



University of Baghdad
College of Education for Pure Science / Ibn AL Haitham
Physics Department/ Four stage
Syllabus of Solid state physics

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References:

- 1- Kittel, C., 2005,. Introduction to solid state physics, 8th ed., Wiley.
- 2- Omar MA., 1975, Elementary solid state physics, principles and applications, Addison-Wesley Publishing Company.
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Textbook, Kittel 8th edition

Chapter one : (Crystalline structure)

- 1- Introduction
- 2- Crystalline structure
- 3- non-crystalline structure
- 4- Unit cell
- 5- Bravais lattice & non-Bravais lattice: kind of lattice structure : a-simple cubic, b-Body center cubic c- Face centre cubic d- NaCl
- d-Hexagonal system
- 6- symmetry
- 6- Miller Indices

Note: Correct typing error in the first chapter for *Introduction to Solid State Physics* by Charles Kittel, 8th Edition: In page (12) "Figure 14 caption" one of the (100)'s should be $(\bar{1}00)$

1- Introduction:

Solid state physics, also known as condensed matter physics, is the study of the behaviour of atoms when they are placed in close proximity to one another. The serious study of solid state physics began with the discovery of x-ray diffraction by crystals and the publication of a series of simple calculations of the properties of crystals and of electrons in crystals.

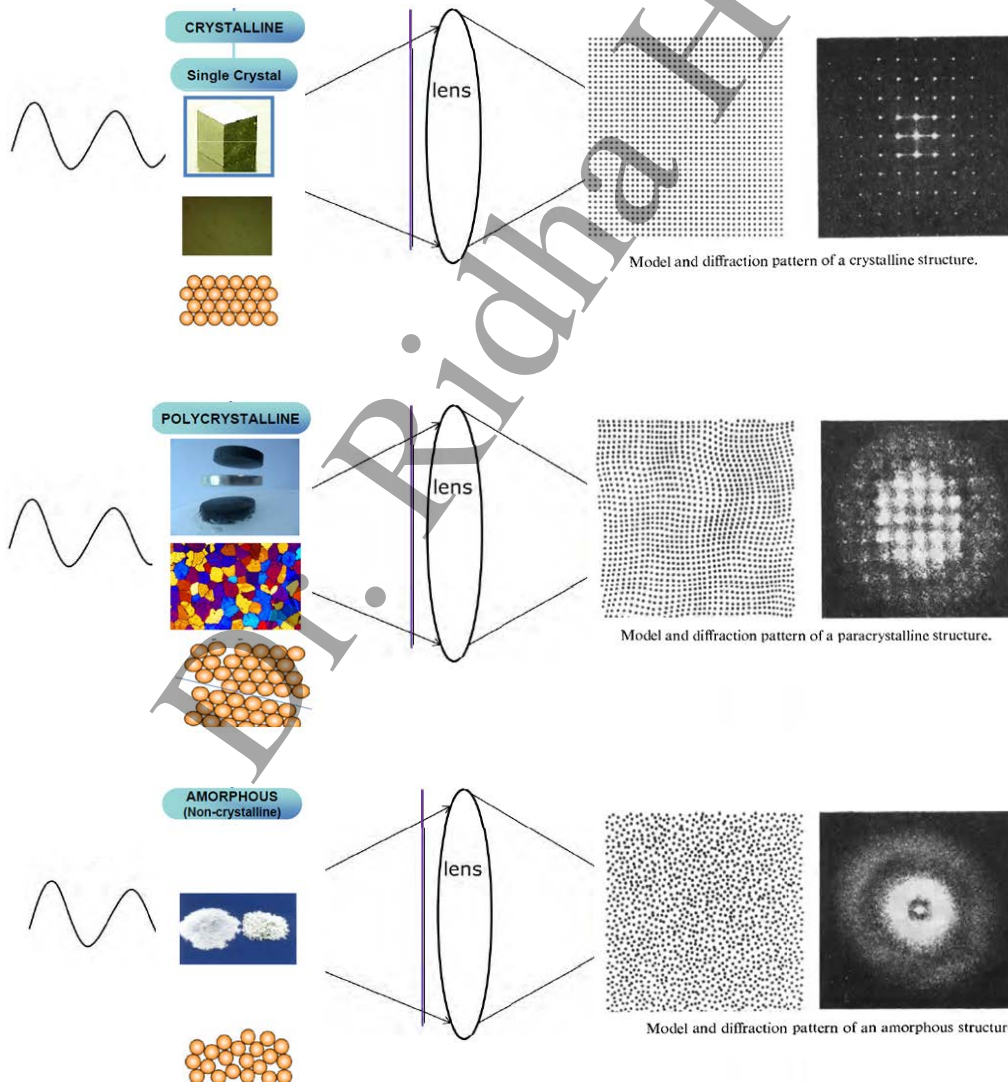
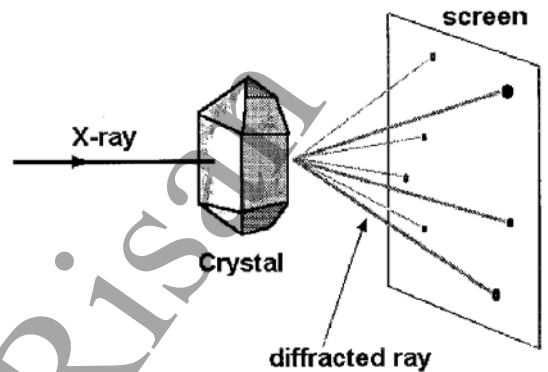
Why crystalline solids rather than noncrystalline solids?

The important electronic properties of solids are best expressed in crystals. Thus the properties of the most important semiconductors depend on the crystalline structure of the host, essentially because electrons have short wavelength components that respond dramatically to the regular periodic atomic order of the specimen.

The original experimental evidence for the periodicity of the structure rests on the discovery by mineralogists that the index numbers that define the orientations of the faces of a crystal are exact integers. This evidence was supported by the discovery in 1912 of x-ray diffraction by crystals, when Laue developed the theory of x-ray diffraction by a periodic array, and his coworkers reported the first experimental observation of x-ray diffraction by crystals.

The importance of x-rays for this task is that they are waves and have a wavelength comparable with the length of a building block of the structure. Such analysis can also be done with neutron diffraction and with electron diffraction, but x-rays are usually the tool of choice.

When a crystal is exposed to a beam of monochromatic X rays, the electron density of any atom diffuses the X ray radiation in all directions. Because of the lattice repetition, the radiation diffused by one atom will interfere with that diffused by all other atoms belonging to the crystal. The result is a diffraction pattern:



2-Crystalline Structure & Non-Crystalline Structure:

A solid is said to be a crystal if the atoms are arranged in such a way that their positions are exactly periodic. Figure 1.1 illustrates the concept. The distance between any two nearest neighbors along the x direction is **a**, and along the y direction is **b** (the x and y axes are not necessarily orthogonal).

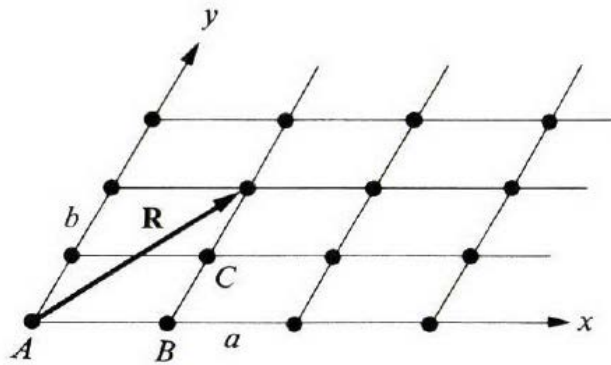
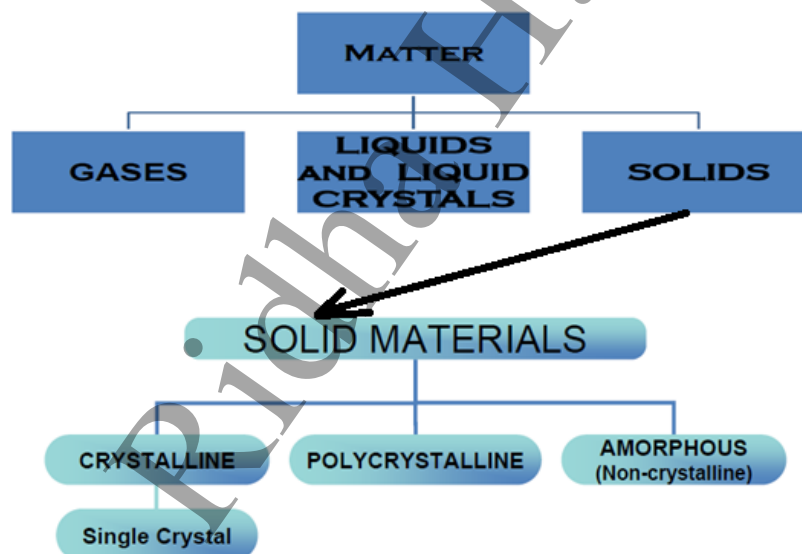


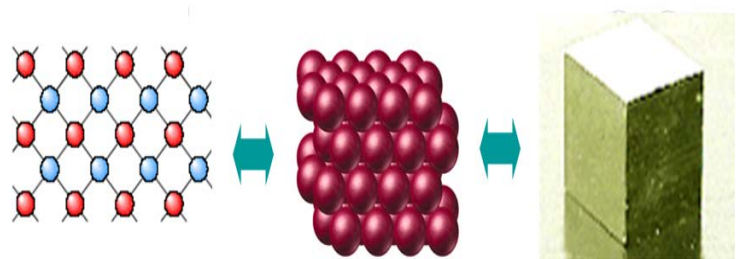
Fig. 1.1: A crystalline solid. All the atoms are arranged periodically.

A perfect crystal maintains this periodicity (or repetitivity) in both the x and y directions from $-\infty$ to ∞ . It follows from the periodicity that the atoms A, B, C, etc., are *equivalent*. In other words, to an observer located at any of these

atomic sites, the crystal appears exactly the same.



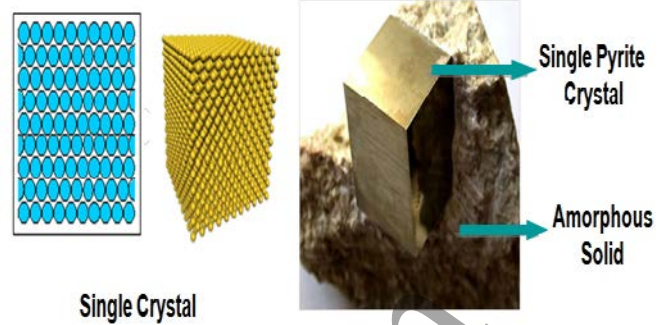
Crystalline Solid is the solid form of a substance in which the *atoms or molecules* are arranged in a definite, repeating pattern in three dimensions.



Crystalline Solid

Single crystals ideally have a high degree of order, or regular geometric periodicity, throughout the *entire volume of the material*.

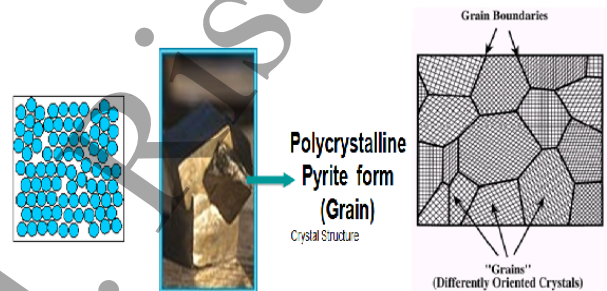
Single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry



Polycrystalline Solid:

Polycrystal is a material made up of an aggregate of *many small single crystals* (also called crystallites or grains).

Polycrystalline material have a high degree of order over many atomic or molecular dimensions.



These *ordered regions*, or single crystal regions, vary in size and orientation with one another.

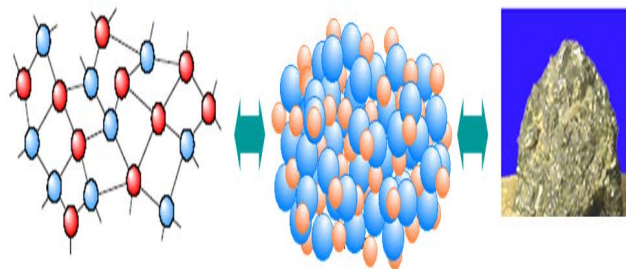
These regions are called as *grains (domain)* and are separated from one another by *grain boundaries*. The atomic order can vary from one domain to the next.

The grains are usually *100 nm - 100 microns in diameter*. Polycrystals with grains that are <10 nm in diameter are called **nanocrystalline**

Amorphous (Non-crystalline) Solid

: is composed of randomly orientated atoms, ions, or molecules that do not form defined patterns or lattice structures.

Amorphous materials have order only within a few atomic or molecular dimensions.



- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples to amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicon can be used in solar cells and thin film transistors.

What is crystallography?

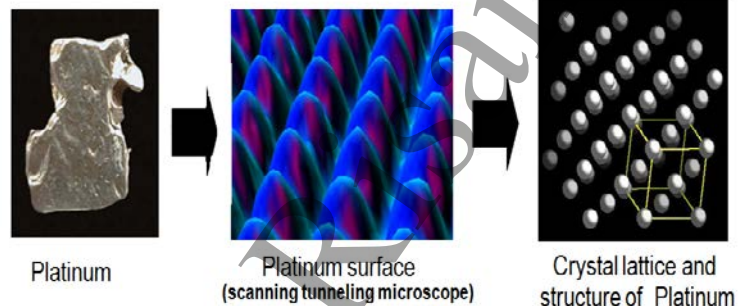
The branch of science that deals with the geometric description of crystals and their internal arrangement. Crystallography is essential for solid state physics.

A basic knowledge of crystallography is essential for solid state physicists;

- to specify any crystal structure and
- to classify the solids into different types according to the symmetries they possess.

What is crystal (space) lattice?

In crystallography, only the geometrical properties of the crystal are of interest, therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom.



Basic Definitions:

In order to talk precisely about crystal structures, we must introduce here a few of the basic definitions which serve as a kind of crystallographic language. These definitions are such that they apply to one-, two-, or three-dimensional crystals. Although most of our illustrative examples will be two-dimensional, the results will be restated later for the 3-D case.

The Crystal Lattice:

In crystallography, only the geometrical properties of the crystal are of interest, rather than those arising from the particular atoms constituting the crystal. Therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom. The result is a pattern of points having the same geometrical properties as the crystal, but which is devoid of any physical contents. **This geometrical pattern is the crystal lattice, or simply the lattice;** all the atomic sites have been replaced by lattice sites.

3- Bravais Lattice:

There are two classes of lattices: the Bravais and the non-Bravais.

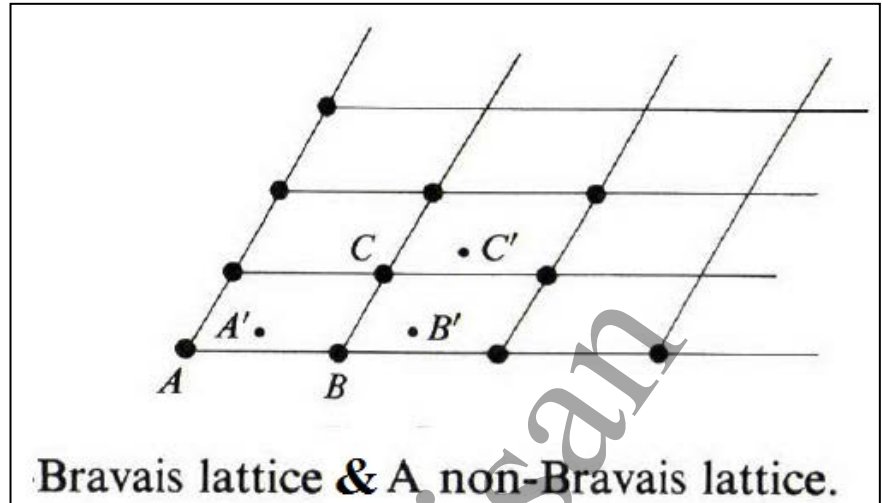
Bravais Lattice : In a **Bravais Lattice**, all lattice points are equivalent, and hence by necessity all atoms in the crystal are of the same kind.

Non-Bravais lattice : In a **non-Bravais lattice**, some of the lattice points are nonequivalent.

The figure shows this clearly.

➡ Here the lattice sites A, B, C are equivalent to each other, and so are the sites A', B', C' among themselves.

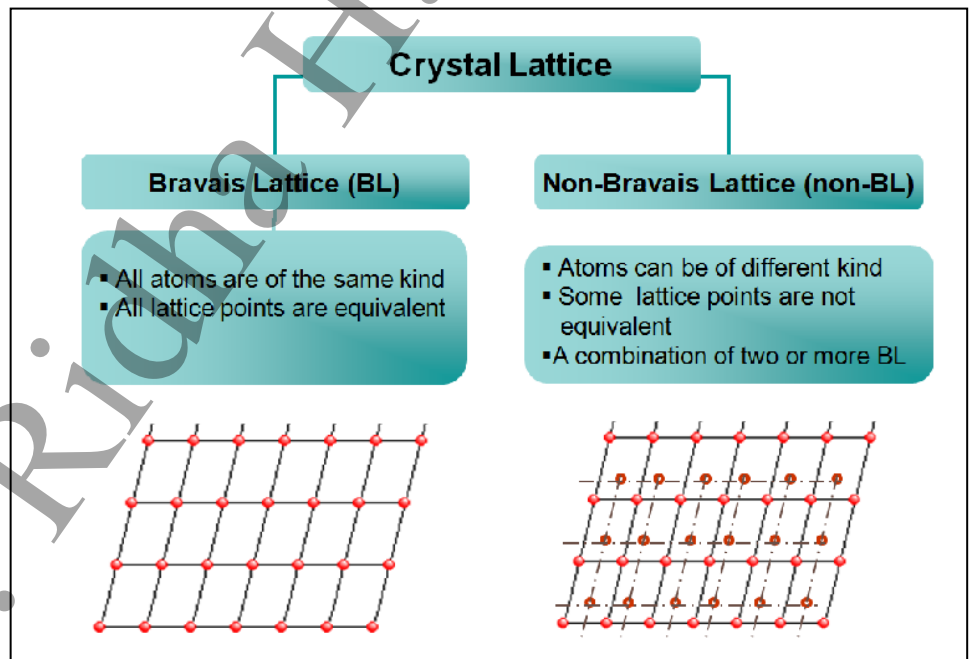
➡ But the two sites A and A' are not equivalent to each other.



➡ As can be seen by the fact that the lattice is not invariant under a translation by AA' . This is so whether the atoms A and A' are of the same kind (for example, two H atoms) or of different kinds (for example, H and Cl atoms).

➡ A non-Bravais lattice is sometimes referred to as a lattice with a basis, the basis referring to the set of atoms stationed near each site of a Bravais lattice. Thus, in this figure, the basis is the two atoms A and A', or any other equivalent set.

➡ The non-Bravais lattice may be regarded as a combination of two or more interpenetrating Bravais lattices with fixed orientations



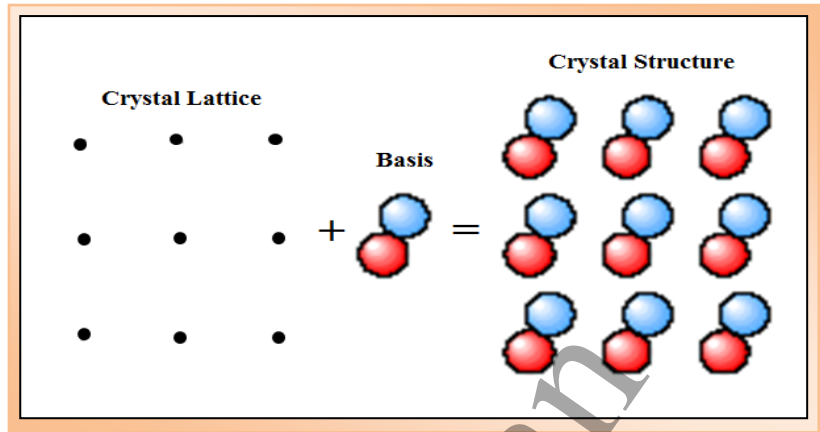
relative to each other. Thus the points A, B, C, etc., form one Bravais lattice, while the points A', B', C' etc., form another.

Crystal structure can be obtained by attaching atoms, groups of atoms or molecules which are called basis to the lattice sides of the lattice point.

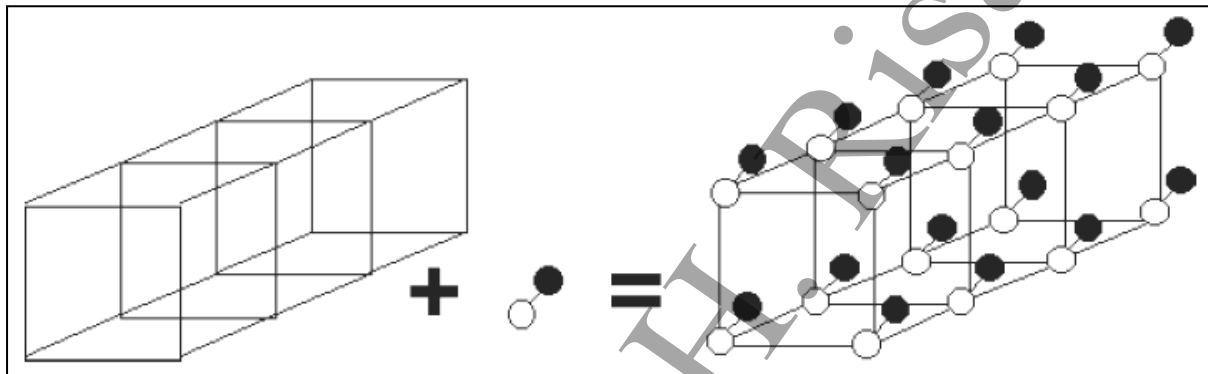
$$\text{Crystal Lattice} + \text{Basis} = \text{Crystal Structure}$$

Crystal structure is formed by the addition of the basis to every lattice point of the space lattice.

This figure shows how a crystal is made by adding a basis to every lattice point of course the lattice points are just mathematical constructions.



Lattice = 3D periodic array of points, unbounded in all directions:



Lattice Translation Vectors:

An ideal crystal is constructed by the infinite repetition of identical groups of atoms. A group is called the **basis**. The set of mathematical points to which the basis is attached is called the **lattice**.

The lattice in three dimensions may be defined by three translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 , such that the arrangement of atoms in the crystal looks the same when viewed from the point \mathbf{r} as when viewed from every point \mathbf{r}' translated by an integral multiple of the \mathbf{a} 's:

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \quad (1)$$

Three Translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 & & u_1 , u_2 , u_3 are arbitrary integers

Here u_1 , u_2 , u_3 are arbitrary integers. The set of points \mathbf{r}' defined by (1) for all u_1 , u_2 , u_3 defines the lattice.

The lattice is said to be **primitive** if any two points from which the atomic arrangement looks the same always satisfy (1) with a suitable choice of the integers u_i .

Basis and the Crystal Structure:

The **basis** of the crystal structure can be identified once the crystal axes have been chosen. Every basis a given crystal is identical to every other in composition, arrangement, and orientation.

The number of atoms in the basis may be one, or it may be more than one. **The position of the center of an atom j** of the basis relative to the associated lattice point is

$$\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3 \quad (2)$$

We may arrange the origin, which we have called the associated lattice point, so that $0 \leq x_j, y_j, z_j \leq 1$.

Primitive Lattice Cell

The parallelepiped defined by primitive axes $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ is called a **primitive cell** as shown in figure. A **primitive cell** is a type of cell or unit cell. The (adjective unit is superfluous and not needed). A cell will fill all space by the repetition of suitable crystal translation operations. A **primitive cell** is a minimum – volume cell.

There are many ways of choosing the **primitive axes** and primitive cell for a given lattice. The number of atoms in a primitive cell or primitive basis is always the same for a given crystal structure.

There is always one lattice point per primitive cell. If the primitive cell is a parallelepiped with lattice points at each of the eight corners, each lattice point is shared among eight cells, so that the total number of lattice points in the cell is one: $8 \times \frac{1}{8} = 1$. The volume of a parallelepiped with axes $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ is

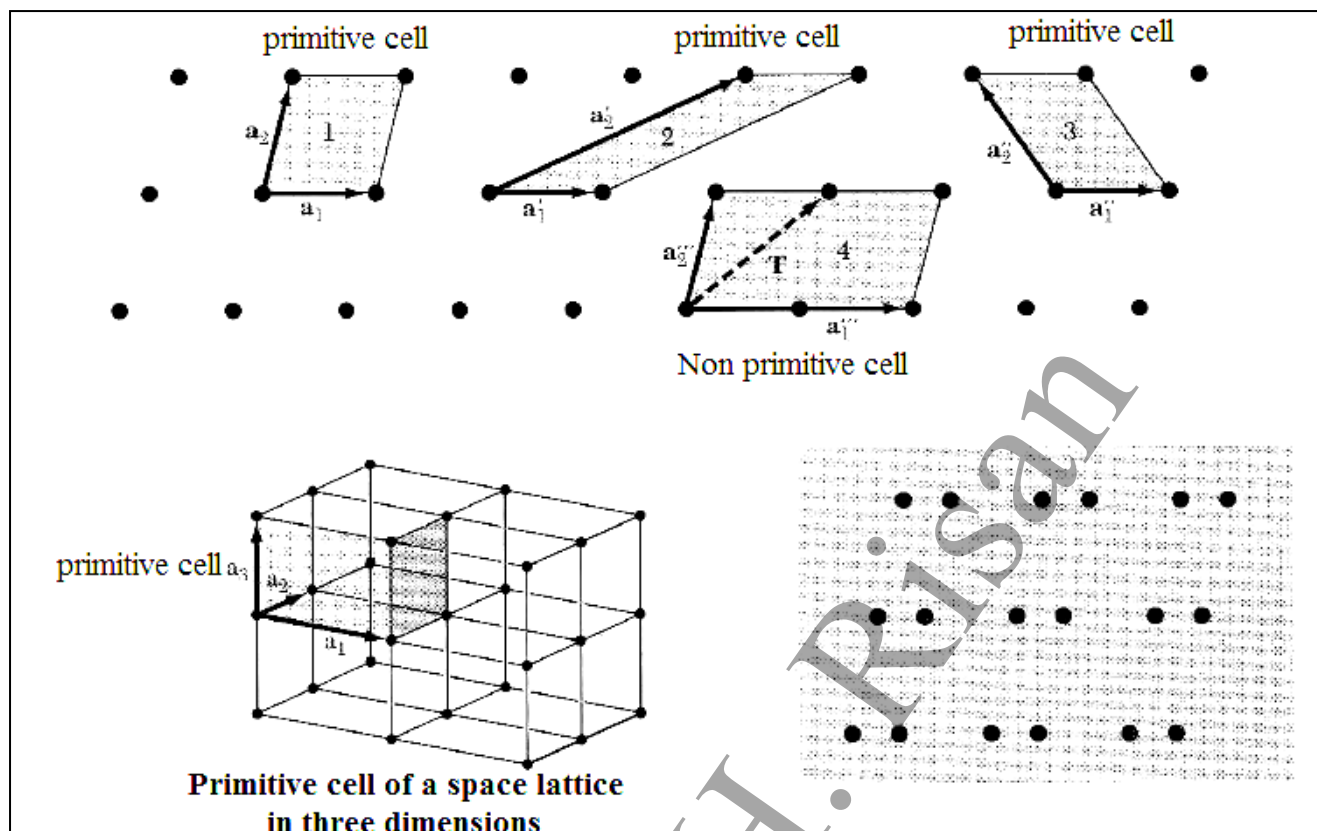
$$V_C = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$$

By elementary vector analysis. The basis associated with a primitive cell is called a primitive basis. No basis contains fewer atoms than a primitive basis contains.

The figure shows Lattice Points of a space lattice in two dimensions. All pairs of vectors $\mathbf{a}_1, \mathbf{a}_2$ are translation vectors of the lattice. But $\mathbf{a}_1''', \mathbf{a}_2'''$ are not primitive translation vectors because we cannot from the lattice translation \mathbf{T} from integral combinations of $\mathbf{a}_1'', \mathbf{a}_2''$.

The other pairs shown of \mathbf{a}_1 and \mathbf{a}_2 may be taken as primitive translation vectors of the lattice. The parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive cell.

The parallelograms 4 have twice the area of a primitive cell.



4- Unit cell:

A volume which, through translation by all of the lattice vectors, can fill the space without overlapping between the replica.

Primitive unit cell: any volume of space which, when translated through all the vectors of the Bravais lattice, fills space without overlap and without leaving voids. Unit cell with the smallest volume • Unit cell can form from fundamental vectors, but it can also be constructed by other methods (e. g. Wigner-Seitz primitive cell).

Non Primitive cells: The units cells, which contain more than one lattice point are called non-primitive cells.

H.W. : As long as the fundamental vectors are fixed, all the unit cells have the same volume (why?)

This statement defines the **primitive translation vectors** \mathbf{a}_i . There is no cell of smaller volume than $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ that can serve as a building block for the crystal structure.

We often use the primitive translation vectors to define the **crystal axes**, which form three adjacent edges of the primitive parallelepiped.

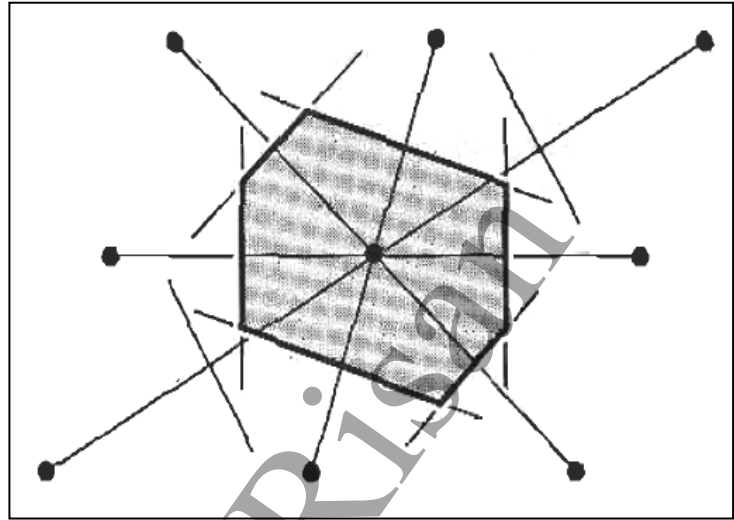
Non primitive axes are often used as crystal axes when they have a simple relation to the symmetry of the structure.

Another way of choosing a primitive is shown in this figure. This is known to physicists as a **Wigner-Seitz cell**.

Wigner-Seitz cell :

A primitive cell may also be chosen following this procedure:

- 1- Draw lines to connect a given lattice point to all nearby lattice points.
- 2- At the midpoint and normal to these lines, draw new lines or planes.
- 3- The smallest volume enclosed in this way is the **Wigner-Seitz primitive cell**.



4- symmetry operations

Crystal lattices can be carried or mapped into themselves by the lattice translations T and by various other symmetry operations.

symmetry operations:

A **typical symmetry** operation is that of **rotation about an axis** that passes through a lattice point. Lattices can be found such that one, two, three, four, and six **fold rotation axes** carry the lattice into itself, corresponding to rotations by 2π , $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations. The rotation axes are denoted by the symbols 1, 2, 3, 4, and 6.

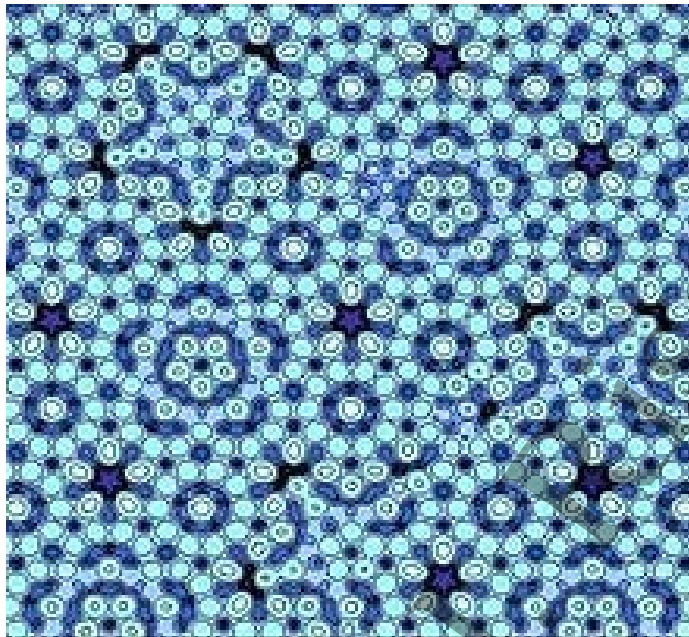
We cannot find a lattice that goes into itself under other rotations, such as by $2\pi/7$ radians.

NOTE:

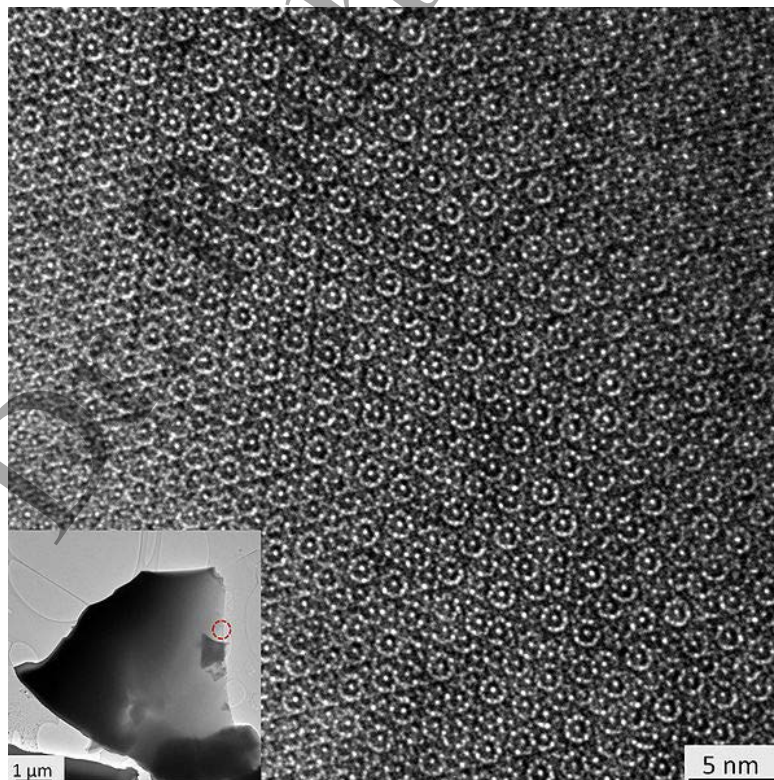
1- The crystallographic restriction theorem in its basic form was based on the observation that the rotational symmetries of a crystal are usually limited to 2-fold, 3-fold, 4-fold, and 6-fold. However, quasicrystals can occur with other diffraction pattern symmetries, such as 5-fold; these were not discovered until 1982 by Dan Shechtman.

2- In 1982 Nobel Laureate Dan Shechtman looked down his microscope and discovered a crystal with 5-fold symmetry - a form that was thought to be impossible. His new crystals, called quasicrystals, caused uproar, and eventually textbooks had to be rewritten across the globe.

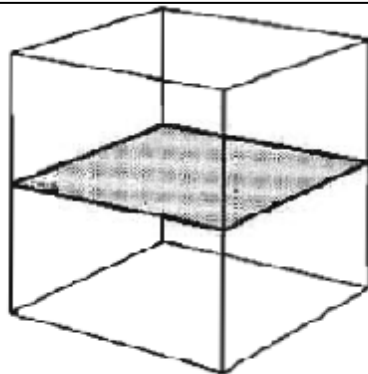
Shechtman's Nobel Prize–winning work was in the area of quasicrystals, ordered crystalline materials lacking repeating structures, such as this Al-Pd-Mn alloy. **aluminium-palladium-manganese (Al-Pd-Mn) quasicrystal**



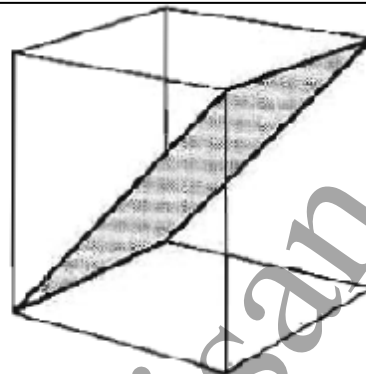
Atomic image of a micron-sized grain of the natural $\text{Al}_{71}\text{Ni}_{24}\text{Fe}_5$ quasicrystal (shown in the inset) from a Khatyrka meteorite. The corresponding diffraction patterns reveal a ten-fold symmetry.



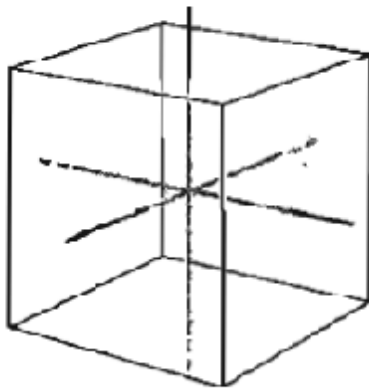
We can have **mirror reflections** m about a plane through a lattice point. The **inversion operation** is composed of π followed by reflection in a plane normal to the rotation axis; the total effect is to replace \mathbf{r} by $-\mathbf{r}$.



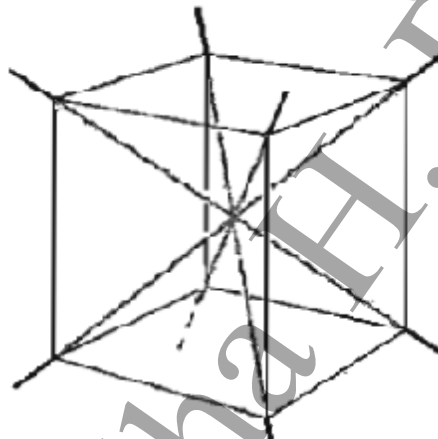
A plane of symmetry parallel to the faces of a cube



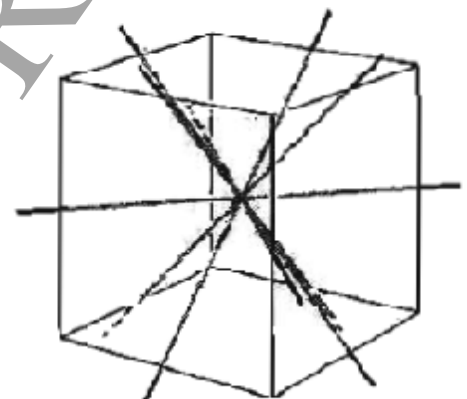
A diagonal plane of symmetry in a cube



The three tetrad axes of a cube



The four triad axes of a cube



The six diad axes of a cube

Crystal Symmetry Operations:

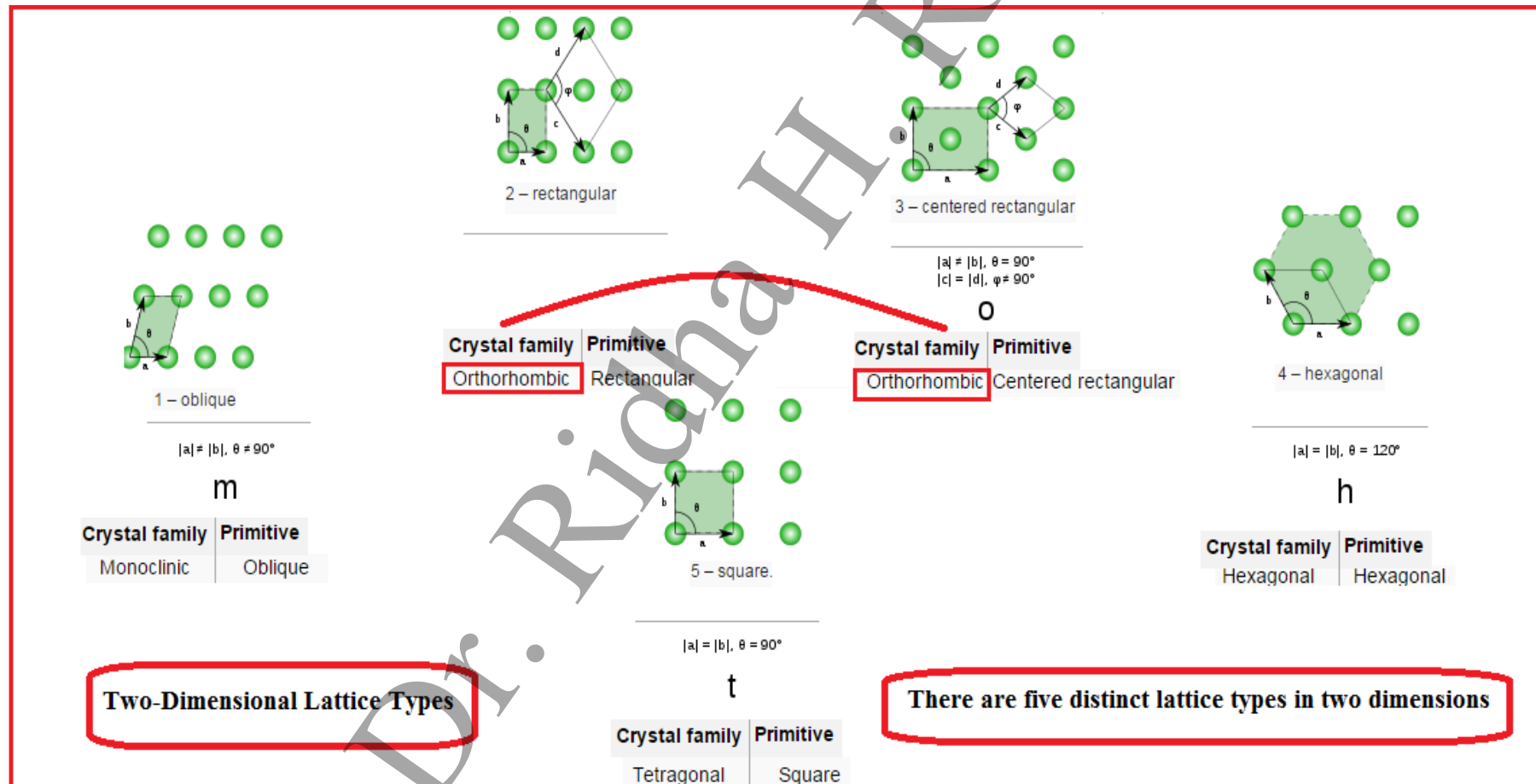
Symmetry operations: Operations under which there is no change in the spatial distances and angles, and there is no distortion, compression or extension, and yet after application of the operation, there is still a lattice point where there were a lattice point and there is not a lattice point where there were no lattice point.

- Translation
- Rotation
- Reflection
- Inversion

6 - kind of lattice structure :

Two Dimensional Lattice Types :

There are four distinct types of restriction, and each leads to what we may call a **special lattice type**. Thus there are five distinct lattice types in two dimensions, the oblique lattice and the four special lattices shown in figure below. There are five Bravais lattice in two dimensions.



Three Dimensional Lattice types:

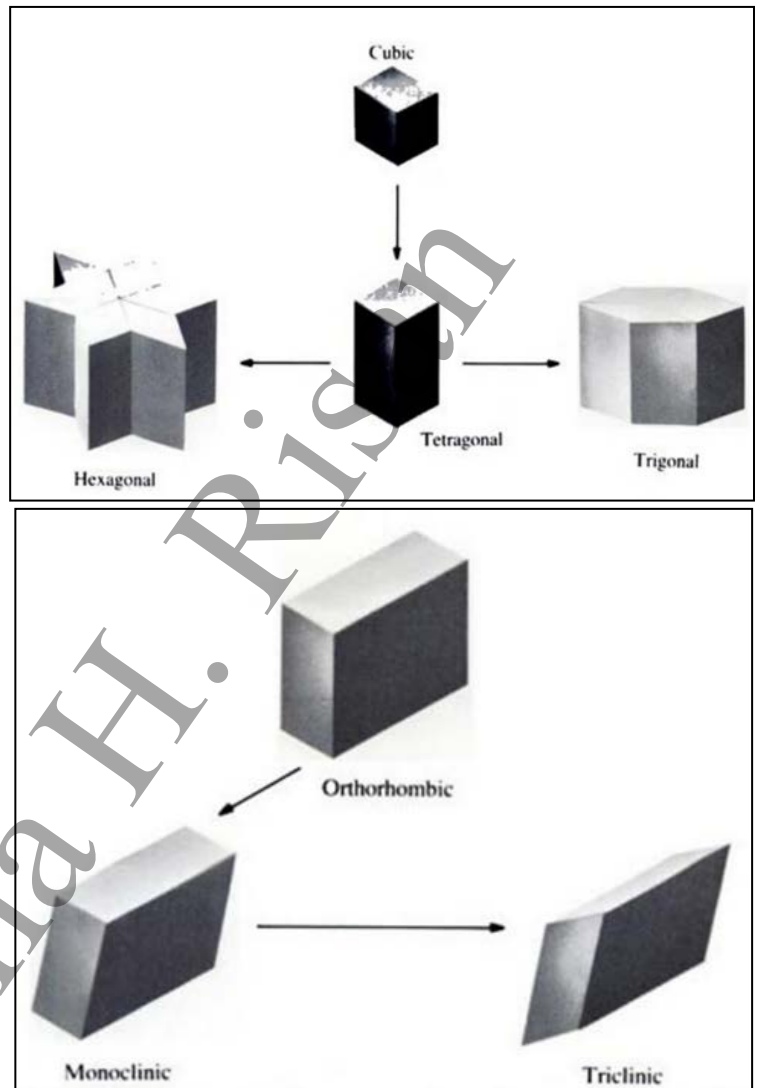
The points symmetry groups in three dimensions require the **14 different lattice types** listed in table below. This gives the **seven crystal systems**, in which all crystal structures can be classified:

1. Cubic System (SC, BCC, FCC)
2. Hexagonal System (S)
3. Triclinic System (S)
4. Monoclinic System (S, Base-C)
5. Orthorhombic System (S, Base-C, BC, FC)
6. Tetragonal System (S, BC)
7. Trigonal (Rhombohedral) System (S)

In three-dimensional space, there are 14 Bravais lattices. These are obtained by combining one of the six **crystal families** with one of the centering types. The centering types identify the locations of the lattice points in the unit cell as follows:

- 1) **Primitive (P):** lattice points on the cell corners only (sometimes called simple)
- 2) **Base-centered (A, B, or C):** lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered)
- 3) **Body-centered (I):** lattice points on the cell corners with one additional point at the center of the cell
- 4) **Face-centered (F):** lattice points on the cell corners with one additional point at the center of each of the faces of the cell
- 5) **Rhombohedrally-centered (R):** lattice points on the cell corners with two additional points along the longest body diagonal (only applies for the hexagonal crystal family).

Primitive cells by definition contain only one lattice point, but the conventional bcc cell contains two lattice points, and the fcc cell contains four points.



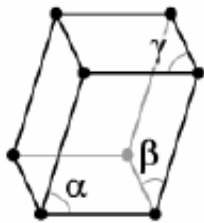
Crystal family	Lattice system	Volume	Axial distances (edge lengths)	Axial angles	Corresponding examples
Triclinic		$abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$	(All remaining cases)		$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3
Monoclinic		$abc \sin \beta$	$a \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic sulfur, $Na_2SO_4 \cdot 10H_2O$
Orthorhombic		abc	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulfur, KNO_3 , $BaSO_4$
Tetragonal		$a^2 c$	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2 , $CaSO_4$
Hexagonal	Rhombohedral	$a^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$ (rhombohedral cell)	$a = b = c$ (rhombohedral cell)	$\alpha = \beta = \gamma \neq 90^\circ$ (rhombohedral cell)	Calcite ($CaCO_3$), cinnabar (HgS)
	Hexagonal	$\frac{\sqrt{3}}{2} a^2 c$	$a = b$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO , CdS
Cubic		a^3	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	$NaCl$, zinc blende, copper metal

7 crystal systems and 14 Bravais lattices in 3D

triclinic

$$a \neq b \neq c$$

$$\alpha, \beta, \gamma \neq 90^\circ$$

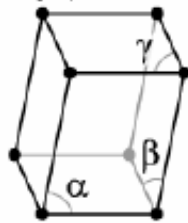


monoclinic

$$a \neq b \neq c$$

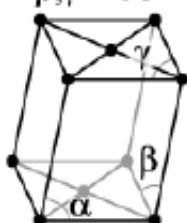
P

$$\alpha \neq 90^\circ, \beta, \gamma = 90^\circ$$



C

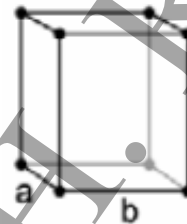
$$\alpha \neq 90^\circ, \beta, \gamma = 90^\circ$$



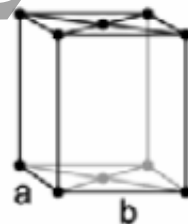
orthorhombic

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

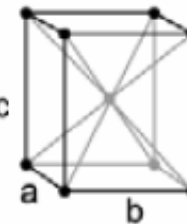
P



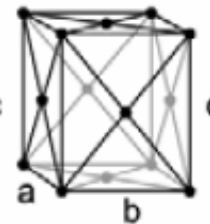
C



I



F

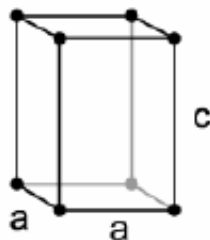


tetragonal

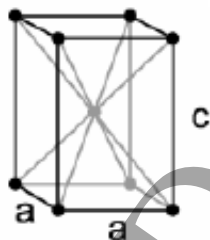
$$a = b \neq c,$$

$$\alpha = \beta = \gamma = 90^\circ$$

P



I

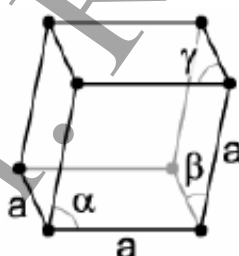


rhombohedral

(trigonal)

$$a = b = c,$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

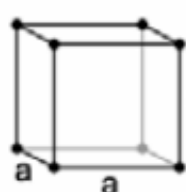


cubic

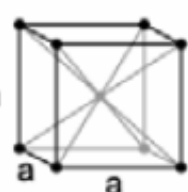
$$a = b = c,$$

$$\alpha = \beta = \gamma = 90^\circ$$

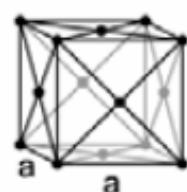
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I



F

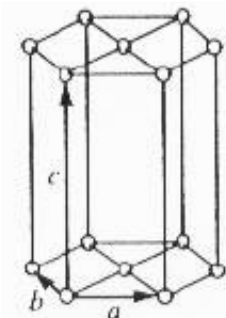


hexagonal

$$a = b \neq c,$$

$$\alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$



The point symmetry groups in three dimensions require the 14 different lattice types listed in this table:

There are three lattice in cubic system: the simple cubic (sc) lattice, the body – centered cubic (bcc) lattice, and the face-centered cubic (fcc) lattice, included in the table shown below.

The 14 lattice types in three dimensions		
System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

Table 2 Characteristics of cubic lattices^a

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2} a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction ^a	$\frac{1}{6}\pi$ =0.524	$\frac{1}{8}\pi\sqrt{3}$ =0.680	$\frac{1}{6}\pi\sqrt{2}$ =0.740

^aThe packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.

As it mentioned previously, the position of the center of an atom \mathbf{j} of the basis relative to the associated lattice point is $\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3$ ---

- (2) ----- $0 \leq x_j, y_j, z_j \leq 1$.

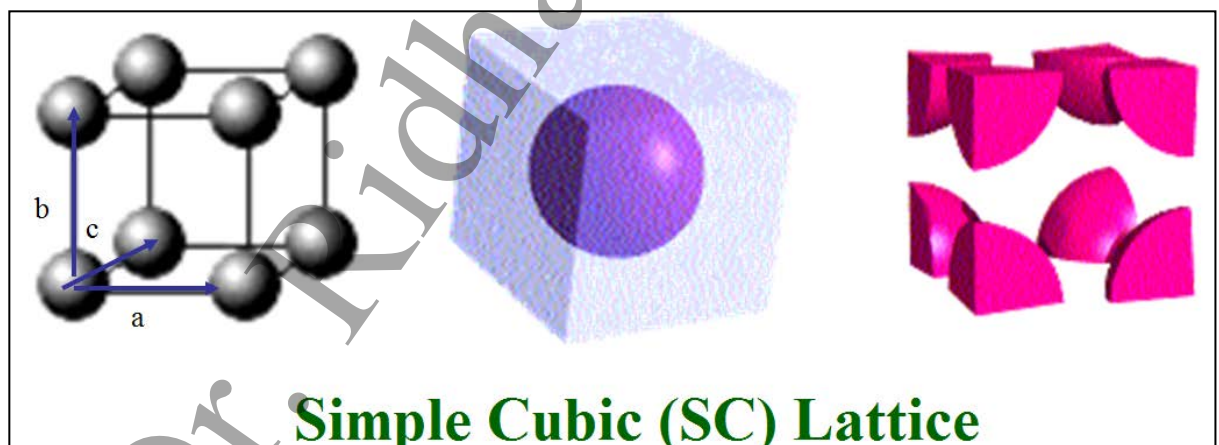
The position of a point in a cell is specified by (2) in terms of the atomic coordinates x, y, z . Here each coordinate is a fraction of axial length $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ in the direction of the coordinate axis, with the origin taken at one corner of the cell.

- ➡ Thus the coordinates of the body center of a cell are $000, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
- ➡ And the fcc center include $000, \frac{1}{2}, \frac{1}{2}, 0, 0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}$.
- ➡ In the hexagonal system the primitive cell is a right prism based on a rhombus with an included angle of 120° .

Simple cubic:

The SC Lattice has one lattice point in its unit cell, so it's unit cell is a primitive cell. In the unit cell on the left, the atoms at the corners are cut because only a portion (in this case 1/8) "belongs" to that cell. The rest of the atom "belongs" to neighboring cells.

Coordination Number of the SC Lattice = 6.



Body Center Cubic:

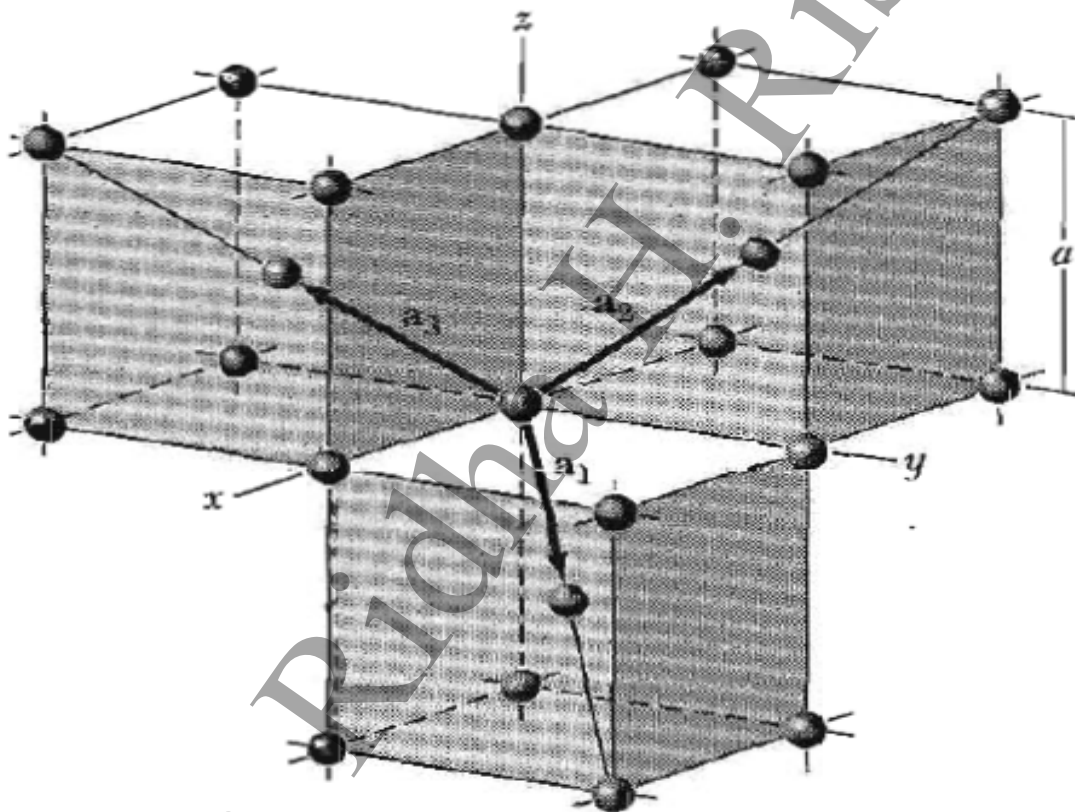
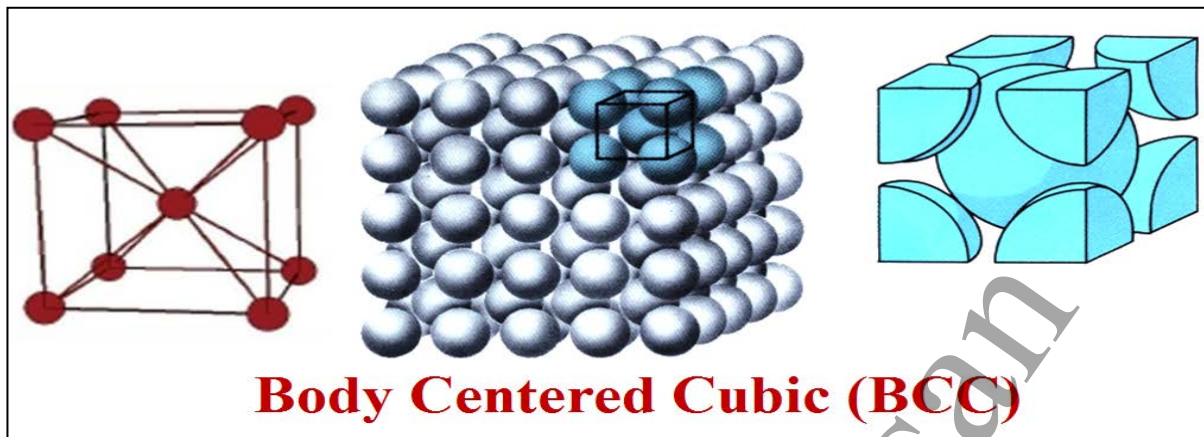
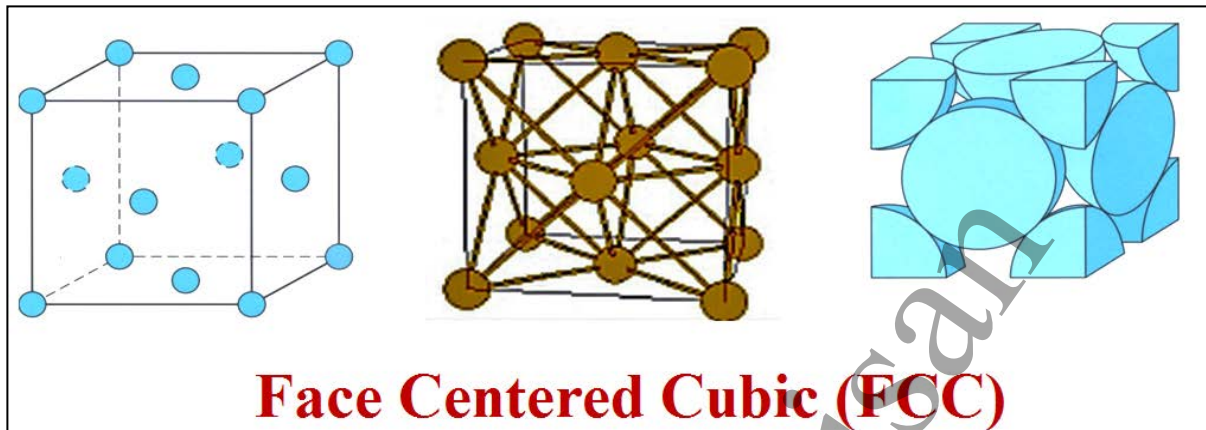


Figure 10 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a , the primitive translation vectors are

$$\begin{aligned} \mathbf{a}_1 &= \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) ; & \mathbf{a}_2 &= \frac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \\ \mathbf{a}_3 &= \frac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) . \end{aligned}$$

Here $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are the Cartesian unit vectors.

C- Face Centre Cubic:



In the the face-centered cubic structure

$$\vec{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y})$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{y} + \hat{z})$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{z})$$

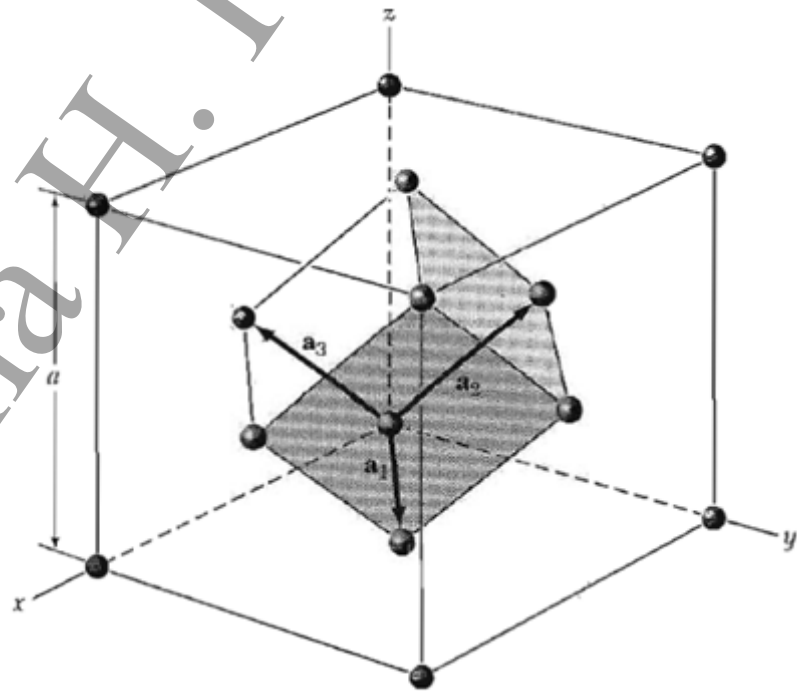


Figure 11 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y}) ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{y} + \hat{z}) ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{z} + \hat{x}) .$$

The angles between the axes are 60° .

Hexagonal Close-Packed Structure (hcp)

There are an infinite number of ways of arranging identical spheres in a regular array that maximizes the packing fraction. One is the face centered cubic structure; another is the hexagonal close-packed structure (Fig. 20). The fraction of the total volume occupied by the spheres is 0.74 for both structures. No structure, regular or not, has denser packing.

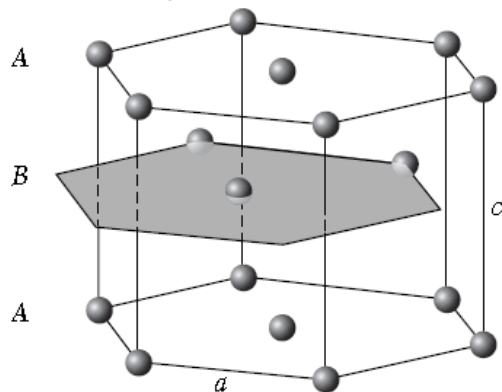


Figure 20 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters a and c are indicated, where a is in the basal plane and c is the magnitude of the axis \mathbf{a}_3 of Fig. 12.

Figure 12 shows the relationship of the rhombic cell to a hexagonal prism.

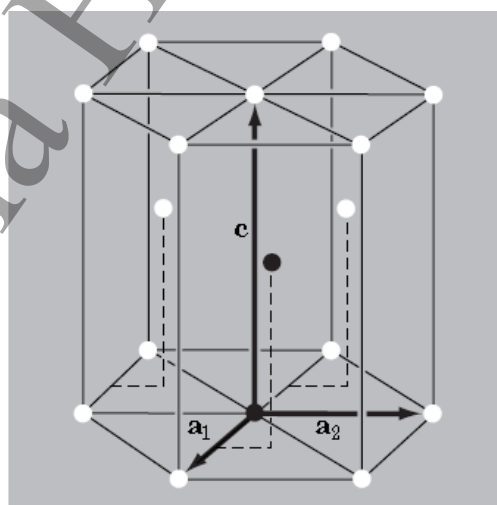
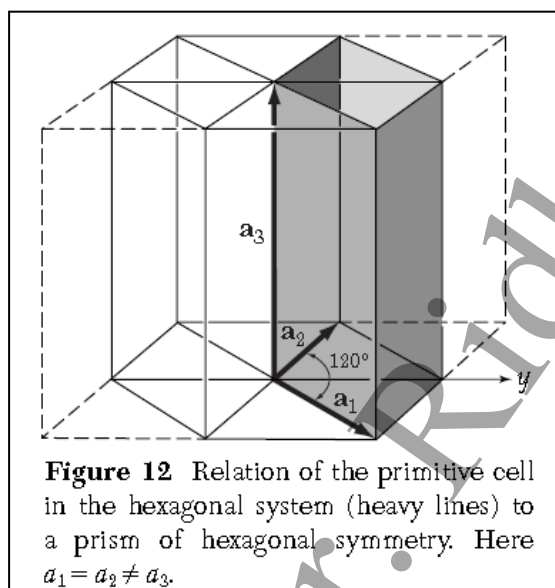
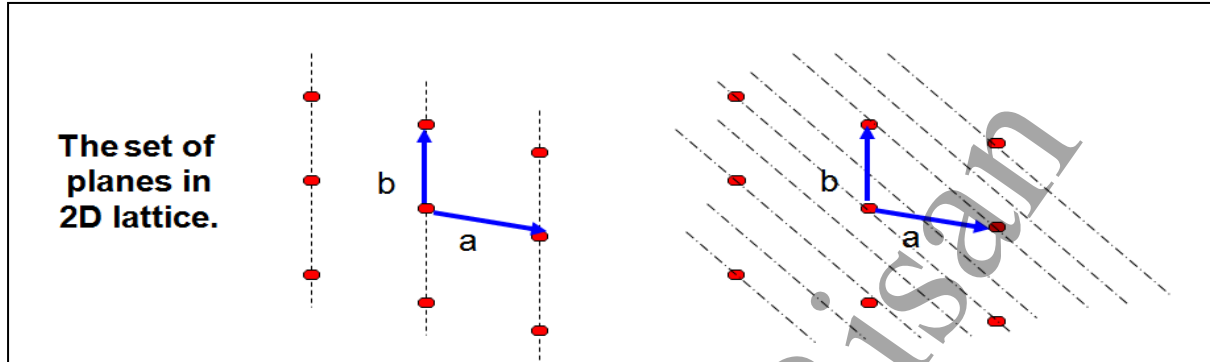


Figure 21 The primitive cell has $a_1 = a_2$, with an included angle of 120° . The c axis (or \mathbf{a}_3) is normal to the plane of \mathbf{a}_1 and \mathbf{a}_2 . The ideal hcp structure has $c = 1.633 a$. The two atoms of one basis are shown as solid circles. One atom of the basis is at the origin; the other atom is at $\frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2$, which means at the position $\mathbf{r} = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$.

The number of nearest-neighbor atoms is 12 for both hcp and fcc structures. If the binding energy (or free energy) depended only on the number of nearest-neighbor bonds per atom, there would be no difference in energy between the fcc and hcp structures.

Crystal Planes:

Within a crystal lattice it is possible to identify sets of equally spaced parallel planes. These are called **lattice planes**. In the figure density of **lattice points on each plane of a set is the same** and all lattice points are contained on each set of planes.

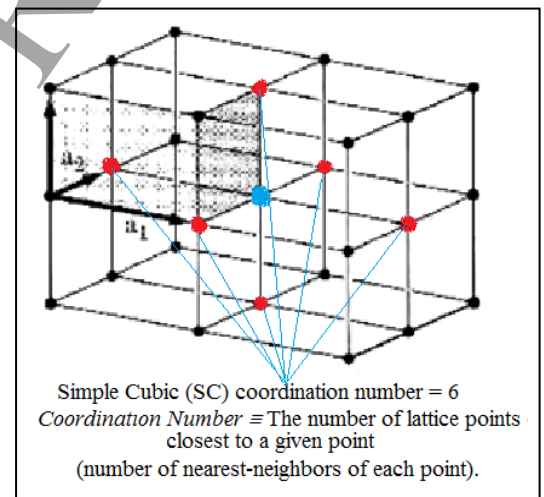


Coordination Number:

- For a Bravais Lattice,
Coordination Number \equiv The number of lattice points closest to a given point (number of nearest-neighbors of each point).
- Because of lattice periodicity, all lattice points have the same number of nearest neighbors or coordination number. (Coordination number is intrinsic to the lattice.)

Examples

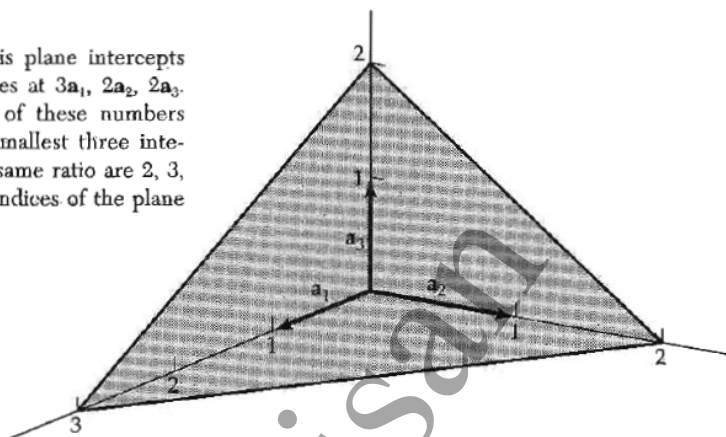
- Simple Cubic (SC) coordination number = 6
- Body-Centered Cubic coordination number = 8
- Face-Centered Cubic coordination number = 12



7- Miller Indices

Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.

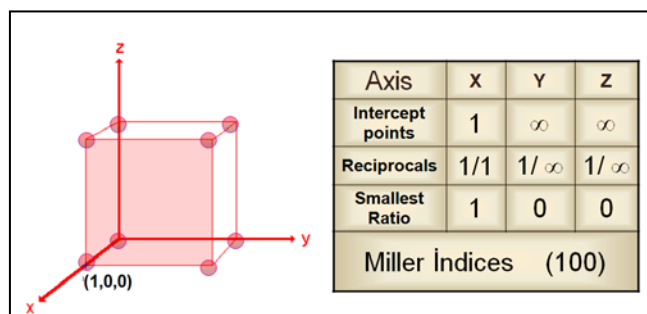
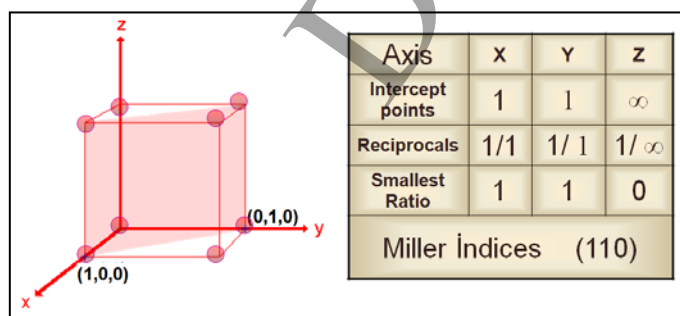
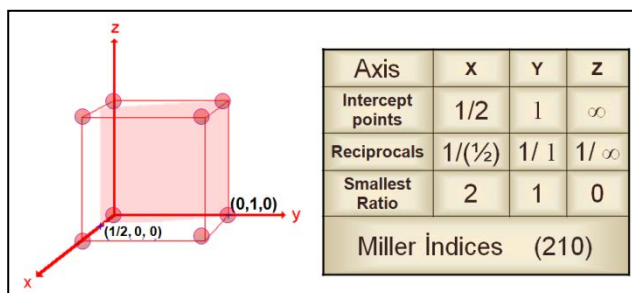
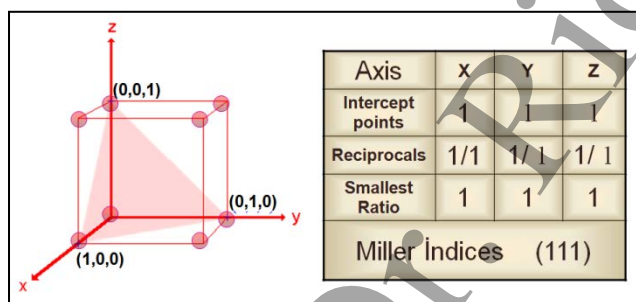
Figure 13 This plane intercepts the a_1 , a_2 , a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

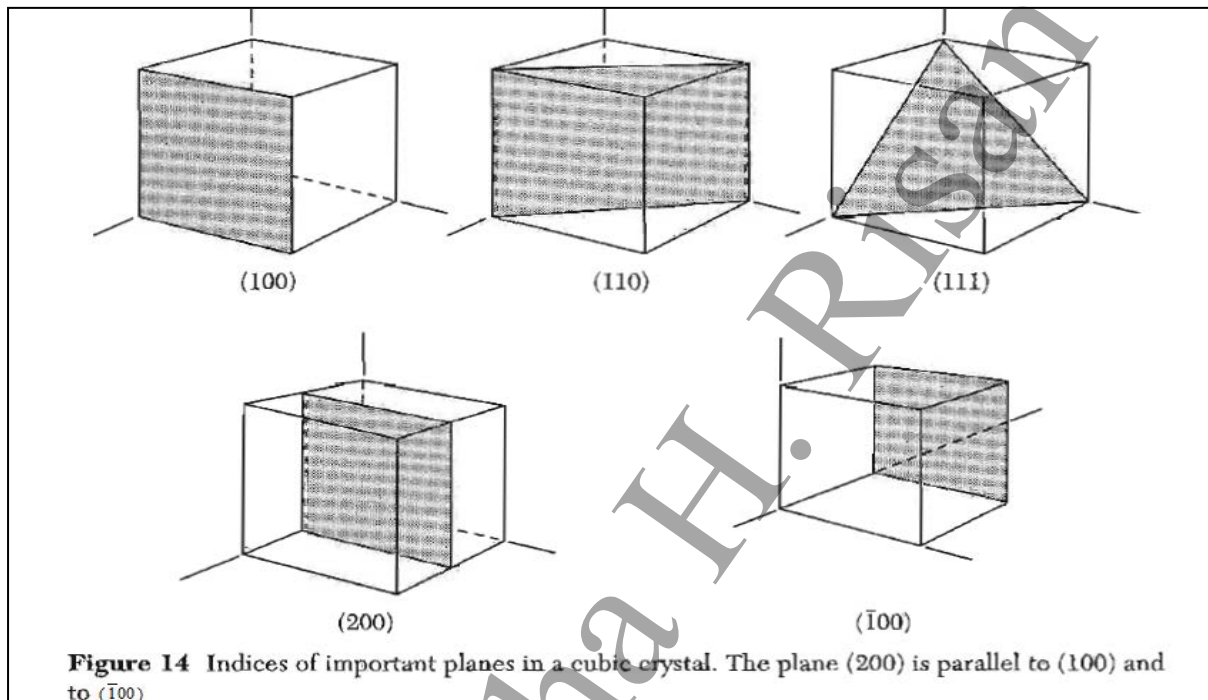
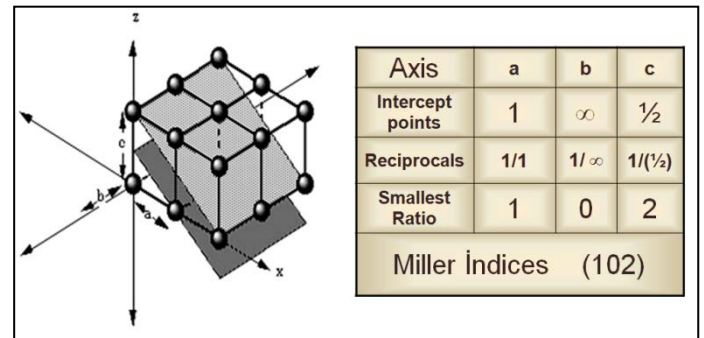
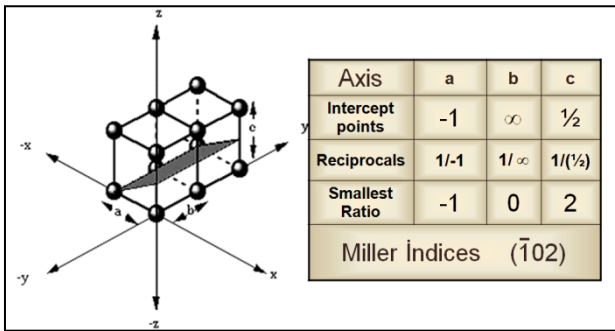


To determine Miller indices of a plane:

- 1) Find the intercepts on the axes in terms of the lattice constants a_1 , a_2 , a_3 . The axes may be those of a primitive or nonprimitive cell.
- 2) Take the reciprocals of these number and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses (hkl), is called the **index of the plane (Miller Indices)**
- 3) If fractions result, multiply each by the denominator of the smallest fraction

Examples:





In Hexagonal System:

$$a_1 = 1 \quad a_2 = -1 \quad a_3 = \infty \quad c = \infty$$

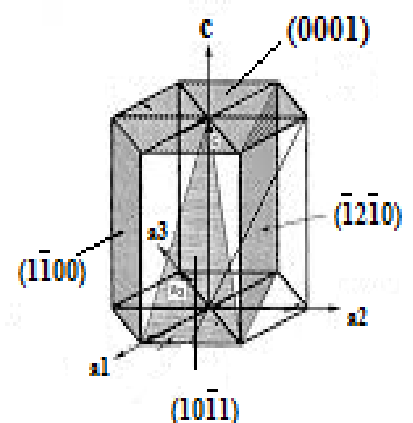
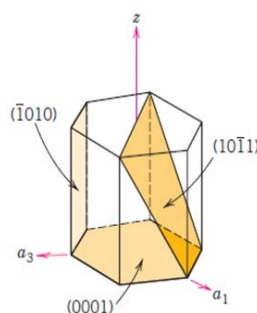
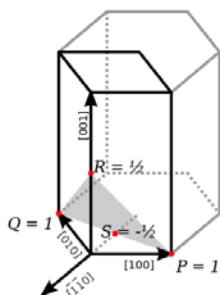
The Intercepts:

$$1 \quad -1 \quad \infty \quad \infty$$

The Reciprocals:

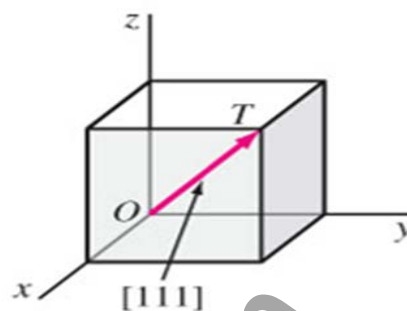
$$1 \quad -1 \quad 0 \quad 0$$

Miller Indices : $(1 \bar{1} 0 0)$

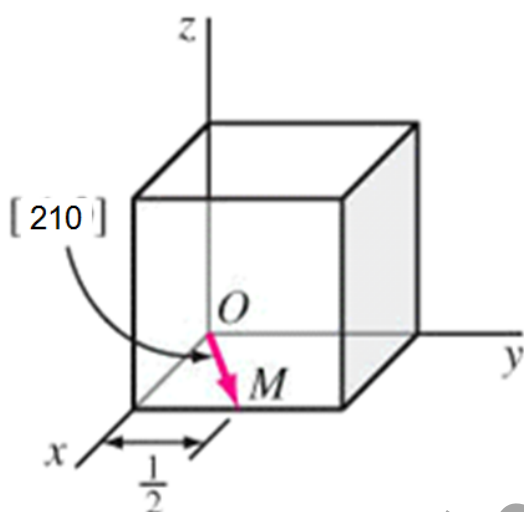


Crystal Directions:

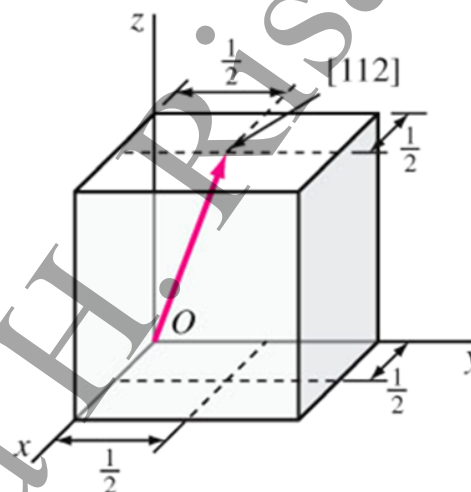
We choose one lattice point on the line as an origin, say the point O. Choice of origin is completely arbitrary, since every lattice point is identical. Then we choose the lattice vector joining O to any point on the line, say point T. To distinguish a lattice direction from a lattice point, the triple is enclosed in square brackets [...] is used. $[u_1u_2u_3]$ or $[n_1n_2n_3]$. $[n_1n_2n_3]$ is the smallest integer of the same relative ratios.



[111] direction

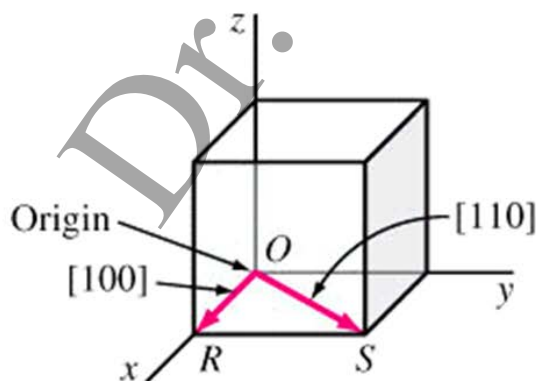


$$X = 1, Y = \frac{1}{2}, Z = 0 \\ [1 \frac{1}{2} 0] \rightarrow [2 \ 1 \ 0]$$

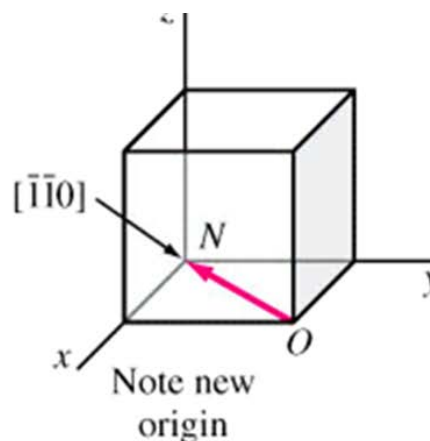


$$X = \frac{1}{2}, Y = \frac{1}{2}, Z = 1 \\ [\frac{1}{2} \ \frac{1}{2} \ 1] \rightarrow [1 \ 1 \ 2]$$

When we write the direction $[n_1n_2n_3]$ depend on the origin, negative directions can be written as $[\bar{n}_1\bar{n}_2\bar{n}_3]$.



$$X = 1, Y = 0, Z = 0 \rightarrow [1 \ 0 \ 0]$$



$$X = -1, Y = -1, Z = 0 \rightarrow [\bar{1}\bar{1}0]$$

Atomic Packing Factor (APF) (Packing Fraction) (PF) (Filling Factor):

For a Bravais Lattice: Packing fraction = $\frac{\text{volume occupied by lattice points}}{\text{volume occupied by unit cell}}$

$$APF = \frac{N_{atoms} V_{atom}}{V_{crystal}}$$

When calculating the APF, the volume of the atoms in the unit cell is calculated as if each atom was a hard sphere, centered on the lattice point & large enough to just touch the nearest-neighbor sphere.

H.W.: Of course, from Quantum Mechanics, we know that this is very unrealistic for any atom ?

- Hexagonal close-packed (hcp): 0.74
- Face-centered cubic (fcc): 0.74 (also called cubic close-packed, ccp)
- Body-centered cubic (bcc): 0.68
- Simple cubic: 0.52
- Diamond cubic: 0.34

The majority of metals take on either the hcp, ccp or bcc structure.

Example 1: How to calculate packing fraction for simple cubic lattice (sc)?

Solution:

To determine the packing fraction, one has to find first the number of lattice points in a given cell.

(i) The lattice point in this case refers to a complete number of atoms that a unit cell contains.

(ii) In a sc, the atoms are in contact with one another only along the edges of the cell as shown in figure :

(iii) All the atoms are at the corners of the cubic lattice.

(iv) Each atom at the corner is shared by 8 cells.

Thus, each atom contributes $\frac{1}{8}$ th of it a unit cell. Since there are 8 atoms at the corners $N = \text{The lattice points sc} = \frac{1}{8} \times 8 = 1$

This means that a unit cell in sc system has one atom to itself. Thus, volume, V , occupied by this atom is,

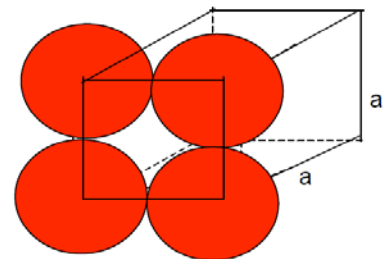
$$V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{a}{2}\right)^3 ,$$

$r = \frac{a}{2}$ (radius of atoms in terms of lattice parameters)

$$\text{Packing fraction} = \frac{\text{volume occupied by lattice points}}{\text{volume occupied by unit cell}} ; APF = \frac{N_{atoms} V_{atom}}{V_{crystal}}$$

$$\text{Packing fraction} = \left(\frac{\frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} \right) = \frac{\pi}{6} = 52\% \quad \text{This means that 48\% of the}$$

volume of a sc is empty, while 52% is filled with atoms.



Example 2 : How to calculate packing fraction for Body-centered cubic (bcc)?**Solution:**

The primitive unit cell for the body-centered cubic crystal structure contains several fractions taken from nine atoms: one on each corner of the cube and one atom in the center. Because the volume of each of the eight corner atoms is shared between eight adjacent cells, each BCC cell contains the equivalent volume of two atoms (one central and one on the corner).

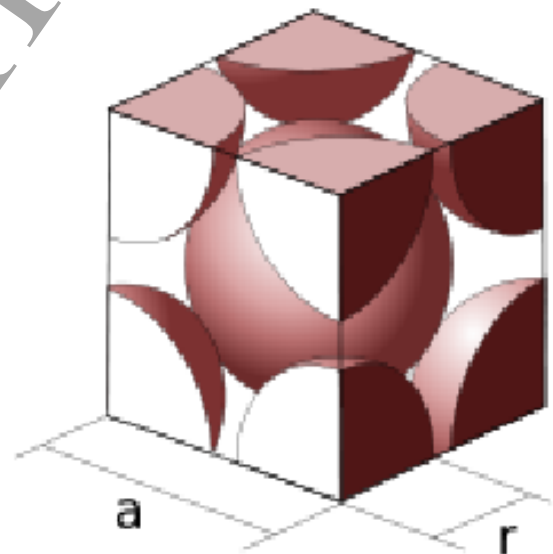
Each corner atom touches the center atom. A line that is drawn from one corner of the cube through the center and to the other corner passes through $4r$, where r is the radius of an atom. By geometry, the length of the diagonal is $a\sqrt{3}$. Therefore, the length of each side of the BCC structure can be related to the radius of the atom by:

$$a = \frac{4r}{\sqrt{3}}$$

Knowing this and the formula for the volume of a sphere, it becomes possible to calculate the APF as follows:

$$APF = \frac{N_{atoms} V_{atom}}{V_{crystal}} = \frac{2 \cdot \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3}$$

$$APF = \frac{\pi\sqrt{3}}{8} \approx 0.68017476$$



Example 3 : How to calculate packing fraction for Face-centered cubic (fcc)?**Solution:**

The FCC unit cell is formed by 4 atoms:

- 8 times one eighth of an atom at the corners of the cube
- 4 times a half of an atom at the center of the of the faces.

At the faces the atoms at the corners and the center atom touch, so that the perfectly fill the face. Hence the length of the face diagonal is

$$D = r + 2r + r = 4r$$

From Pythagorean theorem you get

$$a^2 + a^2 = D^2$$

=>

$$a = \sqrt{8} \cdot r = \sqrt{2} \cdot 2 \cdot r$$

The volume of the cube cell is

$$V_{\text{crystal}} = a^3 = \sqrt{2} \cdot 16 \cdot r^3$$

The volume of the atoms in the cell is

$$V_{\text{atoms}} = 4 \cdot (4 \cdot \pi \cdot r^3 / 3) = 16 \cdot \pi \cdot r^3 / 3$$

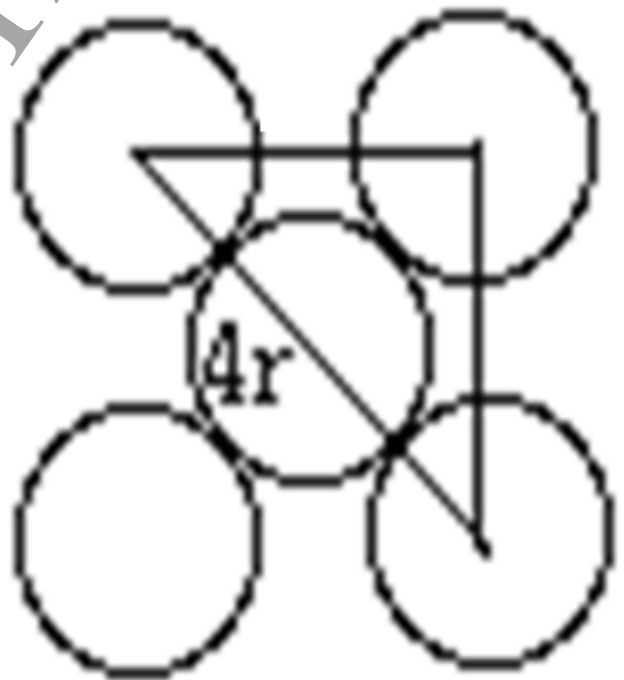
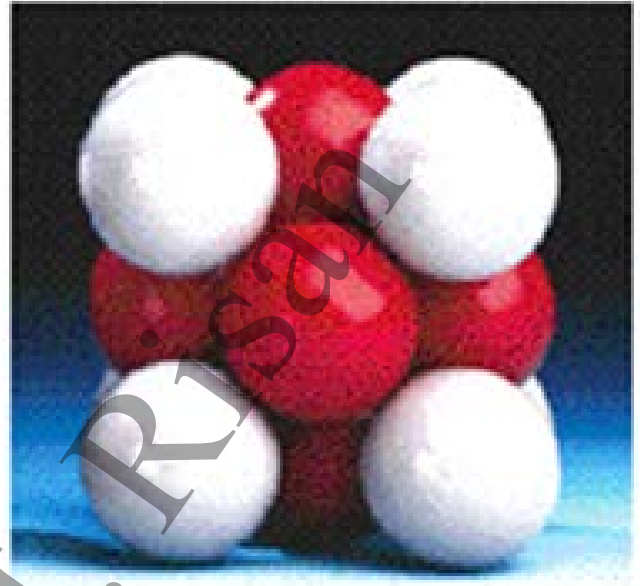
The packing fraction is

$$APF = \frac{N_{\text{atoms}} V_{\text{atom}}}{V_{\text{crystal}}}$$

$$= (16 \cdot \pi \cdot r^3 / 3) / (\sqrt{2} \cdot 16 \cdot r^3)$$

$$= \pi / (3 \cdot \sqrt{2})$$

$$= 0.74$$



Hexagonal System:**Example 4 : How to calculate packing fraction for Hexagonal close-packed?****Solution:**

For the hexagonal close-packed structure the derivation is similar. Here the unit cell (equivalent to 3 primitive unit cells) is a hexagonal prism containing six atoms. Let a be the side length of its base and c be its height. The volume of the unit cell of hcp can be taken as $24\sqrt{2}r^3$. Then:

$$a = 2r \qquad c = 4\sqrt{\frac{2}{3}}r$$

It is then possible to calculate the APF as follows:

$$APF = \frac{N_{atoms}V_{atom}}{V_{crystal}} = \frac{6 \cdot \frac{4}{3}\pi r^3}{\frac{3\sqrt{3}}{2}a^2c}$$

$$APF = \frac{6 \cdot \frac{4}{3}\pi r^3}{\frac{3\sqrt{3}}{2}(2r)^2\sqrt{\frac{2}{3}} \cdot 4r} = \frac{6 \cdot \frac{4}{3}\pi r^3}{\frac{3\sqrt{3}}{2}\sqrt{\frac{2}{3}} \cdot 16r^3} = \frac{\pi}{\sqrt{18}} = \frac{\pi}{3\sqrt{2}} \approx 0.74048$$

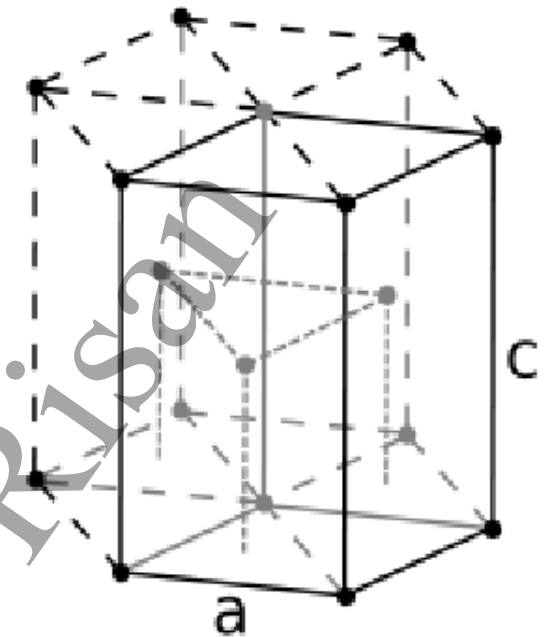
Note: Number of atoms in upper hexagonal plane $= \frac{1}{6} \times 6 = 1$

Number of atoms in lower hexagonal plane $= \frac{1}{6} \times 6 = 1$

We note that each central atom is shared by two unit cells which means upper and lower planes contain $\frac{1}{2}$ atom each.

\therefore Total number of central atoms in both, upper and lower planes $= \frac{1}{2} \times 2 = 1$ and there are three interstitial atoms.

\therefore **Total number of atoms in HCP crystal $= 1 + 1 + 1 + 3 = 6$**



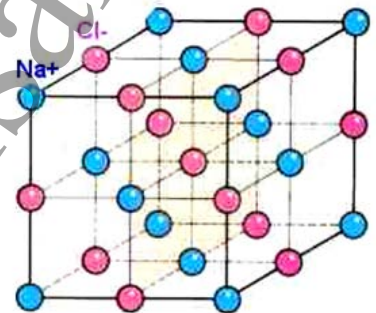
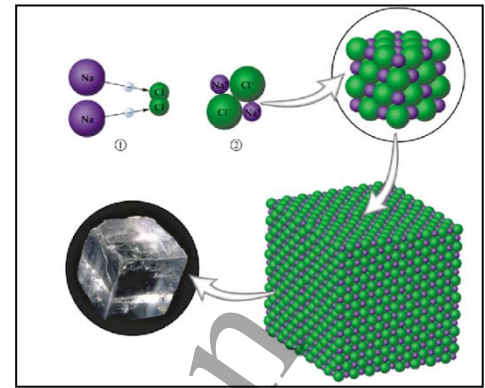
Sodium chloride NaCl:

Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.

Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice.

Each ion has six of the other kind of ions as its nearest neighbours:

This structure can be considered as a face-centered-cubic Bravais lattice with a basis consisting of a sodium ion at 0 and a chlorine ion at the center of the conventional cell.



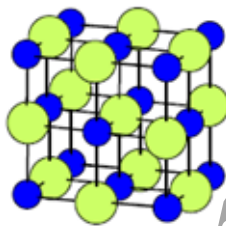
sodium chloride (NaCl)

lattice: cubic F

basis :

Na 000

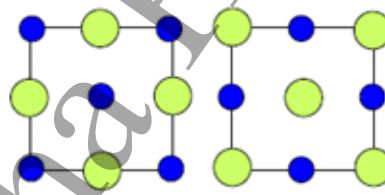
Cl $\frac{1}{2}\frac{1}{2}\frac{1}{2}$



Plan view

$z = 0$ layer

$z = \frac{1}{2}$ layer



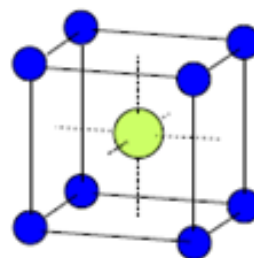
cesium chloride (CsCl)

lattice: cubic P

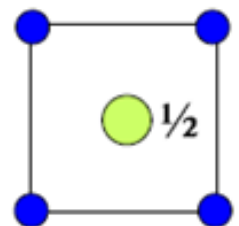
basis :

Cs 000

Cl $\frac{1}{2}\frac{1}{2}\frac{1}{2}$



Plan view

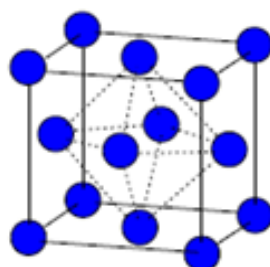


copper (Cu)

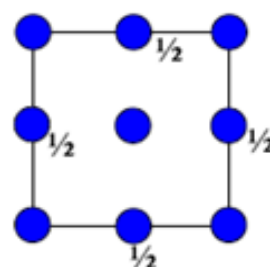
lattice: cubic F

basis :

Cu 000



Plan view



**H.W.: Q1, Q2, and Q3 in *Introduction to Solid State Physics* by Charles Kittel, 8th Edition
Kittel, ch. 1, Q. 1**

Tetrahedral angles. The angles between the tetrahedral bonds of diamond are the same as the angles between the body diagonals of a cube, as in Fig. 10. Use elementary vector analysis to find the value of the angle.

Solution:

Consider the body – centered cubic lattice.

We want the angle made by **acb** call it θ , i.e. we find the angle between any two vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$:

$$\vec{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

$$\vec{a}_2 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z})$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z})$$

Used \vec{a}_1 & \vec{a}_2 ; If θ is the angle between them, their scalar product gives:

$$\vec{a}_1 \cdot \vec{a}_2 = |\vec{a}_1| |\vec{a}_2| \cos\theta$$

$$\vec{a}_1 \cdot \vec{a}_2 = a_{1x}a_{2x} + a_{1y}a_{2y} + a_{1z}a_{2z}$$

$$|\vec{a}_1| = a_1 = \sqrt{a_{1x}^2 + a_{1y}^2 + a_{1z}^2} \quad ; \quad |\vec{a}_2| = a_2 = \sqrt{a_{2x}^2 + a_{2y}^2 + a_{2z}^2}$$

$$\cos\theta = \frac{\vec{a}_1 \cdot \vec{a}_2}{|\vec{a}_1| |\vec{a}_2|} = \frac{a_{1x}a_{2x} + a_{1y}a_{2y} + a_{1z}a_{2z}}{|\vec{a}_1| |\vec{a}_2|} = \frac{\left(\frac{-a^2}{4}\right)}{\left(\frac{a}{2}\sqrt{3}\right)\left(\frac{a}{2}\sqrt{3}\right)} = \frac{-1}{3}$$

$$\theta = \cos^{-1}\left(\frac{-1}{3}\right) = 109.4712206^\circ = 109^\circ \ 28' \ 16.3''$$

In calculator used key \cos^{-1} to obtained

degree min sec

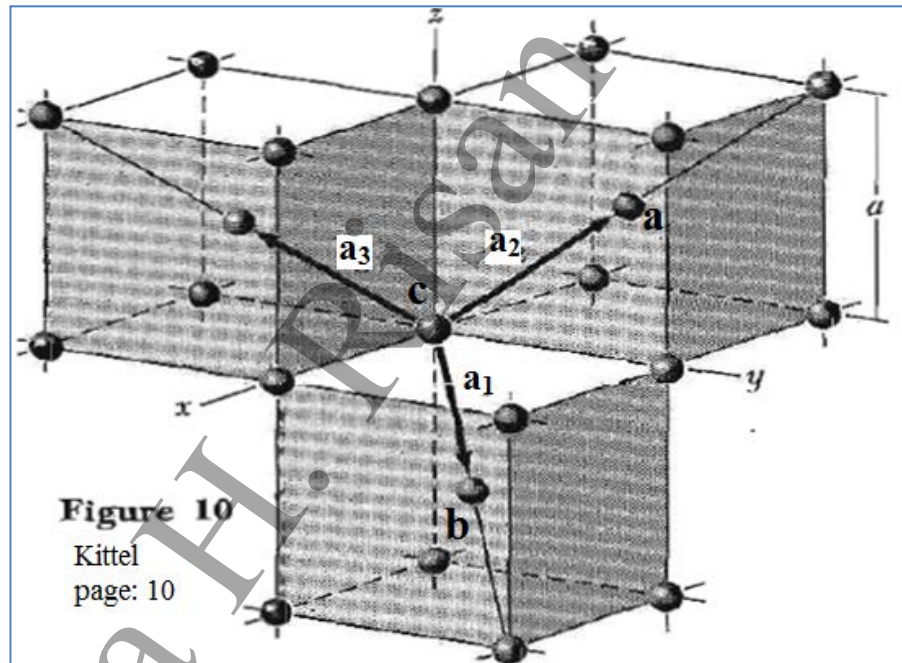


Figure 10
Kittel
page: 10

Kittel, ch. 1, Q. 2

Indices of planes. Consider the planes with indices (100) and (001); the lattice is fcc, and the indices refer to the conventional cubic cell. What are the indices of these planes when referred to the primitive axes of Fig. 11?

Solution:

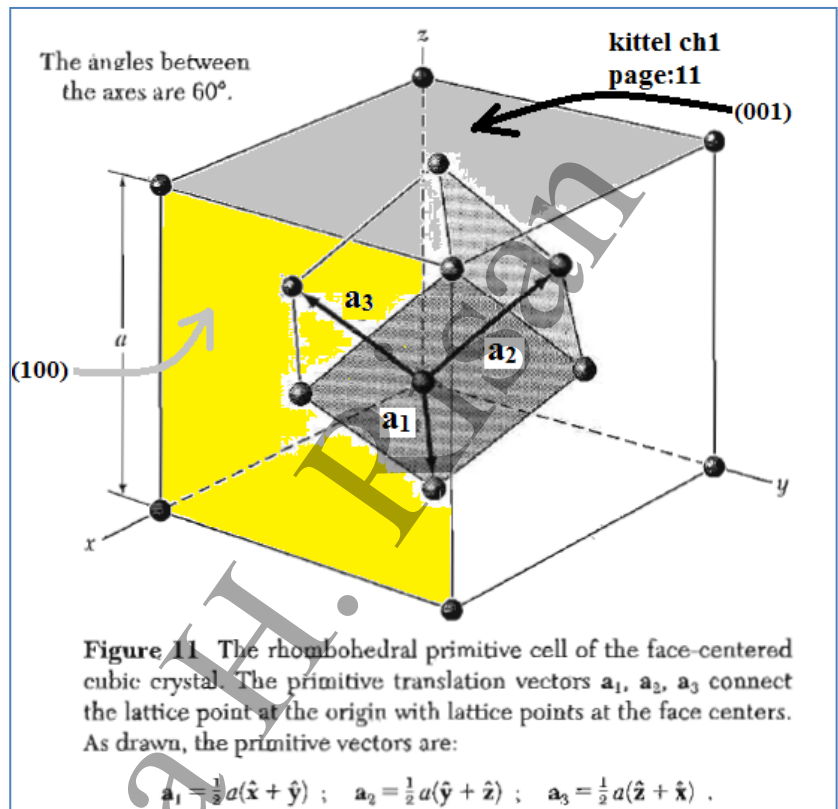
consider the the face-centered cubic structure

$$\vec{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y})$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{y} + \hat{z})$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{z})$$

The (100) plan in the simple cubic basis refers to the plane $x=a$.



The intercepts of this plane on the \vec{a}_1 , \vec{a}_2 , \vec{a}_3 axis is giving by:

$$\left. \begin{array}{l} 2\vec{a}_1 = (a, a, 0) \\ 2\vec{a}_3 = (a, 0, a) \\ \text{No intercept with } \vec{a}_2 \end{array} \right\} \text{The intercepts } 2 \ 0 \ 2$$

The Miller indices are then given by looking at the reciprocals of the intercepts:

$$\text{The reciprocals } \frac{1}{2}, 0, \frac{1}{2}$$

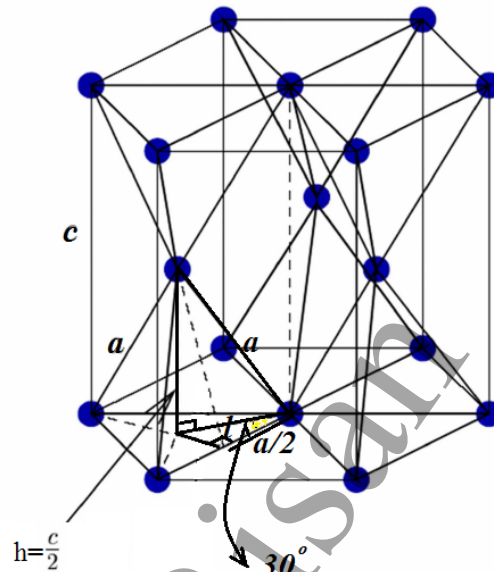
And finding the smallest integers with the same ratio

$$\text{The smallest integers } (1 \ 0 \ 1)$$

In other words, the plane (100) in the simple cubic basis is (101) in the fcc basis. Similary (001) in the simple cubic basis is (011) in the fcc basis.

Kittel, ch. 1, Q. 3

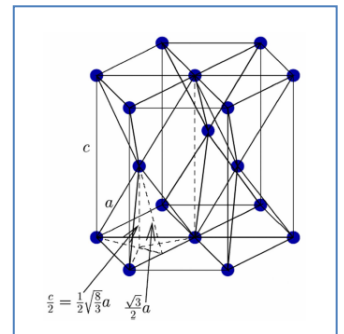
Hcp structure. Show that the c/a ratio for an ideal hexagonal close-packed structure is $\left(\frac{8}{3}\right)^{\frac{1}{2}} = 1.633$. If c/a is significantly larger than this value, the crystal structure may be thought of as composed of planes of closely packed atoms, the planes being loosely stacked.



Solution:

First recognize hexagonal close packing has lattice points arranged in tetrahedral:

This means c is just one-half of the height of one tetrahedron. Consider the following tetrahedron. Looking at the base of the tetrahedron, we have:



$$\cos 30 = \frac{a/2}{l} \quad \text{and} \quad \cos 30 = \frac{\sqrt{3}}{2} \rightarrow l = \frac{a}{\sqrt{3}}$$

Looking at the tip of the tetrahedron, we have:

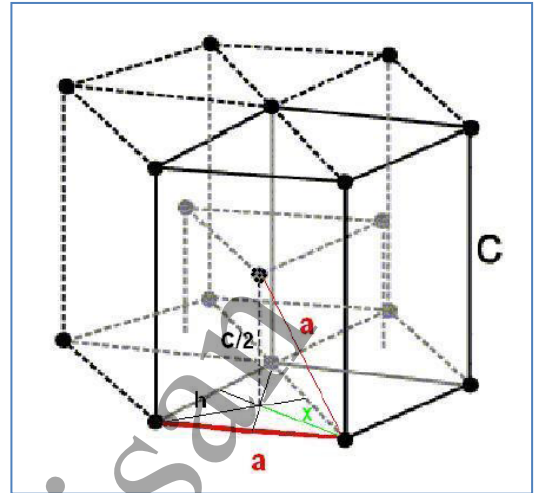
$$h^2 + l^2 = a^2 \rightarrow h^2 + \frac{a^2}{3} = a^2 \rightarrow h^2 = \frac{2}{3}a^2$$

$$\text{Since } c = 2h \rightarrow h = \frac{c}{2} \Rightarrow \frac{c^2}{4} = \frac{2}{3}a^2 \rightarrow c^2 = \frac{8}{3}a^2$$

$$c^2 = \frac{8}{3}a^2 \rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

Kittel, ch. 1, Q. 3

Hcp structure. Show that the c/a ratio for an ideal hexagonal close-packed structure is $\left(\frac{8}{3}\right)^{\frac{1}{2}} = 1.633$. If c/a is significantly larger than this value, the crystal structure may be thought of as composed of planes of closely packed atoms, the planes being loosely stacked.



Another solution:

h...height of the equilateral triangle

a...lattice constant

$$h = \sqrt{a^2 - (a/2)^2} = \sqrt{1 - \frac{1}{4}} * a = \sqrt{\frac{3}{4}} * a$$

Distance x from an atom to the middle of the triangle:

$$x = \frac{2}{3} * h = \frac{2}{3} * \sqrt{\frac{3}{4}} * a$$

$$x = \frac{1}{\sqrt{3}} * a$$

$$\frac{c}{2} = \sqrt{a^2 - x^2} = \sqrt{a^2 - \frac{1}{3}a^2} = \sqrt{\frac{2}{3}} * a$$

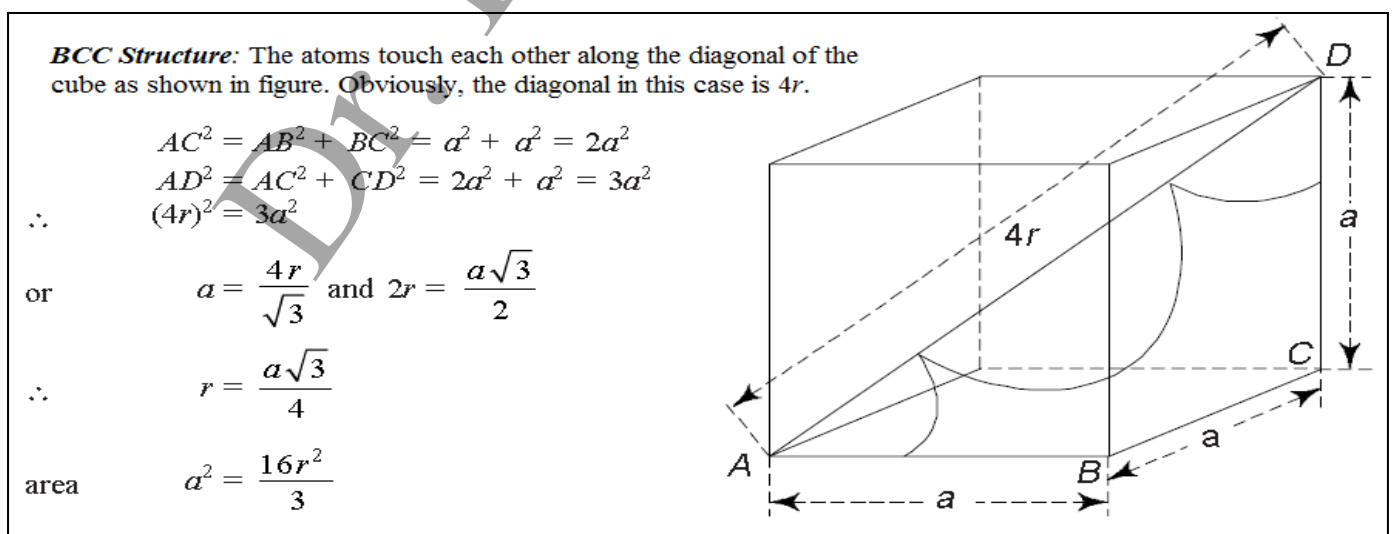
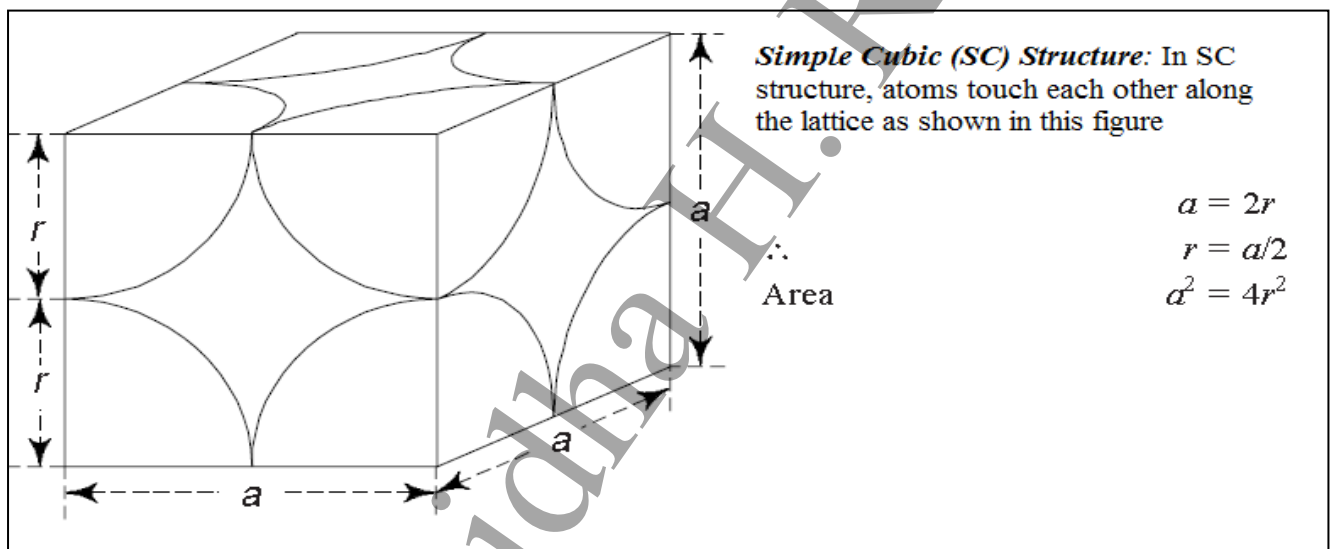
$$\frac{c}{a} = \sqrt{\frac{8}{3}}$$

Chapter One:

Questions & Problem

Q.1 - Determine the relationship between the lattice parameter a and the atomic radius r for monoatomic, SC, BCC and FCC structures

Solution: Atomic radius is defined as half the distance between the nearest neighbours in the crystal structure of a pure element. Atomic radius is denoted by r and expressed in terms of the cube edge element a . One can calculate the atomic radius by assuming that atoms are spheres in contact in a crystal. Calculation of atomic radius in various crystal structures is illustrated as below:



FCC Structure: Atoms within this structure touch along the diagonal of any face of the cube. The diagonal has a length of $4r$.

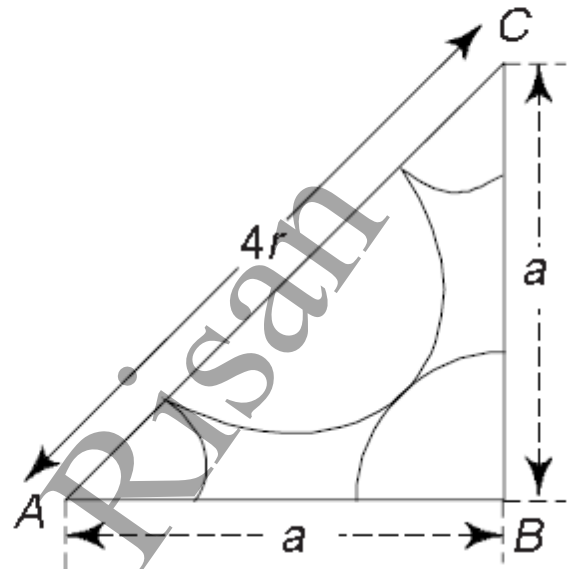
$$AC^2 = AB^2 + BC^2$$

or $(4r)^2 = a^2 + a^2$

$$\therefore r^2 = \frac{2a^2}{16}$$

or $r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$

and area $= a^2 = 8r^2$



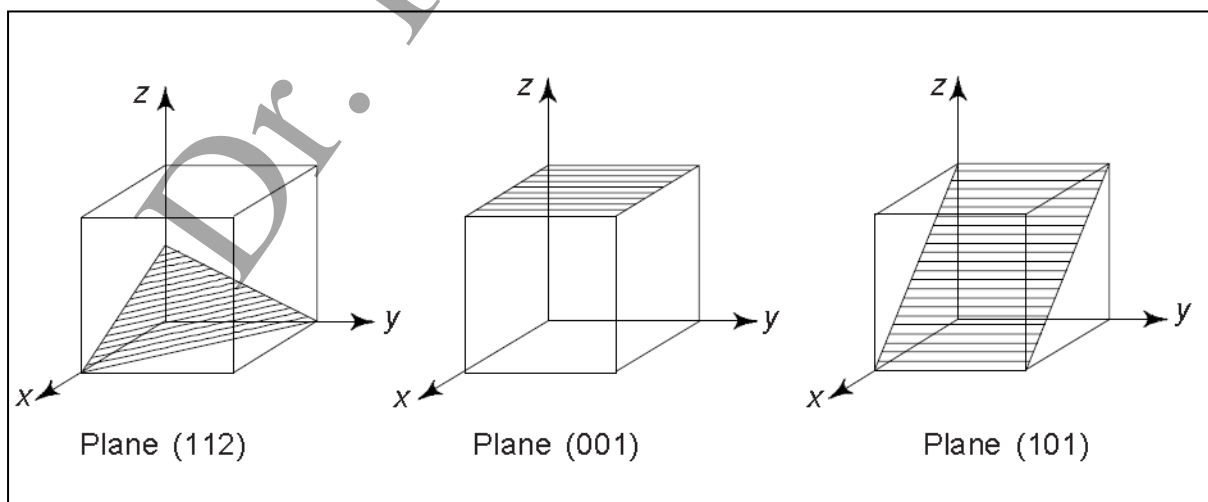
Q.2 - Draw the following planes in the case of a FCC structure: (112), (001) and (101).

Solution

(i) Plane and direction (112): In this, we have $h = 1$, $k = 1$ and $l = 2$. The reciprocals of h , k and l are $1/1$, $1/1$, $1/2$, i.e. 1 , 1 , 0.5 . Now, we can sketch the plane with intercepts 1 , 1 , 0.5 along x - x , y - y and z - z axes respectively.

(ii) Plane of (001): Here $h = 0$, $k = 0$, $l = 1$. The reciprocals are $1/0$, $1/0$, $1/1$ i.e., ∞ , ∞ , 1 . We obtain the sketch of the plane as shown in figure.

(iii) Plane of (101): Here $h = 1$, $k = 0$ and $l = 1$. The reciprocals are $1/1$, $1/0$ and $1/1$, i.e. 1 , ∞ and 1 . We obtain the sketch as shown in figure.



Q. 3 - Draw the planes and directions of FCC structures (321), (102), (201) and (111).

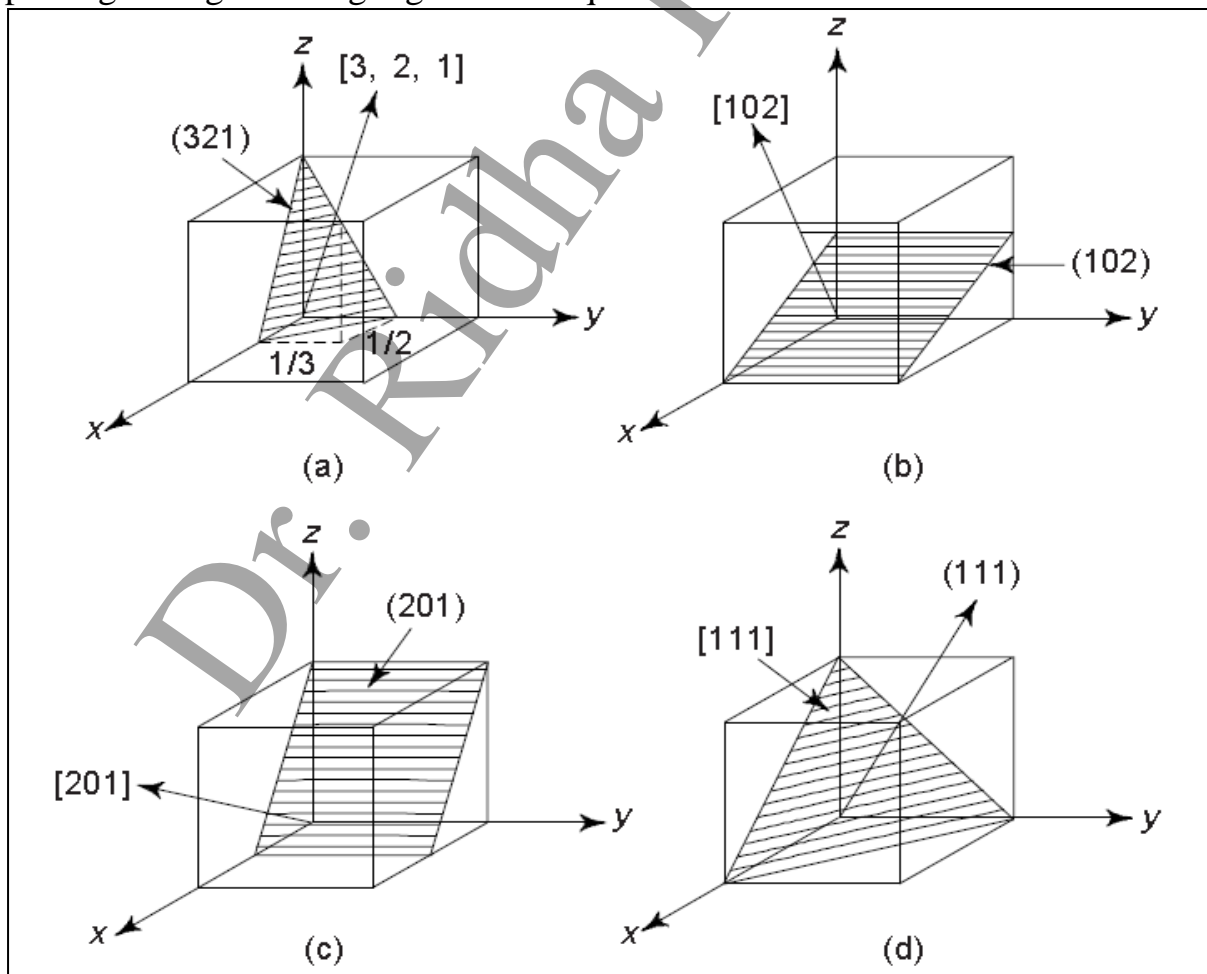
Solution: (For a cubic system lattice, the direction $[hkl]$ is perpendicular to the plane (hkl) .)

(i) *Plane and Direction of (321):* Here $h = 3$, $k = 2$, and $l = 1$. The reciprocals are $1/3$, $1/2$, $1/1$, i.e. 0.3, 0.5, 1. The sketch of the plane with intercepts 0.3, 0.5 and 1 is as shown in Fig. (a). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

(ii) *Plane and Direction of (102):* Here $h = 1$, $k = 0$, and $l = 2$. The reciprocals of these are: $1/1$, $1/0$ and $1/2$, i.e. 1, ∞ , 0.5. The sketch of the plane with these intercepts is as shown in Fig. (b). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

(iii) *Plane and Direction of (201):* Here $h = 2$, $k = 0$, and $l = 1$. The reciprocals of h and k , l are: $1/2$, $1/0$, $1/1$, i.e. 0.5, ∞ , 1. The sketch of the plane with these intercepts is shown in Fig. (c). A line drawn normal to this sketched plane and passing through the origin gives the required direction.

(iv) *Plane and Direction of (111):* Here $h = 1$, $k = 1$, and $l = 1$. The reciprocals of h , k and l are: $1/1$, $1/1$, $1/1$, i.e. 1, 1, 1. The sketch of the plane with these intercepts is shown in Fig. (d). A line drawn normal to this sketched plane and passing through the origin gives the required direction.



Q.4 - An atomic plane in a crystal lattice makes intercept of $3a$, $4b$ and $6c$ with the crystallographic axes where a , b and c are the dimensions of the unit cell. Show that the Miller indices of the atomic plane are (432) .

Solution: In terms of the lattice constants, the intercepts are 3, 4 and 6. Their reciprocals are $1/3$, $1/4$, $1/6$. On reducing to a common denominator, they become 4, 3 and 2. Obviously, the Miller indices of the plane are (432) .

Q.5 - Write short notes on

(i) Bravais Lattices (ii) Coordination number

The answer in the lecture.

Q.6 - The number of lattice points in a primitive cell are

(1) $3/2$

(2) $1/2$

(3) 2

(4) 1

Q.7 - The number of atoms present in the unit cell of HCP structure is

(1) 2

(2) 4

(3) 6

(4) 12

Q.8 - The nearest neighbour distance in BCC structure is

(1) $\frac{a}{\sqrt{2}}$

(2) $\frac{2a}{\sqrt{3}}$

(3) $\frac{a\sqrt{3}}{2}$

(4) $\frac{2a}{\sqrt{3}}$

Q.9 - The atomic diameter of an FCC crystal (lattice parameters a) is

(1) $\frac{2a}{\sqrt{2}}$

(2) $\frac{2a}{\sqrt{3}}$

(3) $\frac{a\sqrt{2}}{2}$

(4) $\frac{4a}{\sqrt{3}}$

Q.10 - The lattice constant of a BCC unit cell with atomic radius of 1.24 \AA is

(1) 1.432 \AA

(2) 2.864 \AA

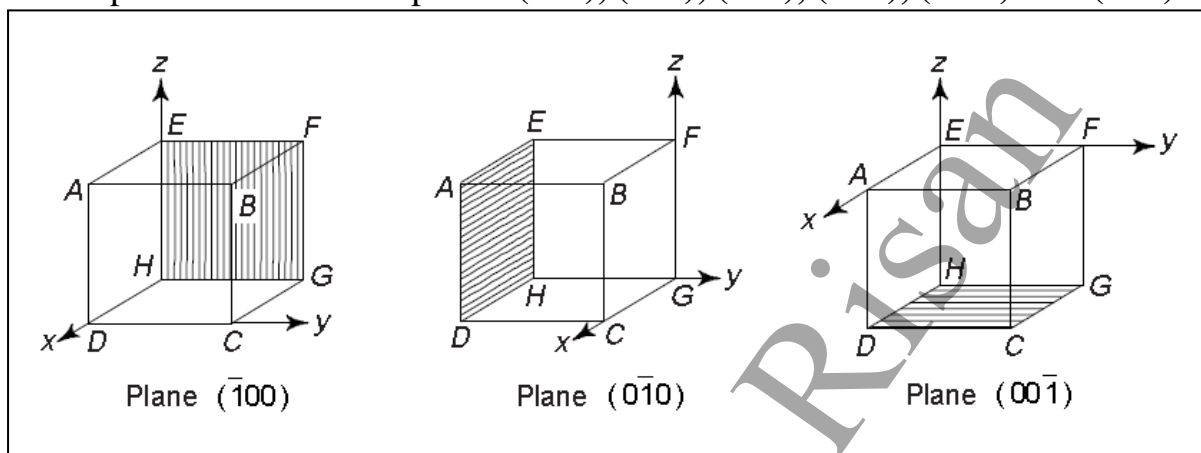
(3) 1.754 \AA

(4) 1.432 \AA

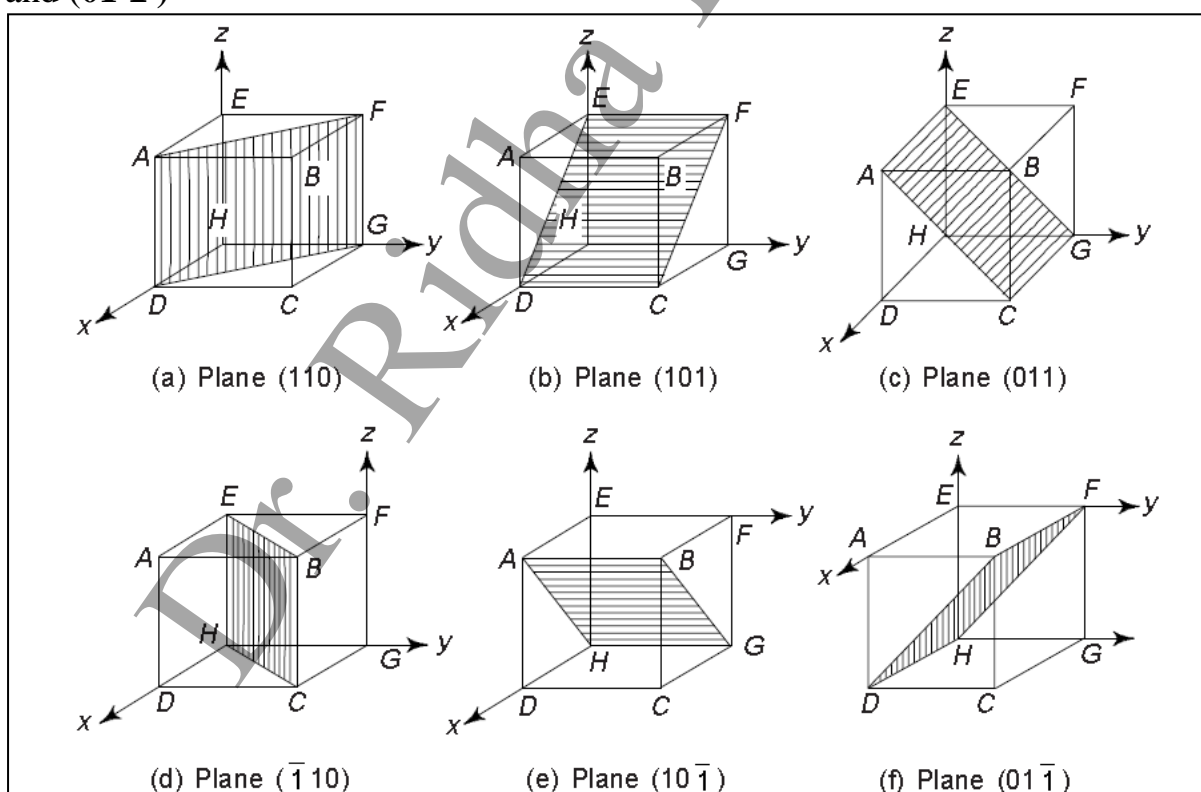
Q.11 – Determined the set of cube faces $\{100\}$?

Planes equivalent by symmetry may be denoted by curly brackets (braces) around indices; the set of cube faces is $\{100\}$.

All the six faces of the cubic unit cell have same geometry, i.e. they are of the same form. Thus Miller indices of all the six planes are represented by $\{100\}$. This represents a set of six planes (100) , (010) , (001) , $(\bar{1}00)$, $(0\bar{1}0)$ and $(00\bar{1})$.



Similarly $\{110\}$ represents a set of six planes (110) , (101) , (011) , $(\bar{1}10)$, $(10\bar{1})$, and $(01\bar{1})$



Q.12 -SHORT QUESTION ANSWERS

1. What is difference between crystalline and non crystalline solids?

Ans. Atoms in crystalline solids are positioned in an orderly and repeated pattern whereas in non crystalline or amorphous materials there is random and disordered atomic distribution.

2. How various crystal structures are specified?

Ans. The various crystal structures are specified in terms of parallelepiped unit cells, which are characterized by geometry and atom positions within.

3. What is a space lattice?

Ans. A space lattice is an infinite array of points, all with identical surroundings.

4. How a crystal structure is obtained?

Ans. A crystal structure is obtained by combining a space lattice with a basis. The basis must give the number of atoms per lattice point, their types, mutual orientations and distances of separation.

5. What is a single crystal?

Ans. Single crystals are materials in which the atomic order extends uninterrupted over the entirety of the specimen; under some circumstances, they may have flat faces and regular geometric shapes. We may note that vast majority of crystalline solids, however, are polycrystalline, being composed of many small crystals or grains having different crystallographic orientations.

6. What are the three relatively simple crystal structures in which most common metals exist?

Ans. FCC, BCC and HCP.

7. Mention two features of crystal structure.

Ans. (i) Coordination number (or number of nearest-neighbour atoms), and (ii) atomic packing (the fraction of solid sphere volume in the unit cell). Coordination number and atomic packing fraction are the same for both FCC and HCP crystal structures, each of which may be generated by the stacking of closed-packed planes of atoms.

8. How crystal directions and crystal planes are denoted?

Ans. These are denoted by Miller indices. A family of crystal directions or planes includes all possible combinations of the indices, both positive and negative. For a given crystal structure, planes having identical atomic packing yet different Miller indices belong to the same family.

Q.13 - Give examples of the following systems

i- Body Centered Cubic (BCC) Crystal Structure:

Examples:-

- Chromium ($a=0.289 \text{ nm}$)
- Iron ($a=0.287 \text{ nm}$)
- Sodium ($a=0.429 \text{ nm}$) , where a is the lattice constant

ii- Face Centered Cubic (FCC) Crystal Structure:

Examples:-

- Aluminum ($a = 0.405 \text{ nm}$)
- Gold ($a = 0.408 \text{ nm}$)

iii- Hexagonal Close-Packed Structure:

Examples:-

- Zinc ($a = 0.2665 \text{ nm}$, $c/a = 1.85$)
- Cobalt ($a = 0.2507 \text{ nm}$, $c/a = 1.62$)

Very few examples of simple cubic lattices are known (alpha - polonium is one of the few known simple cubic lattices).

Q.14 - Determine direction indices of the given vector. Origin coordinates are $(3/4, 0, 1/4)$. Emergence coordinates are $(1/4, 1/2, 1/2)$.

Solution:

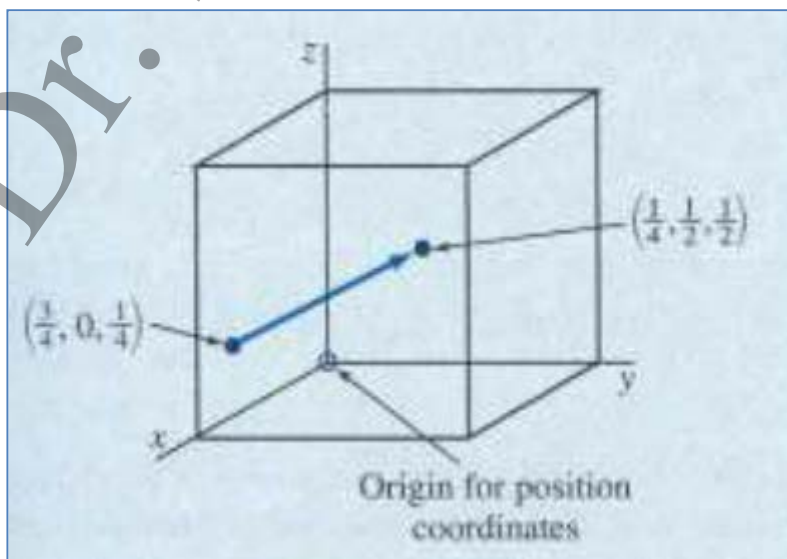
Subtracting origin coordinates from emergence coordinates,

$$(1/4, 1/2, 1/2) - (3/4, 0, 1/4) = (-1/2, 1/2, 1/4)$$

Multiply by 4 to convert all fractions to integers

$$4 \times (-1/2, 1/2, 1/4) = (-2, 2, 1)$$

Therefore, the direction indices are $[\bar{2} 2 1]$



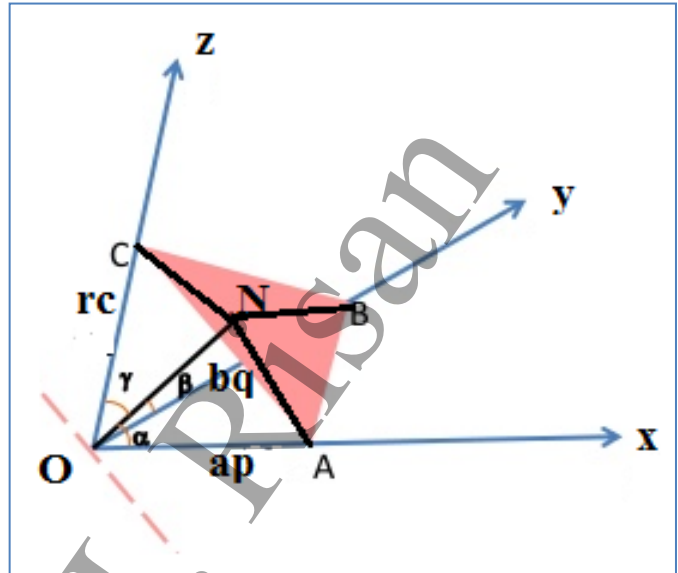
Q.15 - prove that $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ for Cubic System?

In $\triangle ONA$

$$\cos \alpha = \frac{ON}{OA}$$

ON is the length of the normal from the origin, O to the plane ABC and It represent d_{hkl}

$$\cos \alpha = \frac{d_{hkl}}{\frac{a}{h}} = \frac{h}{a} d_{hkl}$$



$$\cos^2 \alpha = \left(\frac{h}{a} \right)^2 d_{hkl}^2 \dots \dots \dots (1)$$

$$OA = ap = a * \frac{1}{h} = \frac{a}{h}$$

$$\triangle ONB : \cos \beta = \frac{ON}{OB} = \frac{d_{hkl}}{\frac{a}{k}} = \frac{k}{a} d_{hkl}$$

$$\cos^2 \beta = \left(\frac{k}{a} \right)^2 d_{hkl}^2 \dots \dots \dots (2)$$

$$\triangle ONC : \cos \gamma = \frac{ON}{OC} = \frac{d_{hkl}}{\frac{a}{l}} = \frac{l}{a} d_{hkl}$$

$$\text{But } \cos^2 \gamma = \left(\frac{l}{a} \right)^2 d_{hkl}^2 \dots \dots \dots (3)$$

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \dots (4)$$

Substituting eq.s 1&2&3 into eq. 4 :

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

In Cubic (a=b=c)

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

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

Crystal systems	Volume conventional cell	$\frac{1}{d^2}$
Cubic	a^3 or L^3	$\frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$a^2 c$	$\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	abc	$\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{\sqrt{3}}{2} a^2 c$	$\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) \frac{l^2}{c^2}$

Q.16 d_{hkl} Planes Spacing for cubic system:

Interplanar spacing between parallel closest planes with same miller indices is given by

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

Where d_{hkl} = interplanar spacing between parallel closest planes with Miller indices h , k , and l

a = lattice constant (edge of unit cube)

h, k, l = Miller indices of cubic planes being considered

Q.17 - Copper has an FCC crystal structure and a unit cell with a lattice constant of 0.361 nm. What is its interplanar spacing d_{220} ?

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

$$d_{hkl} = \frac{0.361}{\sqrt{2^2 + 2^2 + 0^2}} = 0.128 \text{ nm}$$

Q.17- Find the interplanar distance of (200) plane and (111) plane of Nickel crystal. The radius of Nickel atom is 1.245 Å.

Solution:

Nickel has FCC structure. Given radius of Nickel = $r = 1.245 \text{ Å}$

Lattice constant = $a =$

$$\text{Lattice constant} = a = \frac{4r}{\sqrt{2}} = \frac{4 * r}{\sqrt{2}} = \frac{4 * 1.245}{\sqrt{2}} = 3.52 \text{ Å}$$

$$d_{200} = \frac{3.52}{\sqrt{(2^2 + 0^2 + 0^2)}} = 1.76 \text{ Å}$$

$$d_{111} = \frac{3.52}{\sqrt{(1^2 + 1^2 + 1^2)}} = 2.03 \text{ Å}$$

Q.18- The lattice constant of a unit cell of KCl crystal is 3.03 Å. Find the number of atoms/ mm² of planes (100), (110) and (111). KCl has simple cubic structure.

Q.19 - Planar Atomic Density:

Is defined as the number of atoms per unit area that are centered on a given crystallographic plane. The *planar atomic density* is calculated by using the relationship

$$\text{Planar atomic density} = \rho_p = \frac{\text{No. of atoms centered on the plane}}{\text{Area of the plane}}$$

Q.20- Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in BCC chromium, which has a lattice constant of 0.28846 nm : (a) (100), (b) (110).

Solution: To calculate the density, the planar area and the number of atoms contained in that area must first be determined.

(a) The area intersected by the (1 0 0) plane inside the cubic unit cell is a^2 while the number of atoms contained is:

$$(4 \text{ corners}) \times (\frac{1}{4} \text{ atom per corner}) = 1 \text{ atom.}$$

a= lattice constant = 0.28846 nm

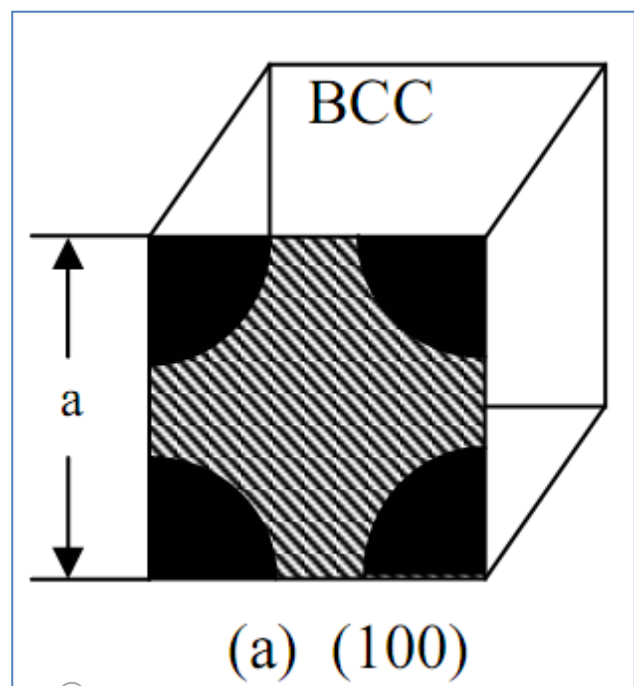
The density is:

planar atomic density = ρ_p

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}}$$

$$\rho_p = \frac{1 \text{ atom}}{(0.28846 \times 10^{-9} \text{ m})^2} = (1.202 \times 10^{19} \text{ atoms/m}^2) \left(\frac{\text{m}}{1000 \text{ mm}} \right)^2$$

$$\rho_p = 1.202 \times 10^{13} \text{ atoms/mm}^2$$



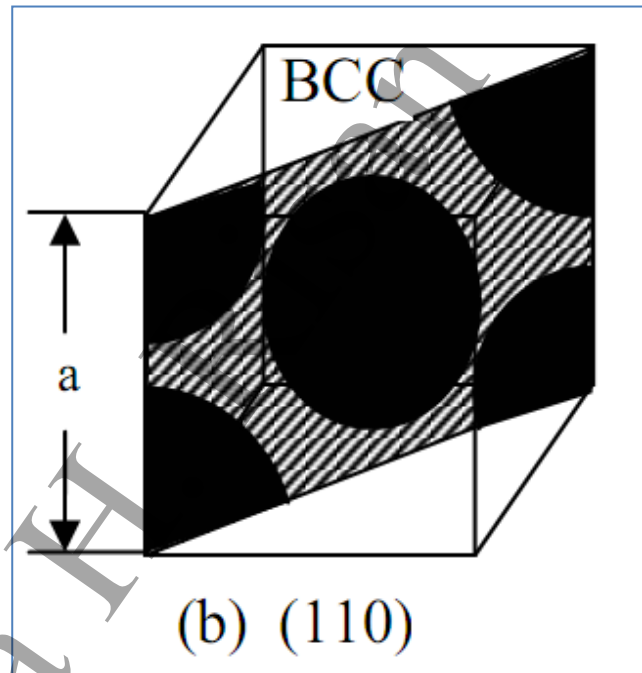
(b) For the more densely packed (1 1 0) plane, there are:
 1 atom at center + (4 corners) \times ($\frac{1}{4}$ atom per corner) = 2 atoms
 And the area is given as

$$(\sqrt{2}a)(a) = \sqrt{2}a^2$$

$$\frac{2 \text{ atom}}{\sqrt{2} * (0.28846 * 10^{-9}m)^2}$$

$$\rho_p = \frac{2 \text{ atom}}{\sqrt{2} * (0.28846 * 10^{-9}m)^2} = (2.35 * 10^{19} \text{ atoms}/m^2)(10^{-6} m^2/mm^2)$$

$$\rho_p = 2.35 * 10^{13} \text{ atoms}/mm^2$$



Q.21- Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in FCC gold, which has a lattice constant of 0.40788 nm: (a) (100), (b) (110).

(a) The area intersected by the (1 0 0) plane inside FCC unit cell is a^2 while the number of atoms contained is:

1 atom at center + (4 corners) \times ($\frac{1}{4}$ atom per corner) = 2 atom.

a= lattice constant = 0.40788 nm

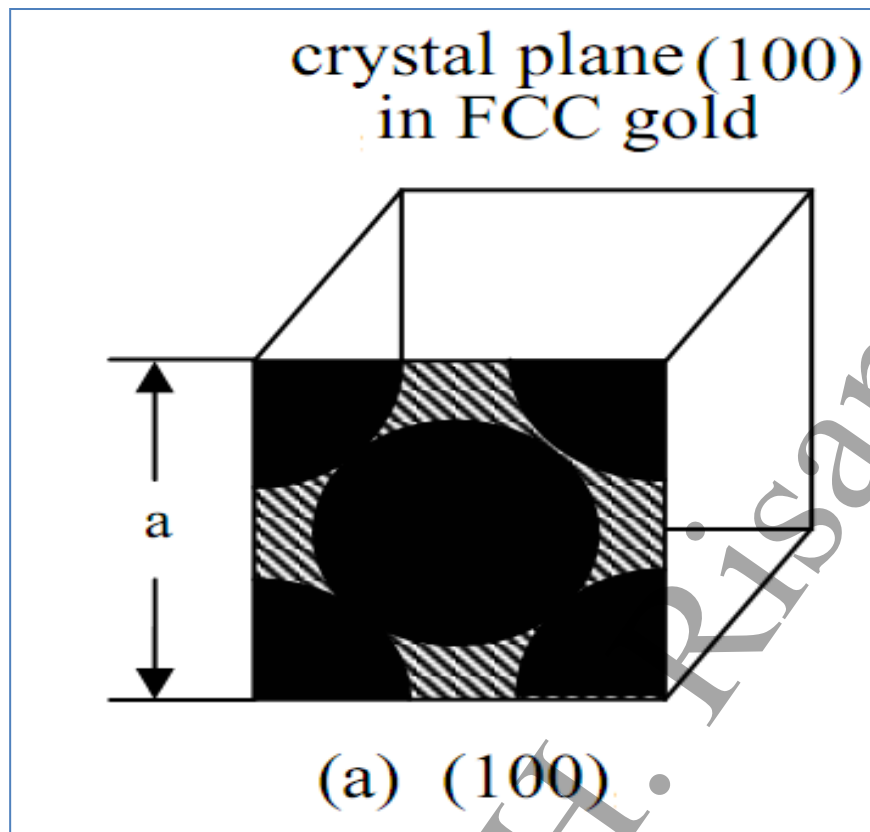
The density is therefore:

planar atomic density = ρ_p

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}}$$

$$\rho_p = \frac{2 \text{ atom}}{(0.40788 * 10^{-9}m)^2} = (1.202 * 10^{19} \text{ atoms}/m^2) \left(\frac{m}{1000 mm} \right)^2$$

$$\rho_p = 1.202 * 10^{13} \text{ atoms}/mm^2$$



(b) For the more densely packed (110) plane, there are:
(2 face atoms) \times ($\frac{1}{2}$ atom) + (4 corners) \times ($\frac{1}{4}$ atom per corner) = 2 atoms

And the area is given as

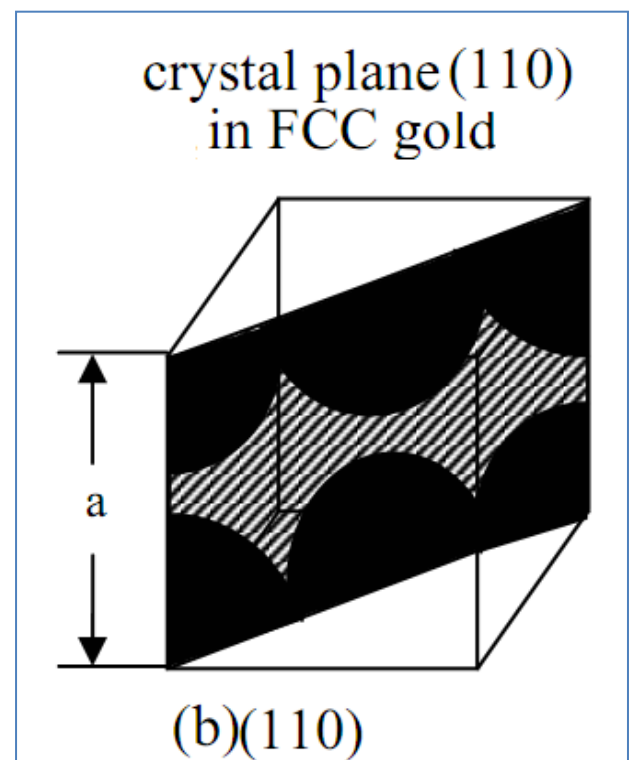
$$(\sqrt{2}a)(a) = \sqrt{2}a^2$$

The density is thus:

$$\rho_p = \frac{2 \text{ atom}}{\sqrt{2} * (0.40788 * 10^{-9} \text{ m})^2}$$

$$= (8.501 * 10^{18} \text{ atoms} / \text{m}^2)(10^{-6} \text{ m}^2 / \text{mm}^2)$$

$$\rho_p = 8.501 * 10^{12} \text{ atoms/mm}^2$$



Q.22- Calculate the planar atomic densities of planes (100) and (110) in FCC unit cell and apply your result for lead (FCC form).

Solution:

(i) *Plane (100):*

Number of atoms contained in (100) plane is $4 \times \frac{1}{4} + 1 = 2$

Let a be the edge of the unit cell and r the radius of the atom, then

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

Planar density of plane (100)

$$\text{Planar density of plane (100)} = \frac{2}{4 \times 2r^2} = \frac{0.25}{r^2}$$

The radius of lead atom is 1.75 \AA .
The planar density of (100) plane of lead

$$\begin{aligned} \text{Planar density of plane (100)} &= \frac{0.25}{(1.75 \times 10^{-7})^2} \\ &= 82 \\ &\times 10^{12} \text{ atoms/mm}^2 \end{aligned}$$

$$\text{Planar density of plane (100)} = 8.2 \times 10^{18} \frac{\text{atoms}}{\text{m}^2}$$

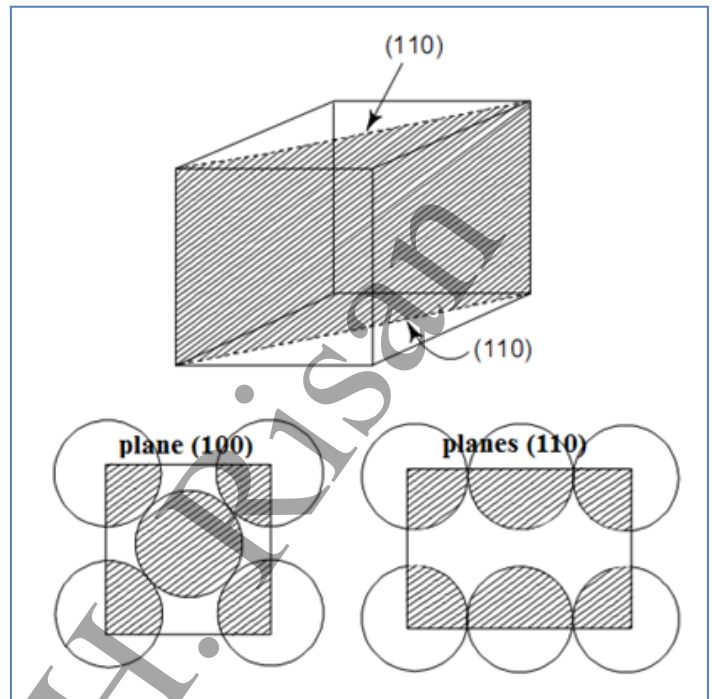
(ii) *Plane (110):* From Fig. (c), we have the number of atoms contained in plane (110):

Number of atoms contained in (110) plane is $4 \times \frac{1}{4} + 2 \times \frac{1}{2} = 2$

The top edge of the plane (110) is $4r$, whereas the vertical edge = $a = 2\sqrt{2}r$. Thus the planar density of (110)

$$\text{Planar density of plane (100)} = \frac{2}{8\sqrt{2}r^2} = \frac{0.177}{r^2}$$

$$\text{In case of (110) plane in lead, we have planar density} = \frac{0.177}{(1.75 \times 10^{-7})^2}$$



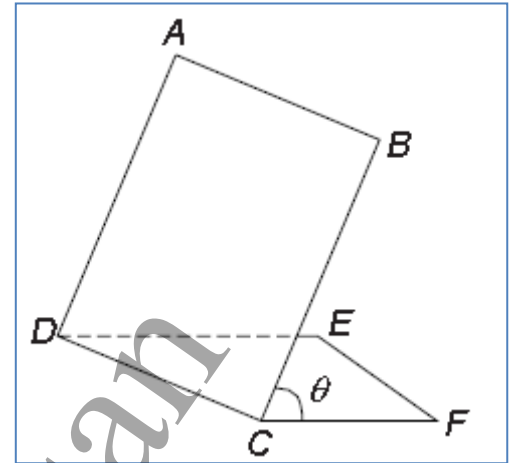
Angle Between Two Planes or Direction:

Let us consider a cube having two planes $ABCD$ and $EFCD$ inclined at an angle with each other. Let h_1, k_1, l_1 are Miller indices of plane $ABCD$ and h_2, k_2, l_2 are Miller indices of plane $EFCD$. The angle between these two planes is given by the relation

$$\cos \theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{(h_1^2 + k_1^2 + l_1^2)^{\frac{1}{2}} (h_2^2 + k_2^2 + l_2^2)^{\frac{1}{2}}}$$

Similarly, the angle ϕ between the two directions having Miller indices (h_1, k_1, l_1) and (h_2, k_2, l_2) respectively is given by the relation

$$\cos \phi = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{(h_1^2 + k_1^2 + l_1^2)^{\frac{1}{2}} (h_2^2 + k_2^2 + l_2^2)^{\frac{1}{2}}}$$



Example : In a cubic unit cell, find the angle between normals to the planes (111) and (121).

Solution:

Since the given crystal is cubic, the normals to the planes (111) and (121) are the directions $[111]$ and $[121]$ respectively. If θ be the angle between the normals, then

$$\begin{aligned} \cos \theta &= \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{(h_1^2 + k_1^2 + l_1^2)^{\frac{1}{2}} (h_2^2 + k_2^2 + l_2^2)^{\frac{1}{2}}} \\ \cos \theta &= \frac{1 \times 1 + 1 \times 2 + 1 \times 1}{(1^2 + 1^2 + 1^2)^{\frac{1}{2}} (1^2 + 2^2 + 1^2)^{\frac{1}{2}}} = 0.9428 \\ \theta &= 19.47^\circ \quad \text{or} \quad 19^\circ 28' \end{aligned}$$

Chapter Two: (Crystal diffraction)

1 - Incident Rays & Braggs Law

2-(X-Ray - Neutrons - Electron)

3-Diffraction Method:

a- Laue Method. b- Powder Method c- Rotating method

4- Reciprocal Lattice

5- Lattice Structure Factor

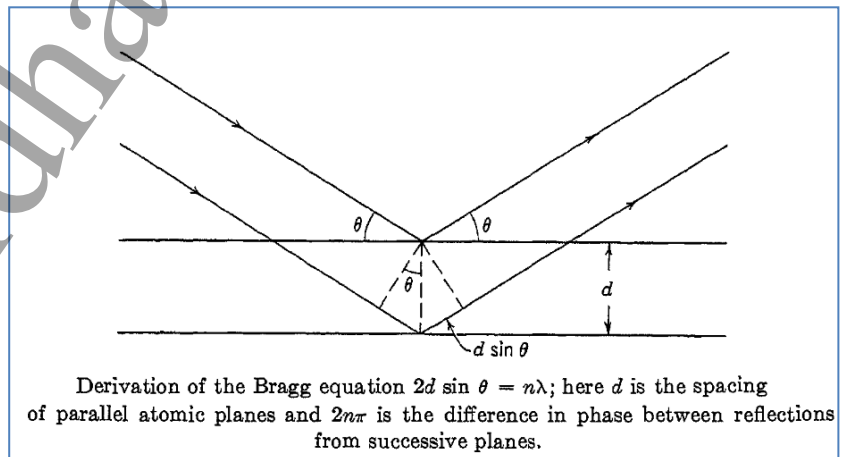
Note: Correct typing error in chapter two "Introduction to Solid State Physics" by Charles Kittel, 8th Edition:

- In page 30 - Figure 6 - The phase factor under the outgoing beam should be $e^{ik \cdot r}$ ---- the prime is missing on k.
- In page 36 – The text between eq (30) and eq (31) - "We have, using (28)," should be "We have, using (29),".
- In page 42 - Equation (50) - the last "=" sign should be deleted; $\sin(G_r)/G_r$ is part of the integrand.

(المقدار $\frac{\sin G_r}{G_r}$ يقع ضمن التكامل)

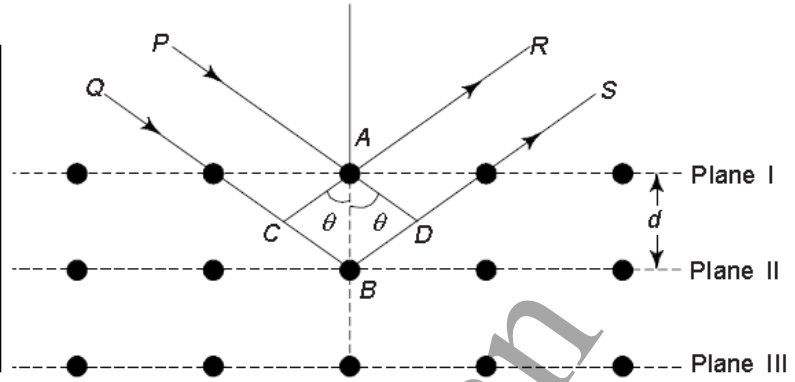
1 - Incident Rays & Braggs Law

Consider parallel lattice planes spaced d apart. The radiation is incident in the plane of the paper. The path difference for rays reflected from adjacent planes is $2d \sin \theta$, where θ is the angle between the incident ray and the planes of reflection and called as *glancing angle*.



Constructive interference of the radiation from successive planes occurs when the path difference is an integral number n of wavelengths (λ).

$CB + BD = n\lambda$
 $CB = BD = d \sin \theta$
 θ is the angle between the incident ray and the planes of reflection
 Therefore, we have
 $2d \sin \theta = n\lambda$
 $n = 1, 2, 3, \dots$
 where d is the interplanar spacing of planes



Reflection of X-rays from lattice planes in a crystal and derivation of Bragg's law

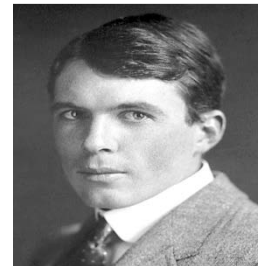
Reflection rules of X-ray diffraction for the common metal structures		
Crystal structure	Diffraction does not occur for	Diffraction occurs for
BCC	$h + k + l = \text{odd number}$	$h + k + l = \text{even number}$
FCC	h, k, l can have both even and odd integer values	h, k, l can be all even or all odd numbers
HCP	$h + 2k = 3n, l \text{ odd } (n \rightarrow \text{integer})$	All other cases

$2d_{hkl} \sin \theta = n\lambda$ ----- Bragg's law

(by William Lawrence Bragg

(1912).

We must note that the Bragg's reflection can occur only for $\lambda \leq 2d$. Although the reflection from each plane is specular, for only certain values of θ will the reflections from all periodic parallel planes add up in phase to give a strong reflected beam. If each plane were perfectly reflecting, only the first plane of a parallel set would see the radiation, and any wavelength would be reflected. But each plane reflects 10^{-3} to 10^{-5} of the incident radiation, so that 10^3 to 10^5 planes may contribute to the formation of the Bragg-reflected beam in a perfect crystal.



The diffraction pattern obtained by them consists of a central spot and a series of spots arranged in a definite pattern around the central spot. This symmetrical pattern of spots is known as Laue pattern. The explanation for this was given by Bragg. According to Bragg, the spots are produced due to the reflection of some of the incident X-rays from the various sets of parallel crystal planes (called as Bragg's planes), which contain a large number of atoms.

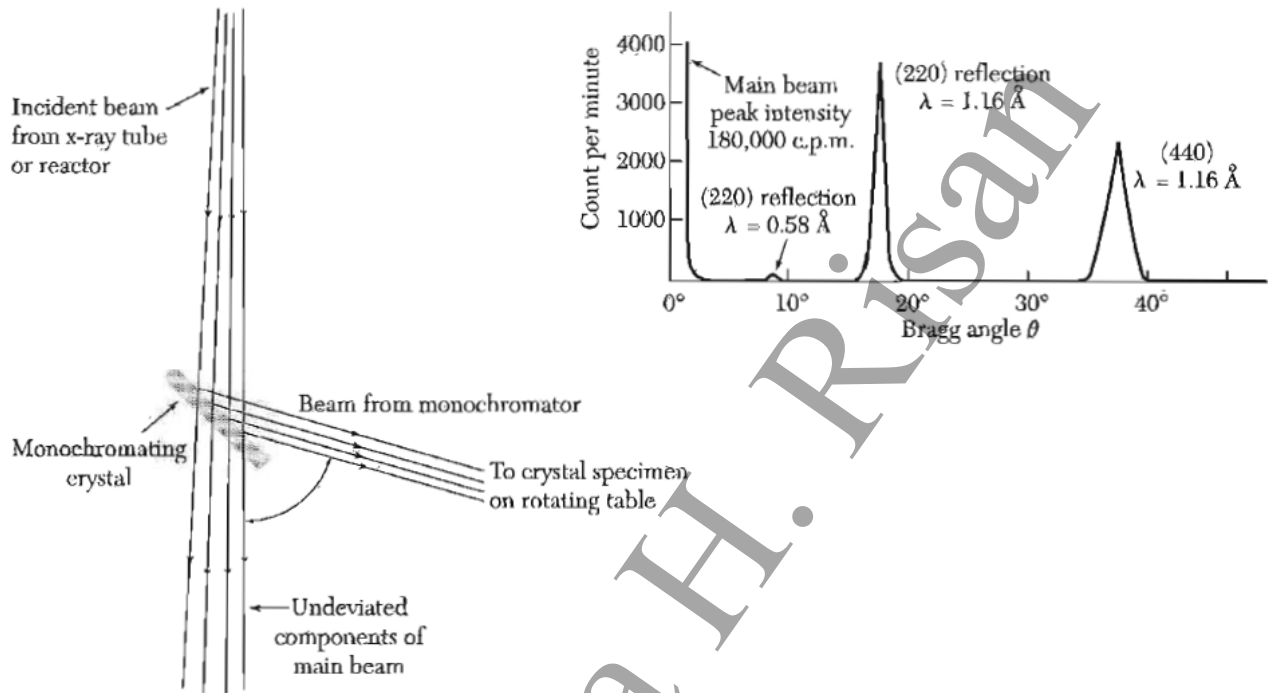


Figure 3 Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of x-ray or neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 Å beam of neutrons from a calcium fluoride crystal monochromator. (After G. Bacon.)

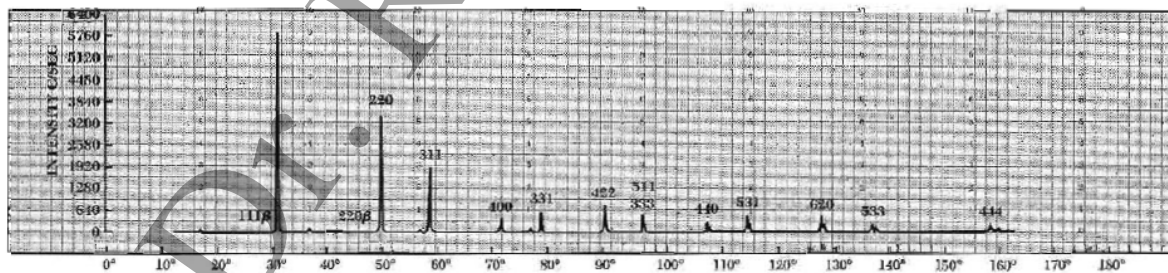


Figure 4 X-ray diffractometer recording of powdered silicon, showing a counter recording of the diffracted beams. (Courtesy of W. Parrish.)

Example: Determine the interplanar spacing when a beam of X-ray of wavelength 1.54 \AA is directed towards the crystal at angle 20.3° to the atomic plane.

Solution:

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

$$\lambda = 1.54 \text{ \AA}$$

$$2d \sin 20.3^\circ = 1 \times 1.54$$

$$\theta = 20.3^\circ$$

$$d = \frac{1.54}{2 \sin 20.3^\circ} = \frac{1.54}{2 \times 0.3469} = 2.22 \text{ \AA}$$

Example: X-rays with wavelength of 0.58 \AA are used for calculating d_{200} in nickel. The reflection angle is 9.5° . What is the size of unit cell?

Solution:

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

$$\lambda = 0.58 \text{ \AA} \quad \& \quad \theta = 9.5^\circ$$

$$d_{200} = \frac{a}{\sqrt{2^2 + 0^2 + 0^2}} = \frac{a}{2} = 0.5a$$

Now, from Bragg's law $2d_{hkl} \sin \theta = n\lambda$ we have

$$2 \times d_{200} \times \sin 9.5^\circ = 1 \times 0.58$$

$$2 \times 0.5a \times 0.165 = 1 \times 0.58$$

$$a = \frac{0.58}{1.165} = 0.52 \text{ \AA}$$

Example Calculate the Bragg angle if (111) planes of a cube ($a = 3.57 \text{ \AA}$) crystal are exposed to X-rays (wavelength = 1.54 \AA)

Solution We have, Miller indices of the (111) planes, $h = 1$, $k = 1$ and $l = 1$; $a = 3.57^\circ$ and $\lambda = 1.54 \text{ \AA}$. Let θ be the Bragg's angle for the first order reflection.

We have

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

$$d_{111} = \frac{3.57}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = 2.06 \text{ \AA}$$

Now, from Bragg's law, we have

$$2d_{111} \sin \theta = n\lambda$$

$$\therefore 2 \times 2.06 \times \sin \theta = 1 \times 0.54$$

$$\sin \theta = \frac{1 \times 0.54}{2 \times 2.06} = 0.131$$

$$\theta = 7^\circ 32'$$

Example For a certain BCC crystal, the (110) plane has a separation of 1.181 Å. These planes are indicated with X-ray of wavelength 1.540 Å. Show that the maximum order of the Bragg's reflection that can be observed is $n = 1$.

Solution

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

$$d = 1.181 \text{ Å}$$

$$\lambda = 1.540 \text{ Å}$$

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

$$= \frac{2 \times 1.181 \sin 90^\circ}{1.540} = 1.53$$

Since the value of 'n' can be integer only, and hence the highest possible value of n in this case is 1.

Example The glancing angle of 10° is observed in first order Bragg's reflection. Show that the angle for 3rd order reflection is 31.39° .

Solution For $n = 1, \theta_1 = 10^\circ$
 For $n = 3, \theta_3 = ?$

From Bragg's law, we have

$$2d \sin \theta_1 = 1\lambda \quad (\text{First order})$$

$$2d \sin \theta_3 = 3\lambda \quad (\text{Third order})$$

$$\therefore \frac{\sin \theta_1}{\sin \theta_3} = \frac{1}{3}$$

or $\sin \theta_3 = 3 \sin \theta_1 = 3 \times \sin 10^\circ = 3 \times 0.1736 = 0.5209$

$$\therefore \theta_3 = 31.39^\circ.$$

Example A diffraction pattern of a cubic crystal of lattice parameter $a = 3.16 \text{ Å}$ is obtained with a monochromatic X-ray beam of wavelength 1.54 Å. The first line on this pattern was observed to have $\theta = 20.3^\circ$. Obtain the interplanar spacing and Miller indices of the reflecting plane.

Solution

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

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

$$= \frac{1 \times 1.54}{2 \times 0.3469}$$

$$= 2.22 \text{ Å}$$

$$\theta = 20.3^\circ$$

$$\lambda = 1.54 \text{ Å}$$

$$n = 1$$

$$a = 3.16 \text{ Å}$$

For cubic crystal, we have

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

or $h^2 + k^2 + l^2 = \frac{a^2}{d^2} = \frac{(3.16)^2}{(2.22)^2} = 2$

Since $(h^2 + k^2 + l^2) = 2$ and hence the Miller indices are (110) or (101) or (011).

Example Determine interatomic spacing when glancing angle of 30° is observed during first order reflection in a crystal having Miller indices as (111). The wavelength of X-rays is 2 \AA .

Solution

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

$$\lambda = 2 \text{ \AA}$$

$$\theta = 30^\circ$$

$$n = 1$$

$$h = k = l = 1$$

\therefore

$$d = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{a}{\sqrt{3}}$$

Now,

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

$$2 \frac{a}{\sqrt{3}} \sin 30^\circ = 1 \times 2 \text{ \AA}$$

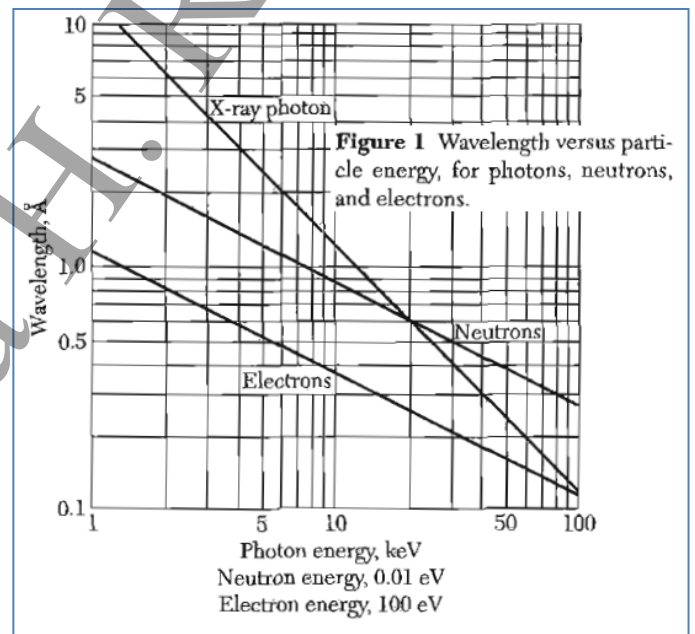
$$a = 2\sqrt{3} \text{ \AA}$$

2- The Incident Beam :(X-Ray - Neutrons - Electron)

We study crystal structure through the diffraction of photons, neutrons, and electrons. The diffraction depends on the crystal structure and on the wavelength.

At optical wavelengths such as 5000 \AA , the superposition of the waves scattered elastically by the individual atoms of a crystal results in ordinary optical refraction.

When the wavelength of the radiation is comparable with or smaller than the lattice constant, we may find diffracted beams in directions quite different from the incident direction



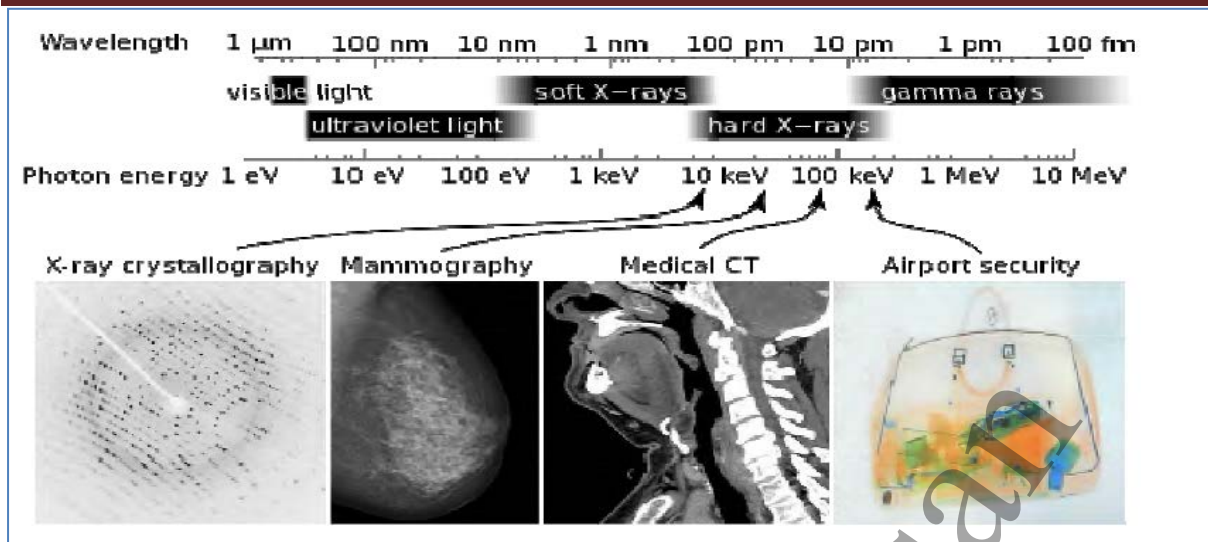
X-rays:

The energy of an x-ray photon is related to its wavelength λ by

$$\epsilon = hf = \frac{hc}{\lambda}$$

$$\lambda (\text{\AA}) = \frac{12.4}{\epsilon(\text{KeV})}$$

Where wavelength λ in angstrom \AA and E is of the order of few keV. X-rays are scattered mostly by the electronic shells of atoms in a solid, since the nuclei are too heavy to respond. Crystal studies require photon energies in the 10 to 50 KeV as shown in above figure.



Neutron:

The energy of a neutron is related to its de Broglie wavelength by

$$\epsilon = \frac{h^2}{2M_n\lambda^2}$$

where $M_n = 1.675 \times 10^{-24}$ g is the mass of the neutron. We recall that $\epsilon = \frac{p^2}{2M_n}$

and the λ is related to the momentum p by $\lambda = \frac{h}{p}$

$$\lambda (\text{\AA}) \cong \frac{0.28}{[\epsilon(\text{eV})]^{\frac{1}{2}}}$$

Where ϵ is the neutron energy in eV. We have $\lambda = 1 \text{ \AA}$ for $\epsilon \cong 0.08 \text{ eV}$.

Because of their magnetic moment, neutrons can interact with the magnetic electrons of a solid, and neutron methods are valuable in structural studies of magnetic crystals. In nonmagnetic materials the neutron interacts only with the nuclei of the constituent atoms.

Electrons:

The energy of an electron is related to its de Broglie wavelength

$$\text{by } \epsilon = \frac{h^2}{2m\lambda^2}$$

where $m = 0.911 \times 10^{-27}$ g is the mass of the electron.

$$\lambda (\text{\AA}) \cong \frac{12}{[\epsilon(\text{eV})]^{\frac{1}{2}}}$$

Electrons interact strongly with matter because they are charged; they penetrate a relatively short distance into a crystal.

3-Diffraction Method:

Max von Laue used a crystal of copper sulfate as the diffraction grating (Nobel Prize 1914). Crystalline solids consist of regular arrays of atoms, ion, or molecules with interatomic spacing on the order of 1\AA .



The wavelength of the incident light has to be on the same order as the spacing of the atoms. Reflection of X-rays only occurs when the conditions for constructive interference are fulfilled.

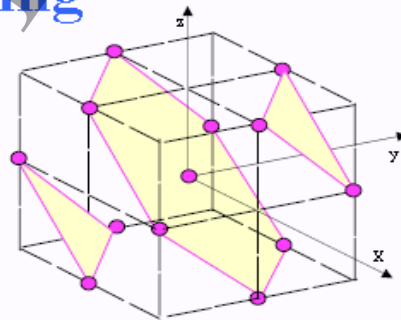
The Bragg law requires that θ and λ be matched: monochromatic x-rays of wavelength λ striking a three dimensional crystal at an arbitrary angle of incidence will not in general be reflected.

There are essentially three methods: The **rotating-crystal method**, the **Laue method**, and the **Powder Method**. Regardless of the method used, the quantities measured are essentially the same.

- i) The scattering angle 2θ between the diffracted and incident beams. By substituting $\sin \theta$ into Bragg's law, one determines the interplanar spacing as well as the orientation of the plane responsible for the diffraction.
- ii) The intensity I of the diffracted beam. This quantity determines the cell-structure factor, F_{hkl} , and hence gives information concerning the arrangement of atoms in the unit cell.

Example of scattering

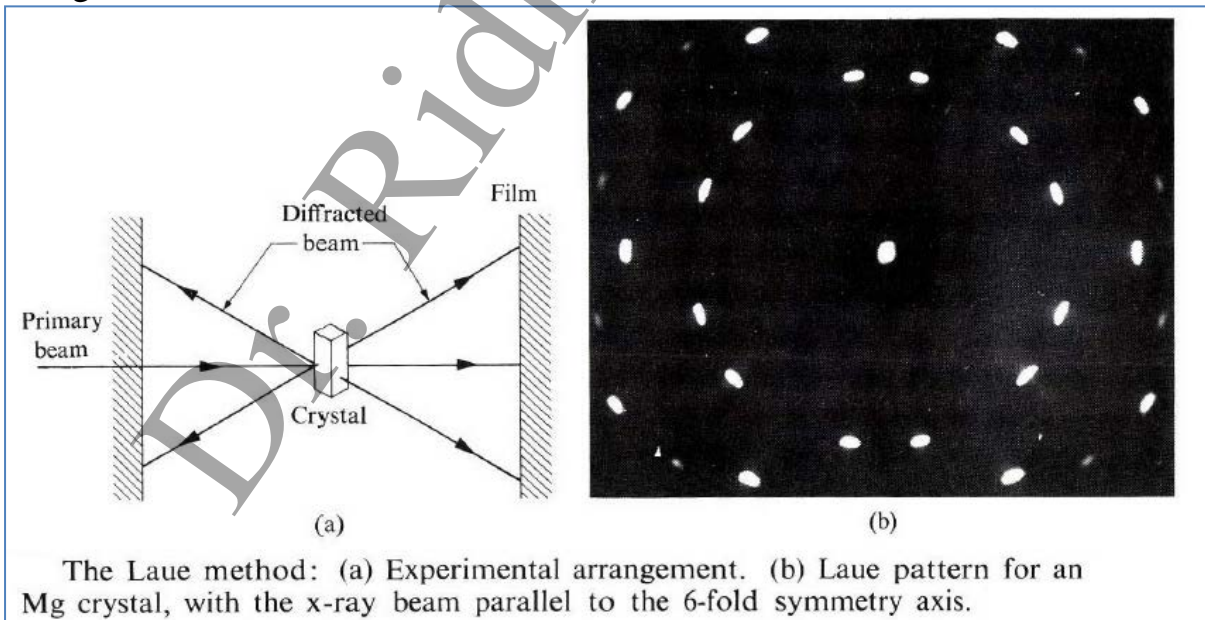
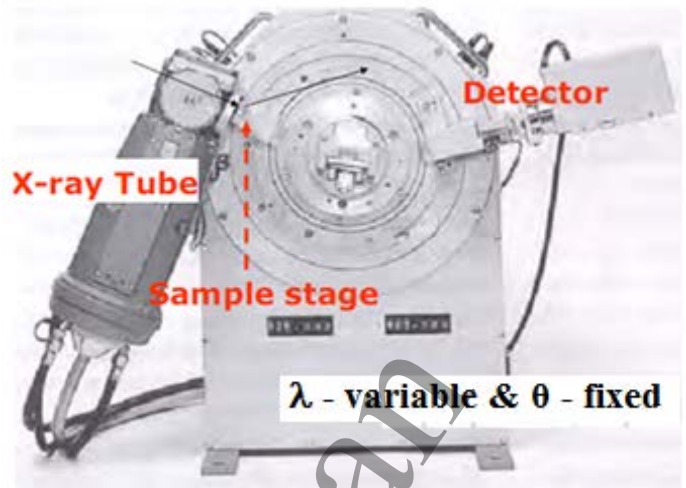
- Aluminum (Al) is fcc with $a = 0.405\text{ nm}$
- What is minimum energy x-ray that can satisfy the Bragg condition?



- The largest distance between planes is for 111 planes:
 $d = (a\sqrt{3})/3 = a/\sqrt{3}$
- Maximum λ is $2d = 2a/\sqrt{3} = 0.468\text{ nm}$
- Using $E = h\nu = hc/\lambda$, ($hc = 1.24 \times 10^{-6}\text{ m} = 1.24 \times 10^3\text{ nm}$), the minimum energy x-ray for Bragg scattering is 2.65 keV .
- Higher energy x-rays are needed for diffraction from all other planes in the crystal

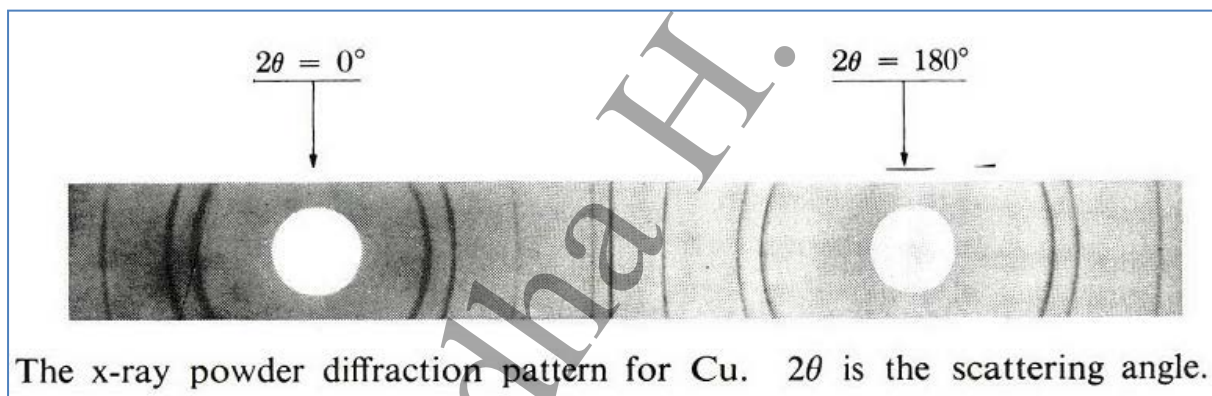
Laue Method.

- ✓ This method can be used for a rapid determination of the symmetry and orientation of a single crystal.
- ✓ The experimental arrangement is shown in Figure. A white x-ray beam - i.e., one with a spectrum of continuous wavelength- is made to fall on the crystal, which has a fixed orientation relative to the incident beam.
- ✓ Flat films are placed in front of and behind the specimen.
- ✓ Since λ covers a continuous range, the crystal selects that particular wavelength which satisfies Bragg's law at the present orientation, and a diffracted beam emerges at the corresponding angle.
- ✓ The diffracted beam is then recorded as a spot on the film.
- ✓ But since the wavelength corresponding to a spot is not measured, one cannot determine the actual values of the interplanar spacings-only their ratios.
- ✓ Therefore one can determine the shape but not the absolute size of the unit cell.
- ✓ A typical Laue photograph is shown in Figure.
- ✓ Note that if the direction of the beam is an axis of symmetry of the crystal, then the diffraction pattern should exhibit this symmetry.
- ✓ Figure shows the 6-fold symmetry of the symmetry axis in Mg, which has the hexagonal structure.

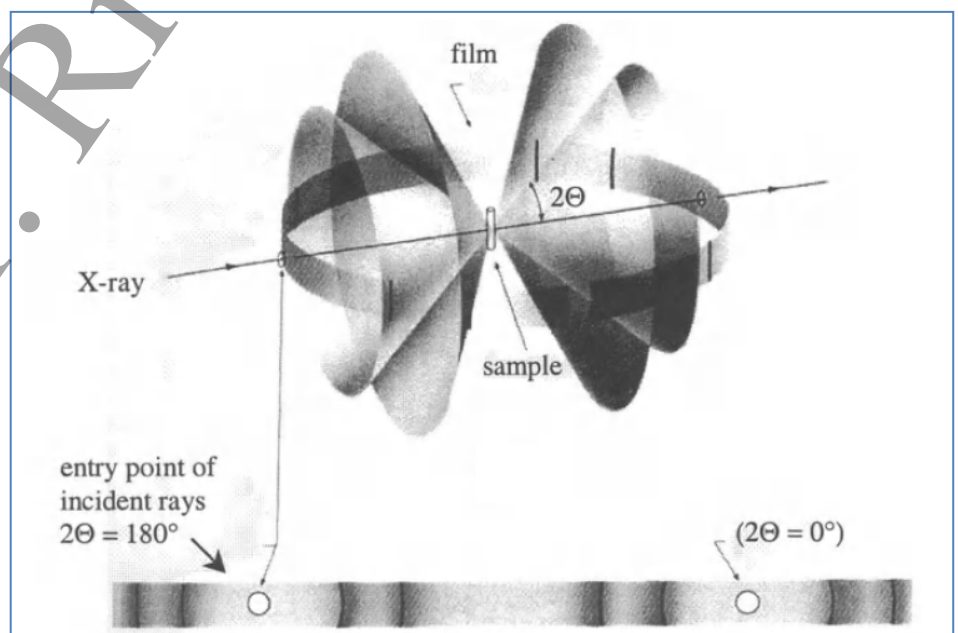


b- Powder Method (Debye Seherrer):

- ✓ This method is used to determine the crystal structure even if the specimen is not a single crystal.
- ✓ The sample may be made up of fine-grained powder packed into a cylindrical glass tube, or it may be polycrystalline, in which case it is made up of a large number of small crystallites oriented more or less randomly.
- ✓ A monochromatic beam impinges on the specimen, and the diffracted beams are recorded on a cylindrical film surrounding it.
- ✓ Because of the large number of crystallites which are randomly oriented, there is always enough of these which have the proper orientation relative to the incident monochromatic beam to satisfy Bragg's law, and hence a diffracted beam emerges at the corresponding angle as shown in figure. Since both, θ and λ are measurable, one can determine the interplanar spacing.
- ✓ Other sets of planes lead to other diffracted beams corresponding to different planar spacing for the same wavelength. Thus one can actually determine the lattice parameters quite accurately, particularly if the crystal structure is already known.

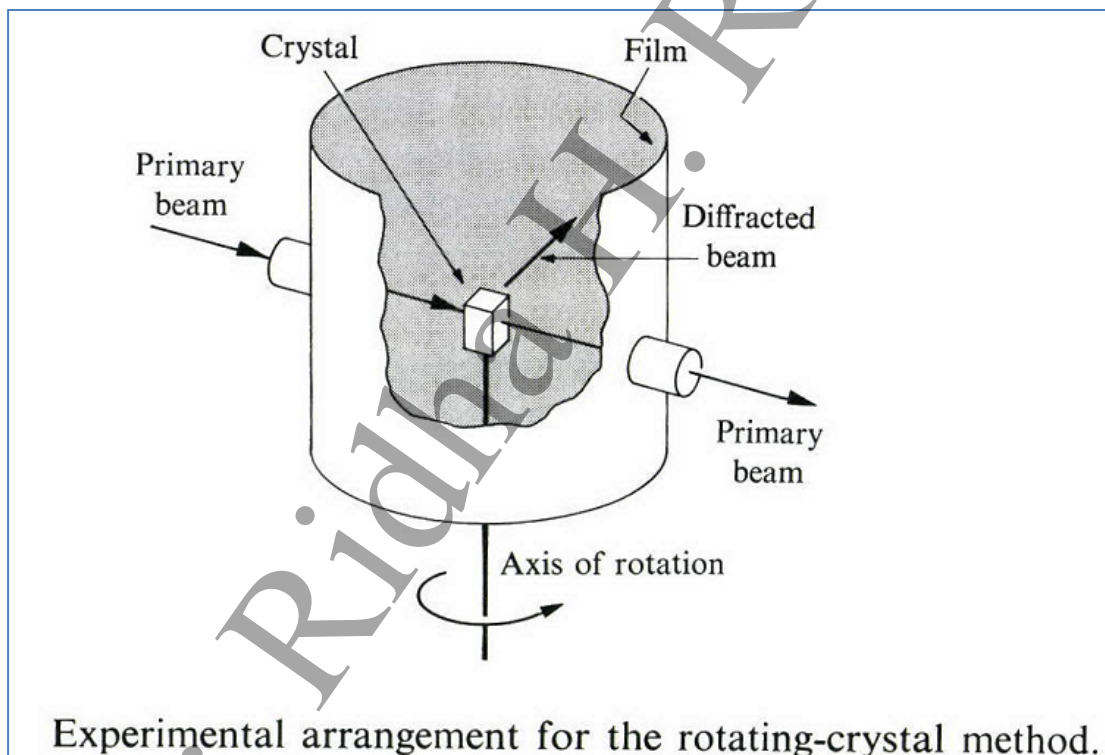


- ✓ Note also that, since the specimen is symmetric under rotation around the incident beam as an axis, the diffracted beam corresponding to each scattering angle 2θ fans out along a cone whose axis lies along the incident beam.



c- Rotating method

- ✓ This method is used for analysis of the structure of a single crystal. The experimental arrangement is shown in Figure. The crystal is usually about 1 mm in diameter, and is mounted on a spindle which can be rotated.
- ✓ A photographic film is placed on the inner side of a cylinder concentric with the axis of rotation.
- ✓ A monochromatic incident beam of wavelength λ is collimated and made to impinge on the crystal. The specimen is then rotated, if necessary, until a diffraction condition obtains, that is λ and θ satisfy Bragg's law.
- ✓ when this occurs, a diffracted beam (or beams) emerges from the crystal and is recorded as a spot on the film.
- ✓ By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of the unit cell as well as the arrangement of atoms inside the cell.



method	λ	θ
a- Laue Method.	variable	fixed
b- Powder Method (Debye Seherrer):	fixed	variable
c- Rotating method	fixed	Partially variable

4- Reciprocal Lattice:

- ❖ We have seen that the diffraction of X-rays occurs from various sets of parallel planes having different orientations (slopes) and interplanar spacings. In certain situations involving the presence of a number of sets of parallel planes with different orientations, it becomes difficult to visualize all such planes because of their two-dimensional nature.
- ❖ To solve the problem, Ewald introduced the new type of lattice known as the *reciprocal lattice*.
- ❖ The idea underlying the development was that each set of parallel planes could be represented by a normal to these planes having length equal to the reciprocal of the interplanar spacing. Thus the direction of each normal represents the orientation of the corresponding set of parallel planes and its length is proportional to the reciprocal of the interplanar spacing. The normals are drawn with reference to an arbitrary origin and points are marked at their ends. These points form a regular arrangement which is called a reciprocal lattice.
- ❖ Obviously, each point in a reciprocal lattice is a representative point of a particular parallel set of planes and it becomes easier to deal with such points than with sets of planes.
- ❖ One can construct a reciprocal lattice to a direct lattice using the following procedure:
 - (i) Take origin at some arbitrary point and draw normals to every set of parallel planes of the direct lattice.
 - (ii) Take length of each normal equal to the reciprocal of the interplanar spacing for the corresponding set of planes. The terminal points of these normals form the reciprocal lattice.

A reciprocal lattice vector, σ_{hkl} , is defined as a vector having magnitude equal to the reciprocal of the interplanar spacing d_{hkl} and direction coinciding with normal to $(h\ k\ l)$ planes. Thus, we have $\sigma_{hkl} = \frac{1}{d_{hkl}} \hat{n}$, where \hat{n} is the unit vector normal to the $(h\ k\ l)$ planes.

Denoting the fundamental reciprocal vector $\sigma_{100}, \sigma_{010}$ and σ_{001} by \vec{b}_1, \vec{b}_2 and \vec{b}_3 respectively, one obtains

$$\vec{b}_1 = \sigma_{100} = \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_2 = \sigma_{010} = \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_3 = \sigma_{001} = \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

Where $\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1 = \vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2$ is the volume of the direct cell.

Reciprocal Lattice Vectors:

As it mentioned previously $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$, where u_1, u_2, u_3 are integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the crystal axes. Any local physical property of the crystal, such as the charge concentration, electron number density, or magnetic moment density is invariant under \vec{T} .

In literature, sometime the primitive translation vectors \vec{a}_1, \vec{a}_2 and \vec{a}_3 of a direct lattice (primitive vectors of crystal lattice) are related to the primitive translation vectors $\vec{b}_1 = \vec{b}_2 = \vec{b}_3$ of the reciprocal lattice as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad \text{--- --- --- --- ---} \quad (*)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

The factors 2π are not used by crystallographer but are convenient in solid state physics.

✓ \vec{a}_1, \vec{a}_2 , and \vec{a}_3 : the primitive translation vectors of a direct lattice (primitive vectors of crystal lattice i.e, crystal axes)

✓ \vec{b}_1, \vec{b}_2 , and \vec{b}_3 : the primitive translation vectors of the reciprocal lattice (the axis vectors of the reciprocal lattice)

Each vector defined by (eq.*) is orthogonal to two axis vectors of the crystal lattice.

\vec{b}_1 is normal to \vec{a}_2 and \vec{a}_3

\vec{b}_2 is normal to \vec{a}_3 and \vec{a}_1

\vec{b}_3 is normal to \vec{a}_1 and \vec{a}_2

Thus \vec{b}_1, \vec{b}_2 , and \vec{b}_3 have the property

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad \text{where} \quad (\delta_{ij} = 1 \text{ if } i = j) \& (\delta_{ij} = 0 \text{ if } i \neq j)$$

$$\vec{b}_1 \cdot \vec{a}_1 = 2\pi, \quad \vec{b}_2 \cdot \vec{a}_1 = 0, \quad \vec{b}_3 \cdot \vec{a}_1 = 0$$

$$\vec{b}_1 \cdot \vec{a}_2 = 0, \quad \vec{b}_2 \cdot \vec{a}_2 = 2\pi, \quad \vec{b}_3 \cdot \vec{a}_2 = 0$$

$$\vec{b}_1 \cdot \vec{a}_3 = 0, \quad \vec{b}_2 \cdot \vec{a}_3 = 0, \quad \vec{b}_3 \cdot \vec{a}_3 = 2\pi$$

Points in the reciprocal lattice are mapped by the set of vectors

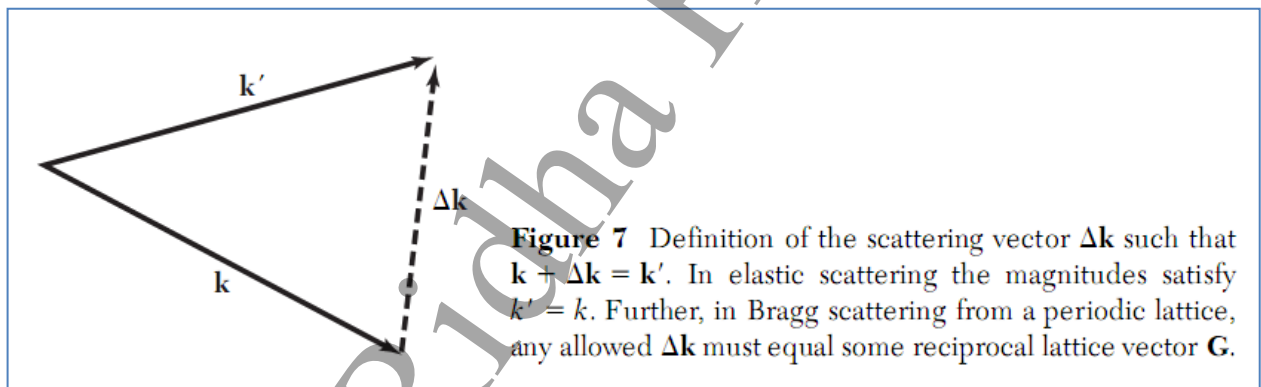
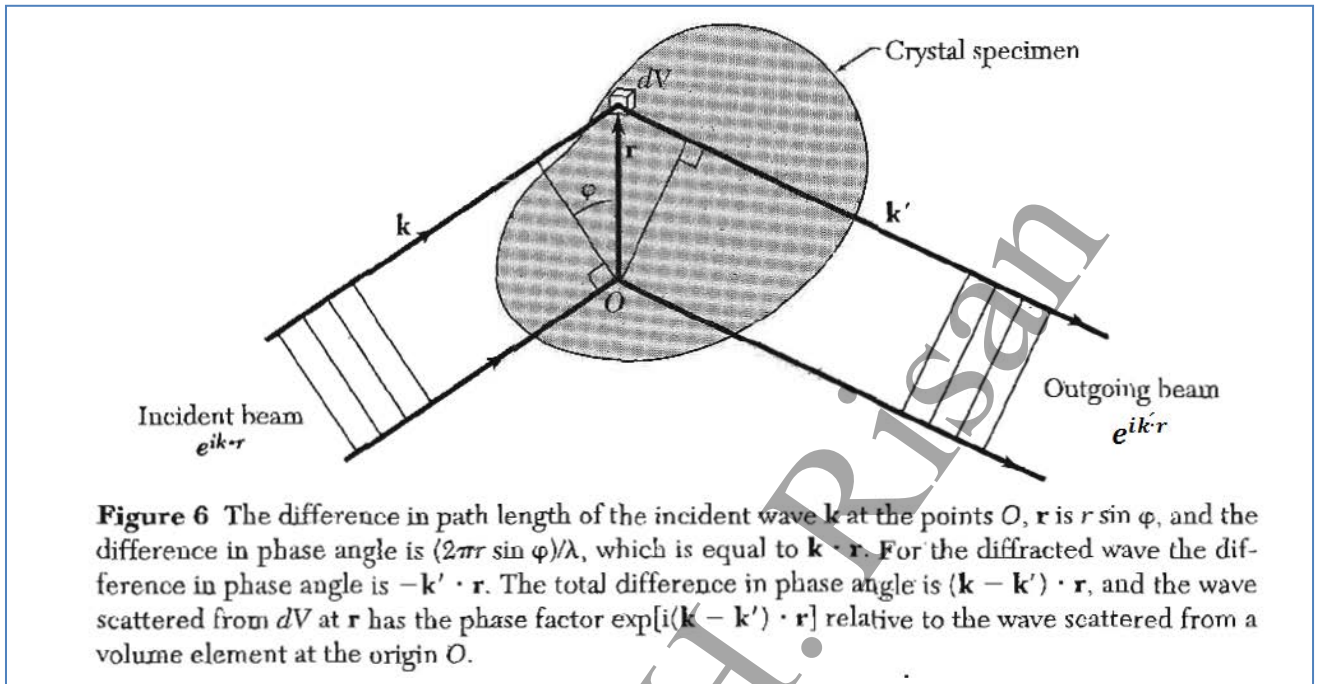
$$\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$$

where v_1, v_2, v_3 are integers. A vector \vec{G} of this form is a reciprocal lattice

vector. $\vec{G}_{hkl} = \frac{2\pi}{d_{hkl}} \hat{n}$ where \hat{n} is the unit vector normal to the $(h k l)$ planes.

Diffraction Conditions:

Theorem. The set of reciprocal lattice vector \vec{G} determines the possible x-ray reflections. The wavevectors of the incoming and outgoing beams are \vec{k} and \vec{k}'



The amplitude of the electric or magnetic field vectors in the scattered electromagnetic wave is proportional to the following integral which defines the quantity F that we call the **scattering amplitude**:

$$F = \int dV n(r) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] = \int dV n(r) \exp[-i\Delta \mathbf{k} \cdot \mathbf{r}]$$

Where $\mathbf{k} - \mathbf{k}' = -\Delta \mathbf{k}$ or $\mathbf{k} + \Delta \mathbf{k} = \mathbf{k}'$

Here $\Delta \mathbf{k}$ measures the change in wavevector and is called the **scattering vector** as shown in previous figure.

When the scattering vector is equal to a particular reciprocal lattice vector,

$$\Delta \mathbf{k} = \mathbf{G}$$

In elastic scattering of a photon its energy $\hbar\omega$ is conserved, so that the frequency of the emergent beam is equal to the frequency of the incident beam. The magnitudes k and k' are equal, and $k^2 = k'^2$, a result that holds also for elastic scattering of electron and neutron beams. From ($\Delta \mathbf{k} = \mathbf{G}$) we found $\mathbf{K} + \mathbf{G} = \mathbf{K}'$ so that the **diffraction condition** is written as $(\mathbf{K} + \mathbf{G})^2 = K'^2$ or

$$2\mathbf{K} \cdot \mathbf{G} + G^2 = 0$$

This is the central result of the theory of elastic scattering of waves in a periodic lattice. If \mathbf{G} is a reciprocal lattice vector, so is $-\mathbf{G}$, and with this substitution we can write the last equation as:

$$2\mathbf{K} \cdot \mathbf{G} = G^2 \dots \dots \dots \text{(The condition for diffraction)}$$

(Another statement of the Bragg condition)

The spacing $d(hkl)$ between parallel lattice planes that are normal to the direction $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is: $\left(d(hkl) = \frac{2\pi}{|\mathbf{G}|}\right)$. Thus the result

$2\mathbf{K} \cdot \mathbf{G} = G^2$ may be written as:

$2\left(\frac{2\pi}{\lambda}\right) \sin \theta = \frac{2\pi}{d(hkl)}$ or $2d(hkl) \sin \theta = \lambda$. Here θ is the angle between the incident beam and the crystal plane.

The integers hkl that define G are not necessarily identical with the indices of an actual crystal plane, because the hkl may contain a common factor n , whereas in the definition of the indices in Chapter 1 the common factor has been eliminated. We thus obtain the Bragg result:

$2d \sin \theta = n\lambda$ Where d is the spacing between adjacent parallel planes with indices $h/n, k/n, l/n$.

Laue Equations:

The original result ($\Delta \mathbf{k} = \mathbf{G}$) of diffraction theory, may be expressed in another way to give what are called the Laue equations. These are valuable because of their geometrical representation. Take the scalar product of both $\Delta \mathbf{k}$ and \mathbf{G} successively with $\mathbf{a}_1, \mathbf{a}_2$ and \mathbf{a}_3 . From (14) and (15) we get

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \dots \dots \dots (14)$$

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3 \dots \dots \dots (15)$$

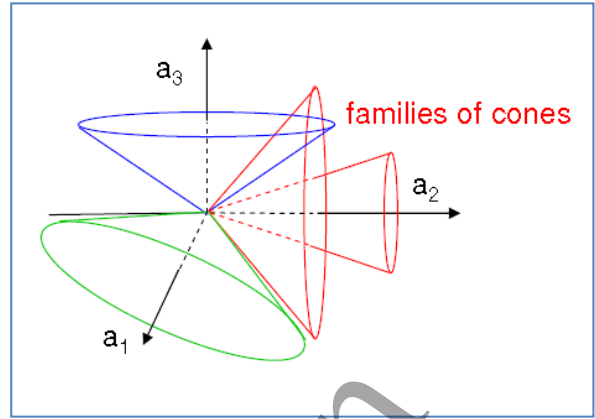
$$\mathbf{a}_1 \cdot \Delta \mathbf{k} = 2\pi v_1 ,$$

$$\mathbf{a}_2 \cdot \Delta \mathbf{k} = 2\pi v_2 ,$$

$$\mathbf{a}_3 \cdot \Delta \mathbf{k} = 2\pi v_3$$

These equations have a simple geometrical interpretation. The first equation $\mathbf{a}_1 \cdot \Delta \mathbf{k} = 2\pi v_1$ tells us that $\Delta \mathbf{k}$ lies on a certain cone about the direction of \mathbf{a}_1 . The second equation tells us that $\Delta \mathbf{k}$ lies on a cone about \mathbf{a}_2 as well, and the third equation requires that $\Delta \mathbf{k}$ lies on a cone about \mathbf{a}_3 .

Thus, at a reflection $\Delta \mathbf{k}$ must satisfy all three equations; it must lie at the common line of intersection of three cones, which is a severe condition that can be satisfied only by systematic sweeping or searching in wavelength or crystal orientation—or by sheer accident.



A beautiful construction, **the Ewald construction**, Illustrated in the figure below. This helps us visualize the nature of the accident that must occur in order to satisfy the diffraction condition in three dimensions:

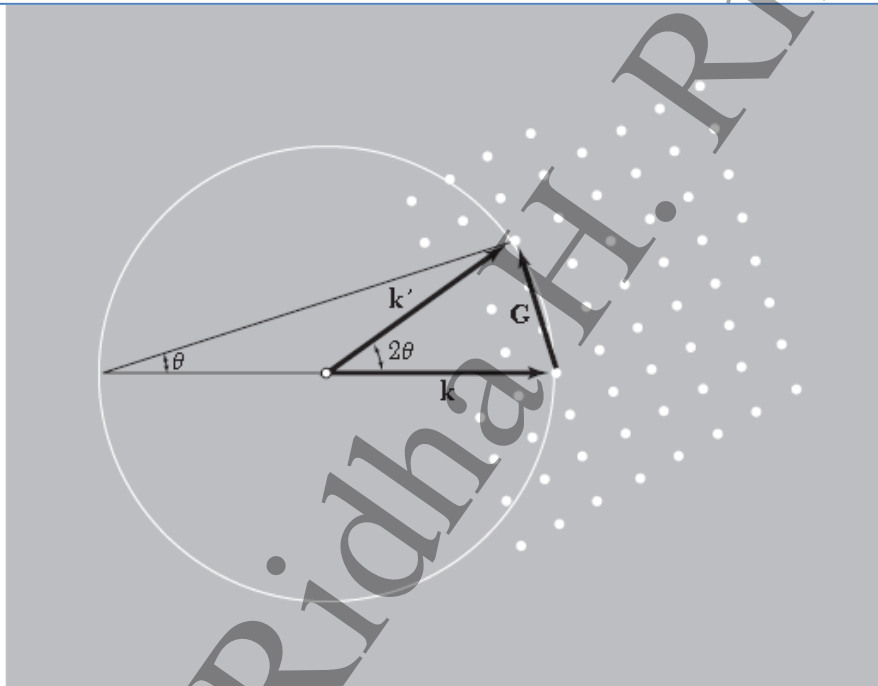


Figure 8 The points on the right-hand side are reciprocal-lattice points of the crystal. The vector \mathbf{k} is drawn in the direction of the incident x-ray beam, and the origin is chosen such that \mathbf{k} terminates at any reciprocal lattice point. We draw a sphere of radius $k = 2\pi/\lambda$ about the origin of \mathbf{k} . A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice. The sphere as drawn intercepts a point connected with the end of \mathbf{k} by a reciprocal lattice vector \mathbf{G} . The diffracted x-ray beam is in the direction $\mathbf{k}' = \mathbf{k} + \mathbf{G}$. The angle θ is the Bragg angle of Fig. 2. This construction is due to P. P. Ewald.

You should know more than Bob. Specifically you should know how to determine the Bravais lattice from an x-ray diffraction measurement and for a very good grade you should be able to explain how to determine the locations of the atoms in the basis.

BRILLOUIN ZONES:

Brillouin gave the statement of the diffraction condition that is most widely used in solid state physics, which means in the description of electron energy band theory and of the elementary excitations of other kinds. **A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice.**

The Brillouin zone gives a *vivid* geometrical interpretation of the diffraction condition

$$2\mathbf{K} \cdot \mathbf{G} = G^2 \dots \dots \dots \text{(The condition for diffraction)}$$

(Another statement of the Bragg condition)

We divide both sides by 4 to obtain: $\mathbf{K} \cdot \left(\frac{1}{2}\mathbf{G}\right) = \left(\frac{1}{2}G\right)^2$

We now work in reciprocal space, the space of the \mathbf{k} 's and \mathbf{G} 's.

- ✓ Select a vector \mathbf{G} from the origin to a reciprocal lattice point.
- ✓ Construct a plane normal to this vector \mathbf{G} at its midpoint.
- ✓ This plane forms a part of a zone boundary as shown in the figure.

An x-ray beam in the crystal will be diffracted if its wavevector \mathbf{k} has the magnitude and direction required by $\left\{\mathbf{K} \cdot \frac{1}{2}\mathbf{G} = \left(\frac{1}{2}G\right)^2\right\}$. The diffracted beam will then be in the direction $\mathbf{k} - \mathbf{G}$, as we see from $(\mathbf{k} + \Delta\mathbf{k} = \hat{\mathbf{k}})$ with $\Delta\mathbf{k} = -\mathbf{G}$. Thus the Brillouin construction exhibits all the wavevectors \mathbf{k} which can be Braggreflected by the crystal.

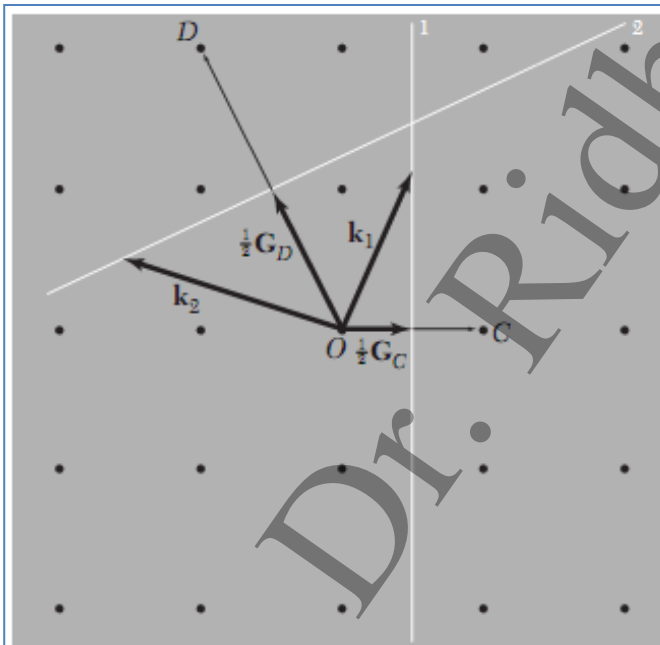
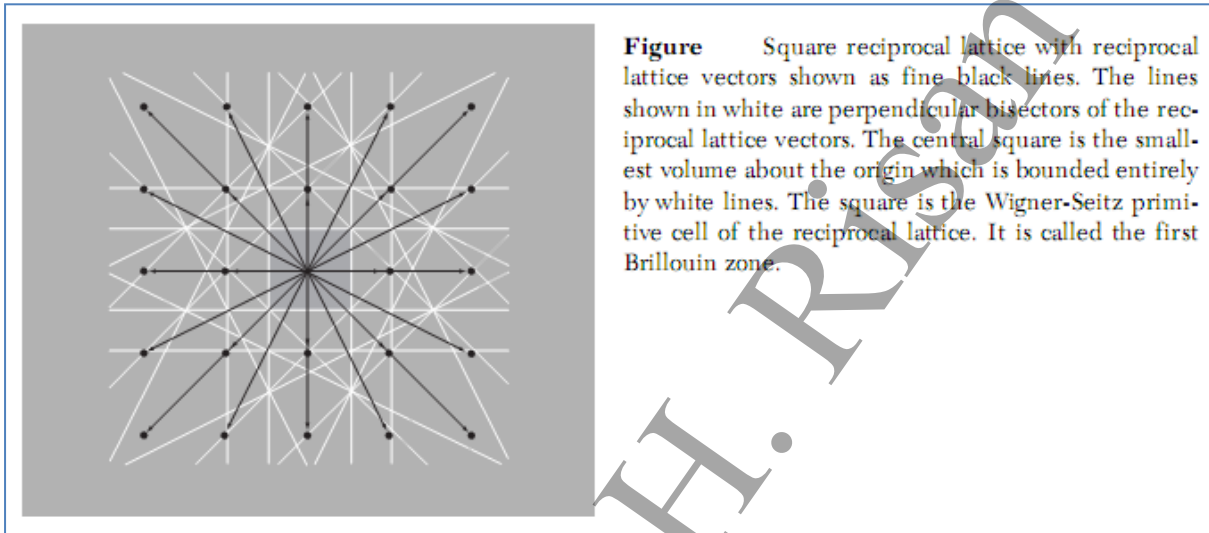


Figure Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector \mathbf{G}_C connects points OC ; and \mathbf{G}_D connects OD . Two planes 1 and 2 are drawn which are the perpendicular bisectors of \mathbf{G}_C and \mathbf{G}_D , respectively. Any vector from the origin to the plane 1, such as \mathbf{k}_1 , will satisfy the diffraction condition $\mathbf{k}_1 \cdot \left(\frac{1}{2}\mathbf{G}_C\right) = \left(\frac{1}{2}G_C\right)^2$. Any vector from the origin to the plane 2, such as \mathbf{k}_2 , will satisfy the diffraction condition $\mathbf{k}_2 \cdot \left(\frac{1}{2}\mathbf{G}_D\right) = \left(\frac{1}{2}G_D\right)^2$.

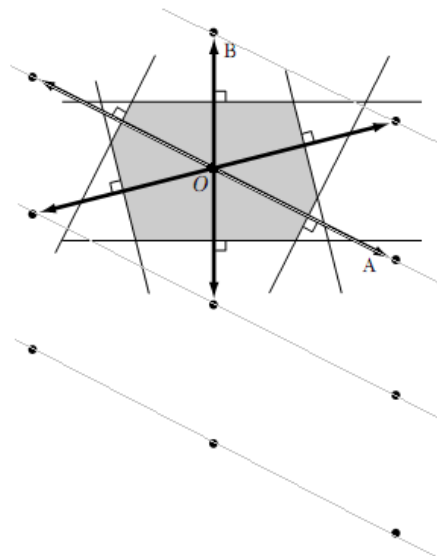
The set of planes that are the perpendicular bisectors of the reciprocal lattice vectors is of general importance in the theory of wave propagation in crystals: A wave whose wavevector drawn from the origin terminates on any of these planes will satisfy the condition for diffraction.

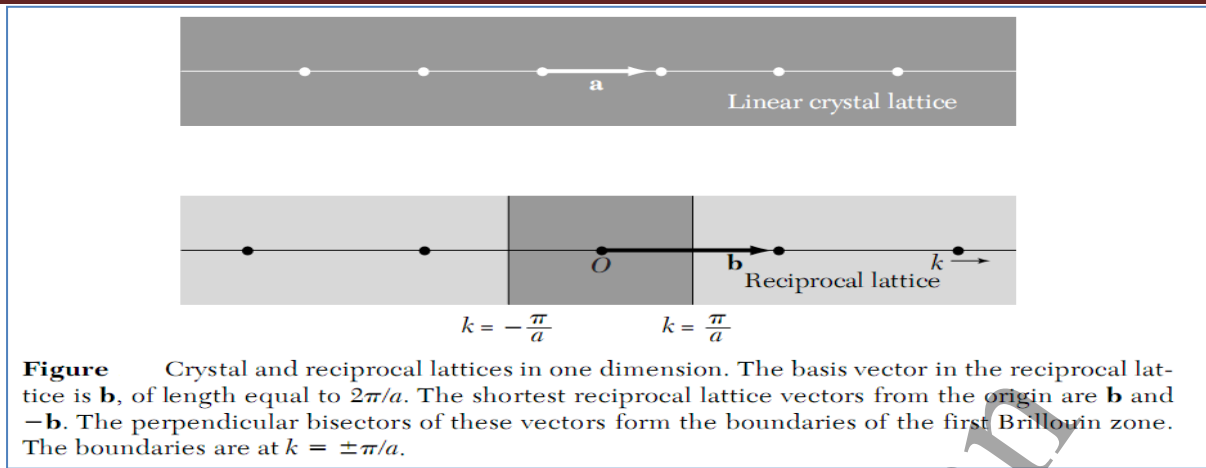
These planes divide the Fourier space of the crystal into fragments, as shown in figure for a square lattice. The central square is a primitive cell of the reciprocal lattice. It is a Wigner-Seitz cell of the reciprocal lattice.



The central cell in the reciprocal lattice is of special importance in the theory of solids, and we call it the first Brillouin zone. **The first Brillouin zone is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.** Examples are shown in figures.

Figure Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from O to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their mid-points. The smallest enclosed area is the first Brillouin zone.





Historically, Brillouin zones are not part of the language of x-ray diffraction analysis of crystal structures, but the zones are an essential part of the analysis of the electronic energy-band structure of crystals.

Reciprocal Lattice to sc Lattice:

The primitive translation vectors of a simple cubic lattice may be taken as the set:

$$\vec{a}_1 = a\hat{x} \quad \vec{a}_2 = a\hat{y} \quad \vec{a}_3 = a\hat{z}$$

Here $\hat{x}, \hat{y}, \hat{z}$ are orthogonal vectors of unit length. The volume of the cell is $\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = a^3$. The primitive translation vectors of the reciprocal lattice are found from the standard prescription:

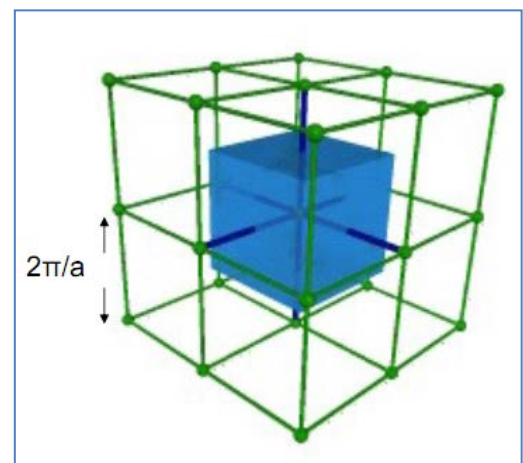
$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_1 = \frac{2\pi}{a} \hat{x} \quad \vec{b}_2 = \frac{2\pi}{a} \hat{y} \quad \vec{b}_3 = \frac{2\pi}{a} \hat{z}$$

Here the reciprocal lattice is itself a simple cubic lattice, now of lattice constant $\left(\frac{2\pi}{a}\right)$. The boundaries of the first Brillouin zones are the planes normal to the six reciprocal lattice vectors $\pm\vec{b}_1, \pm\vec{b}_2, \pm\vec{b}_3$ at their midpoints:

$$\mp \frac{1}{2} \vec{b}_1 = \mp \frac{\pi}{a} \hat{x}, \quad \mp \frac{1}{2} \vec{b}_2 = \mp \frac{\pi}{a} \hat{y}, \quad \mp \frac{1}{2} \vec{b}_3 = \mp \frac{\pi}{a} \hat{z}$$

The six planes bound a cube of edge and of volume this cube is the first Brillouin zone of the sc crystal lattice as shown in figure:



Reciprocal Lattice to bcc Lattice:

The primitive translation vectors of the bcc lattice as shown in this figure are

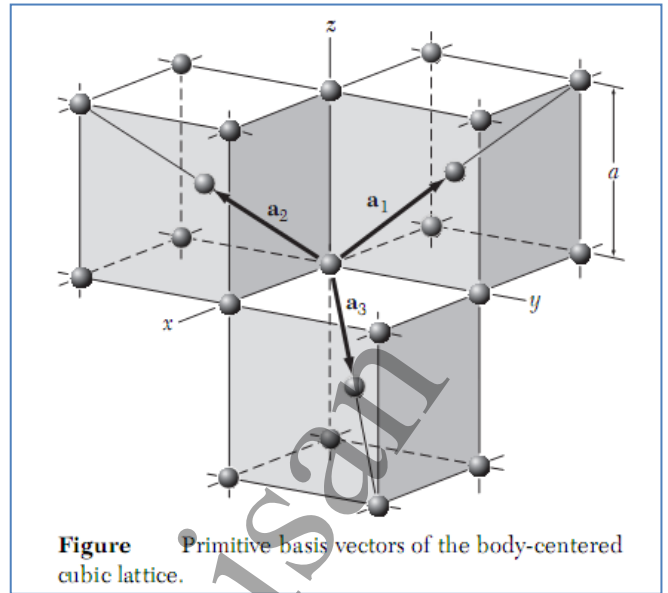
$$\vec{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z})$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z})$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

where a is the side of the conventional cube and $\hat{x}, \hat{y}, \hat{z}$ are orthogonal unit vectors parallel to the cube edges. The volume of the primitive cell is

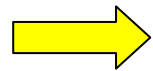
$$V = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = \frac{1}{2}a^3$$



The primitive translations of the reciprocal lattice are defined by (13). We have, using (29),

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} ; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} ; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \dots \dots \dots (13)$$

$$\vec{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) ; \quad \vec{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) ; \quad \vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z}) \dots \dots (29)$$



$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y} + \hat{z}) ; \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{x} + \hat{z}) ; \quad \vec{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y}) \dots \dots (31)$$

The general reciprocal lattice vector is, for integral v_1, v_2, v_3

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$$

$$\vec{G} = \left(\frac{2\pi}{a}\right) [(v_2 + v_3)\hat{x} + (v_1 + v_3)\hat{y} + (v_1 + v_2)\hat{z}]$$

The shortest \vec{G} 's are the following 12 vectors, where all choices of sign are independent:

$$\left(\frac{2\pi}{a}\right)(\mp\hat{y} \mp \hat{z}), \quad \left(\frac{2\pi}{a}\right)(\mp\hat{x} \mp \hat{z}), \quad \left(\frac{2\pi}{a}\right)(\mp\hat{x} \mp \hat{y}) \dots \dots \dots (33)$$

One primitive cell of the reciprocal lattice is the parallelepiped described by the $\vec{b}_1, \vec{b}_2, \vec{b}_3$ defined by (31).

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y} + \hat{z}) ; \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{x} + \hat{z}) ; \quad \vec{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y}) \dots \dots \dots (31)$$

The volume of this cell in reciprocal space is:

$$\vec{b}_1 \cdot \vec{b}_2 \times \vec{b}_3 = 2\left(\frac{2\pi}{a}\right)^3$$

The cell contains one reciprocal lattice point, because each of the eight corner points is shared among eight parallelepipeds. Each parallelepiped contains one-eighth of each of eight corner points.

Another primitive cell is the central (Wigner-Seitz) cell of the reciprocal lattice which is the first Brillouin zone. Each such cell contains one lattice point at the central point of the cell. This zone (for the bcc lattice) is bounded by the planes normal to the 12 vectors of Eq. (33) at their midpoints. The zone is a regular 12-faced solid, a rhombic dodecahedron, as shown in **figure**:

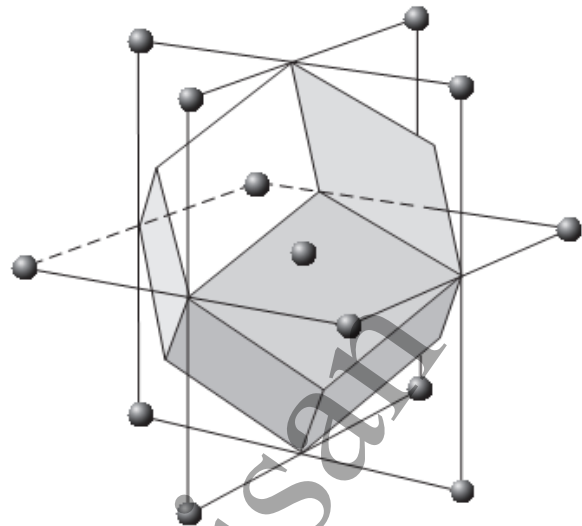


Figure First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

Reciprocal Lattice to fcc Lattice:

The primitive translation vectors of the fcc lattice of this **figure**:

$$\begin{aligned}\vec{a}_1 &= \frac{1}{2}a(\hat{y} + \hat{z}) \\ \vec{a}_2 &= \frac{1}{2}a(\hat{x} + \hat{z}) \\ \vec{a}_3 &= \frac{1}{2}a(\hat{x} + \hat{y}) \quad \dots\dots\dots(34)\end{aligned}$$

The volume of the primitive cell is:

$$V = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = \frac{1}{4}a^3$$

The primitive translation vectors of the lattice reciprocal to the fcc lattice are:

$$\vec{b}_1 = \frac{2\pi}{a}(-\hat{x} + \hat{y} + \hat{z}) ; \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{x} - \hat{y} + \hat{z}) ; \quad \vec{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z})$$

These are primitive translation vectors of a bcc lattice, so that the bcc lattice is reciprocal to the fcc lattice. The volume of the primitive cell of the reciprocal lattice is $4\left(\frac{2\pi}{a}\right)^3$.

The shortest G's are the eight vectors: $\left(\frac{2\pi}{a}\right)(\mp\hat{x} \mp \hat{y} \mp \hat{z})$

The boundaries of the central cell in the reciprocal lattice are determined for the most part by the eight planes normal to these vectors at their midpoints. But

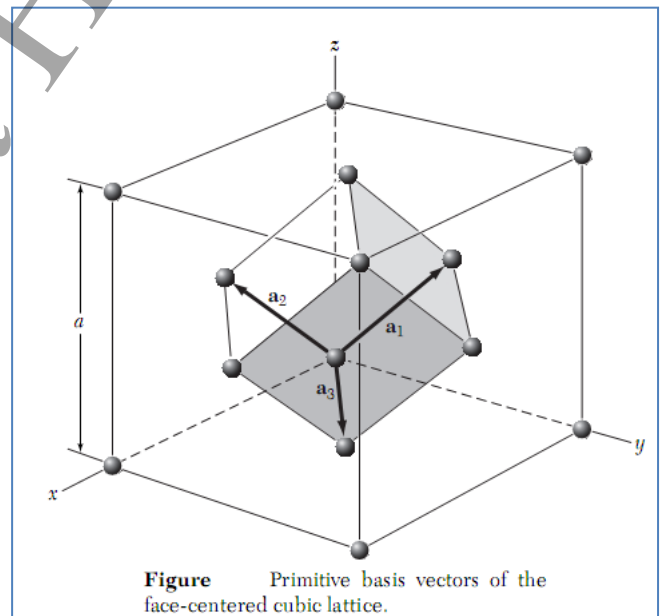


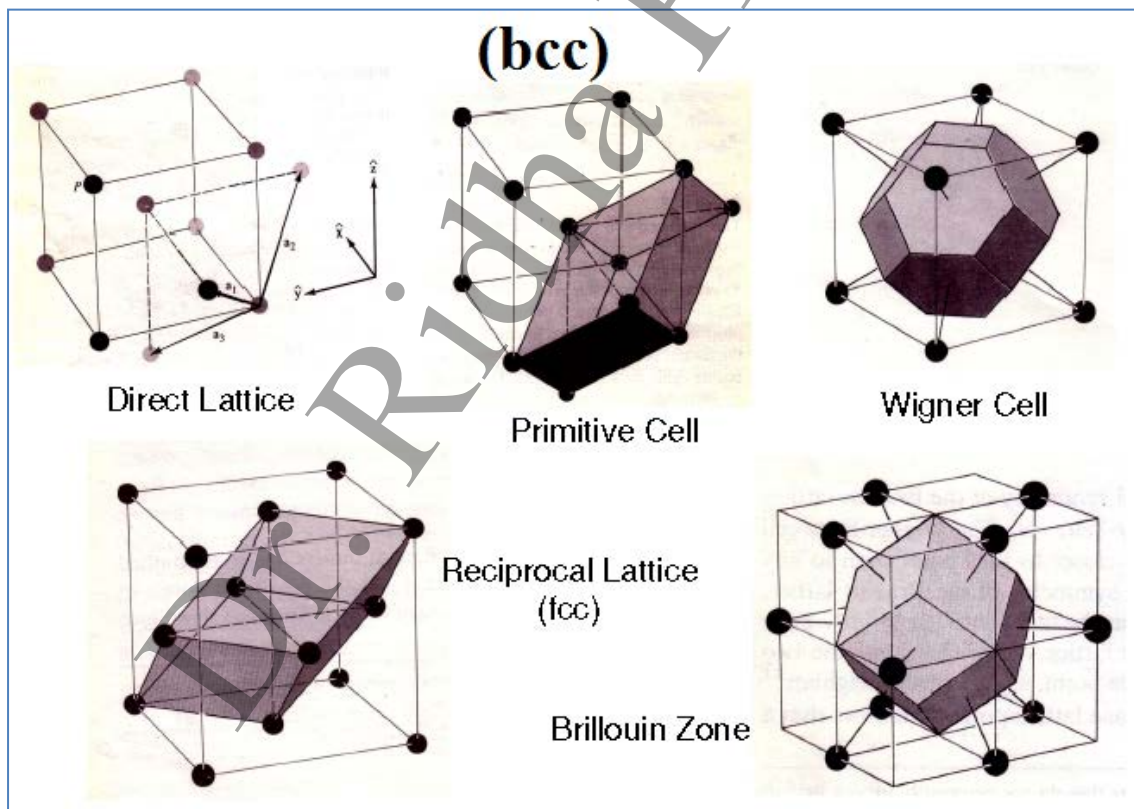
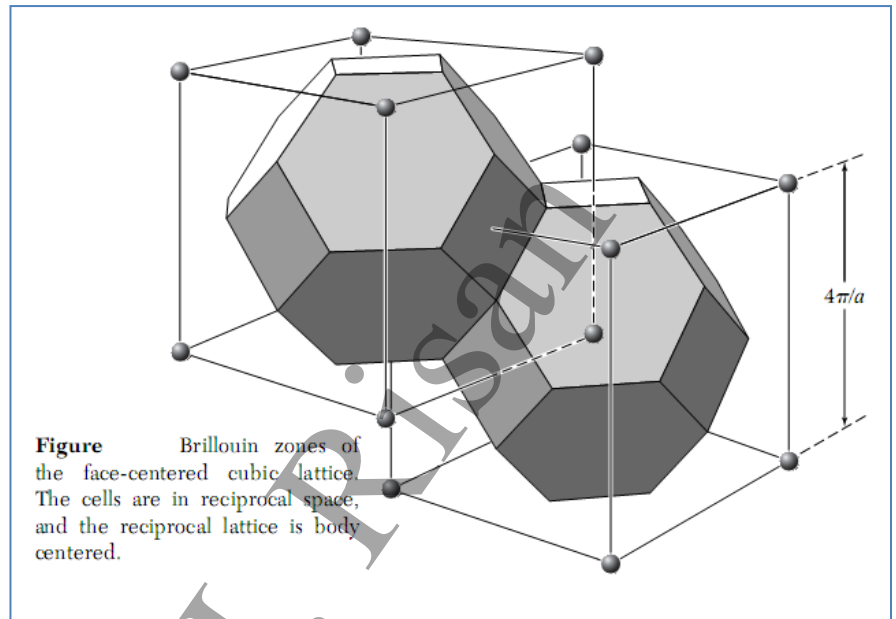
Figure Primitive basis vectors of the face-centered cubic lattice.

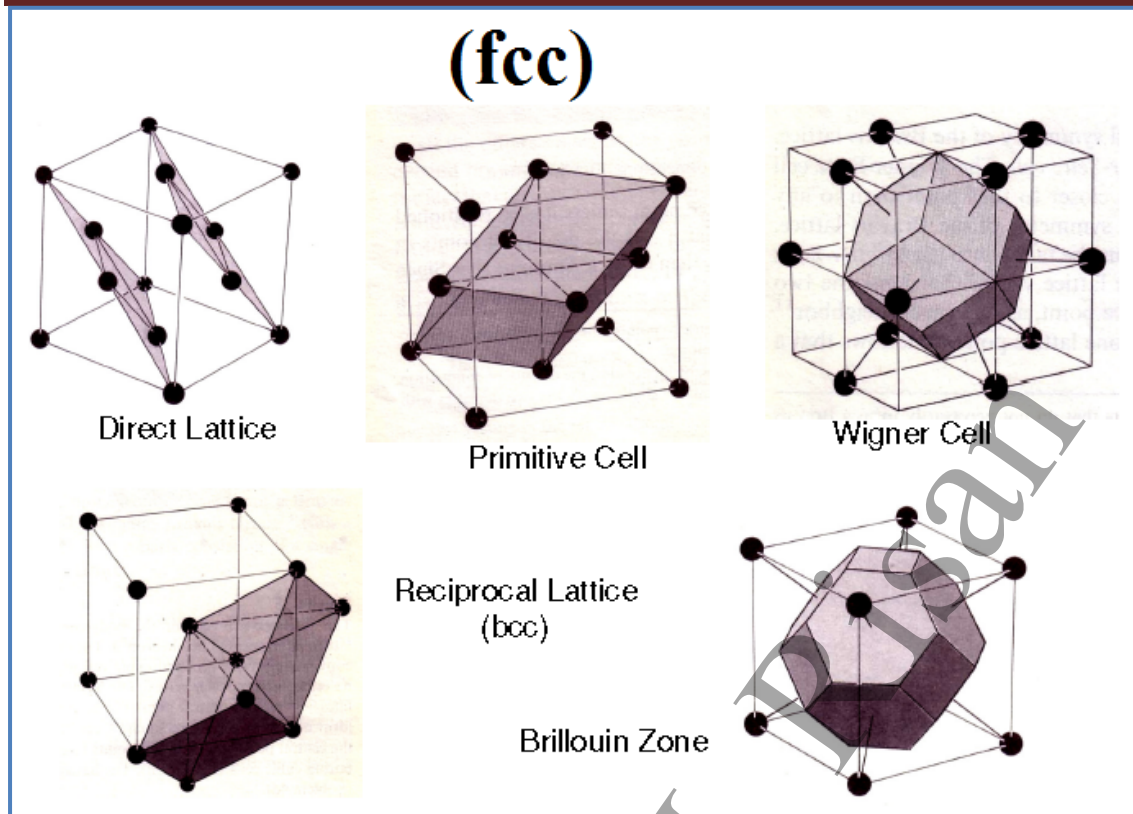
the corners of the octahedron thus formed are cut by the planes that are the perpendicular bisectors of six other reciprocal lattice vectors:

$$\left(\frac{2\pi}{a}\right)(\mp 2\hat{x}), \quad \left(\frac{2\pi}{a}\right)(\mp 2\hat{y}), \quad \left(\frac{2\pi}{a}\right)(\mp 2\hat{z}) \dots\dots\dots(38)$$

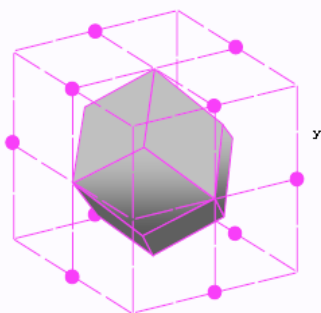
Note that $\left(\frac{2\pi}{a}\right)(2\hat{x})$ is a reciprocal lattice vector because it is equal to $\mathbf{b}_2 + \mathbf{b}_3$.

The first Brillouin zone is the smallest bounded volume about the origin, the truncated octahedron shown in **figure**. The six planes bound a cube of edge $4\pi/a$ and (before truncation) of volume $\left(\frac{4\pi}{a}\right)^3$.

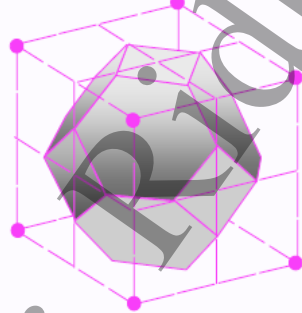




Face Centered Cubic

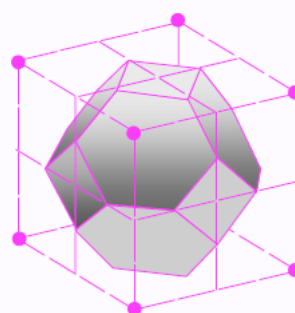


Wigner-Seitz Cell for Face Centered Cubic Lattice

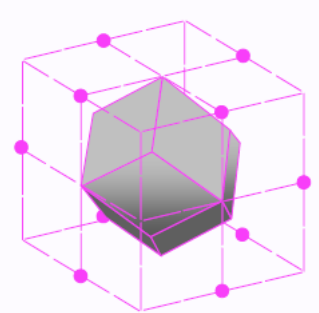


Brillouin Zone = Wigner-Seitz Cell for Reciprocal Lattice

Body Centered Cubic



Wigner-Seitz Cell for Body Centered Cubic Lattice



Brillouin Zone = Wigner-Seitz Cell for Reciprocal Lattice

5- Lattice Structure Factor

When the diffraction condition of Eq. (21) is satisfied, the scattering amplitude (18) for a crystal of N cells may be written as

$$F = \int dV n(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] = \int dV n(\mathbf{r}) \exp[-i\Delta\mathbf{k} \cdot \mathbf{r}] \dots \dots (18)$$

$$\Delta\mathbf{k} = \mathbf{G} \dots \dots \dots (21)$$

$$F = N \int dV n(\mathbf{r}) \exp[-i\mathbf{G} \cdot \mathbf{r}] = NS_C \dots \dots \dots (39)$$

The quantity S_C is called the **structure factor** and is defined as an integral over a single cell, with $\mathbf{r} = 0$ at one corner.

Often it is useful to write the electron concentration $n(\mathbf{r})$ as the superposition of electron concentration functions n_j associated with each atom j of the cell. If \mathbf{r}_j is the vector to the center of atom j , then the function $n_j(\mathbf{r} - \mathbf{r}_j)$ defines the contribution of that atom to the electron concentration at \mathbf{r} . The total electron concentration at \mathbf{r} due to all atoms in the single cell is the sum over the s atoms of the basis.

$$n(\mathbf{r}) = \sum_{j=1}^s n_j(\mathbf{r} - \mathbf{r}_j) \dots \dots \dots (40)$$

over the s atoms of the basis. The decomposition of $n(\mathbf{r})$ is not unique, for we cannot always say how much charge density is associated with each atom. This is not an important difficulty.

The structure factor defined by (39) may now be written as integrals over the s atoms of a cell:

$$S_C = \sum_j \int dV n_j(\mathbf{r} - \mathbf{r}_j) \exp[-i\mathbf{G} \cdot \mathbf{r}]$$

$$S_C = \sum_j \exp[-i\mathbf{G} \cdot \mathbf{r}_j] \int dV n_j(\rho) \exp[-i\mathbf{G} \cdot \rho] \dots \dots (41)$$

where $\rho = \mathbf{r} - \mathbf{r}_j$ We now define **the atomic form factor f_j** as

$$f_j = \int dV n_j(\rho) \exp[-i\mathbf{G} \cdot \rho] \dots \dots \dots (42)$$

integrated over all space. If $n_j(\rho)$ is an atomic property, f_j is an atomic property. We combine (41) and (42) to obtain the **structure factor of the basis** in the form

$$S_C = \sum_j f_j \exp[-i\mathbf{G} \cdot \mathbf{r}_j] \dots \dots \dots (43)$$

The usual form of this result follows on writing for atom j :

$$\vec{r}_j = x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3 \dots \dots \dots (44)$$

Then, for the reflection labelled by v_1, v_2, v_3 , we have

$$\mathbf{G} \cdot \mathbf{r}_j = (v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3) \cdot (x_j \vec{a}_1 + y_j \vec{a}_2 + z_j \vec{a}_3) \dots (45)$$

$$\mathbf{G} \cdot \mathbf{r}_j = 2\pi (v_1 x_j + v_2 y_j + v_3 z_j)$$

so that (43) becomes

$$S_C(v_1 v_2 v_3) = \sum_j f_j \exp[-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)] \dots \dots \dots (46)$$

The structure factor S need not be real because the scattered intensity will involve $S^* S$ where S^* is the complex conjugate of S so that $S^* S$ is real.

NOT:

$$e^{i\theta} = \cos \theta + i \sin \theta$$

$$e^{i2\pi} = \cos 2\pi + i \sin 2\pi = 1 + 0 = 1 = e^{-i2\pi}$$

$$e^{i\pi} = \cos \pi + i \sin \pi = -1 + 0 = -1 = e^{-i\pi}$$

Structure Factor of the bcc Lattice

The bcc basis referred to the cubic cell has identical atoms at $x_1=y_1=z_1=0$ and at $x_2=y_2=z_2=1/2$. i.e., $\left(000 \ \& \ \frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$; Thus (46) becomes

$$S_C(v_1 \ v_2 \ v_3) = \sum_j f_j \exp[-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)] \dots \dots \dots (46)$$

$$S_C(v_1 \ v_2 \ v_3) = S|_{000} + S|_{\frac{111}{222}} \Rightarrow S_C(v_1 \ v_2 \ v_3) = f_j \{1 + \exp[-i\pi(v_1 + v_2 + v_3)]\}$$

but :

$$e^{i2\pi} = \cos 2\pi + i \sin 2\pi = 1 + 0 = 1 = e^{-i2\pi}$$

$$e^{i\pi} = \cos \pi + i \sin \pi = -1 + 0 = -1 = e^{-i\pi}$$

Where f is the form factor of an atom. The value of S is zero whenever the exponential has the value -1, which is whenever the argument is $-i\pi \times (\text{odd integer})$. Thus we have

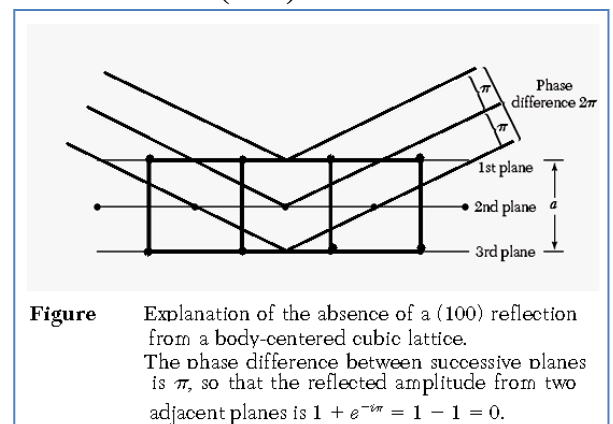
- $S = 0$ when $(v_1 + v_2 + v_3) = \text{odd integer} =$
Reflections absent (reflection vanishes – cancellation)
- $S = 2f$ when $(v_1 + v_2 + v_3) = \text{even integer} =$
Reflections present (reflection occurs)

Planes	$(v_1 + v_2 + v_3)$	S_C	Notes
(100)	odd	0	Reflections absent ×
(110)	even	$2f$	Reflections present
(111)	odd	0	Reflections absent ×
(200)	even	$2f$	Reflections present
(210)	odd	0	Reflections absent ×
(220)	even	$2f$	Reflections present

Metallic sodium has a bcc structure. The diffraction pattern **does not contain lines such as (100), (300), (111), or (221)**, but lines such as **(200), (110), and (222) will be present**; here the indices $(v_1 \ v_2 \ v_3)$ are referred to a cubic cell.

What is the physical interpretation of the result that the (100) reflection vanishes?

The (100) reflection normally occurs when reflections from the planes that bound the cubic cell differ in phase by 2π . In the bcc lattice there is an intervening plane (as shown in figure) of atoms, labeled the second plane in the figure, which is equal in scattering power to the other planes. Situated midway between them, it gives a reflection retarded in phase by π with respect to the first plane, thereby canceling the contribution from that plane. The cancellation of the (100) reflection occurs in the bcc lattice because the planes are identical in composition.



Structure Factor of the fcc Lattice

The basis of the fcc structure referred to the cubic cell has identical atoms at $000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0$. Thus (46) becomes :

$$S_C(v_1 v_2 v_3) = \sum_j f_j \exp[-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)] \dots \dots \dots (46)$$

$$S_C(v_1 v_2 v_3) = S|_{000} + S|_{0\frac{1}{2}\frac{1}{2}} + S|_{\frac{1}{2}0\frac{1}{2}} + S|_{\frac{1}{2}\frac{1}{2}0}$$

$$S_C(v_1 v_2 v_3) = f_j \{1 + \exp[-i\pi(v_2 + v_3)] + \exp[-i\pi(v_1 + v_3)] + \exp[-i\pi(v_1 + v_2)]\}$$

- If all indices are even integers, $S = 4f$; similarly if all indices are odd integers.
- But if only one of the integers is even, two of the exponents will be odd multiples of π and S will vanish.
- If only one of the integers is odd, the same argument applies and S will also vanish.
- Thus in the fcc lattice no reflections can occur for which the indices are partly even and partly odd.
- **$S = 0$ when $(v_1 \& v_2 \& v_3) =$ If one of them different (even or odd) for the other two i.e., (mixed) = Reflections absent (reflection vanishes – cancellation)**
- **$S = 2f$ when $(v_1 \& v_2 \& v_3) =$ are even integers or are odd integers = Reflections present (reflection occurs)**

$S = 0$ when $(v_1 \& v_2 \& v_3)$ not all odd or all even = Reflections absent

$S = 2f$ when $(v_1 \& v_2 \& v_3)$ all odd or all even = Reflections present

Planes	$(v_1 \& v_2 \& v_3)$	S_C	Notes
(100)	mixed	0	Reflections absent ×
(110)	mixed	0	Reflections absent ×
(111)	are odd integers	$2f$	Reflections present
(200)	are even integers	$2f$	Reflections present
(210)	mixed	0	Reflections absent ×
(220)	are even integers	$2f$	Reflections present
(112)	mixed	0	Reflections absent ×

The point is beautifully illustrated by this figure: both KCl and KBr have an fcc lattice, but $n(\mathbf{r})$ for KCl simulates an sc lattice because the K^+ and Cl^- ions have equal numbers of electrons.

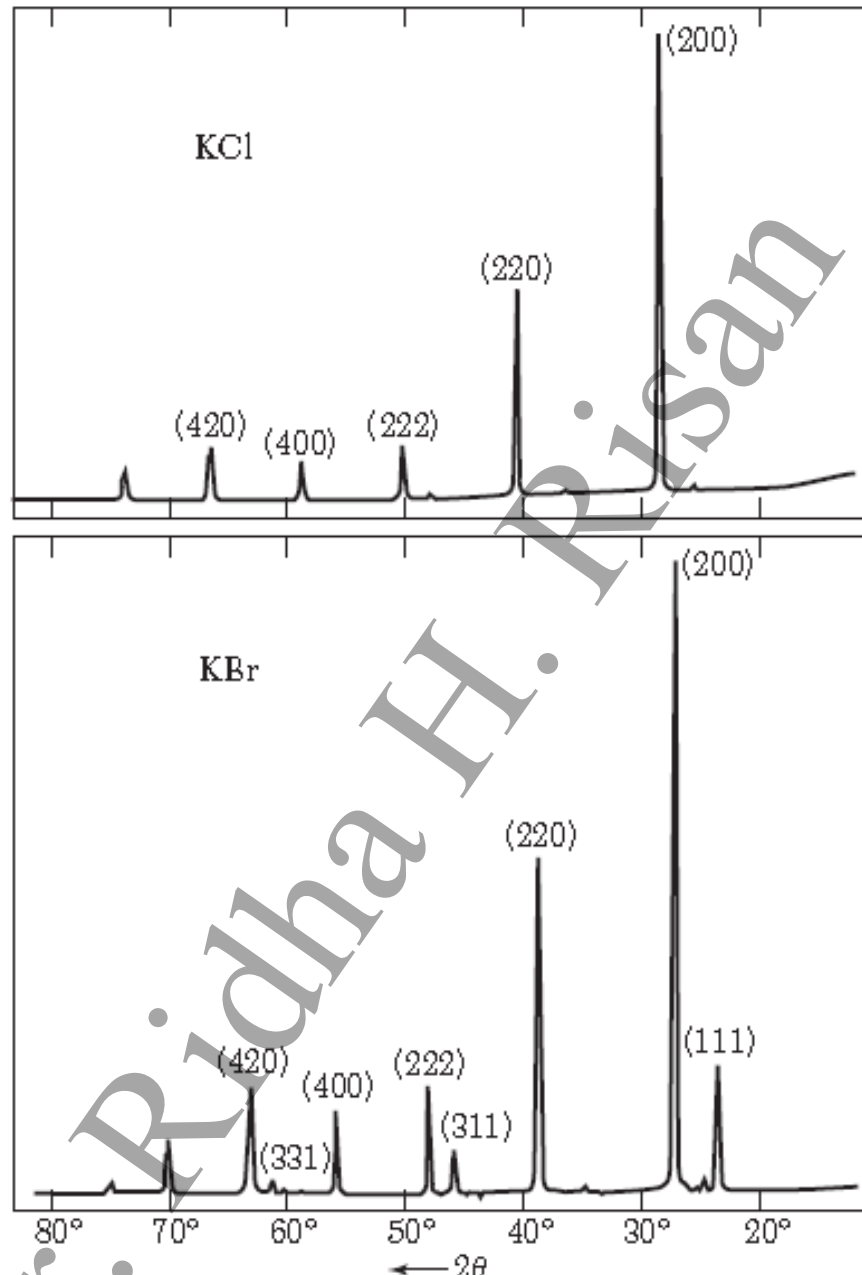


Figure Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(\text{K}^+)$ and $f(\text{Cl}^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a . In KBr the form factor of Br^- is quite different to that of K^+ , and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

Atomic Form Factor:

In the expression (46) for the structure factor, there occurs the quantity f_j , which is a measure of the scattering power of the j_{th} atom in the unit cell. The value of f involves the number and distribution of atomic electrons, and the wavelength and angle of scattering of the radiation. We now give a classical calculation of the scattering factor.

The scattered radiation from a single atom takes account of interference effects within the atom. We defined the form factor in (42):

$$f_j = \int dV n_j(\mathbf{r}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \dots \dots \dots (49)$$

with the integral extended over the electron concentration associated with a single atom. Let \mathbf{r} make an angle α with \mathbf{G} ; then $\mathbf{G} \cdot \mathbf{r} = Gr \cos \alpha$. If the electron distribution is spherically symmetric about the origin, then

$$f_j = 2\pi \int dr r^2 d(\cos \alpha) n_j(r) \exp[-iGr \cos \alpha]$$

$$f_j = 2\pi \int dr r^2 n_j(r) \frac{e^{iGr} - e^{-iGr}}{-iGr}$$

after integration over $d(\cos \alpha)$ between -1 and 1. Thus the form factor is given by

$$f_j = 4\pi \int dr n_j(r) r^2 \frac{\sin Gr}{Gr} \dots \dots \dots (50)$$

If the same total electron density were concentrated at $r = 0$, only $Gr = 0$ would contribute to the integrand. In this limit $\frac{\sin Gr}{Gr} = 1$, and

$$f_j = 4\pi \int dr n_j(r) r^2 = Z \dots \dots \dots (51)$$

the number of atomic electrons. Therefore f_j is the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by one electron localized at a point. In the forward direction $G = 0$, and f reduces again to the value Z .

The overall electron distribution in a solid as seen in x-ray diffraction is fairly close to that of the appropriate free atoms. This statement does not mean that the outermost or valence electrons are not redistributed somewhat in forming the solid; it means only that the x-ray reflection intensities are represented well by the free atom values of the form factors and are not very sensitive to small redistributions of the electrons.

Diffraction Conditions for Cubic Unit Cells:

The analysis of x-ray diffraction data for cubic unit cells can be simplified by $d_{hkl} = \frac{a}{\sqrt{(h^2+k^2+l^2)}}$ with the Bragg equation ($\lambda = 2d \sin \theta$) or $\left(d = \frac{\lambda}{2 \sin \theta}\right)$ giving $\lambda = \frac{2a \sin \theta}{\sqrt{(h^2+k^2+l^2)}}$.

This equation can be used along with x-ray diffraction data to determine if a cubic crystal structure is body-centered or face-centered cubic.

To use the last equation for diffraction analysis, we must know which crystal planes are the diffracting planes for each type of crystal structure. For the simple cubic lattice, reflections from all (hkl) planes are possible.

✓ However, for the BCC structure diffraction occurs only on planes whose Miller indices **when added together ($h + k + l$) total to an even number** (as shown in the table below. Thus, for the BCC crystal structure the principal diffracting planes are $\{110\}$, $\{200\}$, $\{211\}$, etc., which are listed in the table.

✓ In the case of the FCC crystal structure, the principal diffracting planes are those whose Miller indices **are either all even or all odd (zero is considered even)**. Thus, for the FCC crystal structure the diffracting planes are $\{111\}$, $\{200\}$, $\{220\}$, etc., which are listed in the table.

Table Rules for Determining the Diffracting $\{hkl\}$ Planes in Cubic Crystals

Bravais lattice	Reflections present	Reflections absent
BCC	$(h + k + l) = \text{even}$	$(h + k + l) = \text{odd}$
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

Table Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes $\{hkl\}$	$h^2 + k^2 + l^2$	Sum $\Sigma[h^2 + k^2 + l^2]$	Cubic diffracting planes $\{hkl\}$	
			FCC	BCC
$\{100\}$	$1^2 + 0^2 + 0^2$	1	...	110
$\{110\}$	$1^2 + 1^2 + 0^2$	2
$\{111\}$	$1^2 + 1^2 + 1^2$	3	111	...
$\{200\}$	$2^2 + 0^2 + 0^2$	4	200	200
$\{210\}$	$2^2 + 1^2 + 0^2$	5
$\{211\}$	$2^2 + 1^2 + 1^2$	6	...	211
...	...	7
$\{220\}$	$2^2 + 2^2 + 0^2$	8	220	220
$\{221\}$	$2^2 + 2^2 + 1^2$	9
$\{310\}$	$3^2 + 1^2 + 0^2$	10	...	310

Diffraction Conditions for Cubic Unit Cells:

The analysis of x-ray diffraction data for cubic unit cells can be simplified by combining: $\left\{d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}\right\}$ with Bragg equation $\{\lambda = 2d\sin\theta\}$. We get: $\left\{\lambda = \frac{2a\sin\theta}{\sqrt{h^2+k^2+l^2}}\right\}$. This equation can be used along with x-ray diffraction data to determine if a cubic crystal structure is body-centered or face-centered cubic. The rest of this subsection will describe how this is done.

Interpreting Experimental X-Ray Diffraction Data for Metals with Cubic Crystal Structures

By squaring both sides of $\left\{\lambda = \frac{2a\sin\theta}{\sqrt{h^2+k^2+l^2}}\right\}$ and solving for $\sin^2\theta$, we obtain

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

From x-ray diffraction data we can obtain experimental values of 2θ for a series of principal diffracting $\{hkl\}$ planes. Since the wavelength of the incoming radiation and the lattice constant a are both constants, we can eliminate these quantities by forming the ratio of two $\sin^2\theta$ values as

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h_A^2 + k_A^2 + l_A^2}{h_B^2 + k_B^2 + l_B^2}$$

where θ_A and θ_B are two diffracting angles associated with the principal diffracting planes $\{h_A k_A l_A\}$ and $\{h_B k_B l_B\}$, respectively.

Using last equation and the Miller indices of the first two sets of principal diffracting planes listed in Table for BCC and FCC crystal structures.

Table Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes $\{hkl\}$	$h^2 + k^2 + l^2$	Sum $\Sigma[h^2 + k^2 + l^2]$	Cubic diffracting planes $\{hkl\}$	
			FCC	BCC
$\{100\}$	$1^2 + 0^2 + 0^2$	1		
$\{110\}$	$1^2 + 1^2 + 0^2$	2	...	110
$\{111\}$	$1^2 + 1^2 + 1^2$	3	111	
$\{200\}$	$2^2 + 0^2 + 0^2$	4	200	200
$\{210\}$	$2^2 + 1^2 + 0^2$	5		
$\{211\}$	$2^2 + 1^2 + 1^2$	6	...	211
...		7		
$\{220\}$	$2^2 + 2^2 + 0^2$	8	220	220
$\{221\}$	$2^2 + 2^2 + 1^2$	9		
$\{310\}$	$3^2 + 1^2 + 0^2$	10	...	310

We can determine values for the $\sin^2\theta$ ratios for both BCC and FCC structures. For the BCC crystal structure the first two sets of principal diffracting planes are the $\{110\}$ and $\{200\}$ planes (Table). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. $\left\{\left(\frac{\sin \theta_A}{\sin \theta_B}\right)^2 = \frac{h_A^2+k_A^2+l_A^2}{h_B^2+k_B^2+l_B^2}\right\}$ gives

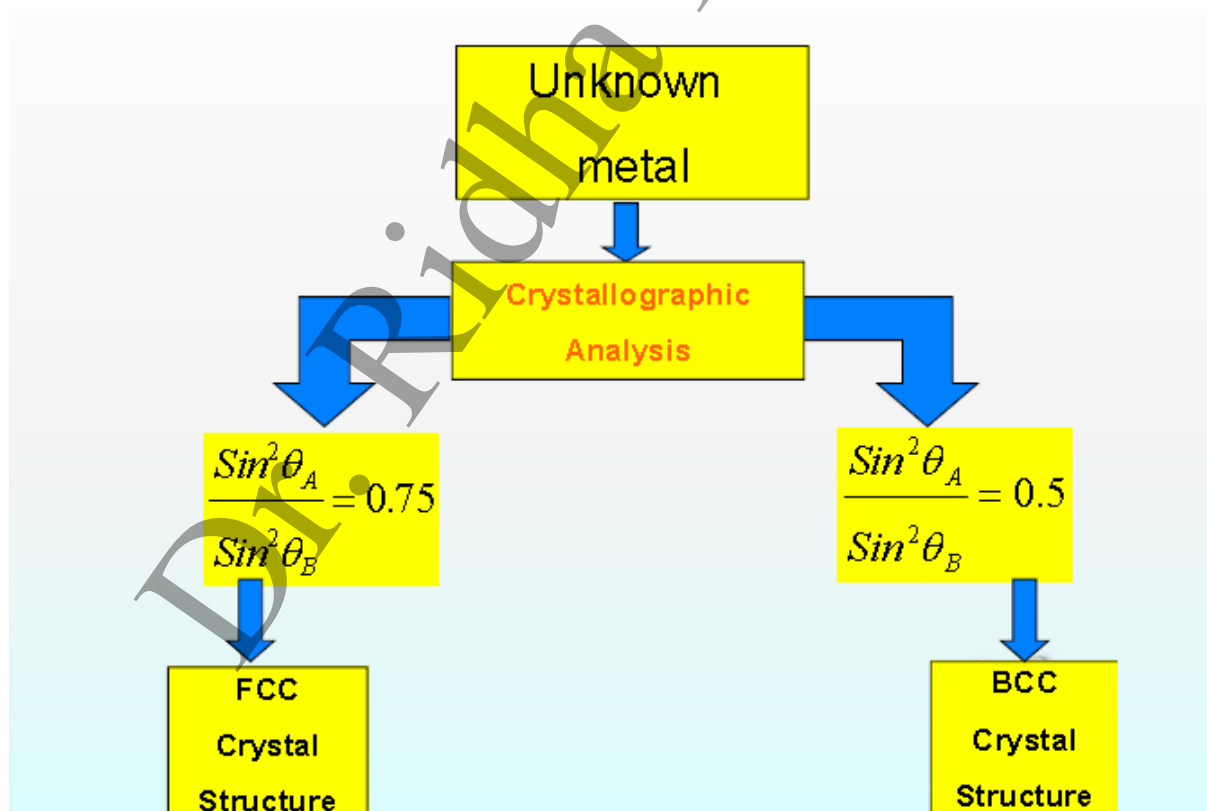
$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{1^2 + 1^2 + 0^2}{2^2 + 0^2 + 0^2} = 0.5$$

Thus, if the crystal structure of the unknown cubic metal is BCC, the ratio of the $\sin^2\theta$ values that correspond to the first two principal diffracting planes will be 0.5.

For the FCC crystal structure the first two sets of principal diffracting planes are the $\{111\}$ and $\{200\}$ planes (Table). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. $\left\{\left(\frac{\sin \theta_A}{\sin \theta_B}\right)^2 = \frac{h_A^2+k_A^2+l_A^2}{h_B^2+k_B^2+l_B^2}\right\}$ gives

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{1^2 + 1^2 + 1^2}{2^2 + 0^2 + 0^2} = 0.75$$

Thus, if the crystal structure of the unknown cubic metal is FCC, the ratio of the $\sin^2\theta$ values that correspond to the first two principal diffracting planes will be 0.75.



Problem:

An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure shows diffraction peaks at the following 2θ angles: 40, 58, 73, 100.4, 86.8, and 114.7. The wavelength of the incoming x-ray used was 0.154 nm.

- Determine the cubic structure of the element.
- Determine the lattice constant of the element.
- Identify the element.

■ Solution

- (a) *Determination of the crystal structure of the element.* First, the $\sin^2 \theta$ values are calculated from the 2θ diffraction angles.

$2\theta(\text{deg})$	$\theta(\text{deg})$	$\sin \theta$	$\sin^2 \theta$
40	20	0.3420	0.1170
58	29	0.4848	0.2350
73	36.5	0.5948	0.3538
86.8	43.4	0.6871	0.4721
100.4	50.2	0.7683	0.5903
114.7	57.35	0.8420	0.7090

Next the ratio of the $\sin^2 \theta$ values of the first and second angles is calculated:

$$\frac{\sin^2 \theta}{\sin^2 \theta} = \frac{0.117}{0.235} = 0.498 \approx 0.5$$

The crystal structure is BCC since this ratio is ≈ 0.5 . If the ratio had been ≈ 0.75 , the structure would have been FCC.

- (b) *Determination of the lattice constant.* Rearranging Eq. 3.12 and solving for a^2 gives

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

or

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

Substituting into Eq. 3.17 $h = 1$, $k = 1$, and $l = 0$ for the h, k, l Miller indices of the first set of principal diffracting planes for the BCC crystal structure, which are the $\{110\}$ planes, the corresponding value for $\sin^2 \theta$, which is 0.117, and 0.154 nm for λ , the incoming radiation, gives

$$a = \frac{0.154 \text{ nm}}{2} \sqrt{\frac{1^2 + 1^2 + 0^2}{0.117}} = 0.318 \text{ nm} \blacktriangleleft$$

- (c) *Identification of the element.* The element is tungsten since this element has a lattice constant of 0.316 nm and is BCC.

Q.1) Explain how with the help of X-ray diffraction techniques, the lattice dimensions are determined.

Q.2) Write short notes on

(i) Bragg's law. (ii) Electron and neutron diffraction.

Q.3) Discuss Bragg's law of X-ray diffraction. Describe how the powder method is used for the determination of crystal structure.

Q.4) State and explain the Bragg's law of X-ray diffraction. What are its uses?

Q.5) Derive Bragg's law by using the simple case of incident x-ray beams being diffracted by parallel planes in a crystal.

Q.6) Name the three most important kinds of probes used in diffraction experiments on crystal. (Hint: See figure page "50" in the lectures). *Discuss* the essential condition that the wavelength of each probe must satisfy if it is to be useful in understanding crystal structure.

Q.7): Briefly (in a few English sentences) *Define or Explain* the following terms:

- (1) Reciprocal Lattice.**
- (2) Reciprocal Lattice Vector**
- (3) Brillouin Zones**
- (4) Structure Factor**
- (5) Atomic Form Factor**
- (6) Bragg's law of Diffraction**
- (7) Laue Condition (Laue Equations)**
- (8) Ewald construction**

Q.8): Derive Reciprocal Lattice to sc Lattice

Q.9): Derive Reciprocal Lattice to bcc Lattice

Q.10): Reciprocal Lattice to fcc Lattice

Q.11) Consider a crystal with the simple cubic (SC) lattice structure. The primitive lattice vectors are $\vec{a}_1 = a\hat{x}$; $\vec{a}_2 = a\hat{y}$; $\vec{a}_3 = a\hat{z}$ where a is the lattice constant and $\hat{x}, \hat{y}, \hat{z}$ are the usual unit vectors for a Cartesian coordinate system. Prove that the reciprocal lattice is simple cubic also.

Ans. : page "69" in the lectures

Kittel - ch. 2 - Q.1 : Interplanar separation. Consider a plane hkl in a crystal lattice. (a) Prove that the reciprocal lattice vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is perpendicular to this plane. (b) Prove that the distance between two adjacent parallel planes of the lattice is $d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|}$. (c) Show for a simple

cubic lattice that $d^2 = \frac{a^2}{(h^2+k^2+l^2)}$.

Solution:

To prove that the reciprocal lattice vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is perpendicular to this plane, it suffices to show that G is perpendicular to two nonparallel vectors in this plane. The crystal plane with Miller indices hkl is a plane defined by the intercept points $\frac{a_1}{h}, \frac{a_2}{k}, \text{ and } \frac{a_3}{l}$. Two vectors that lie in the plane may be taken as $(\frac{a_1}{h} - \frac{a_2}{k})$ and $(\frac{a_1}{h} - \frac{a_3}{l})$. But each of these vectors gives zero as its scalar product with $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$, so that \vec{G} must be perpendicular to the plane hkl .

If we prove that

$$\vec{G} \cdot \left(\frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k} \right) = 0 \quad \rightarrow \quad (\theta = 0) \quad \rightarrow \quad (\vec{G} \perp \text{plane } hkl)$$

$$\begin{aligned} \vec{G} \cdot \left(\frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k} \right) &= (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot \left(\frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k} \right) \\ &= \frac{h}{h} (\vec{b}_1 \cdot \vec{a}_1) - \frac{h}{k} (\vec{b}_1 \cdot \vec{a}_2) + \frac{k}{h} (\vec{b}_2 \cdot \vec{a}_1) - \frac{k}{k} (\vec{b}_2 \cdot \vec{a}_2) + \frac{l}{h} (\vec{b}_3 \cdot \vec{a}_1) \\ &\quad - \frac{l}{k} (\vec{b}_3 \cdot \vec{a}_2) \end{aligned}$$

But $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$ where $(\delta_{ij} = 1 \text{ if } i = j) \& (\delta_{ij} = 0 \text{ if } i \neq j)$

$$\vec{b}_1 \cdot \vec{a}_1 = 2\pi, \quad \vec{b}_2 \cdot \vec{a}_1 = 0, \quad \vec{b}_3 \cdot \vec{a}_1 = 0$$

$$\vec{b}_1 \cdot \vec{a}_2 = 0, \quad \vec{b}_2 \cdot \vec{a}_2 = 2\pi, \quad \vec{b}_3 \cdot \vec{a}_2 = 0$$

$$\vec{b}_1 \cdot \vec{a}_3 = 0, \quad \vec{b}_2 \cdot \vec{a}_3 = 0, \quad \vec{b}_3 \cdot \vec{a}_3 = 2\pi$$

$$\therefore \vec{G} \cdot \left(\frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k} \right) = 0$$

$$\text{Similarly } \vec{G} \cdot \left(\frac{\vec{a}_1}{h} - \frac{\vec{a}_3}{l} \right) = 0$$

so that \vec{G} must be perpendicular to the plane hkl .

Kittel - ch. 2 - Q.1 – (b) Prove that the distance between two adjacent parallel planes of the lattice is $d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|}$.

See: solid state physics by BLAKMORE – Page: 69-70)

If \hat{n} is the unit normal to the plane, the interplanar spacing is $\left(\frac{\hat{n} \cdot \vec{a}_1}{h}\right)$ & $\left(\hat{n} = \frac{\vec{G}}{|\vec{G}|}\right)$.

Referring to figure, we can see that both \vec{G}_{hkl} and the vector from the origin of direct space to the (hkl) plane can be expressed as multiples of a unit vector \hat{n} . The equation of the (hkl) plane is that

$$d_{hkl} = \vec{r} \cdot \hat{n} = \vec{r} \cdot \frac{\vec{G}_{hkl}}{|\vec{G}_{hkl}|}$$

For any vector \vec{r} whose magnitude is larger than d_{hkl} , and the vector (\vec{a}_1/h) obviously qualifies as being of adequate length. Thus

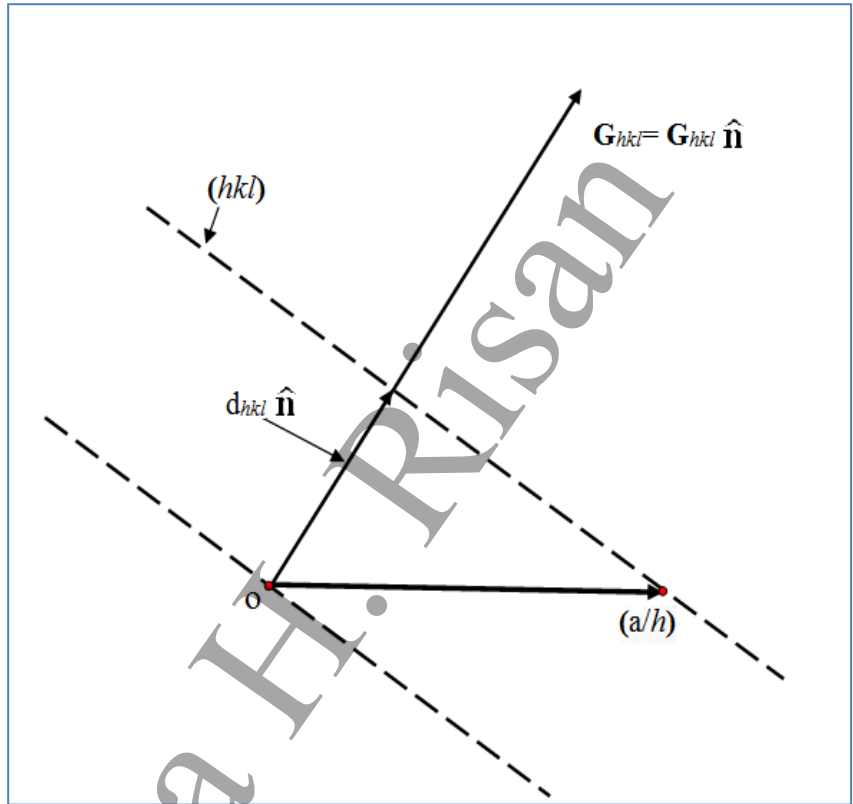
$$d_{hkl} = \frac{\vec{a}_1 \cdot \vec{G}_{hkl}}{h|\vec{G}_{hkl}|} = \frac{\vec{a}_1 \cdot (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)}{h|\vec{G}_{hkl}|}$$

$$d_{hkl} = \frac{h(\vec{a}_1 \cdot \vec{b}_1) + k(\vec{a}_1 \cdot \vec{b}_2) + l(\vec{a}_1 \cdot \vec{b}_3)}{h|\vec{G}_{hkl}|} = \frac{h(2\pi) + k(0) + l(0)}{h|\vec{G}_{hkl}|}$$

But $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$ where $(\delta_{ij} = 1 \text{ if } i = j)$ & $(\delta_{ij} = 0 \text{ if } i \neq j)$

$$\vec{b}_1 \cdot \vec{a}_1 = 2\pi, \quad \vec{b}_2 \cdot \vec{a}_1 = 0, \quad \vec{b}_3 \cdot \vec{a}_1 = 0$$

$$d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|}$$



Kittel - ch. 2 - Q.1- (c) Show for a simple cubic lattice that $d^2 = \frac{a^2}{(h^2+k^2+l^2)}$.

For simple cubic (SC) lattice

$$\vec{\mathbf{b}}_1 = \frac{2\pi}{a} \hat{\mathbf{x}}$$

$$\vec{\mathbf{b}}_2 = \frac{2\pi}{a} \hat{\mathbf{y}}$$

$$\vec{\mathbf{b}}_3 = \frac{2\pi}{a} \hat{\mathbf{z}}$$

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

$$\vec{\mathbf{G}} = \left(h \frac{2\pi}{a}\right) \hat{\mathbf{x}} + \left(k \frac{2\pi}{a}\right) \hat{\mathbf{y}} + \left(l \frac{2\pi}{a}\right) \hat{\mathbf{z}} \quad \text{for sc}$$

$$|\vec{\mathbf{G}}| = \sqrt{\left(\frac{2\pi h}{a}\right)^2 + \left(\frac{2\pi k}{a}\right)^2 + \left(\frac{2\pi l}{a}\right)^2} = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}$$

$$d_{hkl} = \frac{2\pi}{|\vec{\mathbf{G}}_{hkl}|} = \frac{2\pi}{\frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}}$$

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

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

Kittel - ch. 2 - Q.2 : Hexagonal space lattice. The primitive translation vectors of the hexagonal space lattice may be taken as

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}a}{2}\right)\hat{x} + \left(\frac{a}{2}\right)\hat{y} \quad ; \quad \mathbf{a}_2 = \left(\frac{-\sqrt{3}a}{2}\right)\hat{x} + \left(\frac{a}{2}\right)\hat{y} \quad ; \quad \mathbf{a}_3 = c\hat{z}$$

(a) Show that the volume of the primitive cell is $\left(\frac{\sqrt{3}a^2c}{2}\right)$.

(b) Show that the primitive translations of the reciprocal lattice are

$$\mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}\right)\hat{x} + \left(\frac{2\pi}{a}\right)\hat{y} \quad ; \quad \mathbf{b}_2 = \left(\frac{-2\pi}{\sqrt{3}a}\right)\hat{x} + \left(\frac{2\pi}{a}\right)\hat{y} \quad ; \quad \mathbf{b}_3 = \frac{2\pi}{c}\hat{z}$$

so that the lattice is its own reciprocal, but with a rotation of axes.

(c) Describe and sketch the first Brillouin zone of the hexagonal space lattice.

Solution:

$$\text{Volume of primitive cell} = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

$$\vec{a}_2 \times \vec{a}_3 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix}$$

$$\vec{a}_2 \times \vec{a}_3 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix} = \begin{vmatrix} \hat{x} & \hat{y} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix}$$

$$\vec{a}_2 \times \vec{a}_3 = \left(\frac{ac}{2}\hat{x} - 0\right) + \left[0 - \frac{-\sqrt{3}ac}{2}\right] + (0 - 0)$$

$$\vec{a}_2 \times \vec{a}_3 = \frac{ac}{2}\hat{x} + \frac{\sqrt{3}ac}{2}\hat{y}$$

$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \left[\left(\frac{\sqrt{3}a}{2}\right)\hat{x} + \left(\frac{a}{2}\right)\hat{y}\right] \cdot \left(\frac{ac}{2}\hat{x} + \frac{\sqrt{3}ac}{2}\hat{y}\right)$$

\therefore

$$\hat{x} \cdot \hat{x} = |\hat{x}||\hat{x}|\cos 0 = 1$$

$$\hat{x} \cdot \hat{y} = |\hat{x}||\hat{y}|\cos 90 = 0$$

$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \left(\frac{\sqrt{3}a}{2}\right)\left(\frac{a}{2}\right) + \left(\frac{a}{2}\right)\left(\frac{\sqrt{3}ac}{2}\right)$$

$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \left(\frac{\sqrt{3}a^2c}{4}\right) + \left(\frac{\sqrt{3}a^2c}{4}\right) = \frac{2\sqrt{3}a^2c}{4}$$

$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{\sqrt{3}a^2c}{2}$$

Kittel - ch. 2 - Q.2 : Hexagonal space lattice. (b) Show that the primitive translations of the reciprocal lattice are

$$\mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}\right)\hat{x} + \left(\frac{2\pi}{a}\right)\hat{y} \quad ; \quad \mathbf{b}_2 = \left(\frac{-2\pi}{\sqrt{3}a}\right)\hat{x} + \left(\frac{2\pi}{a}\right)\hat{y} \quad ; \quad \mathbf{b}_3 = \frac{2\pi}{c}\hat{z}$$

so that the lattice is its own reciprocal, but with a rotation of axes.

Solution:

$$\vec{\mathbf{b}}_1 = 2\pi \frac{\vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3}{\vec{\mathbf{a}}_1 \cdot \vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3} \quad ; \quad \vec{\mathbf{b}}_2 = 2\pi \frac{\vec{\mathbf{a}}_3 \times \vec{\mathbf{a}}_1}{\vec{\mathbf{a}}_1 \cdot \vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3} \quad ; \quad \vec{\mathbf{b}}_3 = 2\pi \frac{\vec{\mathbf{a}}_1 \times \vec{\mathbf{a}}_2}{\vec{\mathbf{a}}_1 \cdot \vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3}$$

$$\vec{\mathbf{a}}_1 \cdot (\vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3) = \frac{\sqrt{3}a^2c}{2}$$

$$\& \vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix}$$

$$\vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix} = \begin{vmatrix} \hat{x} & \hat{y} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix} + \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} + \begin{vmatrix} \hat{x} & \hat{y} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix}$$

$$\vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3 = \left(\frac{ac}{2} - 0\right)\hat{x} + \left[0 - \frac{-\sqrt{3}ac}{2}\right]\hat{y} + (0 - 0)\hat{z}$$

$$\vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3 = \frac{ac}{2}\hat{x} + \frac{\sqrt{3}ac}{2}\hat{y}$$

$$\vec{\mathbf{b}}_1 = 2\pi \frac{\vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3}{\vec{\mathbf{a}}_1 \cdot \vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3} = 2\pi \frac{\left(\frac{ac}{2}\hat{x} + \frac{\sqrt{3}ac}{2}\hat{y}\right)}{\left(\frac{\sqrt{3}a^2c}{2}\right)}$$

$$\therefore \mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}\right)\hat{x} + \left(\frac{2\pi}{a}\right)\hat{y}$$

$$\vec{\mathbf{b}}_2 = 2\pi \frac{\vec{\mathbf{a}}_3 \times \vec{\mathbf{a}}_1}{\vec{\mathbf{a}}_1 \cdot \vec{\mathbf{a}}_2 \times \vec{\mathbf{a}}_3}$$

$$\vec{\mathbf{a}}_3 \times \vec{\mathbf{a}}_1 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 0 & c \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \end{vmatrix}$$

$$\vec{\mathbf{a}}_3 \times \vec{\mathbf{a}}_1 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 0 & c \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \end{vmatrix} = \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix} + \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} + \begin{vmatrix} \hat{x} & \hat{y} \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix} \begin{vmatrix} \hat{x} & \hat{y} \\ 0 & 0 \end{vmatrix}$$

$$\vec{\mathbf{a}}_3 \times \vec{\mathbf{a}}_1 = \left(\frac{-ac}{2}\right)\hat{x} + \left(\frac{\sqrt{3}ac}{2}\right)\hat{y}$$

$$\vec{b}_2 = 2\pi \frac{\left(\frac{-ac}{2}\right)\hat{x} + \left(\frac{\sqrt{3}ac}{2}\right)\hat{y}}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad \& \quad \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{\sqrt{3}a^2c}{2}$$

$$\vec{b}_2 = 2\pi \frac{\left(\frac{-ac}{2}\right)\hat{x} + \left(\frac{\sqrt{3}ac}{2}\right)\hat{y}}{\frac{\sqrt{3}a^2c}{2}}$$

$$\vec{b}_2 = \frac{\left(\frac{-2\pi ac}{2}\right)\hat{x} + \left(\frac{2\pi\sqrt{3}ac}{2}\right)\hat{y}}{\frac{\sqrt{3}a^2c}{2}} = \frac{(-\pi ac)\hat{x} + (\pi\sqrt{3}ac)\hat{y}}{\frac{\sqrt{3}a^2c}{2}}$$

$$\therefore b_2 = \left(\frac{-2\pi}{\sqrt{3}a}\right)\hat{x} + \left(\frac{2\pi}{a}\right)\hat{y}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad \vec{a}_1 \times \vec{a}_2 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} & c \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \end{vmatrix}$$

$$\vec{a}_1 \times \vec{a}_2 = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \end{vmatrix} = \begin{vmatrix} \hat{x} & \hat{y} \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} \end{vmatrix}$$

$$\vec{a}_1 \times \vec{a}_2 = 0 + 0 + \left(\frac{\sqrt{3}a^2}{4} - \frac{-\sqrt{3}a^2}{4}\right)\hat{z}$$

$$\vec{a}_1 \times \vec{a}_2 = \left(\frac{\sqrt{3}a^2}{4} + \frac{\sqrt{3}a^2}{4}\right)\hat{z} = \left(\frac{\sqrt{3}a^2}{2}\right)\hat{z}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = 2\pi \frac{\left(\frac{\sqrt{3}a^2}{2}\right)\hat{z}}{\frac{\sqrt{3}a^2c}{2}} = 2\pi \frac{\left(\frac{\sqrt{3}a^2}{2}\right)\hat{z}}{\frac{\sqrt{3}a^2c}{2}}$$

$$b_3 = \frac{2\pi}{c}\hat{z}$$

Kittel - ch. 2 - Q.3 : Volume of Brillouin zone. Show that the volume of the first Brillouin zone is $\left\{\frac{(2\pi)^3}{V_c}\right\}$ where V_c is the volume of a crystal primitive cell.

Hint: The volume of a Brillouin zone is equal to the volume of the primitive parallelepiped in Fourier space. Recall the vector identity

$$(c \times a) \times (a \times b) = (c \cdot a \times b)a.$$

$$\text{i.e., : } (a_3 \times a_1) \times (a_1 \times a_2) = (a_3 \cdot a_1 \times a_2)a_1$$

solution:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} ; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} ; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\begin{aligned} V_{B.Z} &= \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \\ &= \left(2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}\right) \cdot \left(2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}\right) \times \left(2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}\right) \end{aligned}$$

$$V_{B.Z} = \left\{ \frac{(2\pi)^3}{(\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3)^3} \right\} [(\vec{a}_2 \times \vec{a}_3) \cdot (\vec{a}_3 \times \vec{a}_1) \times (\vec{a}_1 \times \vec{a}_2)]$$

$$\because (c \times a) \times (a \times b) = (c \cdot a \times b)a.$$

$$\text{i.e., : } (a_3 \times a_1) \times (a_1 \times a_2) = (a_3 \cdot a_1 \times a_2)a_1$$

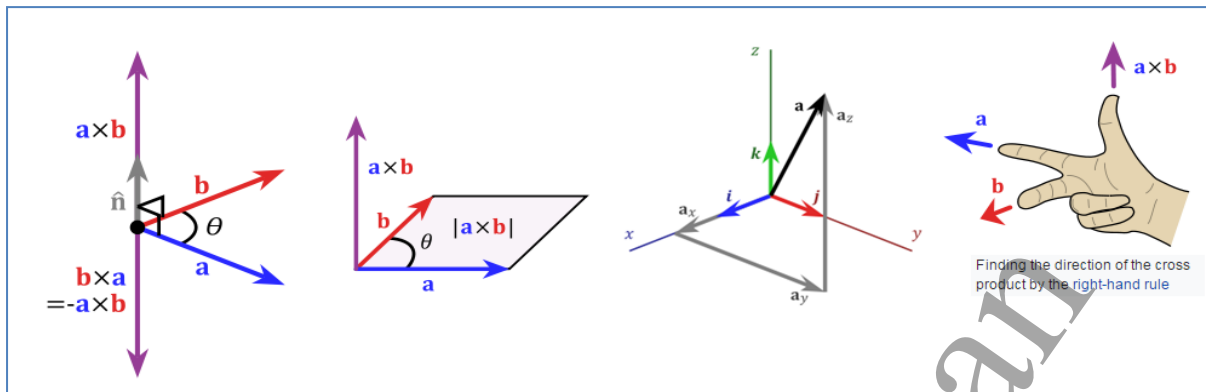
$$V_{B.Z} = \left\{ \frac{(2\pi)^3}{(\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3)^3} \right\} [(\vec{a}_2 \times \vec{a}_3) \cdot \{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2\} \vec{a}_1]$$

$$\begin{aligned} V_c = \text{Volume of primitive cell} &= \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = a_3 \cdot a_1 \times a_2 \\ &= a_2 \cdot a_3 \times a_1 = \text{Scalure quantity} \end{aligned}$$

$$V_{B.Z} = \left\{ \frac{(2\pi)^3}{\{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3\}^3} \right\} [\{(\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1\} \{ \vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2 \}]$$

$$V_{B.Z} = \frac{(2\pi)^3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

Remember



This little cycle diagram can help you remember these results.

$$\begin{array}{lcl} \mathbf{i} \times \mathbf{j} = \mathbf{k} & \mathbf{j} \times \mathbf{i} = -\mathbf{k} \\ \mathbf{j} \times \mathbf{k} = \mathbf{i} & \mathbf{k} \times \mathbf{j} = -\mathbf{i} \\ \mathbf{k} \times \mathbf{i} = \mathbf{j} & \mathbf{i} \times \mathbf{k} = -\mathbf{j} \end{array}$$

$$\mathbf{a} = (a_1, a_2, a_3) = a_1\mathbf{i} + a_2\mathbf{j} + a_3\mathbf{k}$$

$$\mathbf{b} = (b_1, b_2, b_3) = b_1\mathbf{i} + b_2\mathbf{j} + b_3\mathbf{k}$$

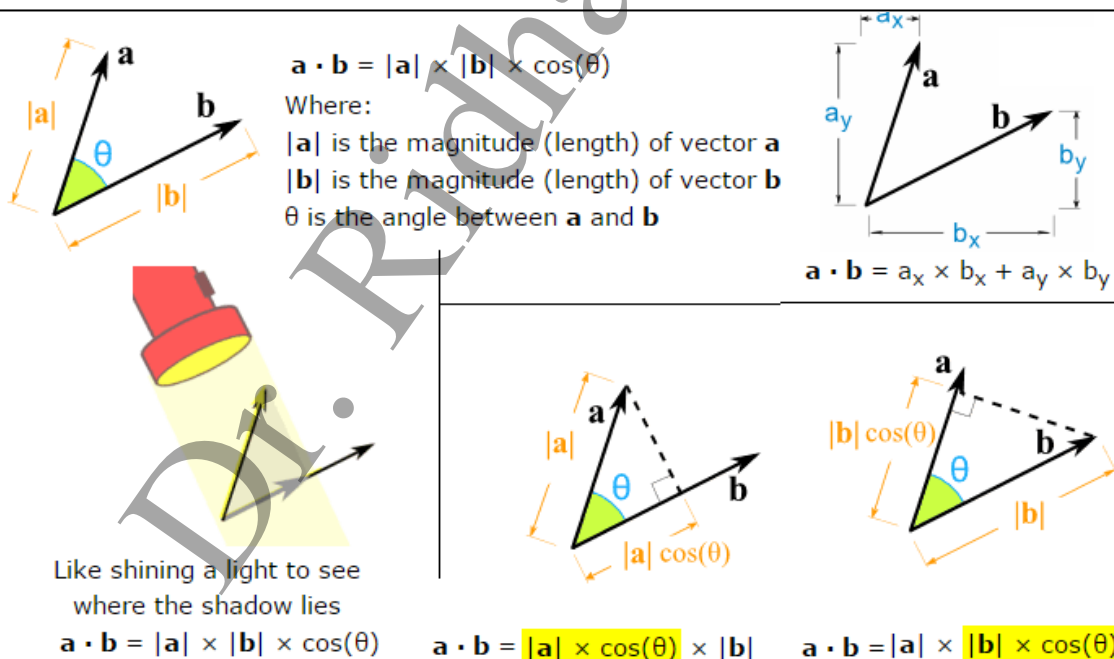
$$\begin{aligned} \mathbf{a} \times \mathbf{b} &= (a_1\mathbf{i} + a_2\mathbf{j}) \times (b_1\mathbf{i} + b_2\mathbf{j}) \\ &= a_1b_1(\mathbf{i} \times \mathbf{i}) + a_1b_2(\mathbf{i} \times \mathbf{j}) + a_2b_1(\mathbf{j} \times \mathbf{i}) + a_2b_2(\mathbf{j} \times \mathbf{j}) \end{aligned}$$

$$\mathbf{i} \times \mathbf{i} = \mathbf{0} = \mathbf{j} \times \mathbf{j} \text{ and that } \mathbf{i} \times \mathbf{j} = \mathbf{k} = -\mathbf{j} \times \mathbf{i},$$

$$\begin{aligned} \mathbf{a} \times \mathbf{b} &= (a_1b_2 - a_2b_1)\mathbf{k} \\ &= \begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} \mathbf{k}. \end{aligned}$$

$$\begin{aligned} \mathbf{a} \times \mathbf{b} &= (a_1\mathbf{i} + a_2\mathbf{j} + a_3\mathbf{k}) \times (b_1\mathbf{i} + b_2\mathbf{j} + b_3\mathbf{k}) \\ &= a_1b_1(\mathbf{i} \times \mathbf{i}) + a_1b_2(\mathbf{i} \times \mathbf{j}) + a_1b_3(\mathbf{i} \times \mathbf{k}) \\ &\quad + a_2b_1(\mathbf{j} \times \mathbf{i}) + a_2b_2(\mathbf{j} \times \mathbf{j}) + a_2b_3(\mathbf{j} \times \mathbf{k}) \\ &\quad + a_3b_1(\mathbf{k} \times \mathbf{i}) + a_3b_2(\mathbf{k} \times \mathbf{j}) + a_3b_3(\mathbf{k} \times \mathbf{k}) \\ \mathbf{a} \times \mathbf{b} &= a_1b_2\mathbf{k} - a_1b_3\mathbf{j} - a_2b_1\mathbf{k} + a_2b_3\mathbf{i} + a_3b_1\mathbf{j} - a_3b_2\mathbf{i} \\ &= (a_2b_3 - a_3b_2)\mathbf{i} - (a_1b_3 - a_3b_1)\mathbf{j} + (a_1b_2 - a_2b_1)\mathbf{k}. \end{aligned}$$

$$\mathbf{a} \times \mathbf{b} = \begin{vmatrix} a_2 & a_3 \\ b_2 & b_3 \end{vmatrix} \mathbf{i} - \begin{vmatrix} a_1 & a_3 \\ b_1 & b_3 \end{vmatrix} \mathbf{j} + \begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} \mathbf{k}.$$



The dot or scalar product $\Rightarrow \mathbf{A} \cdot \mathbf{B} = |\mathbf{A}| \cdot |\mathbf{B}| \cdot \cos \Theta$

Where $|\mathbf{A}|$ and $|\mathbf{B}|$ represents the magnitudes of vectors \mathbf{A} and \mathbf{B} and Θ is the angle between vectors \mathbf{A} and \mathbf{B} .

$\mathbf{A} = a_1\mathbf{i} + a_2\mathbf{j}$ and $\mathbf{B} = b_1\mathbf{i} + b_2\mathbf{j} \Rightarrow \mathbf{A} \cdot \mathbf{B} = a_1 \cdot b_1 + a_2 \cdot b_2$

Chapter Three: (Lattice Dynamics)

1- Lattice Vibration

Elastic Waves

2- Vibrational Modes of Linear Monatomic Lattice

First Brillouin Zone

Phase and Group Velocity

3- Diatomic Linear Lattice (Two Atoms per Primitive Basis)

Vibrational Modes of Diatomic Linear Lattice

4- Acoustic Phonon Branch

5- Optical Phonon Branch






6- Quantization of Elastic Waves

Phonon Momentum

7- Inelastic Scattering by Phonons

Note: Correct typing error in (ch. 4) "*Introduction to Solid State Physics*" by Charles Kittel, 8th Edition:

- ➡ In page 97, Eq. (19), Left side equation should be v_s not v_2 .
- ➡ In page 98, Eq. (21), upper right matrix entry should be $-C(1+e^{-ika})$; the minus sign is missing in the exponent.
- ➡ In page 104, the minus sign between ω^2/ω_0^2 and the sine-squared term should be an equals sign; also, below the summation sign, $p-1$ should be $p=1$.

	Name	Field
	Electron	—
	Photon	Electromagnetic wave
	Phonon	Elastic wave
	Plasmon	Collective electron wave
	Magnon	Magnetization wave
—	Polaron	Electron + elastic deformation
—	Exciton	Polarization wave

Important elementary excitations in solids.

1-lattice Vibration:

In studying crystal structures in the last two chapters, we have assumed that the atoms were at rest at their lattice sites. Atoms, however, are not quite stationary, but oscillate around their equilibrium positions as a result of thermal energy. Let us now discuss these lattice vibrations in detail .

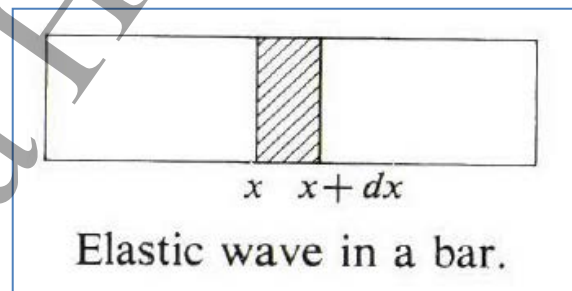
Consider the elastic vibrations of a crystal with one atom in the primitive cell. We want to find the frequency of an elastic wave in terms of the wavevector that describes the wave and in terms of the elastic constants.

The mathematical solution is simplest in the [100], [110], and [111] propagation directions in cubic crystals. These are the directions of the cube edge, face diagonal, and body diagonal. When a wave propagates along one of these directions, entire planes of atoms move in phase with displacements either parallel or perpendicular to the direction of the wavevector.

ELASTIC WAVES:

A solid is composed of discrete atoms, and this discreteness must be taken into account in the discussion of lattice vibrations. However, when the wave length is very long, one may disregard the atomic nature and treat the solid as a continuous medium. Such vibrations are referred to as *elastic waves*.

Let us now examine the propagation of an elastic wave in a sample in the shape of a long bar.



Suppose that the wave is longitudinal, and denote the elastic displacement at the point x by $u(x)$. The strain is defined as $\left\{e = \frac{du}{dx}\right\}$ which is the change of length per unit length. The stress (S) is defined as the force per unit area, and is also a function of x . According to *Hooke's law*, the stress is proportional to the strain. That is,

$$S = Ye$$

where the elastic constant Y is known as *Young's modulus*.

To examine the dynamics of the bar, we choose an arbitrary segment of length dx , as shown in the figure. Using *Newton's second law*, we can write for the motion of this segment:

$$(\rho A dx) \frac{\partial^2 u}{\partial x^2} = [S(x + dx) - S(x)]A \dots \dots \dots (*)$$

where ρ is the mass density and A the cross-sectional area of the bar. The term on the left is simply the mass times the acceleration, while that on the right is the net force resulting from the stresses at the ends of the segment. Writing $S(x + dx) - S(x) = \partial S / \partial x dx$ for a short segment, substituting for

$S = Ye$, and then using $\left\{e = \frac{du}{dx}\right\}$ for the strain, one can rewrite the dynamical equation (*) as

$$\frac{\partial^2 y}{\partial x^2} - \frac{\rho}{Y} \frac{\partial^2 y}{\partial t^2} = 0 \dots \dots \dots (*)$$

which is the well-known *waue equation in one dimension*.

We now attempt a solution in the form of a propagating plane wave

$$u = Ae^{i(Kx - \omega t)}$$

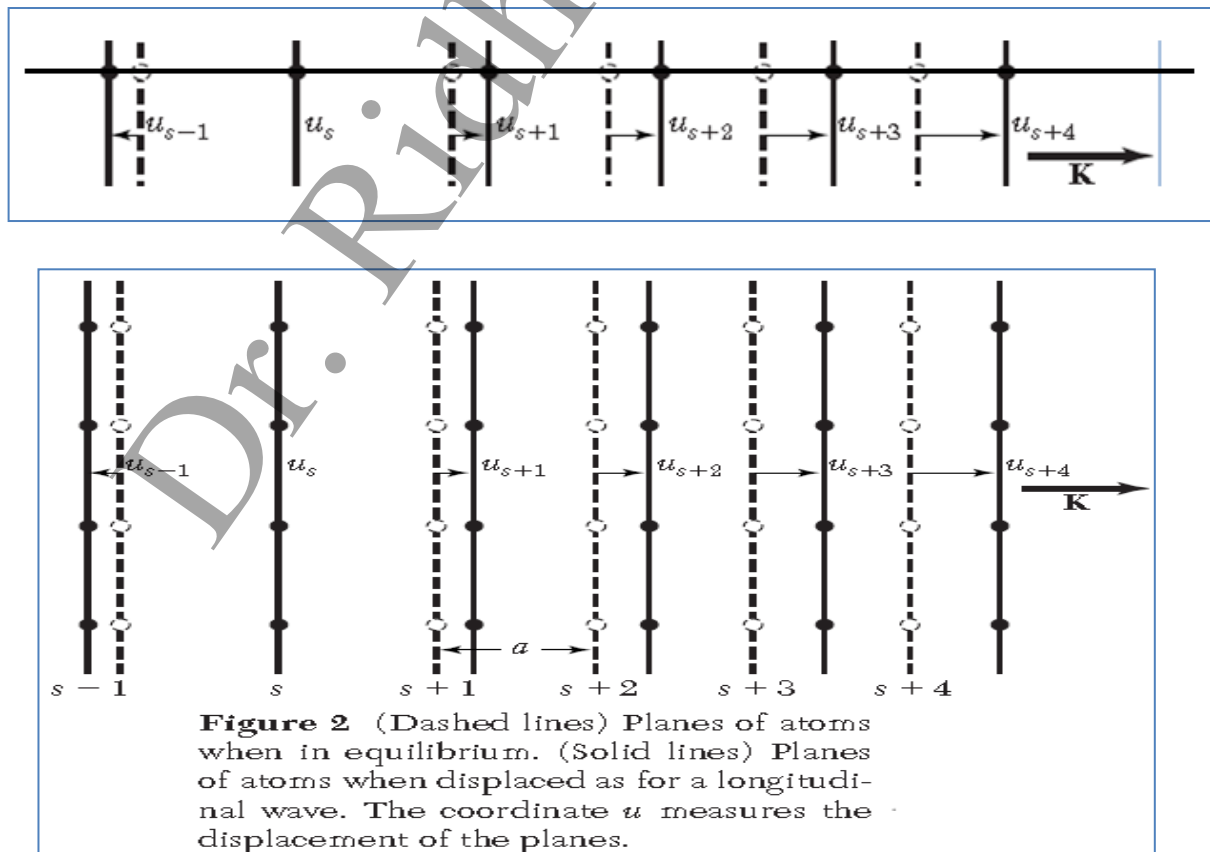
where K , of course, is the wave number $K = 2\pi/\lambda$, ω the frequency of the wave, and A is its amplitude. Substitution in (*) leads to

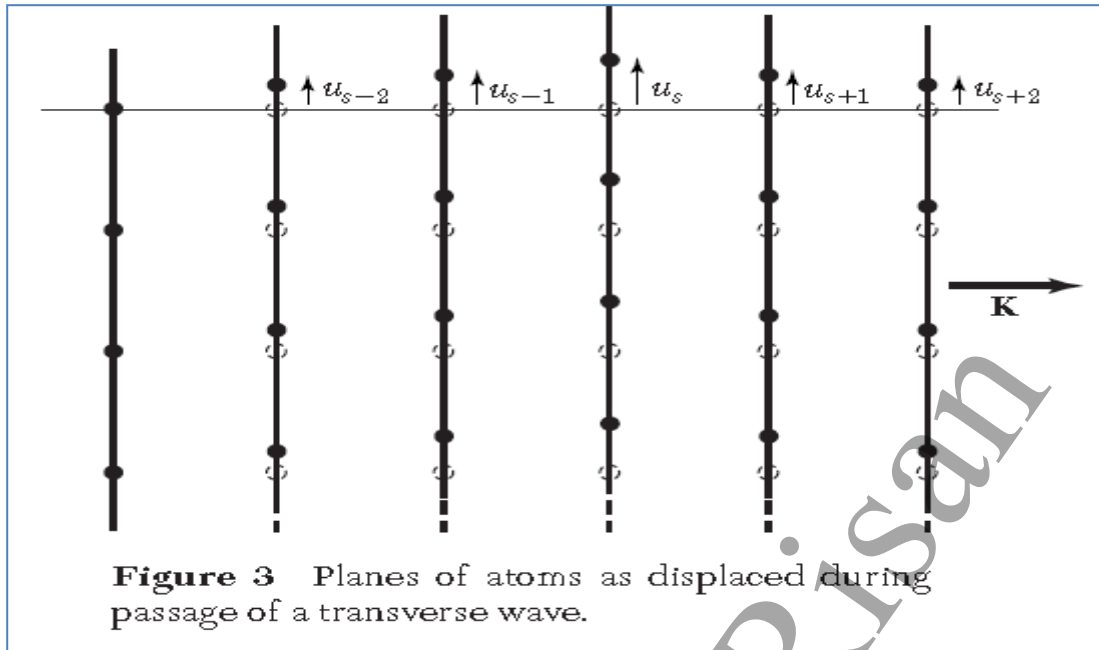
$$\omega = v_s K \quad \text{where} \quad v_s = \sqrt{Y/\rho}$$

The relation $\{\omega = v_s K\}$ connecting the frequency and wave number is known as the dispersion relation.

2- Vibrational modes of linear monatomic lattice

We can describe with a single coordinate u_s the displacement of the plane s from its equilibrium position. The problem is now one dimensional. For each wavevector there are three modes as solutions for u_s , one of longitudinal polarization (Fig. 2) and two of transverse polarization (Fig. 3).





We assume that the elastic response of the crystal is a linear function of the forces. That is equivalent to the assumption that the elastic energy is a quadratic function of the relative displacement of any two points in the crystal. Terms in the energy that are linear in the displacements will vanish in equilibrium.

We assume that the force on the plane s caused by the displacement of the plane $s + p$ is proportional to the difference $u_{s+p} - u_s$ of their displacements.

$$F_s = \sum_p C_p (u_{s+p} - u_s) \dots \dots \text{Hooke's law} \quad \& \quad F = M \frac{d^2 u_s}{dt^2}$$

For brevity we consider only nearest-neighbor interactions, with $p = \pm 1$. The total force on s from planes $s \pm 1$:

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s) \dots \dots (1)$$

This expression is linear in the displacements and is of the form of Hooke's law.

The constant C is the **force constant** between nearest-neighbor planes and will differ for longitudinal and transverse waves. It is convenient hereafter to regard C as defined for one atom of the plane, so that F_s is the force on one atom in the plane s .

The equation of motion of an atom in the plane s is

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s) \dots \dots (2) \quad u_s = u e^{-i\omega t}$$

where M is the mass of an atom.

We look for solutions with all displacements having the time dependence

$$e^{-i\omega t}. \text{ Then } \frac{du_s}{dt} = -i\omega u e^{-i\omega t} \Rightarrow \frac{d^2 u_s}{dt^2} = -\omega^2 u_s, \text{ and (2) becomes}$$

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) \dots \dots (3)$$

This is a difference equation in the displacements u and has traveling wave solutions of the form:

$$u_s = u e^{isKa} \dots \dots (4)$$

$$u_{s\pm 1} = u e^{i(s\pm 1)Ka} = u e^{isKa} e^{\pm iKa} \dots \dots \dots (4)$$

where a is the spacing between planes and K is the wavevector. The value to use for a will depend on the direction of K .

With (4), we have from (3):

$$\begin{aligned} -\omega^2 M u \exp(isKa) \\ = Cu\{\exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2 \exp(isKa)\} \\ \dots \dots \dots (5) \end{aligned}$$

$$\begin{aligned} -\omega^2 M u e^{isKa} &= Cu(e^{i(s+1)Ka} + e^{i(s-1)Ka} - 2 e^{isKa}) \\ &= Cu(e^{isKa} e^{iKa} + e^{isKa} e^{-iKa} - 2 e^{isKa}) \dots \dots \dots (5) \end{aligned}$$

We cancel $u e^{isKa}$ from both sides, to leave

$$\omega^2 M = -C[\exp(iKa) + \exp(-iKa) - 2] \dots \dots \dots (6)$$

With the identity $\{2 \cos ka = \exp(ika) + \exp(-ika)\}$, we have the **dispersion relation** $\omega(k)$.

$$\omega^2 M = -C[2 \cos Ka - 2] = -2C[\cos Ka - 1] = 2C[1 - \cos Ka]$$

$$\omega^2 = \frac{2C}{M} [1 - \cos Ka] \dots \dots \dots (7)$$

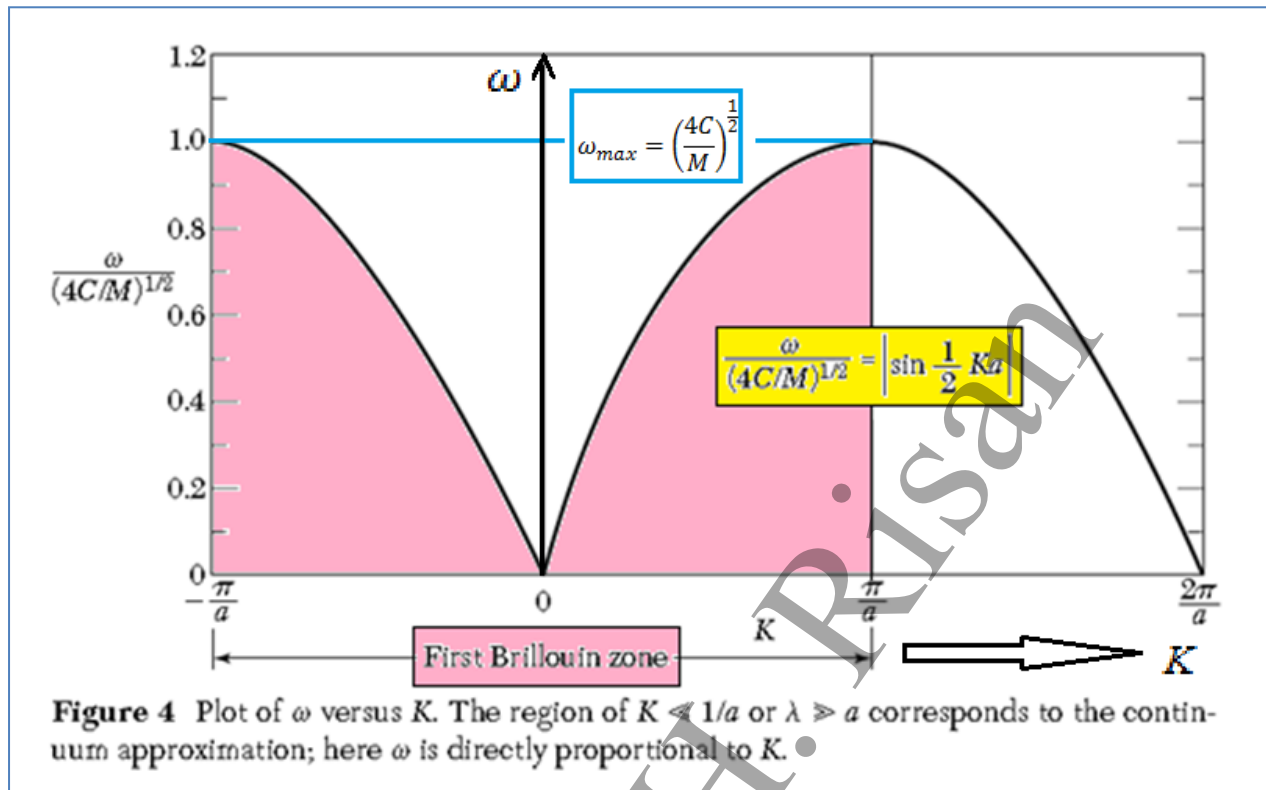
By a trigonometric identity $\{1 - \cos(Ka) = 2 \sin^2\left(\frac{Ka}{2}\right)\}$, (7) may be written as

$$\omega^2 = \frac{4C}{M} \sin^2\left(\frac{1}{2}ka\right) \dots \dots (9)$$

$$\omega = \left(\frac{4C}{M}\right)^{\frac{1}{2}} \left|\sin \frac{1}{2}ka\right| \dots \dots \text{(phonon dispersion relation)} - \omega(k) \dots \dots (9)$$

$$\omega_{max} = \left(\frac{4C}{M}\right)^{\frac{1}{2}}$$

A plot of ω versus K is given in Fig. 4.



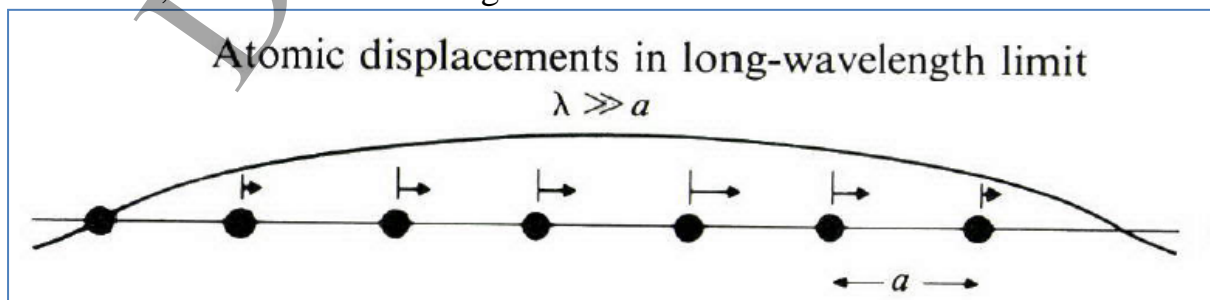
Q.) Show from dispersion relation $\omega(k)$ for monatomic lattice in one dimensional that the slope of ω versus K is zero at the zone boundary?

Solution: The boundary of the first Brillouin zone lies at $K = \pm \pi/a$. We show from (7): $\omega^2 = \frac{2C}{M} [1 - \cos Ka]$ (7)

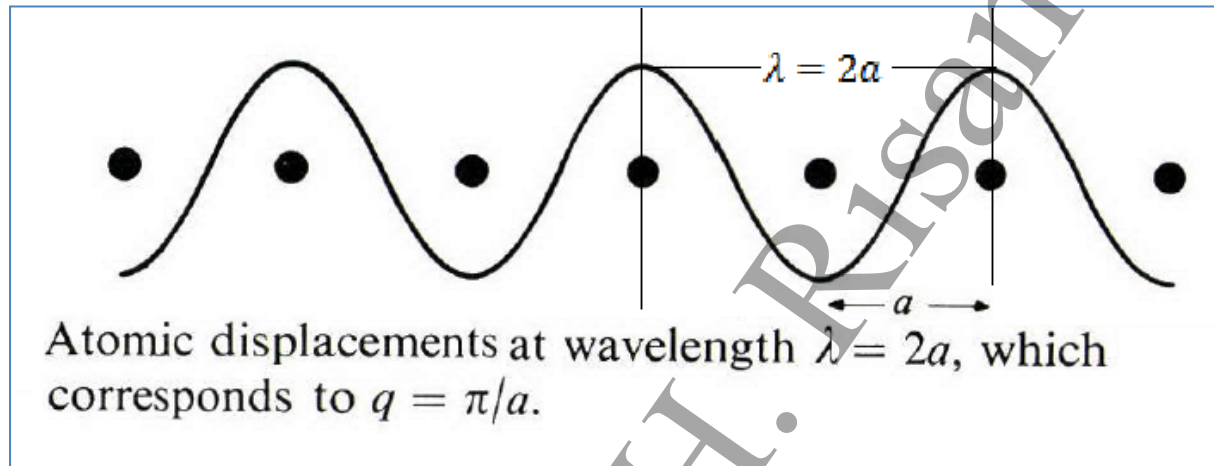
$$\frac{d\omega^2}{dK} = \frac{2Ca}{M} \sin Ka = 0 \quad \dots \dots \dots (8)$$

at $K = \pm \frac{\pi}{a}$, for here $\sin ka = \sin(\pm\pi) = 0$.

The above results for the behavior of the dispersion curve (Fig. 4) in the range $\{0 < K \leq \frac{\pi}{a}\}$ may also be understood from the following qualitative argument. For small K , $\lambda \gg a$, and the atoms move essentially in phase with each other, as indicated in the figure below.



The restoring force on the atom due to its neighbors is therefore small, which is the reason why ω is also small. In fact for $K = 0$ at $\lambda = \infty$, and the whole lattice moves as a rigid body, which results in the vanishing of the restoring force. This explains why $\omega = 0$ at $K = 0$. The opposite limit occurs at $\left\{K = \frac{\pi}{a}\right\}$ (as shown in the figure below), where, $\{\lambda = 2a\}$. As we see from the figure, the neighboring atoms are now out of phase, and consequently the restoring force and the frequency are at a maximum.



First Brillouin Zone:

What range of K is physically significant for elastic waves? Only those in the first Brillouin zone. From (4) the ratio of the displacements of two successive planes is given by

$$\frac{u_{s+1}}{u_s} = \frac{u e^{i(s+1)Ka}}{u e^{isKa}} = \frac{u e^{isKa} e^{iKa}}{u e^{isKa}} = \exp(iKa) \dots \dots (10)$$

The range $-\pi$ to $+\pi$ for the phase Ka covers all independent values of the exponential. The range of independent values of K is specified by

$$-\pi < Ka \leq \pi, \quad \text{or} \quad -\frac{\pi}{a} < K \leq \frac{\pi}{a}$$

This range is the first Brillouin zone of the linear lattice, as defined in Chapter 2. The extreme values are $\left\{K_{max} = \pm \frac{\pi}{a}\right\}$. Values of K outside of the first Brillouin zone (Fig. 5) merely reproduce lattice motions described by values within the limits $\pm \frac{\pi}{a}$.

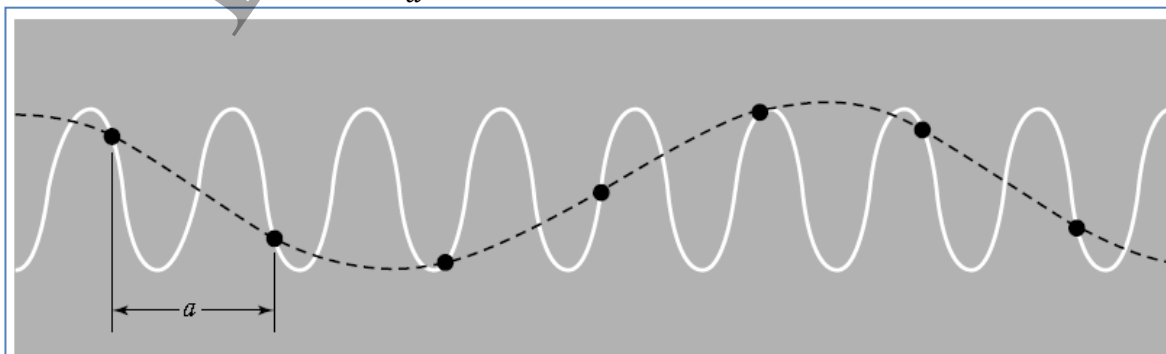


Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

We may treat a value of K outside these limits by subtracting the integral multiple of $\left\{\frac{2\pi}{a}\right\}$ that will give a wavevector inside these limits. Suppose K lies outside the first zone, but a related wavevector \hat{K} defined $\left\{\hat{K} = K - \frac{2\pi n}{a}\right\}$ lies within the first zone, where n is an integer. Then the displacement ratio (10) becomes

$$\frac{u_{s+1}}{u_s} = \frac{u e^{[i(s+1)Ka]}}{u \exp(isKa)} = \frac{u e^{isKa} e^{iKa}}{u e^{isKa}} = \exp(iKa) \dots \dots (10)$$

$$\frac{u_{s+1}}{u_s} = \exp(iKa) \equiv \exp(i2\pi n) \exp(iKa - 2\pi n) \equiv \exp(i\hat{K}a) \dots \dots (11)$$

because $\{\exp(i2\pi n) = 1\}$. Thus the displacement can always be described by a wavevector within the first zone. We note that $\left\{\frac{2\pi n}{a}\right\}$ is a reciprocal lattice vector because $\left\{\frac{2\pi}{a}\right\}$ is a reciprocal lattice vector. Thus by subtraction of an appropriate reciprocal lattice vector from K , we always obtain an equivalent wavevector in the first zone.

At the boundaries $\left\{K_{max} = \pm \frac{\pi}{a}\right\}$ of the Brillouin zone the solution $\{u_s = u \exp(isKa)\}$ does not represent a traveling wave, but a standing wave. At the zone boundaries $\{sK_{max}a = \pm s\pi\}$, whence $u_s = u \exp(\pm is\pi) = u(-1)^s \dots \dots \dots (12)$

This is a standing wave: alternate atoms oscillate in opposite phases, because $u_s = \pm 1$ according to whether s is an even or an odd integer. The wave moves neither to the right nor to the left.

This situation is equivalent to Bragg reflection of x-rays: when the Bragg condition is satisfied a traveling wave cannot propagate in a lattice, but through successive reflections back and forth, a standing wave is set up.

The critical value $\left\{K_{max} = \pm \frac{\pi}{a}\right\}$ found here satisfies the Bragg condition $2d \sin \theta = n\lambda$: we have $\theta = \frac{1}{2}\pi$, $d = a$, $K = \frac{2\pi}{\lambda}$, $n = 1$, so that $\lambda = 2a$. With x-rays it is possible to have n equal to other integers besides unity because the amplitude of the electromagnetic wave has a meaning in the space between atoms, but the displacement amplitude of an elastic wave usually has a meaning only at the atoms themselves.

Phase and Group Velocity:

In wave theory, a distinction is made between two, kinds of velocities phase velocity v_p and group velocity v_g . For an arbitrary dispersion relation, phase velocity is given by

$$v_p = \frac{\omega}{K}$$

and group velocity by

$$v_g = \frac{d\omega}{dK}$$

The physical distinction between these velocities is that (v_p) phase velocity is the velocity of propagation for a pure wave of an exactly specified frequency ω and a wave vector. While (v_g) group velocity describes the velocity of a wave pulse whose average frequency and wave vector are specified by ω and K .

Q) Briefly Discuss the reasons that group velocity is physically the more significant from the phase velocity?

Solution: Since energy and momentum are transmitted, in practice, via pulses rather than by pure waves, group velocity is physically the more significant.

The transmission velocity of a wave packet is the group velocity, given as

$$v_g = \frac{d\omega}{dK}$$

or

$$v_g = \text{grad}_K \omega(K) \dots \dots \dots (13)$$

the gradient of the frequency with respect to \mathbf{K} . This is the velocity of energy propagation in the medium.

With the particular dispersion relation (9), the group velocity (Fig. 6) is

$$v_g = \left(\frac{Ca^2}{M} \right)^{\frac{1}{2}} \cos\left(\frac{1}{2}Ka\right) \dots \dots \dots (14)$$

This is zero at the edge of the zone where $K = \pi/a$. Here the wave is a standing wave, as in (12), and we expect zero net transmission velocity for a standing wave.

Long Wavelength Limit

When $ka \ll 1$ we expand $\cos(Ka) \equiv 1 - \frac{1}{2}(Ka)^2$, so that the dispersion relation (7) becomes

$$\omega^2 = \left(\frac{C}{M} \right) k^2 a^2 \dots \dots \dots (15)$$

The result that the frequency is directly proportional to the wavevector in the long wavelength limit is equivalent to the statement that the velocity of sound is independent of frequency in this limit. Thus $v = \frac{\omega}{K}$, exactly as in the continuum theory of elastic waves—in the continuum limit $ka \ll 1$.

3- Diatomic linear lattice (TWO ATOMS PER PRIMITIVE BASIS):

The phonon dispersion relation shows new features in crystals with two or more atoms per primitive basis. Consider, for example, the NaCl or diamond structures, with two atoms in the primitive cell. For each polarization mode in a given propagation direction the dispersion relation ω versus K develops two branches, known as the acoustical and optical branches.

The numerology of the branches follows from the number of degrees of freedom of the atoms. With p atoms in the primitive cell and N primitive cells, there are pN atoms. Each atom has three degrees of freedom, one for each of the x, y, z directions, making a total of $3pN$ degrees of freedom for the crystal. The number of allowed K values in a single branch is just N for one Brillouin zone.

Thus the LA and the two TA branches have a total of $3N$ modes, thereby accounting for $3N$ of the total degrees of freedom. The remaining $(3p - 3)N$ degrees of freedom are accommodated by the optical branches.

Vibrational modes of Diatomic linear lattice

We consider a cubic crystal where atoms of mass M_1 lie on one set of planes and atoms of mass M_2 lie on planes interleaved between those of the first set (Fig. 9). It is not essential that the masses be different, but either the force constants or the masses will be different if the two atoms of the basis are in nonequivalent sites. Let a denote the repeat distance of the lattice in the direction normal to the lattice planes considered. We treat waves that propagate in a symmetry direction such that a single plane contains only a single type of ion; such directions are $[111]$ in the NaCl structure and $[100]$ in the CsCl structure.

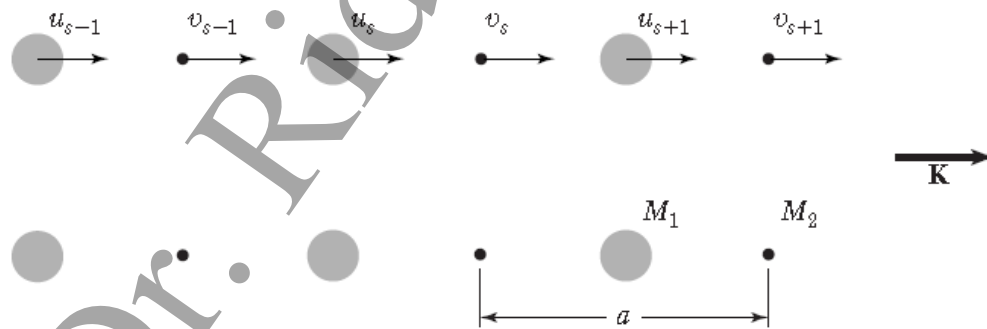


Figure 9 A diatomic crystal structure with masses M_1, M_2 connected by force constant C between adjacent planes. The displacements of atoms M_1 are denoted by $u_{s-1}, u_s, u_{s+1}, \dots$, and of atoms M_2 by v_{s-1}, v_s, v_{s+1} . The repeat distance is a in the direction of the wavevector K . The atoms are shown in their undisplaced positions.

We write the equations of motion under the assumption that each plane interacts only with its nearest-neighbor planes and that the force constants are identical between all pairs of nearest-neighbor planes. We refer to Fig. 9 to obtain

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s) \dots \dots \dots (18)$$

We look for a solution in the form of a traveling wave, now with different amplitudes u, v on alternate planes:

$$u_s = u \exp(isk_a) \exp(-i\omega t), \quad v_s = v \exp(isk_a) \exp(-i\omega t) \dots \dots (19)$$

We define a in Fig. 9 as the distance between nearest identical planes, not nearest-neighbor planes.

$$\left. \begin{aligned} -\omega^2 M_1 u &= Cv[1 + \exp(-ika)] - 2Cu \\ -\omega^2 M_2 v &= Cu[1 + \exp(ika)] - 2Cv \end{aligned} \right\} \dots \dots \dots (20)$$

The homogeneous linear equations have a solution only if the determinant of the coefficients of the unknowns u, v vanishes:

$$\begin{vmatrix} 2C - M_1 \omega^2 & -C[1 + \exp(-ika)] \\ -C[1 + \exp(ika)] & 2C - M_2 \omega^2 \end{vmatrix} = 0 \dots \dots \dots (21)$$

or

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0 \dots \dots (22)$$

We can solve this equation exactly for ω^2 , but it is simpler to examine the limiting cases $Ka \ll 1$ and $Ka = \pm\pi$ at the zone boundary. For small Ka we have $\left\{ \cos Ka \cong 1 - \frac{1}{2}K^2 a^2 + \dots \right\}$. This approximation is in fact the Taylor expansion of the cosine function near zero. We therefore obtain successively

$$1 - \cos Ka \cong \frac{1}{2}K^2 a^2$$

and the two roots are:

$$\omega^2 \cong 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (\text{optical branch}) \dots \dots \dots (23)$$

$$\omega^2 \cong \frac{\frac{1}{2}C}{M_1 + M_2} K^2 a^2 \quad (\text{acoustical branch}) \dots \dots \dots (24)$$

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 4C^2 - 4C^2 \sin^2 \left(\frac{ka}{2} \right) = 0 \dots \dots \dots (22 *)$$

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \sqrt{1 - \frac{2M_1 M_2}{(M_1 + M_2)^2} (1 - \cos ka)} \right] \dots (22 **)$$

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \left(1 - \frac{M_1 M_2}{2(M_1 + M_2)^2} (K^2 a^2) \right) \right] \dots (22 ***)$$

This expression (22 **) always has a meaning since the argument of the square root is always positive because we have, for any value of masses M_1 and M_2 , and value of wavenumber k :

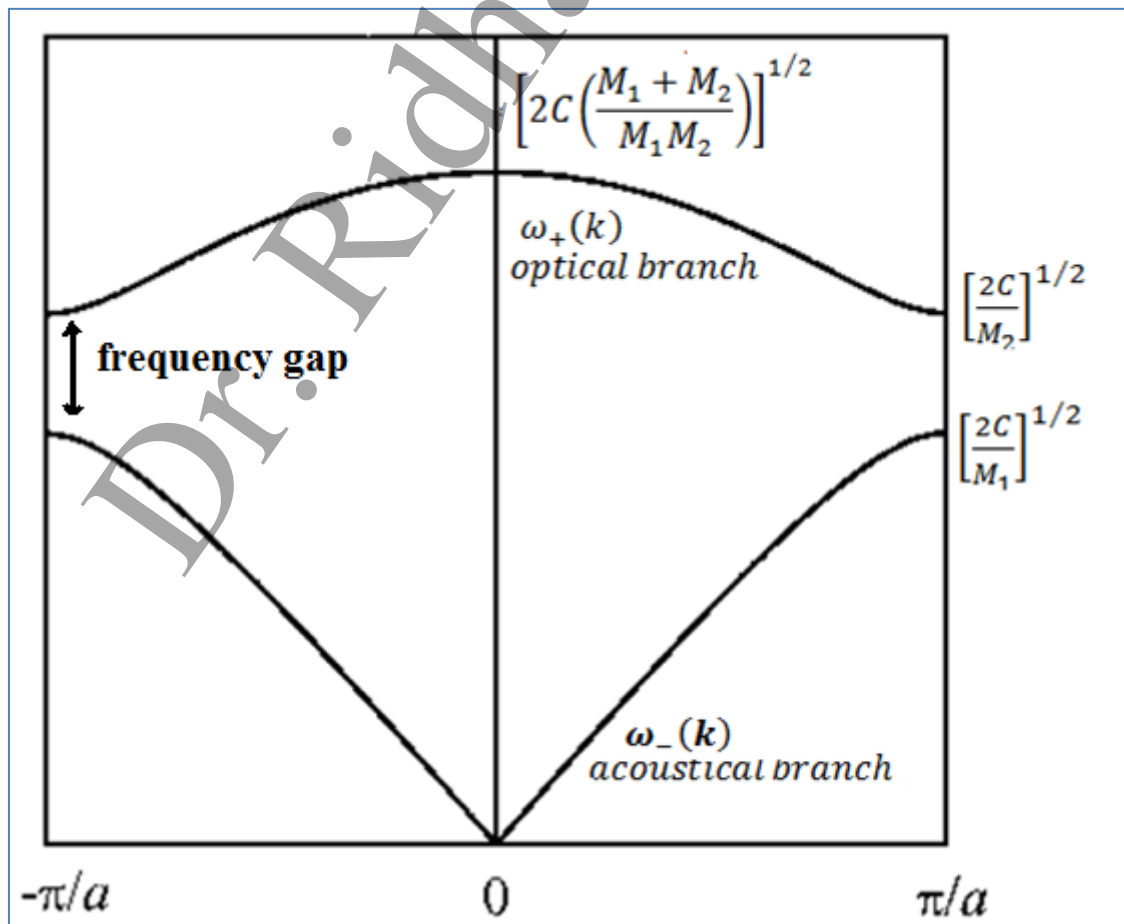
$$0 \leq (1 - \cos ka) \leq 2$$

and therefore:

$$0 \leq \frac{2M_1 M_2}{(M_1 + M_2)^2} (1 - \cos ka) \leq 1$$

There are thus two possible dispersion relations, denoted $\omega_+(k)$ and $\omega_-(k)$, relating the angular frequency to the wavenumber. Both are plotted in the first Brillouin zone as shown in figure. These plots represent the so-called phonon spectrum of a one-dimensional diatomic harmonic crystal.

The values for $\omega_+(k)$ and $\omega_-(k)$ at $k = 0$ and $k = \pm \frac{\pi}{2}$ can be easily calculated from Eq. (22**) (note that we have chosen $M_1 > M_2$). The top curve in figure corresponds to $\omega_+(k)$ and is called the optical phonon branch or simply optical phonon, while the bottom branch corresponds to $\omega_-(k)$ and is called the acoustic phonon branch or simply acoustic phonon.



The frequency range between the top of the acoustic branch and the bottom of the optical branch is forbidden, and the lattice cannot transmit such a wave; waves in this region are strongly attenuated. One speaks here of a **frequency gap**. Therefore the diatomic lattice acts as a band-pass mechanical filter.

as in Fig. 7. We have:

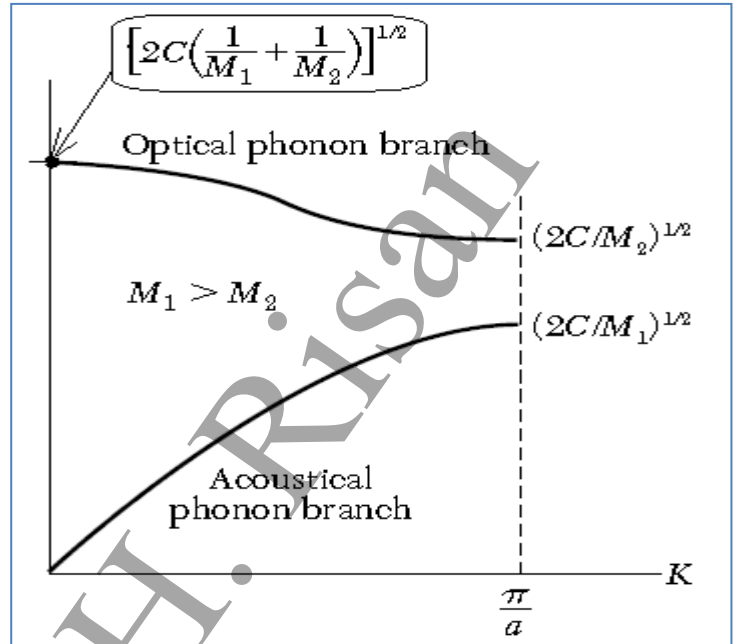
longitudinal acoustical = LA

transverse acoustical = TA modes.

longitudinal optical = LO

transverse optical = TO modes.

Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K=0$ and $K=K_{\max}=\pi/a$. The lattice constant is a .



4- Acoustic phonon branch:

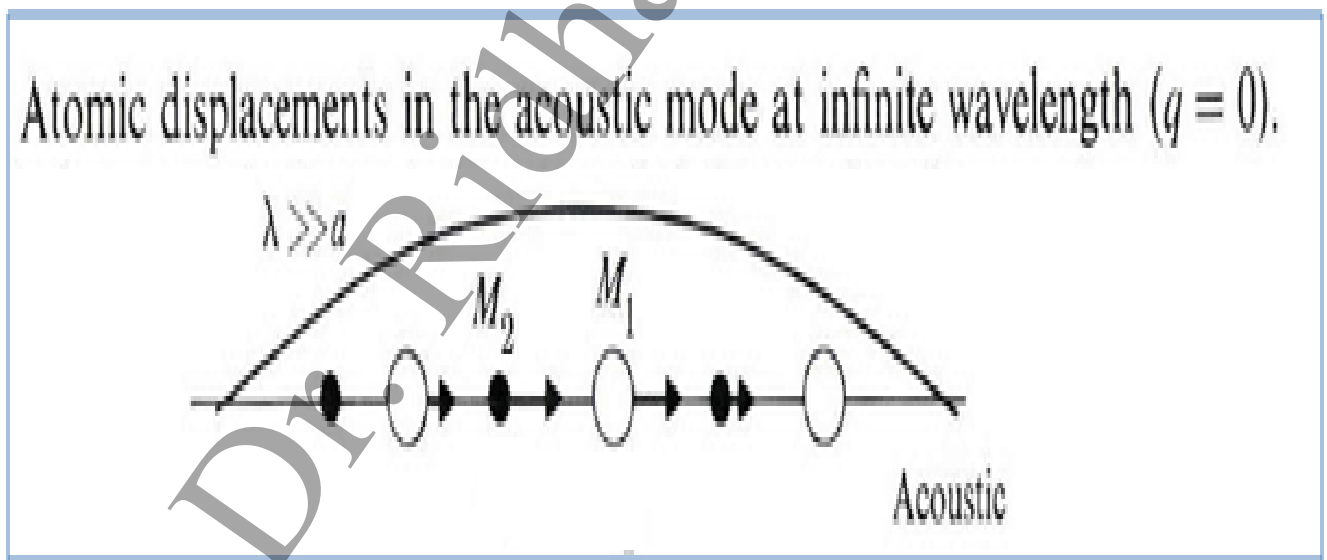
Consequently, in the long wave limit, the angular frequency acoustic phonon branch can be written as:

$$\omega_{-}^2(k) \approx \frac{\frac{1}{2}C}{(M_1 + M_2)} K^2 a^2 \quad \dots \dots \text{(acoustical branch)} \dots \dots (24)$$

Which means that the angular frequency $\omega_{-}(k)$ for the acoustic phonon branch is proportional to the wavenumber k . The shape of the acoustic branch is similar, but the increased mass lowers the frequency. For the acoustic branch in the long wave limit, the traveling wave is equivalent to the elastic wave of a one-dimensional atomic chain regarded as a continuous media.

The nature of the vibrations in this region is just like sound waves. The two atoms in the unit cell move in the same direction and over a small region it seems as if the entire crystal has been compresses or stretched. This is why the $\omega_{-}(k)$ is called the acoustic branch.

For this branch the two atoms in the cell, or molecule, have the same amplitude, and are also in phase (The diatomic lattice may be viewed as an array of diatomic molecules) . In other words, the molecule (and indeed the whole lattice) oscillates as a rigid body, with the center of mass moving back and forth, as shown in the figure below



5- Optical phonon branch:

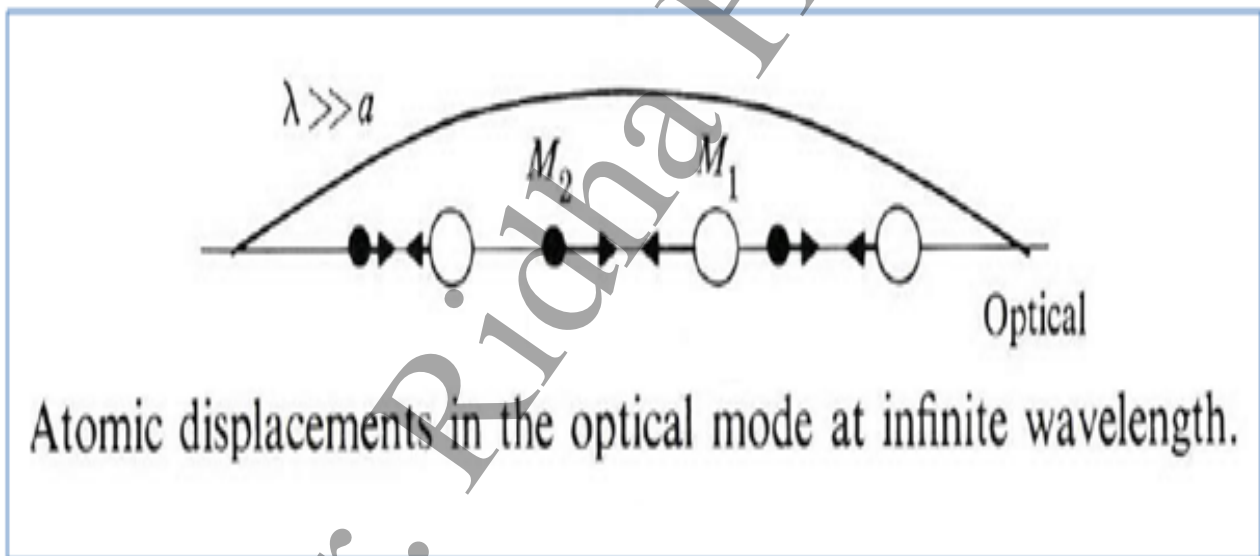
In the same limit $k \rightarrow 0$, the angular frequency of the optical phonon branch can be expressed from Eq. (22**):

$$\omega_+^2(k) = 2C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \quad (\text{optical branch}) \dots \dots \dots (23)$$

$$\omega^2 \cong 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (\text{optical branch}) \dots \dots \dots (23)$$

Which shows that the angular frequency $\omega_+(k)$ in the optical phonon branch is a constant in the long wave limit. The nature of the vibrations in this region is that the two atoms in the unit cell move in opposite directions. This is similar to the top of the band in the monatomic case, where there is maximum distortion and frequency of vibration.

As K increases, they still move approximately in phase with each other. This means that the optical oscillation takes place in such a way that the center of mass of the cell remains fixed. The two atoms move π out of phase with each other., as shown in the figure below.



The ratio of their amplitudes $\frac{u}{v} = -\frac{M_2}{M_1}$. This type of oscillation around the center of mass is well known in the study of molecular vibrations. As K increases beyond zero, the frequency of the diatomic vibration decreases, but the decrease is not large because the atoms continue to oscillate approximately π out of phase with each other throughout the entire K -range.

The extent of the first Brillouin zone is $-\frac{\pi}{a} \leq K \leq \frac{\pi}{a}$, where a is the repeat distance of the lattice. At $\{K_{max} = \pm \frac{\pi}{a}\}$ the roots are

$$\omega^2 = \frac{2C}{M_1} \Rightarrow \omega = \left[\frac{2C}{M_1}\right]^{1/2} ; \quad \omega^2 = \frac{2C}{M_2} \Rightarrow \omega = \left[\frac{2C}{M_2}\right]^{1/2} .$$

The dependence of ω on K is shown in Fig. 7 for $M_1 > M_2$.

The particle displacements in the transverse acoustical (TA) and transverse optical (TO) branches are shown in Fig. 10. For the optical branch at $k=0$ we find, on substitution of (23) in (20),

$$\frac{u}{v} = -\frac{M_2}{M_1} \dots \dots \dots (26)$$

The atoms vibrate against each other, but their center of mass is fixed. If the two atoms carry opposite charges, as in Fig. 10, we may excite a motion of this type with the electric field of a light wave, so that the branch is called the optical branch. At a general K the ratio u/v will be complex, as follows from either of the equations (20). Another solution for the amplitude ratio at small K is $u = v$, obtained as the $K = 0$ limit of (24). The atoms (and their center of mass) move together, as in long wavelength acoustical vibrations, whence the term acoustical branch.

Wave like solutions do not exist for certain frequencies, here between $\left(\frac{2C}{M_1}\right)^{1/2}$ and $\left(\frac{2C}{M_2}\right)^{1/2}$. This is a characteristic feature of elastic waves in polyatomic lattices. There is a frequency gap at the boundary $\{K_{max} = \pm \frac{\pi}{a}\}$ of the first Brillouin zone.

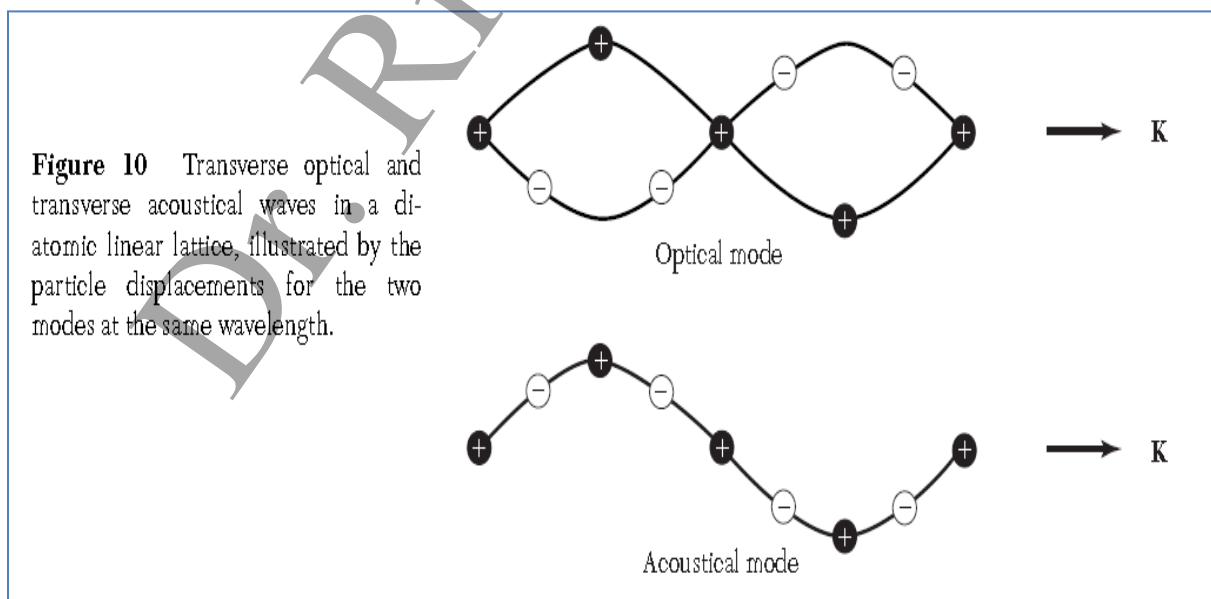


Figure 10 Transverse optical and transverse acoustical waves in a diatomic linear lattice, illustrated by the particle displacements for the two modes at the same wavelength.

6- QUANTIZATION OF ELASTIC WAVES:

The energy of a lattice vibration is quantized. The quantum of energy is called a **phonon** in analogy with the photon of the electromagnetic wave. The energy of an elastic mode of angular frequency ω is

$$\epsilon = \left(n + \frac{1}{2}\right) \hbar \omega \dots \dots \dots (27)$$

when the mode is excited to quantum number n ; that is, when the mode is occupied by n phonons. The term $\frac{1}{2} \hbar \omega$ is the zero point energy of the mode.

It occurs for both phonons and photons as a consequence of their equivalence to a quantum harmonic oscillator of frequency ω , for which the energy eigenvalues are also $\left(n + \frac{1}{2}\right) \hbar \omega$

We can quantize the mean square phonon amplitude. Consider the standing wave mode of amplitude

$$u = u_0 \cos kx \cos \omega t$$

Here u is the displacement of a volume element from its equilibrium position at x in the crystal. The energy in the mode, as in any harmonic oscillator, is half kinetic energy and half potential energy, when averaged over time. The kinetic energy density is $\frac{1}{2} \rho \left(\frac{\partial u}{\partial t}\right)^2$, where ρ is the mass density. In a crystal of volume V , the volume integral of the kinetic energy is $\frac{1}{4} \rho V \omega^2 u_0^2 \sin^2 \omega t$. The time average kinetic energy is

$$\frac{1}{8} \rho V \omega^2 u_0^2 = \frac{1}{2} \left(n + \frac{1}{2}\right) \hbar \omega \dots \dots \dots (28)$$

Because $\langle \sin^2 \omega t \rangle = \frac{1}{2}$. The square of the amplitude of the mode is

$u_0^2 = 4 \left(n + \frac{1}{2}\right) \hbar / \rho V \omega$. This relates the displacement in a given mode to the phonon occupancy n of the mode.

What is the sign of ω ? The equations of motion such as (2) are equations for ω^2 , and if this is positive then ω can have either sign, + or -. But the energy of a phonon must be positive, so it is conventional and suitable to view ω as positive. If the crystal structure is unstable, then ω^2 will be negative and ω will be imaginary.

PHONON MOMENTUM

A phonon of wavevector K will interact with particles such as photons, neutrons, and electrons as if it had a momentum $\hbar K$. However, a phonon does not carry physical momentum. The reason that phonons on a lattice do not carry momentum is that a phonon coordinate (except for $K=0$) involves relative coordinates of the atoms. Thus in an H_2 molecule the internuclear vibrational coordinate $r_1 - r_2$ is a relative coordinate and does not carry linear momentum; the center of mass coordinate $\frac{1}{2}(r_1 + r_2)$ corresponds to the uniform mode $K=0$ and can carry linear momentum.

In crystals there exist wavevector selection rules for allowed transitions between quantum states. We saw in Chapter 2 that the elastic scattering of an x-ray photon by a crystal is governed by the wavevector selection rule

$$\mathbf{\hat{k}} = \mathbf{k} + \mathbf{G} \dots \dots \dots (30)$$

where \mathbf{G} is a vector in the reciprocal lattice, \mathbf{k} is the wavevector of the incident photon, and $\mathbf{\hat{k}}$ is the wavevector of the scattered photon. In the reflection process the crystal as a whole will recoil with momentum $-\hbar\mathbf{G}$, but this uniform mode momentum is rarely considered explicitly.

Equation (30) is an example of the rule that the total wavevector of interacting waves is conserved in a periodic lattice, with the possible addition of a reciprocal lattice vector \mathbf{G} . The true momentum of the whole system always is rigorously conserved.

If the scattering of the photon is **inelastic**, with the creation of a phonon of wavevector \mathbf{K} , then the wavevector selection rule becomes

$$\mathbf{\hat{k}} + \mathbf{K} = \mathbf{k} + \mathbf{G} \dots \dots \dots (31)$$

If a phonon \mathbf{K} is absorbed in the process, we have instead the relation

$$\mathbf{\hat{k}} = \mathbf{k} + \mathbf{K} + \mathbf{G} \dots \dots \dots (32)$$

Relations (31) and (32) are the natural extensions of (30).

7- INELASTIC SCATTERING BY PHONONS

Phonon dispersion relations $\omega(\mathbf{K})$ are most often determined experimentally by the inelastic scattering of neutrons with the emission or absorption of a phonon. A neutron sees the crystal lattice chiefly by interaction with the nuclei of the atoms. The kinematics of the scattering of a neutron beam by a crystal lattice are described by the general wavevector selection rule:

$$\mathbf{k} + \mathbf{G} = \mathbf{\hat{k}} \pm \mathbf{K} \dots \dots \dots (33)$$

and by the requirement of conservation of energy. Here \mathbf{K} is the wavevector of the phonon created (+) or absorbed (-) in the scattering process, and \mathbf{G} is any reciprocal lattice vector. For a phonon we choose \mathbf{G} such that \mathbf{K} lies in the first Brillouin zone. The kinetic energy of the incident neutron is $p^2/2M_n$, where M_n is the mass of the neutron. The momentum \mathbf{p} is given by $\hbar\mathbf{k}$, where \mathbf{k} is the wavevector of the neutron. Thus $\hbar^2\mathbf{k}^2/2M_n$ is the kinetic energy of the incident neutron. If $\mathbf{\hat{k}}$ is the wavevector of the scattered neutron, the energy of the scattered neutron is $\hbar^2\mathbf{\hat{k}}^2/2M_n$. The statement of conservation of energy is

$$\frac{\hbar^2\mathbf{k}^2}{2M_n} = \frac{\hbar^2\mathbf{\hat{k}}^2}{2M_n} \pm \hbar\omega \dots \dots \dots (34)$$

where $\hbar\omega$ is the energy of the phonon created (+) or absorbed (-) in the process.

In More Detail for Two Atoms Per Primitive Basis:

We write the equations of motion under the assumption that each plane interacts only with its nearest-neighbor planes and that the force constants are identical between all pairs of nearest-neighbor planes. We refer to Fig. 9 to obtain

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s) \dots \dots \dots (18)$$

We look for a solution in the form of a traveling wave, now with different amplitudes u, v on alternate planes:

$$u_s = u \exp(isk_a) \exp(-i\omega t), \quad v_s = v \exp(isk_a) \exp(-i\omega t) \dots \dots (19)$$

We define a in Fig. 9 as the distance between nearest identical planes, not nearest-neighbor planes.

On substitution of (19) in (18) we have

$$\left. \begin{aligned} -\omega^2 M_1 u &= Cv[1 + \exp(-iKa)] - 2Cu \\ -\omega^2 M_2 v &= Cu[1 + \exp(iKa)] - 2Cv \end{aligned} \right\} \dots \dots \dots (20)$$

$$\left. \begin{aligned} -\omega^2 M_1 u + 2Cu - Cv[1 + \exp(-iKa)] &= 0 \\ -\omega^2 M_2 v + 2Cv - Cu[1 + \exp(iKa)] &= 0 \end{aligned} \right\} \dots \dots \dots (20)$$

$$\left. \begin{aligned} (2C - \omega^2 M_1)u - C(1 + e^{-iKa})v &= 0 \\ -C(1 + e^{iKa})u + (2C - \omega^2 M_2)v &= 0 \end{aligned} \right\} \dots \dots \dots (20)$$

The homogeneous linear equations have a solution only if the determinant of the coefficients of the unknowns u, v vanishes:

$$\begin{vmatrix} 2C - M_1 \omega^2 & -C[1 + \exp(-iKa)] \\ -C[1 + \exp(iKa)] & 2C - M_2 \omega^2 \end{vmatrix} = 0 \dots \dots \dots (21)$$

$$\begin{aligned} (2C - M_1 \omega^2)(2C - M_2 \omega^2) - (-C[1 + \exp(-iKa)])(-C[1 + \exp(iKa)]) \\ = 0 \\ (4C^2 - 2CM_2 \omega^2 - 2CM_1 \omega^2 + M_2 M_1 \omega^4) \\ - C^2(1 + \exp(iKa) + \exp(-iKa) + e^0) = 0 \end{aligned}$$

Use : $\{2 \cos ka = \exp(ika) + \exp(-ika)\}$ & $\{1 - \cos \theta = 2 \sin^2 \frac{\theta}{2}\}$

$$4C^2 - 2C(M_1 + M_2)\omega^2 + M_2M_1\omega^4 - C^2(2 + 2 \cos ka) = 0$$

Or:

$$M_1M_2\omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0 \dots \dots (22)$$

$$M_1M_2\omega^4 - 2C(M_1 + M_2)\omega^2 + 4C^2 - 2C^2(1 + \cos ka) = 0$$

$$M_1M_2\omega^4 - 2C(M_1 + M_2)\omega^2 + 4C^2 - 4C^2 \sin^2 \left(\frac{ka}{2}\right) = 0 \dots \dots \dots (22 *)$$

This equation is of the form $\alpha\omega^4 - 2\beta\omega^2 + \gamma = 0$, with α, β , and $\gamma > 0$ and has two solutions for ω^2 , denoted ω_+^2 and ω_-^2 such that:

$$\omega_{\pm}^2(k) = \frac{\beta \pm \sqrt{\beta^2 - \alpha\gamma}}{\alpha}$$

Therefore, the solution of Eq. (22 *) are:

$$\omega_{\pm}^2(k) = \frac{C(M_1 + M_2) \pm \sqrt{C^2(M_1 + M_2)^2 - 4C^2M_1M_2 \sin^2 \left(\frac{ka}{2}\right)}}{M_1M_2}$$

Which can be simplified into:

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1M_2} \right) \pm C \sqrt{\left(\frac{M_1 + M_2}{M_1M_2} \right)^2 - \frac{4 \sin^2 \left(\frac{ka}{2}\right)}{M_1M_2}}$$

Using the trigonometric identity $\{\cos(2x) = 1 - 2 \sin^2(x)\}$, this equation becomes:

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1M_2} \right) \left[1 \pm \sqrt{1 - \frac{2M_1M_2}{(M_1 + M_2)^2} (1 - \cos ka)} \right] \dots \dots (22 **)$$

This expression always has a meaning since the argument of the square root is always positive because we have, for any value of masses M_1 and M_2 , and value of wavenumber k :

$$0 \leq (1 - \cos ka) \leq 2$$

and therefore:

$$0 \leq \frac{2M_1M_2}{(M_1 + M_2)^2} (1 - \cos ka) \leq 1$$

There are thus two possible dispersion relations, denoted $\omega_+(k)$ and $\omega_-(k)$, relating the angular frequency to the wavenumber.

We can solve this equation exactly for ω^2 , but it is simpler to examine the limiting cases $K_a \ll 1$ and $Ka = \pm\pi$ at the zone boundary.

For small Ka we have $\left\{ \cos Ka \cong 1 - \frac{1}{2}K^2a^2 \right\}$. This approximation is in fact the Taylor expansion of the cosine function near zero.

We therefore obtain successively

$$1 - \cos Ka \cong \frac{1}{2} K^2 a^2$$

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \sqrt{1 - \frac{2M_1 M_2}{(M_1 + M_2)^2} (1 - \cos ka)} \right] \dots (22 **)$$

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \sqrt{1 - \frac{2M_1 M_2}{(M_1 + M_2)^2} \left(\frac{1}{2} K^2 a^2 \right)} \right] \dots (22 **)$$

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \sqrt{1 - \frac{M_1 M_2}{(M_1 + M_2)^2} (K^2 a^2)} \right] \dots (22 **)$$

by using the approximation $\sqrt{1-x} \approx 1 - \frac{1}{2}x$ for $x \rightarrow 0$ (a gain this comes from the Taylor expansion of $\sqrt{1-x}$ small values of (x)). Eq. (22**) can than be approximated by the following expression:

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \left(1 - \frac{M_1 M_2}{2(M_1 + M_2)^2} (K^2 a^2) \right) \right] \dots (22 ***)$$

Acoustic phonon branch:

Consequently, in the long wave limit, the angular frequency acoustic phonon branch can be written as:

$$\omega_{-}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 - \left(1 - \frac{M_1 M_2}{2(M_1 + M_2)^2} (K^2 a^2) \right) \right]$$

$$\omega_{-}^2(k) \approx C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[\frac{M_1 M_2}{2(M_1 + M_2)^2} (K^2 a^2) \right]$$

$$\omega_{-}^2(k) \approx \left[\frac{C(K^2 a^2)}{2(M_1 + M_2)} \right]$$

$$\omega_{-}^2(k) \approx \frac{\frac{1}{2} C}{(M_1 + M_2)} K^2 a^2 \dots \dots (acoustical branch) \dots \dots (24)$$

$$\omega^2 \cong \frac{\frac{1}{2} C}{M_1 + M_2} K^2 a^2 \dots \dots (acoustical branch) \dots \dots (24)$$

$$\omega_{-}(k) \approx k \sqrt{\frac{C a^2}{2(M_1 + M_2)}}$$

Optical phonon branch:

In the same limit $k \rightarrow 0$, the angular frequency of the optical phonon branch can be expressed from Eq. (22**):

$$\omega_{\pm}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 \pm \left(1 - \frac{M_1 M_2}{2(M_1 + M_2)^2} (K^2 a^2) \right) \right] \dots (22 **)$$

$$\omega_{+}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \left[1 + \left(1 - \frac{M_1 M_2}{2(M_1 + M_2)^2} (K^2 a^2) \right) \right]$$

$$\because k \rightarrow 0 \quad \Rightarrow \quad \omega_{+}^2(k) = C \left(\frac{M_1 + M_2}{M_1 M_2} \right) [1 + 1] =$$

$$\omega_{+}^2(k) = 2C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \quad (\text{optical branch}) \dots (23)$$

$$\omega_{+}(k) = \left[2C \left(\frac{M_1 + M_2}{M_1 M_2} \right) \right]^{1/2}$$

$$\omega^2 \cong 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (\text{optical branch}) \dots (23)$$

Chapter Four : Crystal Defects

1-Point defects

2-Schottky defects

3-Frenkel defects

4-Linear defects

5-Dislocation a- Edge dislocation b-Screw dislocation

6- Surface defects

7- Volume defects

Introduction:

The common point imperfections in crystals are chemical impurities, vacant lattice sites, and extra atoms not in regular lattice positions. Linear imperfections are treated under dislocations. The crystal surface is a planar imperfection, with electron, phonon, and magnon surface states.

- Some important properties of crystals are controlled as much by imperfections as by the composition of the host crystal, which may act only as a solvent or matrix or vehicle for the imperfections.
- The conductivity of some semiconductors is due entirely to trace amounts of chemical impurities.
- The color and luminescence of many crystals arise from impurities or imperfections.
- Atomic diffusion may be accelerated enormously by impurities or imperfections.
- Mechanical and plastic properties are usually controlled by imperfections.
- In some situations defects are, in fact, highly desirable, as in the case of donor and acceptor impurities, which are essential to the operation of the transistor.

Types of imperfections:

By taking great pains, one can reduce crystal imperfections, or defects, considerably, but one can never eliminate them entirely. In As the name implies, a defect is a region involving a break, or an irregularity, in the crystal structure. The most important types of defects are:

Point defects (Zero dimensional defects)

Vacancies (Schottky defects , Frenkel defects), Extra atoms

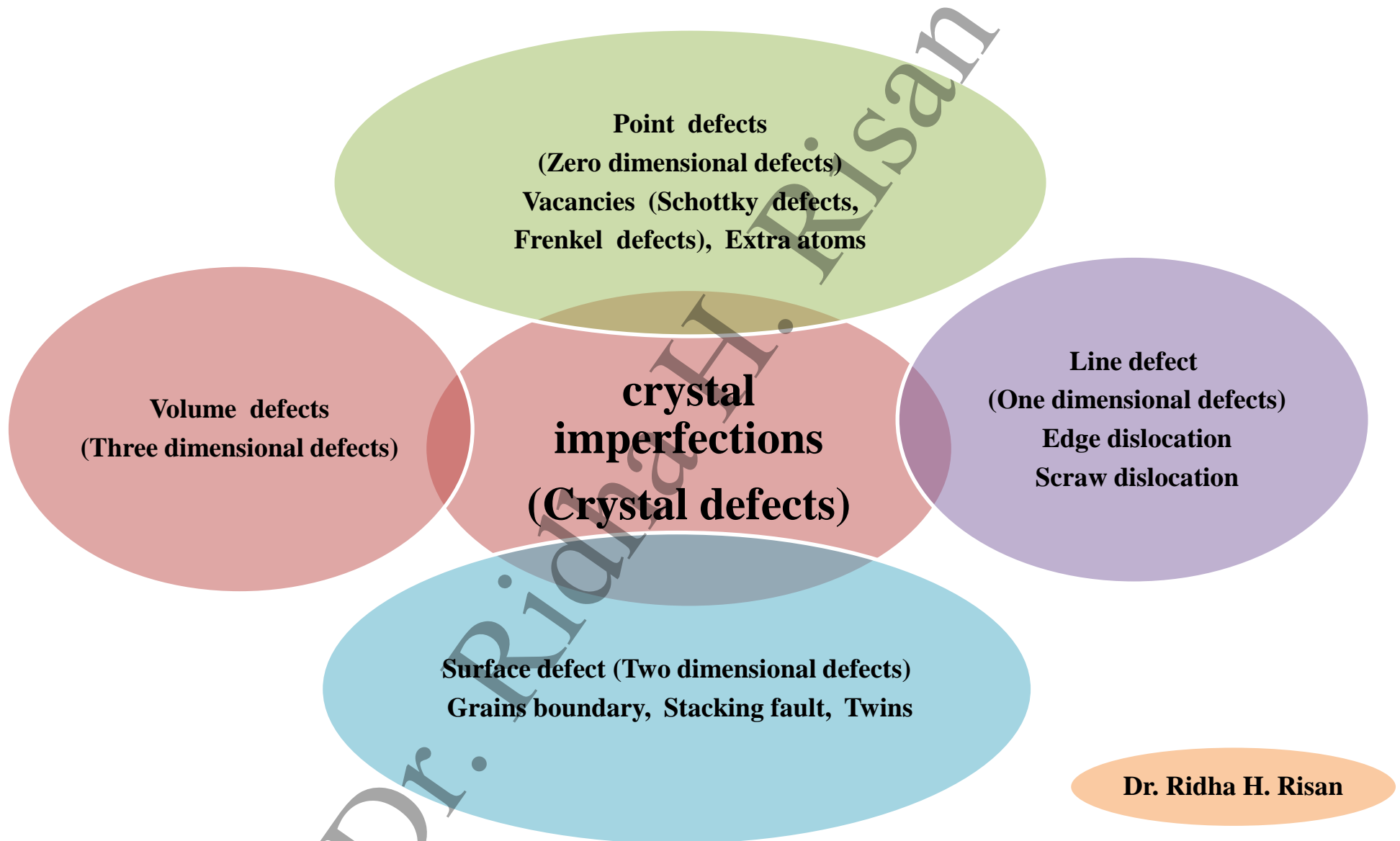
Line defect (One dimensional defects)

1- Edge dislocation. 2- Screw dislocation

Surface defect (Two dimensional defects)

1- Grains boundary. 2- Stacking fault. 3- Twins

Volume defects (Three dimensional defects)



Point defects (Zero dimensional defects):

An irregularity in the crystal structure, localized in the lattice. An example is a foreign atom, or impurity, in the crystal. A crystal usually contains all sorts of impurities which attach themselves to it during the crystallization process, particularly small atoms present in the atmosphere in which the crystal is grown, such as oxygen, hydrogen, and nitrogen.

An impurity is **substitutional** if it occupies a lattice site from which a host atom has been expelled and interstitial if it occupies a position between the host atoms.

The region surrounding an impurity is strained, the extent of the strain depending on the kind of impurity atom and its location. An appreciable number of substitutional impurities may be present only if the size of the impurity is not far from that of the host atom, otherwise the strain energy required would be prohibitive. Similarly, only small atoms can exist in large numbers as **interstitial impurities** because the space between host atoms is small, especially in metals, in which the atoms are tightly packed.

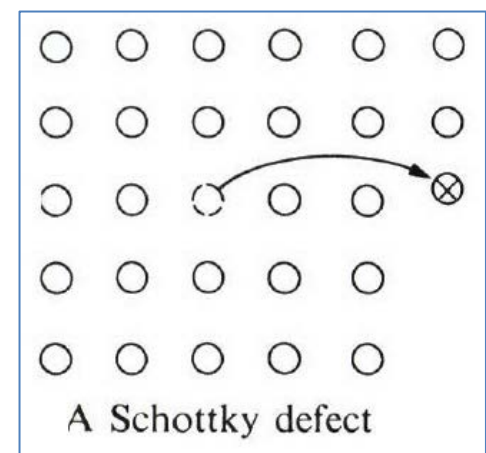
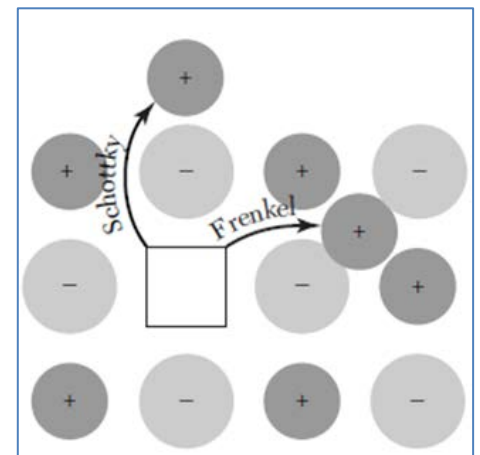
The defect which arises due to the irregularity in the arrangement of atoms or ions is called point defect.

Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies.

1- Vacancies: An empty lattice site from which the regular atom has been removed. In metals, as in other solids, vacancies are created by thermal excitation, provided the temperature is sufficiently high, because, as the atoms vibrate around their regular positions, some acquire enough energy to leave the site completely. When the regular atom leaves, the region surrounding a vacancy is distorted because the lattice relaxes, as it were, in order to partially fill the void left by the atom. This contributes further to the irregularity of the lattice in the immediate neighborhood of the vacancy. There are two types of vacancy:

- ❖ Schottky defects
- ❖ Frenkel defects)

Schottky defects: which is a missing atom or ion, also known as a **Schottky defect**. We create a Schottky defect in a perfect crystal by transferring an atom from a lattice site in the interior to a lattice site on the surface of the crystal. In pure alkali halides the most common lattice vacancies are Schottky defects.



The probability that a given site is vacant is proportional to the Boltzmann factor for thermal equilibrium: $P = \exp(-E_V/k_B T)$, where E_V is the energy required to take an atom from a lattice site inside the crystal to a lattice site on the surface. If there are N atoms, the equilibrium number n of vacancies is given by the Boltzmann factor

$$\frac{n}{N-n} = \exp(-E_V/k_B T) \quad \text{---(1)}$$

If $n \ll N$, then

$$n = N \exp(-E_V/k_B T) \quad \text{---(2)}$$

If $E_V \approx 1 \text{ eV}$ and $T \approx 1000 \text{ K}$, then $\frac{n}{N} \approx e^{-12} \approx 10^{-5}$

The equilibrium concentration of vacancies decreases as the temperature decreases. The actual concentration of vacancies will be higher than the equilibrium value if the crystal is grown at an elevated temperature and then cooled suddenly, thereby freezing in the vacancies.

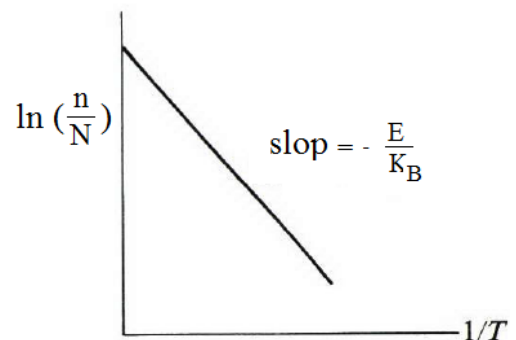
In ionic crystals it is usually energetically favorable to form roughly equal numbers of positive and negative ion vacancies. The formation of pairs of vacancies keeps the crystal electrostatically neutral on a local scale. From a statistical calculation we obtain

$$n = N \exp(-E_p/2k_B T) \quad \text{---(3)}$$

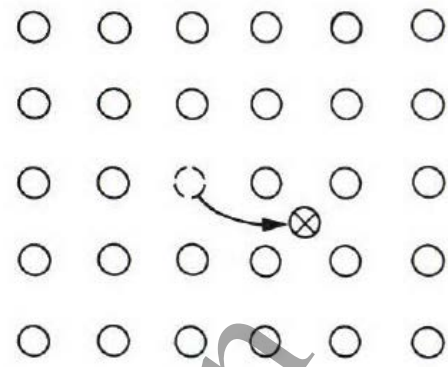
for the number of pairs, where E_p is the energy of formation of a pair.

At low temperature the number of vacancies is small because $kT \ll E_v$, but this number increases rapidly as the temperature rises. Thus for $N = 10^{29}$ atoms/m³ and $E_v = 1 \text{ eV}$, the number of vacancies at 300 K is $N \cdot 10^{12}$ vacancies/m³, while at 900 K it is about 10^{22} vacancies/m³. Therefore raising the temperature by only a factor of three causes the number of vacancies to increase by ten orders of magnitude.

$$\begin{aligned} n &= N \exp(-E_V/k_B T) \\ \left(\frac{n}{N}\right) &= \exp(-E_V/k_B T) \\ \ln\left(\frac{n}{N}\right) &= \frac{-E_V}{k_B T} = \left(-\frac{E}{k_B}\right) \frac{1}{T} \\ \text{slop} &= -\frac{E}{k_B} \end{aligned}$$



Frenkel defects : Another vacancy defect is the Frenkel defect in which an atom is transferred from a lattice site to an interstitial position, a position not normally occupied by an atom. In pure silver halides the most common vacancies are Frenkel defects.



A Frenkel defect

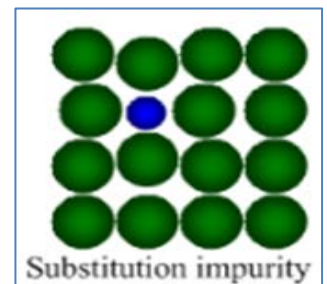
The calculation of the equilibrium number of Frenkel defects proceeds along the lines of Problem 1. If the number n of Frenkel defects is much smaller than the number of lattice sites N and the number of interstitial sites, N' the result is

$$n \cong (NN')^{1/2} \exp(-E_f/2k_B T) \quad \text{--- -- -- -- -- (4)}$$

where E_f is the energy necessary to remove an atom from a lattice site to an interstitial position.

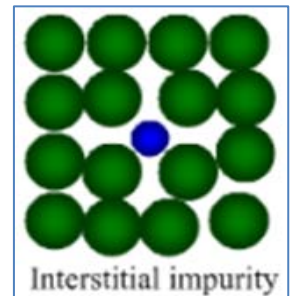
2- Extra atoms:

A **substitutional impurity atom**: (ذرة شائبة استبدالية) is an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. Substitutional impurity atoms are usually close in size (within approximately 15%) to the bulk atom. An example of substitutional impurity atoms is the zinc atoms in brass. In brass, zinc atoms with a radius of 0.133 nm have replaced some of the copper atoms, which have a radius of 0.128 nm.



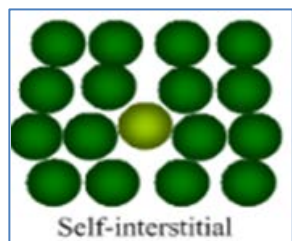
Substitution impurity

Interstitial impurity atoms: (ذرة شائبة بينية) are much smaller than the atoms in the bulk matrix. Interstitial impurity atoms fit into the open space between the bulk atoms of the lattice structure. An example of interstitial impurity atoms is the carbon atoms that are added to iron to make steel. Carbon atoms, with a radius of 0.071 nm, fit nicely in the open spaces between the larger (0.124 nm) iron atoms.



Interstitial impurity

A **self-interstitial atom**: (ذرة ذاتية بينية) is an **extra atom** that has crowded its way into an interstitial void in the crystal structure. Self-interstitial atoms occur only in low concentrations in metals because they distort and highly stress the tightly packed lattice structure.



Self-interstitial

Q.) Briefly discuss the reasons that , the Frenkel defect is not usually present in metals except under special circumstances?

Because of the additional elastic energy involved in squeezing an atom into an interstitial position, the Frenkel defect requires a large amount of energy, and for this reason is not usually present in metals except under special circumstances.

Q.) Why the vacancies usually exist only near free surfaces, grain boundaries, and dislocations, rather than inside a perfect crystal?

Because only at surfaces, boundaries, or dislocations can they be created without a concomitant formation of interstitials. In other words, these extended defects act as vacancy sources.

Q.2) Schottky vacancies. Suppose that the energy required to remove a sodium atom from the inside of a sodium crystal to the boundary is 1eV . Calculate the concentration of Schottky vacancies at 300K. Hint: N is the total number of atoms in the sodium $N = 2.5 \times 10^{22}$ atoms/cm³ .

Solution:

From $n = N \exp(-E_V/k_B T)$ & $k_B T(300 \text{ K}) = 0.025 \text{ eV}$

E_V = is the energy required to form a vacancy = 1 eV

Thus, $n = (2.5 \times 10^{22})(4 \times 10^{-18}) \cong 10^5$ per cm³

Q.1) Frenkel defects. Show that the number n of interstitial atoms in equilibrium with n lattice vacancies in a crystal having N lattice points and N' possible interstitial positions is given by the equation

$$E_I = k_B T \ln [(N - n)(N' - n)/n^2] ,$$

whence, for $n \ll N, N'$, we have $n = (NN')^{1/2} \exp(-E_I/2k_B T)$. Here E_I is the energy necessary to remove an atom from a lattice site to an interstitial position.

Solution:

$U = nE_I$. The number of ways to pick n from N is $N!/(N - n)!n!$. The number of ways to put n into $N' = n!/(N' - n)!n!$. Entropy:

$$S = k_B \left[\log \frac{N!}{(N - n)!n!} + \log \frac{N'!}{(N' - n)!n!} \right]$$

$$\log \frac{N!}{(N - n)!n!} \approx N \log N - (N - n) \log (N - n) - n \log n$$

$$\log \frac{N'!}{(N' - n)!n!} \approx N' \log N' - (N' - n) \log (N' - n) - n \log n$$

$(\frac{\partial F}{\partial n})_T = \frac{\partial U}{\partial n} - T \frac{\partial S}{\partial n} = 0$, in equilibrium; thus:

$$E_I = k_B T \left(\log \frac{N - n}{n} + \log \frac{N' - n}{n} \right) = k_B T \log \frac{(N - n)(N' - n)}{n^2}$$

for, $n \ll N, N'$, $E_I = k_B T \log (NN'/n^2)$; $n = \sqrt{NN'} e^{-E_I/2k_B T}$.

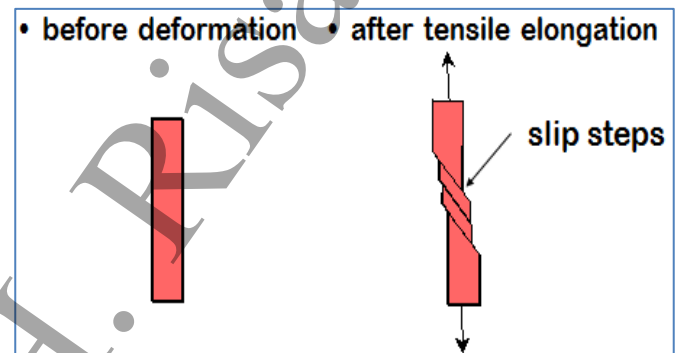
✚ Line defect (One dimensional defects):

When the deviation from the perfect arrangement is present in the entire row of lattice points, then the defect is known as line defect. These are commonly called as dislocation.

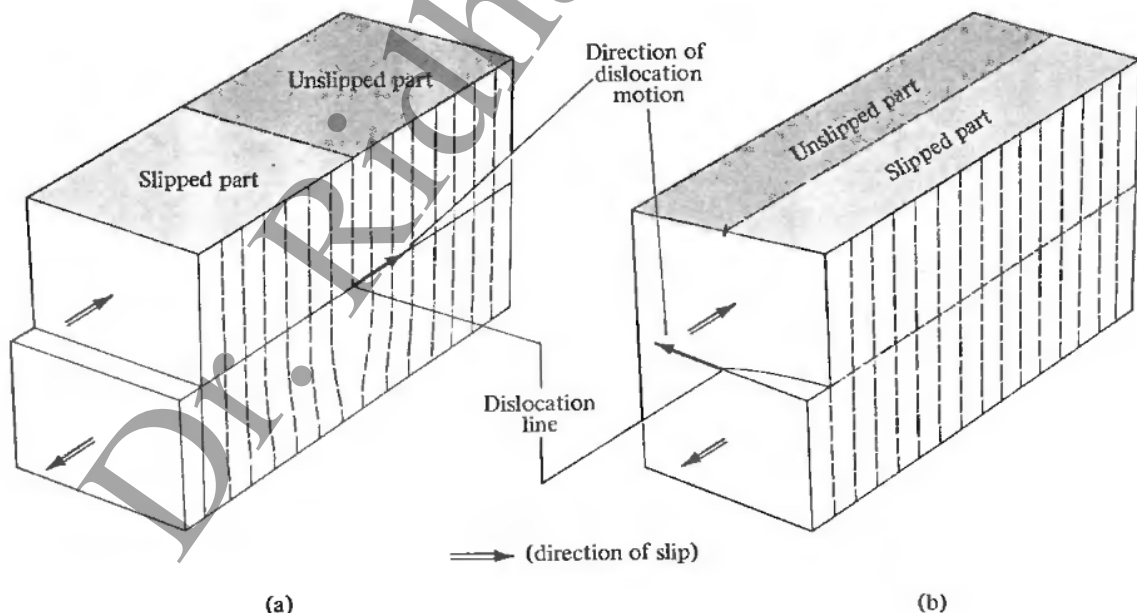
Dislocation:

- are line defects,
- cause slip between crystal plane when they move,
- produce permanent (plastic) deformation.

Line defects are dislocations. Dislocations are areas where the atoms are out of position in the crystal lattice and cause the crystal defects. They are generated and displaced by applying stress. The motion of dislocations allows slip - plastic deformation to occur.



The two main types of dislocations are the edge dislocation and the screw dislocation.



(a) Slip in a crystal via the motion of an edge dislocation.

(b) Slip in a crystal via the motion of a screw dislocation.

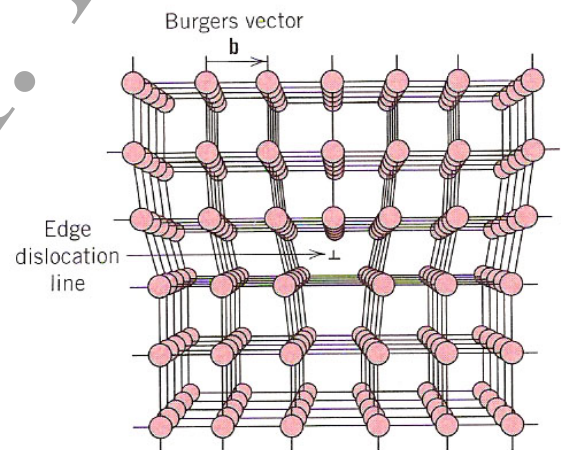
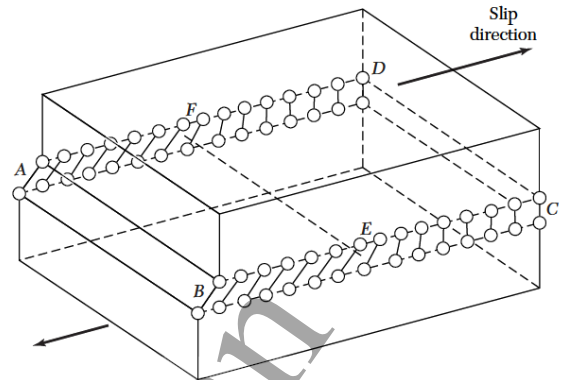
1- Edge Dislocation:

Figure shows a simple cubic crystal in which slip of one atom distance has occurred over the left half of the slip plane but not over the right half. The boundary between the slipped and unslipped regions is called the dislocation.

An edge dislocation EF in the glide plane $ABCD$. The figure shows the slipped region $ABEF$ in which the atoms have been displaced by more than half a lattice constant and the unslipped region $FECD$ with displacement less than half a lattice constant.

Its position is marked by the termination of an extra vertical half-plane of atoms crowded into the upper half of the crystal as shown in Figure. Near the dislocation the crystal is highly strained. The simple edge dislocation extends indefinitely in the slip plane in a direction normal to the slip direction.

This dislocation is a line defect because distortion is present only in the immediate vicinity of the dislocation line. This area is called dislocation core or area. Dislocation lines are along the top of extra half plane. This type of dislocation can distort the perfect crystal with a small stress. **This dislocation moves parallel to the direction of stress.**



The magnitude and the direction of distortion in crystal lattice is given by the burger vector B . In edge dislocation, burger vector is perpendicular to dislocation line.

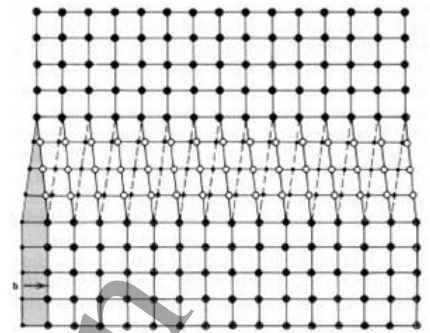
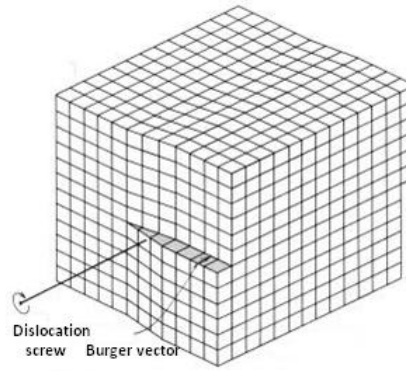
The magnitude and the direction of distortion in a crystal lattice is given by burger vector B . **In edge dislocation, burger vector is perpendicular to the dislocation line.**

2.Screw Dislocation

This is the second type of line defect which can't be easily envisioned. The movement of screw dislocation is a result of shear stress **but the defect moves in perpendicular direction of the stress** of the atom displacement. This can be explained with a metal block shown in the figure below by applying shear stress.

If a shear stress is applied to the block of metal as shown in figure (a). The plane of atoms of top side will not move from their original position as shown in figure (b). The atoms of the bottom side have moved to their new position in

the lattice and have re-established metallic bonds. The middle side atoms are in the process of moving. In this, only a small portion of the bonds are broke at a time. This movement requires a much smaller force than breaking all the bonds



across the middle plane and edge dislocation. The atoms will continue the movement with increasing shear stress.

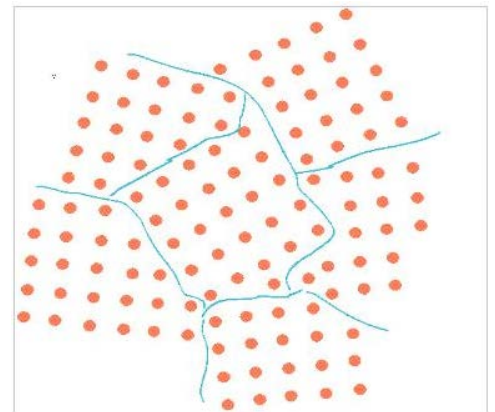
The burgers vector, b , is parallel to the slip plane

✚ Surface defect (Two dimensional defects) Planar Defects:

A planar defect is distortion in a perfect crystal across the plane. The two main types of defects are Stacking & grain boundary.

1- Grain boundary: This is another type of planar defect which is found in poly crystals. Single crystal is found in specially controlled growth conditions. Solids are made of a number of small crystallizes which are also known as Grains. The size range of grains is up to nanometers to millimeters. The orientations of atomic planes rotate with respect to their neighboring grains. All the grains are separated by boundaries which are called Grain boundaries and the atoms in this region are not in perfect arrangement. In the crystallization process of solid, these boundaries give the uneven growth to the solid.

These boundaries are important as they develop the opaque property in the material and also affect the mechanical properties. They limit the lengths and the movement of dislocations. It means more grain boundary surface area or small grain give more strength than a larger grain. Grain's size can be controlled by temperature cooling. Rapid cooling gives the small grains while slow cooling produces larger grains. This is the reason for the low strength, hardness and ductility of large grains at room temperature.



2- Stacking Fault: A distortion in the long-range stacking sequence can produce two other types of crystal defects.

1. a stacking fault.
2. a twin region

Stacking faults occur: during crystal growth as part of other defects because they evolve from other defects

It is sometimes useful to distinguish three kinds of stacking fault. An **extrinsic stacking fault** is one that can be created by inserting an extra plane of atoms into the structure. In the ...ABC|B|ABC... pattern given above the plane marked |B| is an extrinsic stacking fault.

An **intrinsic stacking fault** is one that can be created by removing a plane of atoms. In the sequence ...ABC||BCABC.. the defect marked || corresponds to a missing A-plane, and is hence an intrinsic stacking fault.

The third kind of stacking fault is called a **twin boundary**, and is a surface that separates two volumes of crystal that are mirror images of one another. In the sequence ...ABCAB|C|BACBA... the plane marked C is a twin boundary;

Volume defects (Three dimensional defects):

Volume defects as name suggests are defects in 3-dimensions. These include pores, cracks, foreign inclusions and other phases. These defects are normally introduced during processing and fabrication steps. All these defects are capable of acting as stress raisers, and thus deleterious to parent metal's mechanical behavior. However, in some cases foreign particles are added purposefully to strengthen the parent material.