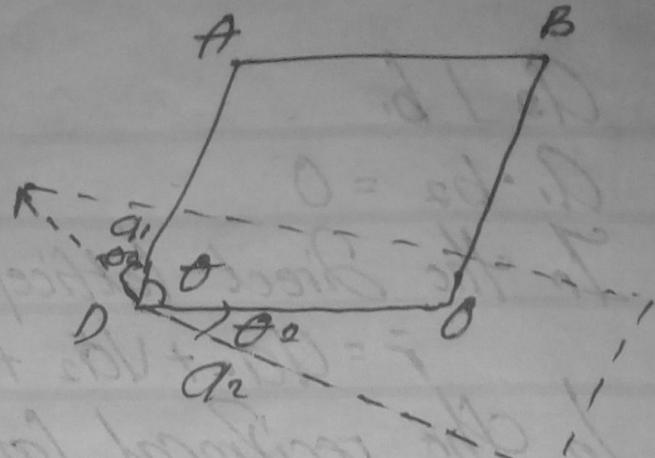
Assume  $AD = \vec{a}_1$   $DC = \vec{a}_2$

$$\vec{a}_1 \cdot \vec{b}_1 = 2\pi$$

$$|a_1||b_1|\cos\theta = 2\pi$$

$$|b_1| = \frac{2\pi}{|a_1|\cos\theta}$$

In real space  
 $\vec{a}_1 \cdot \vec{b}_2 = 0$



$$\Rightarrow \vec{a}_1 \perp \vec{b}_2$$

$$\text{Similarly } \vec{a}_2 \cdot \vec{b}_2 = 2\pi$$

$$|\vec{a}_1||\vec{b}_2| \cos \theta_3 = 2\pi$$

$$|\vec{b}_2| = \frac{2\pi}{|\vec{a}_2| \cos \theta_2}$$

$$|\vec{a}_2| \cos \theta_2 = ad \cdot cd = id \cdot id$$

$$\vec{a}_2 \perp \vec{b}_2$$

$$\theta_1 = \theta_2$$

$$90^\circ - \theta$$

$$= 90^\circ - 60^\circ$$

$$= 30^\circ$$

$$b_1 = \frac{2\pi}{\vec{a}_1 \cos 30} = \frac{2\pi}{4 \cos 30} = 1.81 \text{ \AA}$$

$$b_2 = \frac{2\pi}{\vec{a}_2 \cos 0} = \frac{2\pi}{3 \cos 30} = 2.42 \text{ \AA}$$

### Brillouin Zone

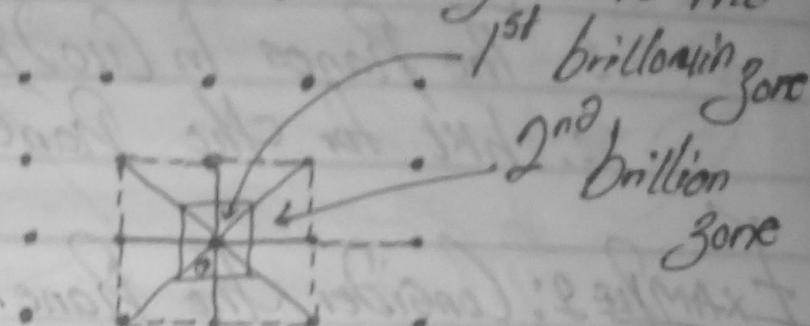
The reciprocal lattice vector is expressed as

$$g = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

Steps in Drawing a Brillouin Zone

N.B:

- \* Draw Planes which are 1 bisector of all reciprocal lattice vectors around the reference point O.
- \* There will be small volume of reciprocal space which is bound by planes which are perpendicular bisectors of the vectors connecting O to the nearest neighbours.

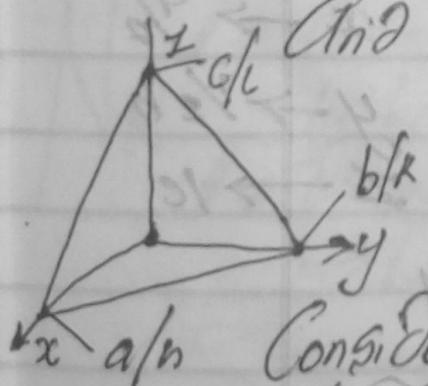


- \* The smallest volume is defined as the first Brillouin zone for a Simple Cubic (Sc) lattice.
- \* The reciprocal lattice is also cubic - 1<sup>st</sup> Brillouin zone is also a cube.
- \* For FCC real lattice the reciprocal lattice is BCC.

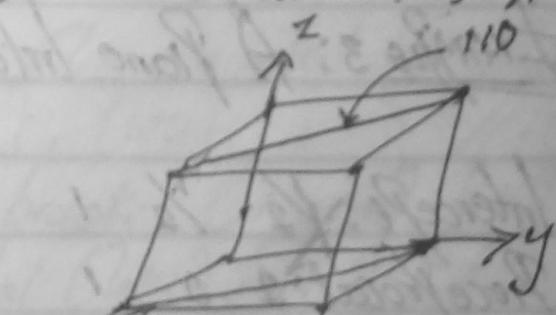
### MILLER INDICES

- \* This is a rational way of describing planes in a crystal.

Consider a plane cutting the axis at  $a/h$ ,  $b/k$  and  $c/l$



Consider a plane that cut the axis at  $x=a$ ,  $y=b$ ,  $z=c$



$\Rightarrow$  Three steps for calculating Miller Indices

Intercept at  $1a \ 1b \ \infty$

Or  $1 \ 1 \ \infty$   
reciprocal  $\frac{1}{1} \ \frac{1}{1} \ \frac{1}{\infty}$

Clear fraction  $1 \ 1 \ 0$

The Planes In  $(110)$  Plane.

$\therefore$  hkl for the Plane  $(110)$

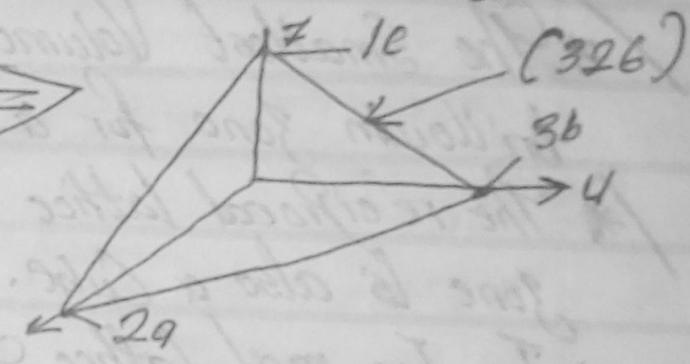
Example 2: Consider the plane that cuts the axis at



$$x \rightarrow 2a$$

$$y \rightarrow 3b$$

$$z \rightarrow 1c$$



Intercepts  $2 \ 3 \ 1$

Reciprocal  $(\frac{1}{2} \ \frac{1}{3} \ \frac{1}{1}) \times 6$

Clear fraction  $3 \ 2 \ 6$

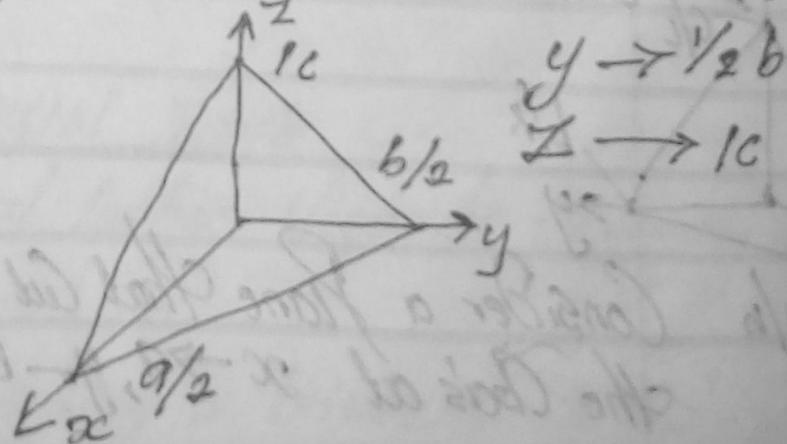
$\therefore$  The Plane is  $(326)$

Example 3: A Plane intercept the axis at  $x \rightarrow \frac{a}{2}$

Intercept:  $\frac{1}{2} \ \frac{1}{2} \ 1$

Reciprocal:  $2 \ 2 \ 1$

No fraction to clear



$\therefore$  The Plane Is  $(221)$

$hkl$  Is  $(221)$

We Can Similarly have negative Integers which we Denote with a bar e.g.  $-k, \bar{k}$

Example: A Plane Intercept that Axis at  $x \rightarrow (-2a)$

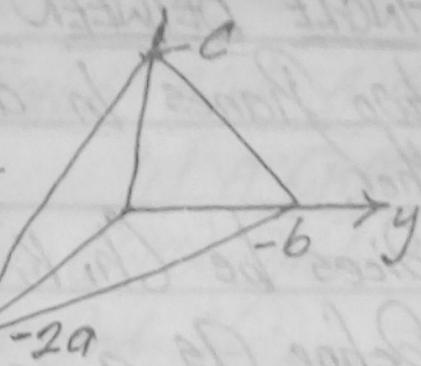
Intercept:  $\{-2 -1 1\}$

Reciprocal:  $\{-\frac{1}{2} -\frac{1}{2} \frac{1}{2}\}$

Clear fraction:  $-1 -2 2$

The Plane Is  $(\bar{1}\bar{2}2)^x$

$\therefore hkl$  Is  $(\bar{1}\bar{2}2)$



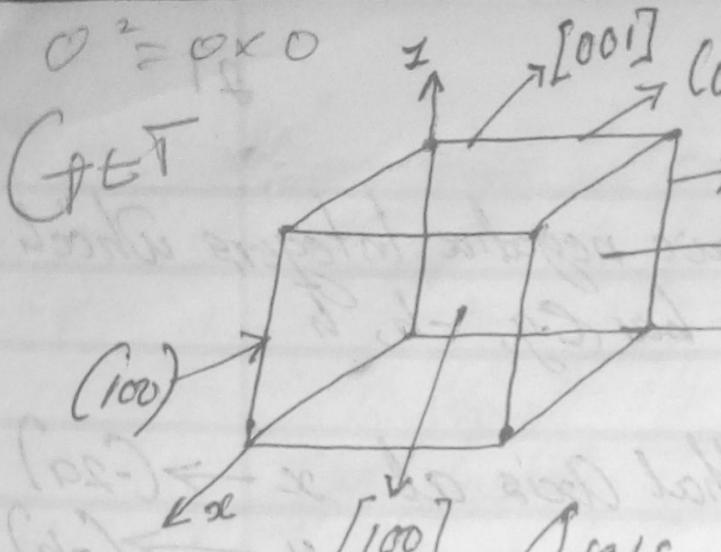
Ques

The General form for Describing Crystal Planes Are the method of reciprocal lattice ( $a/\alpha, b/\beta, c/\gamma$ ) allows all Intercept tube related to the Unit cell Specified by the Edge length ( $a, b, c$ ).

\* Planes Are Indicated by round bracket  $()$

\* A Set of Parallel Planes Are Denoted by a Curly bracket  $\{\}$  —  $\{hkl\}, \{100\},$

N.B: \* Direction Is Denoted by a bracket (square)  $[ ]$   
 $\rightarrow [hkl]$  In a Cubic Crystal  $(hkl) \equiv [hkl]$ .



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GET

### ANGLE BETWEEN TWO PLANES

\* Consider two planes in a crystal inclined at  $\theta$  to each other.

Let the indices be  $(h_1 k_1 l_1)$ ,  $(h_2 k_2 l_2)$

The angle  $\theta$  is defined as  $\cos \theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \cdot \sqrt{h_2^2 + k_2^2 + l_2^2}}$

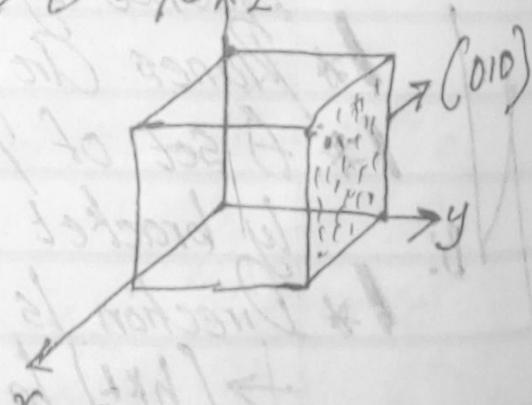
EXAMPLE 1: Find the angle between the planes  $(100)$  and  $(010)$

Solution

$$(100) \Rightarrow (h_1 k_1 l_1)$$

$$(010) \Rightarrow (h_2 k_2 l_2)$$

$$\therefore \cos \theta = \frac{(100) + 0 + 0}{\sqrt{1+0+0}} = 0 \Rightarrow \theta = 90^\circ$$



ANSWER

$$\frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \cdot \sqrt{h_2^2 + k_2^2 + l_2^2}} = \cos \theta$$

Example 2: Find the angle between the plane (111) And (110).

Solution

$$\cos \theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \cdot \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

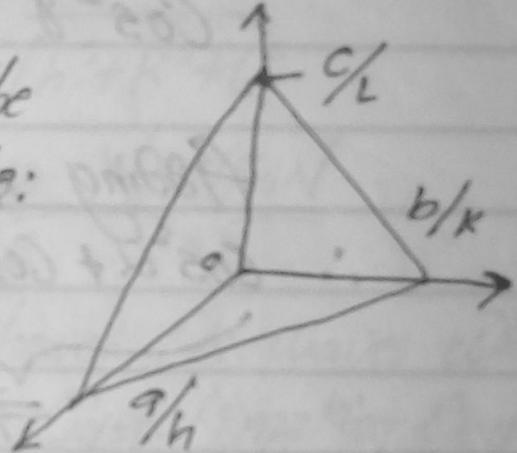
$$= \frac{1+1+0}{\sqrt{3} \cdot \sqrt{2}} = \frac{2}{\sqrt{6}} \Rightarrow \theta = 35.26^\circ$$

Distance b/w A SET OF PLANES  
IN A CRYSTAL

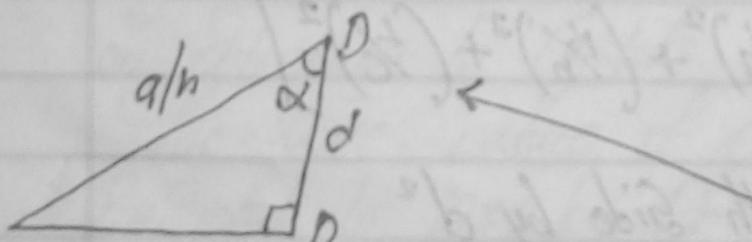


Consider Plane (hkl) which cuts the x, y and z-axis at  $a/h$ ,  $b/k$  and  $c/l$ .

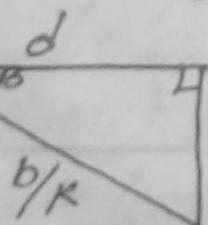
- Suppose the normal from the origin to the plane makes Angle:
- α with the x-axis
  - β with the y-axis
  - γ with the z-axis



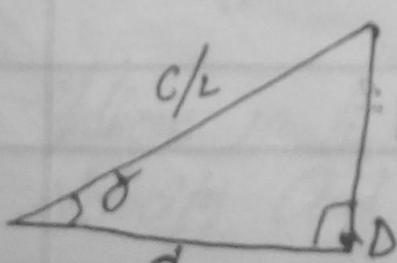
(1)



(2)



(3)



$$\begin{aligned} 1 \Rightarrow \cos \alpha &= \frac{d/a}{h} \Rightarrow \frac{dh}{a} \\ 2 \Rightarrow \cos \beta &= \frac{d/b}{k} \Rightarrow \frac{dk}{b} \\ 3 \Rightarrow \cos \gamma &= \frac{d/c}{l} \Rightarrow \frac{dl}{c} \end{aligned}$$

Squaring both sides of Equation 1, 2 And 3

$$\cos^2 \alpha = \left( \frac{dh}{a} \right)^2 \quad \text{--- (4)}$$

$$\cos^2 \beta = \left( \frac{dk}{b} \right)^2 \quad \text{--- (5)}$$

$$\cos^2 \gamma = \left( \frac{dl}{c} \right)^2 \quad \text{--- (6)}$$

Adding 4+5+6 from above

$$\therefore \cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = \left( \frac{dh}{a} \right)^2 + \left( \frac{dk}{b} \right)^2 + \left( \frac{dl}{c} \right)^2$$

\$\Rightarrow 1 \qquad \qquad \qquad = d^2 \left[ \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 \right]\$.

$$\therefore 1 - 1 = d^2 \left[ \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 \right]$$

Dividing both sides by  $d^2$

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

Taking reciprocal of both sides

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

Taking Square root of both sides.

$$d = \frac{1}{\sqrt{(\frac{h}{a})^2 + (\frac{k}{b})^2 + (\frac{l}{c})^2}}$$

Where  $d$  is the Interplaner Spacing  
In the special case  $a=b=c$

$$d = \frac{1}{\sqrt{(\frac{h}{a})^2 + (\frac{k}{a})^2 + (\frac{l}{a})^2}}$$

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

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

### X-RAYS, ELECTRONS AND NEUTRON WAVES IN CRYSTALS

The fact that Electrons behaves As waves when they interact with Atoms in a Crystal making Electron Diffraction In Crystals Structural studies Possible. The wave nature of Electron Or matter was Predicted In 1924 by De Broglie.

The De-broglie relation between the momentum ( $P=mv$ ) of an Electron And its associated de-broglie wave length ( $\lambda$ ) is given by.

$$\lambda = \frac{h}{P} = \frac{h}{mv} \quad \text{--- 2.21}$$

Where  $m$  is the mass of Electron And  $v$  is the Velocity And  $h$  is Planck's Constant

If a stream of Electron is accelerated by a, applied Electric Potential  $V$ , the Kinetic Energy ( $E_k$ ) of the Electron is  $\frac{1}{2}mv^2$  is given by.

$$\frac{1}{2}mv^2 = ev \quad \text{--- 2.22}$$

where  $e$  is electric charge.

from Equation (2.21/2.22) we obtain

$$\lambda = \frac{h}{\sqrt{2mev}} = \sqrt{\frac{150}{V}} = \frac{12.27}{\sqrt{V}} \quad \text{--- 2.23}$$

### Assignment

Prove

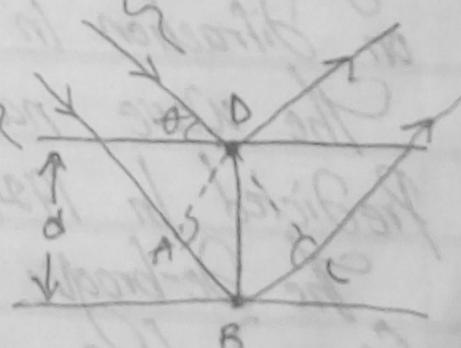
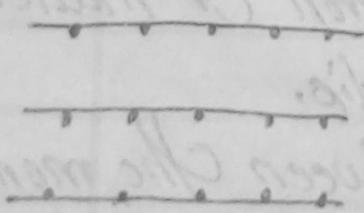
$$\lambda = \frac{h}{\sqrt{2ev}} = \sqrt{\frac{150}{V}}$$

TRY knowing  
the proving.

02/09/

### BRAGG'S LAW

If the Path  $AB + BC$  in the fig. below is a multiple of the X-ray wavelength  $\lambda$ , then two waves will give a Constructive Interference.



$$\Rightarrow n\lambda = AB + BC = 2ds\sin\theta$$

$$\Rightarrow n\lambda = 2ds\sin\theta \Rightarrow \text{Bragg's law}$$

The Incident and Diffracted beam and Always Coplanar  
The angle between the Diffracted beam and the transm-

## Monochromator

mitted beam is always 2θ

Since  $\sin \theta \leq 1$

$$\frac{n\lambda}{2d} = \sin \theta \leq 1$$

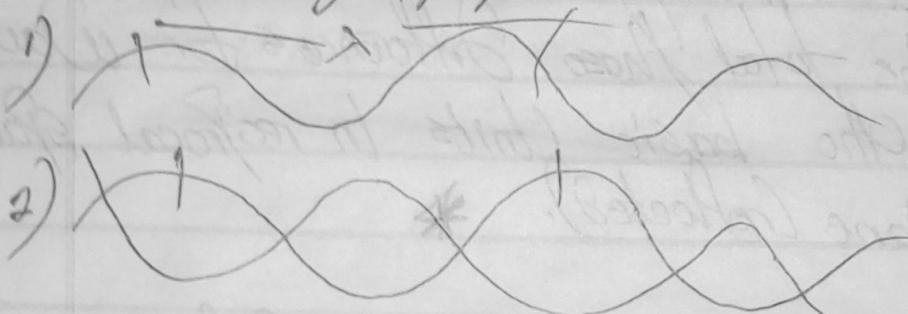
$\therefore$  for  $n=1, \lambda < 2d$

Remember;

- Diffraction, Interference
- X-rays - Origin / Properties.



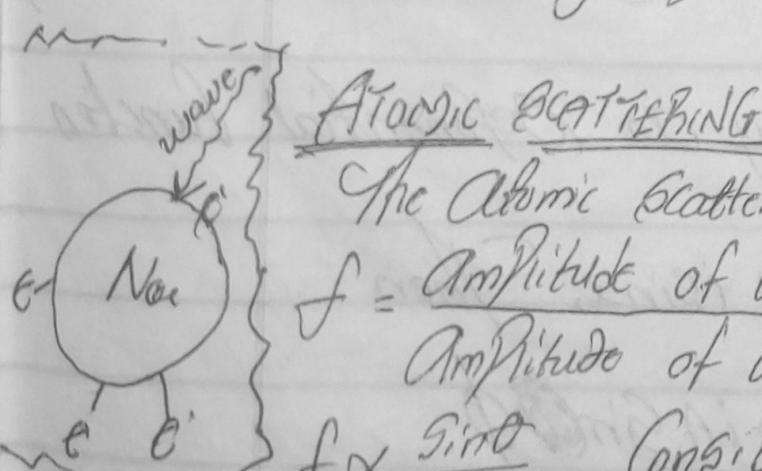
Transmitted beam.



## SCATTERING BY AN ELECTRON

• Elementary Scattering Ch't. In an atom is an electron.

• Classically, scattering by an atom by the Thomson Scattering Equation Or Compton Effect.



## Atomic Scattering

The Atomic Scattering factor  $f$  is defined

$f = \frac{\text{Amplitude of wave scattered by an Atom}}{\text{Amplitude of wave scattered by an Electron}}$

$f \propto \frac{f_{\text{int}}}{1}$ , Considering atom containing several Electrons.  $f$  is also called Atomic form factor

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$f$  is calculated using quantum mechanics scattering by a unit cell

$F_{hkl}$  = Amplitude of waves scattered by a Unit cell

where  $F_{hkl}$  is called the Structure Factor

Assignment: Show that for a 3-D System {Submit On  
 $\phi = 2\pi (hu + kv + lw)$

Where  $\phi$  is the total Phase Difference for wave in 3D.  $u, v, w$  as the basic units in reciprocal space and  $hkl$  are the plane reflected). \*

So, for 3-D System of atom, we define,

$$\phi = 2\pi (hu + kv + lw)$$

where  $\phi$  is the Phase Difference between waves scattered from different diffraction planes ( $hkl$ ) are  $u, v, w$  and integers representing coordinate of atom reciprocal lattice vectors.

Represent the waves by an exponential function of the type

$$C^{ix} = \cos x + i \sin x, \text{ Then}$$

$$AC^{ix} = A \cos \phi + i A \sin \phi$$

where  $A$  is the Amplitude of the wave.

$$\text{But, } |AC^{i\phi}|^2 = |AC^{i\phi} \cdot AC^{-i\phi}| = A^2$$

We can write.

$$AC^{i\phi} = F \exp[2\pi i(hu + kv + lw)]$$

Summing over all atoms in the unit cell, we obtain

$$F = f_1 C^{i\phi_1} + f_2 C^{i\phi_2} + f_3 C^{i\phi_3}$$

$$\bar{F} = \sum_n f_n C^{i\phi_n} = \sum_i f_n C^{2\pi i(hu + kv + lw)}.$$

Since Intensity  $\propto F_{hkl} * F_{hkl}^* = |F_{hkl}|^2$

$\therefore$  Recall the ff useful relations when solving Process

$$C^{ix} = \cos x + i \sin x$$

$$C^{3\pi i} = C^{3\pi i} = C^{3\pi i} = \dots = -1$$

$$C^0 = C^{2\pi i} = C^{4\pi i} = \dots = +1$$

$$C^{n\pi i} = (-1)^n$$

$$C^{n\pi i} = C^{-n\pi i}$$

$$C^{ix} + C^i$$

### STRUCTURE FACTORS FOR CRYSTAL STRUCTURES

#### 1. FCC Lattice.

If the atom are the same, their location are at  $(0,0,0)$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$  and  $(0, \frac{1}{2}, \frac{1}{2})$ .

Hence from  $\text{Eq } 3^{\circ}$

$$F_{hkl} = \sum_n f_n \left( e^{2\pi i(hu_n + kv_n + lu_n)} \right)$$

$$F = [1 + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(l+k)}]$$

If  $h, k, l$  All  $\neq 0$  EVEN Or All ODD (Unmixed)  
 Then the Exponential term all equal = +1  $\Rightarrow$

$$F_{hkl} = 4F$$

If  $h, k, l$  Are mixed (EVEN And ODD), Then two of the Exponential term will Equal = -1, While One will Equal = +1  $\Rightarrow F_{hkl} = 0$

Summarizing

$$|F_{hkl}|^2 = \begin{cases} 16F^2 & h, k, l \text{ Unmixed EVEN Or ODD} \\ 0 & h, k, l \text{ mixed EVEN And ODD} \end{cases}$$

No reflection.

## 2. Bcc Lattice.

It has a (different atoms) e.g. CsCl structure  
 $Cs^+$  ions for a cubic lattice

$Cl^-$  ions are located at the center of each cubic unit cell. We can now say  $Cl^-$  forms a cubic lattice.  $Cs^+$  are located at the center of each cube above all  $Cs^+$ .  $Cl^-$  acts as corner atom and  $Cl^-$  acts as body atom

(000)  $\xrightarrow{\text{Cs}^+ \text{ Corner}}$

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$(\frac{1}{2} \frac{1}{2} \frac{1}{2}) \xrightarrow{\text{Cs}^+ \text{ Center}}$

For more atomic species the diffraction Amplitude  $F(h,k,l)$  is considered separately in the individual summation of atom defining the unit cell.

$$F(h,k,l) = f_{\text{Cs}}(N) \sum_j e^{2\pi i (hv_j + kv_j + lw_j)} + f_{\text{Cl}}(N) \sum_j \exp^{2\pi i (hv_j + kv_j + lw_j)}$$

Since Cs atom at (0,0,0) Cl atoms are at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = (u, v, w)$

for  $h+k+l$  Add

$$f_{\text{Cs}}(N) [e^{2\pi i (h+k+l)}] + f_{\text{Cl}}(N) = -1$$

for  $h+k+l$

Given

~~$$F(h,k,l) = f_{\text{Cs}}(N) + f_{\text{Cl}}(N) [e^{2\pi i (h+k+l)}] = +1$$~~

Note ①: The structure factor contain information regarding the types and location ( $u, v, w$ ) of atoms within the unit cell. ② X-ray structural analysis lower the observed and calculated structural factor.

③ The observed intensities must be located for experimental and geometric effect before analysis.

### Atomic Bonding in Crystals

The crystals are categorized depending on the type of forces existing among the atom.

The description of the classical theory of ionic crystal and inert gasses is also given the attractive electrostatic interaction between the negative charge of the electron and positive charge of the nucleus is entirely responsible for the cohesion of solids.

Magnetic forces have only a very weak effect on cohesion while gravitational forces are negligible.

The observed differences between the form of induced water are caused in the final analysis by different distribution of outermost electron and ion cores.

The cohesive energy of a crystal is defined as the energy that must be added to the crystal to

Separate its Components into neutral free Electrons / atom at rest. At Infini te Separation, with the same Electronic Configuration\*

### Lattice Energy

It is used in the discussion of ionic Crystal. In the Energy that must be added to the Crystal to Separate its Component ions into free ions at rest. There is a wide variation of cohesive Energy between different columns of the Periodic table. The Inert gasses Crystal are weakly bond with Cohesive Energy less than a few percent of the cohesive Energy of the elements in group 14, Period 6, 14, 32, 32.

(Carbon, Sodium, Germanium, lead). The alkaline metal Crystal have Intermediate Values of Cohesive Energy in group 1-6 hydrogen while the transition Element Metals are quite strongly bind, melting temps varies as cohesive Energy are applied.

### \*Crystals of Inert Gasses

The Inert gasses form the Smallest Crystal, the Electron Distribution is very close to that of a free atom.

### Properties of Inert gas As Crystal

⇒ The Crystal are Insulator, weakly bond, with low melting temperature.

(ii) The Atoms have Very high Ionization Energy,  
 (iii) The Outermost Electron Shell Are Completely filled  
 And Distribution of Electron charge In the free Atom Is spherical Symmetric.

•v In the Crystals, the Inert gas Atom Are packed together As closely As Possible v. The Crystal Structure Pro Cube close-packed fcc. ( $\text{He}^3 \& \text{He}^4$ )

What holds the Inert gases together i-e

1. The Cohesive Energy of ~~An~~ an atom In Crystal Is Only less 1% Or less of the Ionization Energy of An Atomic Electron, Also, the Electron Distribution In Crystal Is not Significantly Distorted from the Electron Distribution Around The free Atom because not much Energy Could Distort the free Atom, Distortion Part of this Distortion gives the Van der Waal's Interaction.

### Ionic Crystals

\* They Are made up of Positive And negative ions, the long bonds Are got from the Electrostatic Interaction of oppositely charged ion. There Are two Common Crystal Structure for Ionic Crystals.

- { i) NaCl Structure.
- ii) CaCl Structure

The electronic configuration of all ions of a sample ionic crystals correspond to that of close electron shell has [In the Inert gas Atom lone bond + NaCl] transfer of

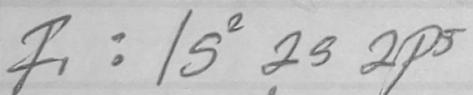
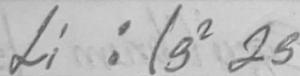
$\text{CsCl}$  - Valence Electron

Covalent bond  $\rightarrow$  Diamond + sharing of Valence Electron  
hydrogen bond  $\rightarrow$  ICB.

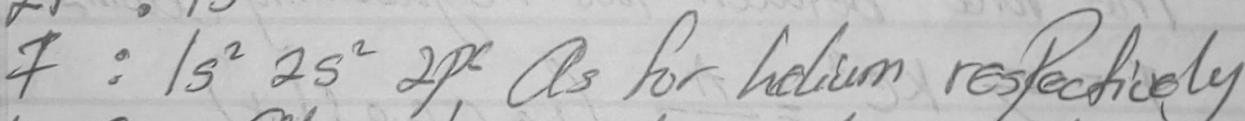
Metallic bond  $\rightarrow$  Ag  $\rightarrow$  free nature of Valence Electron  
Vander-wall forces  $\rightarrow$  In Solid  $\rightarrow$  Electron remain Associated  
With original molecules.

### Example

For Lithium Fluoride (LiF), the Configuration of the new  
far Atom Are



The Single Charged ion have Configuration



As for helium respectively  
Inert Gas Atoms have, close shell And the charge-distribution Are Spherically Symmetric. We expect  
that the charge distribution In each ion In Ionic Crystals will have approximately Spherical Symmetry  
With Some Distortion Near the region of Contact  
With neighboring Atom.

16/09/

## Electrostatic And Madelung Energy

Consider two atoms (A and B) in the ground state with infinite separation (i.e. zero interaction potential). As they are brought together, the potential energy of either atom  $U = P.E.$ , attraction + P.E. separation (Increasing) (Decreasing)

Let the separation be  $r$

$$\text{Force of Attraction, } F = \frac{e^2}{4\pi\epsilon_0 r^2} \text{ (SI Unit)}$$

$$\text{And } P.E. = \frac{e^2}{4\pi\epsilon_0 r}$$

The minimum displacement at equilibrium is

$$\frac{\partial U}{\partial r} = 0, r \rightarrow r_0$$

The force between two neighbouring atoms.

$$F = \sum_{i=j} \frac{k e^2}{r_{ij}^n} = \frac{A}{r^n} \text{ (i.e. C.G.S Unit)}$$

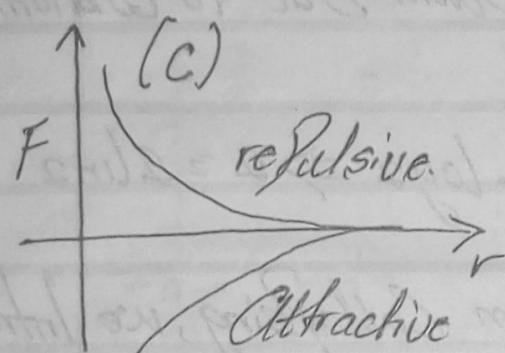
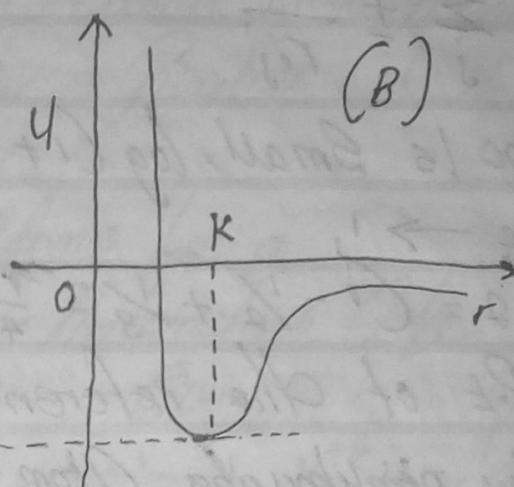
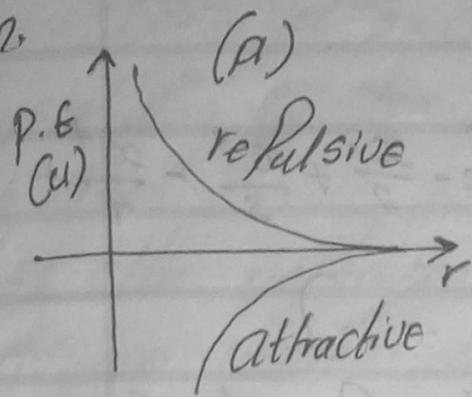
Where  $i \Rightarrow i^{th}$  Atom and  $j \Rightarrow j^{th}$  Atom

If the atom is neutral,  $\frac{A}{r^n}$  converges and P.E. between

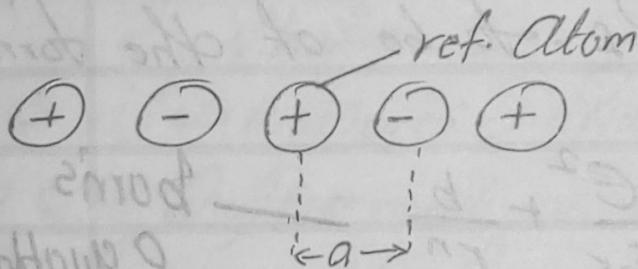
$$U = k e^2$$

$$\therefore \text{Total P.E. } U = \sum \frac{k e^2}{r_{ij}}$$

figures A And B <sup>depict</sup> represent the Energy Diagram, While (C) Is the force Diagram.



For a chosen reference Atom Consider a One-Dimensional Case



Taking the Atom In Pairs, with respect to the reference Atom And Summing.

$$U = \frac{ke^2}{a} \left( -\frac{1}{1} + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \frac{1}{5} + \dots \right) \quad \textcircled{1}$$

$$U = \frac{k2e^2}{a} \left( -1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \frac{1}{5} + \dots \right) \quad \textcircled{2}$$

The 2 arises because the atom are taken in pairs

$$\therefore \textcircled{2} \Rightarrow U = \frac{k\alpha e^2}{a}, \text{ Where } \alpha = 2 \left( -1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right) \quad \textcircled{3}$$

$\alpha$  Is Called The Madelung Constant.

$$\alpha = \sum_j \pm \frac{1}{r_{ij}}$$

When  $x$  Is Small,  $\log(1+x) = (\alpha - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots)$

$$\text{If } x \rightarrow 1$$

$$\log 2 = (1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \dots)$$

The P.E of the reference Atom Due to Coulomb forces Existed by neighbouring Atom.

$$U(r) = \frac{\alpha e^2}{4\pi \epsilon_0 r}, \quad \alpha \Rightarrow \log 2 \approx 2 \ln 2$$

To Prevent the Crystal from Collapsing, we Introduce repulsive force And the Associated P.E

Assume repulsive P.E. to be of the form:

$$U'' = \frac{b}{r^n}$$

$$\text{Total Energy, } U = \frac{-\alpha e^2}{4\pi \epsilon_0 r} + \frac{b}{r^n} \quad \text{born's equation}$$

This Is Called born's Equation.

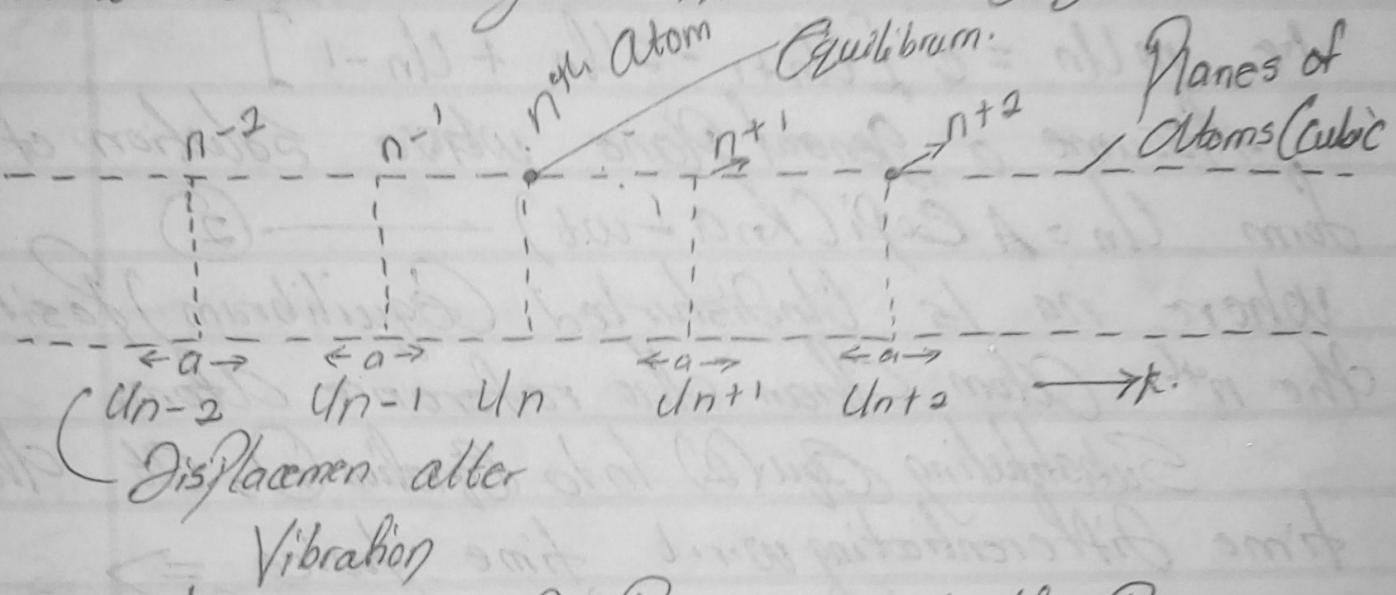
### LATTICE VIBRATION

The look at the Contribution of lattice vibration for thermal, Electrical And optical Properties. We treat the vibration As Vibrational Waves Described by frequency  $f$  and wavevector  $k$  ( $k = 2\pi/\lambda$ ,  $w = 2\pi f$ ) OR this lattice vibration Is Planes With Energy  $E = \hbar w$ ,  $P = \hbar k$ .

## Vibrational Spectra (Mono Atomic).

Consider a chain of atoms in a mono atomic crystal, e.g.  $\text{Cs}$  atom. Consider a primitive U unit cell with one atom.

Let the separation of atoms be  $a$ .  
Assume nearest neighbour interactions only.



$\therefore U \Rightarrow$  measures Displacement of the Planes.

Let the Displacement of the atoms from their Equilibrium Positions  $U_n, U_{n+1}$  etc.

Assume that the force constant  $k$  is the same for all atoms in C and subsequently apply Hooke's law for the system of atoms ( $F = -kx$ )

Force on the  $n^{\text{th}}$  atom to the right:

$$= -c(U_n - U_{n+1}) = c(U_{n+1} - U_n) \quad (\text{A})$$

Force on the  $n^{\text{th}}$  atom to the left:

$$= -c(U_n - U_{n-1}) = c(U_{n-1} - U_n) \quad (\text{B})$$

Net force on the  $n$ th Atom.

$$c(U_{n+1} - 2U_n + U_{n-1}) \quad (\text{C.C.}, A+B)$$

Let the mass of each atom be  $m$ ,

Equation of motion of the  $n$ th atom is

$$\frac{md^2U}{dt^2} = c[U_{n+1} - 2U_n + U_{n-1}] \quad (1)$$

$$\text{i.e., } mU_n = c[U_{n+1} - 2U_n + U_{n-1}]$$

Assume a general plane wave solution of the form  $U_n = A \exp(iKna - wt) \quad (2)$

where  $na$  is undisturbed equilibrium position of the  $n$ th atom than the reference atom.

Substituting Eqn(2) into Equation (1), at the same time differentiating w.r.t. time twice  $\Rightarrow$

$$\begin{aligned} -mw^2 A \exp(iKna - wt) &= c[A \exp(iK(n+1)a - wt) - 2A \exp(iKna - wt) + A \exp(iK(n-1)a - wt)] \\ -mw^2 \exp(iKna - wt) &= c\{2\exp(iKa - wt) - 2\exp(-iKa) \\ &+ \exp(i(-Ka - wt))\} \end{aligned}$$

$$-mw^2 = c(\exp(iKa) - 2 + \exp(-iKa))$$

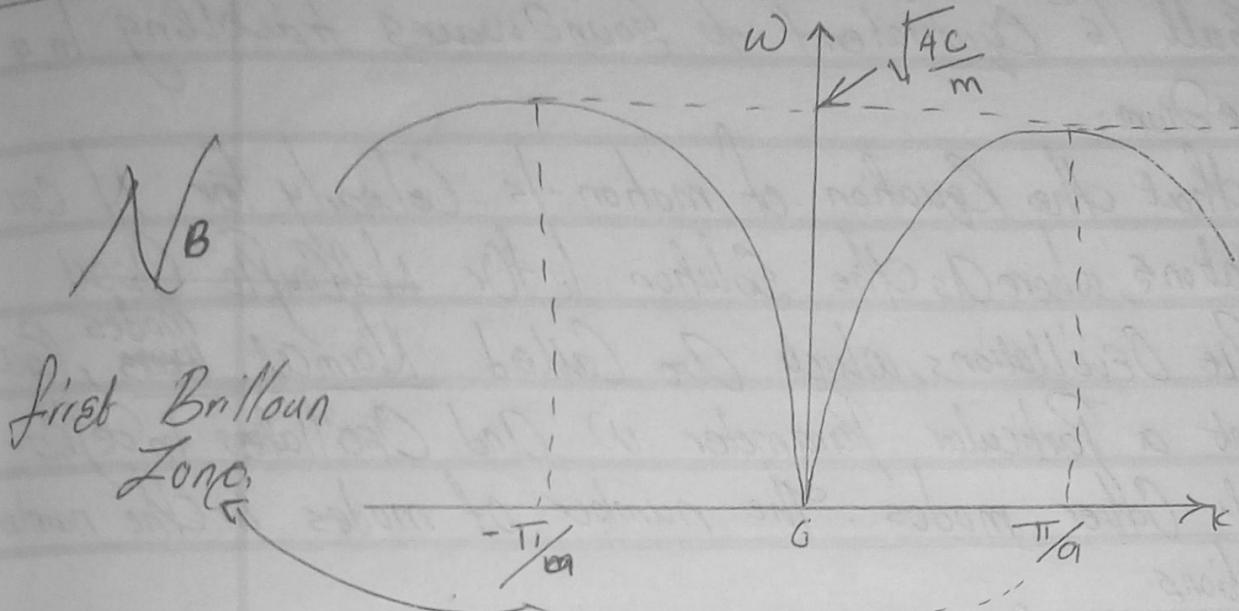
$$-w^2 m = 2c \{ \cos Ka - 1 \}$$

$$= 4c \sin^2 \frac{Ka}{2}$$

$$w = \sqrt{\frac{4c}{m} \cdot \sin^2 \frac{Ka}{2}} \Rightarrow \text{Dispersion Relation (} w(K) \text{)}$$

NB know this from sound wave

13/09  $\omega = \sqrt{\frac{4c}{m}} \cdot \sin \frac{ka}{2} \Rightarrow$  Dispersion relation.



The formula above formular is the dispersion relation for an elastic wave of wavevector  $k$  and of frequency  $\omega$  is the frequency maximum  $\omega_{\max}$  oscillation

$$\sin \frac{ka}{2} = 1, i.e. \frac{ka}{2} = \frac{\pi}{2} \Rightarrow k = \frac{\pi}{a}$$

$\Rightarrow \omega_{\max} = \sqrt{\frac{4c}{m}}$ . This is called the range of Acoustic. It shows that vibration travels through the crystal as continuum i.e. that all frequencies are possible and hence there is no dispersion. It is the cut-off frequency.

Let us consider limiting condition of  $k$ , that is, small  $k$  values that is, when  $k$  is in the long wavelength region.

$$k = \frac{2\pi}{\lambda} \gg a, i.e., ka \ll 1 \Rightarrow$$

$$\omega \approx \sqrt{\frac{4c}{m}} \cdot \frac{ka}{2} \quad (\text{as } \sin \theta \approx \theta, \text{ limit } \theta -)$$

$$\Rightarrow \text{Phase Velocity}, V_p = \frac{\omega}{k} = \sqrt{\frac{c}{m}} \cdot a \quad \text{And}$$

$$\text{group Velocity}, V_g = \frac{d\omega}{dk} = \sqrt{\frac{c}{m}} \cdot a$$

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$\therefore$  for long wavelength  $V_g = V_p \Rightarrow$  no dispersion.

This result is equivalent to sound waves travelling in a continuous medium.

Note that the equation of motion is clearly for N coupled oscillations, whereas the solution is for N uncoupled oscillations, which are called Normal modes, each representing a particular parameter  $\omega$  and oscillates independent with other modes. The number of modes is the number of oscillations.

### Lattice Vibration (Di-atomic)

Consider a diatomic crystal such as CsCl which is BCC lattice with  $Cs^+$  at the vertices and  $Cl^-$  is the centro-clinic crystal).

As in the monoatomic case, suppose we have a wave propagation ~~in~~ of one of the planes of atoms. Consider all the assumptions made in the case of monoatomic and in particular nearest neighbour concept. This is the

