

Solid State Physics

Chapter 1: Crystal Structure

(4)

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Introduction:

The material (elements and compounds) in three cases as we knew earlier or is the case of solid, liquid and gaseous matter varies in that it possesses one of these cases in different distances and the strength of the bond between their atoms. It is important to note here that pressure and temperature are the main causes of the change in the state of matter. A fourth case of matter is the state of the plasma, in which the substance is ionized gas, and a fifth case in which the material appears in high-energy atomic particles. From the above, we can come to the conclusion that "the kinetic energy of the molecule or the atom is responsible for determining the state in which the substance appears."

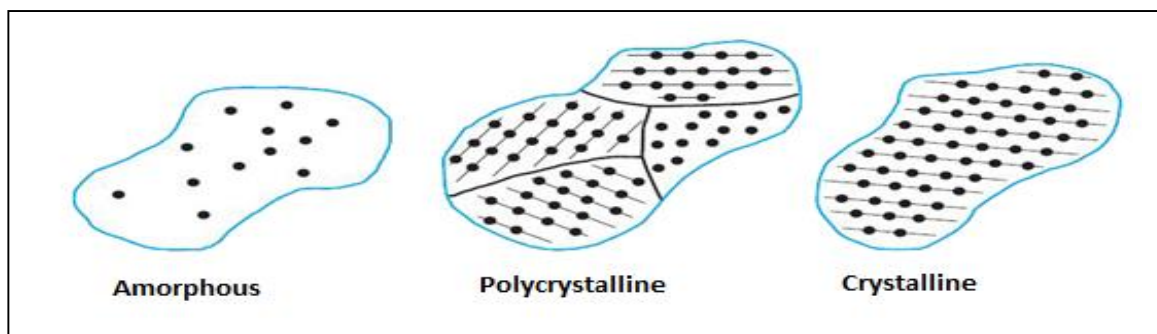
Solid and non-crystallized solids:

Crystalline materials: are the solids whose atoms are geometrically arranged so that their positions are borderline in this shape. This is a long-range order, either in two dimensions of two-dimensional integers or three dimensions of three-dimensional ones.

The crystallized material contains rows of atoms collected and periodically arranged and have a similarity symmetry and can be considered as a duplicate of any cell unit of these materials are iron, gold and sodium chloride and others.

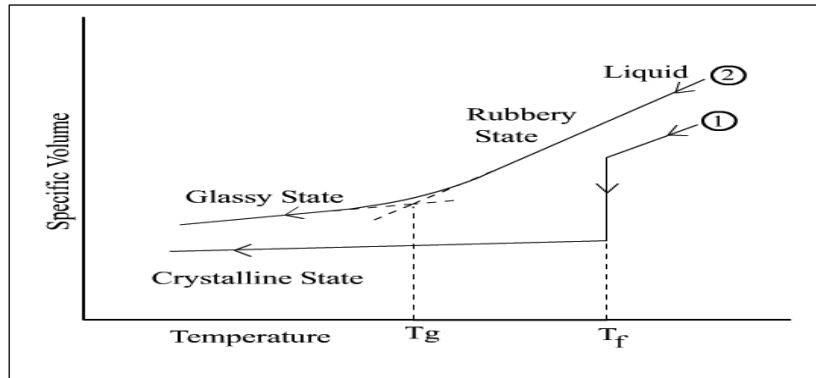
Non-Crystalline Materials: Also called amorphous substances: substances that accumulate their atoms randomly and without arrangement, such materials glass.

There are both amorphous and amorphous substances such as silicon and germanium and the reason is the way they are prepared or how they are made.

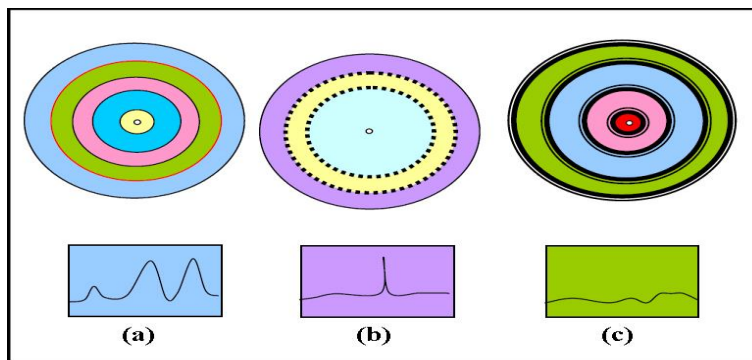


Practical distinction can be made between crystallized and non-crystallized materials by three independent criteria:

1 - Crystallized material crystallized suddenly and at a certain temperature constant always non-crystalline materials fused over a certain temperature range.



2. Non-crystallized materials will be dispersed at x-ray diffraction in the form of concentric rings, while this formation will be of crystallized materials, distinct and separate spots, with identical symmetry.



(XRD) of (a) Polycrystalline (b) single crystal (c) Amorphous crystal

3. All crystallized materials are differentiated by the **anisotropic** directional properties of varying degrees. The non-crystallized materials are all the same as the **isotropic** properties, which does not show any effect of the direction on their properties.

Basic terms:

Crystallography: is a science that is interested in studying solid materials in all its forms and phenomena and is divided into:

- 1 - Science of crystalline engineering: and is interested in studying the symmetry of crystals and their external forms.
- 2- Chemistry of chemical crystals: It is interested in studying the origin of crystals and how to grow them.

Crystal: A solid object that contains a number of atoms aligned geometrically and consists of very small units that are regularly repeated in the three dimensions, called **unit cell**.



The basis of crystalline construction is repetition and there are crystals on the types:

1- Real crystals represent most of the crystals in nature and contain some defects and distortions.

2 - Perfect crystals, which is a supposed crystalline, where we assume the existence of a perfect crystal free of defects and distortions for the study and there is no perfect crystal in nature and is similar to the idea of ideal gas and has the ideal crystal:

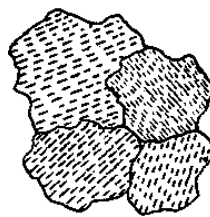
A) Periodicity of three-dimensional, as identical groups of atoms repeat themselves at exactly equal intervals.

(B) They may have large formations of periodic arrangements.

Types of real crystals:

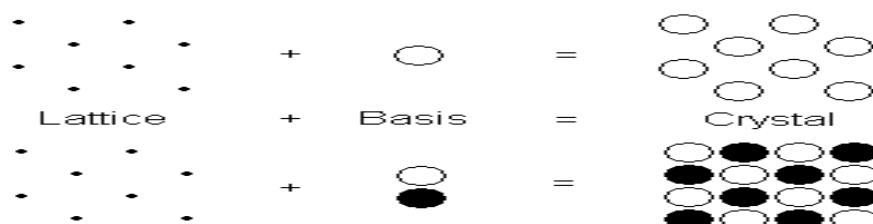
1-A single crystal: has a periodicity of three-dimensional crystal model extends through the entire crystal.

2-Polycrystalline crystals where the periodicity of the model does not extend throughout the crystal but ends at the limits of the crystal called **grain boundaries**.



Crystal structure: It can be defined by the relationship between the Basis and the Lattice.

Basis + Lattice = Crystal Structure



Basis: An atom, ion, molecule or group of atoms is called a point and each point is connected with the other points to form a specific body. The basis for each point should be:

- 1 - Symmetrical parts in terms of structure, arrangement and direction.
2. The number of atoms in the primary unit cell is equal to the number of base atoms.

Lattice: A group of points arranged by a specific system, not a group of atoms. For the crystalline structure, an atom or group of atoms must be attached to each of the splicing points, which is called the base.

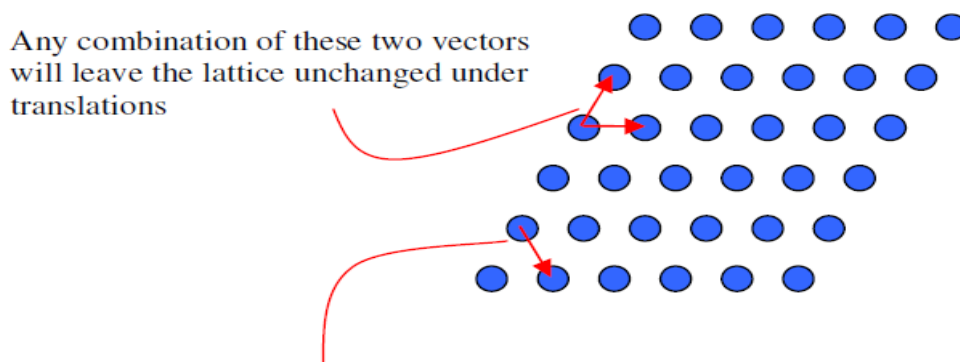
What is the difference between the atomic structure and the crystal structure?

Atomic structure is the number of neutrons and protons in the nucleus of the atom and the number of electrons in electronic orbits. Crystalline structure means the formation of atoms within crystalline solids in certain formations.

Translation Symmetry and Bravais Lattices

At the heart of solid state (crystal) physics is the assumption of translation symmetry. A non-trivial translation will leave any structure (a 2D object) or any pattern (a 3D object) and leave it unchanged.

For example, let's consider an infinite lattice;



We need to ask which points are equivalent. The vector between any two equivalent points leaves the lattice unchanged under translations. These vectors characterize the symmetry of the pattern. Equivalent points have the same environment in the same orientation.

Translation symmetry: 2D can be characterized by a two dimensional lattice or net and in three dimensions by a Bravais Lattice.

Definitions

1. A Bravais Lattice is an infinite array of points which appears exactly the same

when viewed from any one of the points.

2. A Bravais Lattice consists of all points with position vector \vec{T} of the form

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \quad \dots\dots\dots (1)$$

$$\vec{r} = \vec{r} + \vec{T} \quad \dots\dots\dots (2)$$

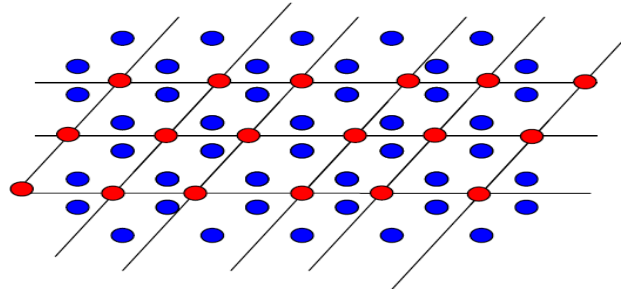
$$\vec{r} = \vec{r} + n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \quad \dots\dots\dots (3)$$

The translational operator \vec{T} connects two locations within the crystal so that the surrounding atoms appear to be similar to the two positions, and this is called the translational or creep operator.

Where (\vec{r}) and (\vec{r}) two locations within the crystal, where a, b, c are any three non-coplanar vectors and n_1, n_2, n_3 range through all integer values (positive, negative and zero).

Basis and unit cell

What is it that repeats to give the whole pattern/ structure?



There are two blue blobs in each parallelogram. The corners of each parallelogram (the red dots) are equivalent points.

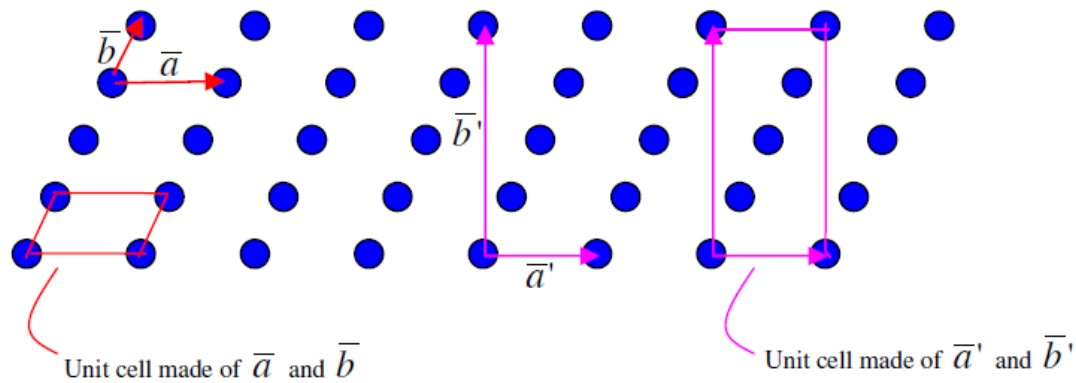
“The lattice plus the basis equals the structure”.

We start with a parallelogram (or a parallelepiped in three dimensions) whose edges are the lattice vectors. We associate the contents with all the lattice points. The choice is not unique, just like the choice of the lattice vectors.

Sometimes the basis is defined within a shape other than a parallelogram or a parallelepiped which tessellates the plane (or equivalent in three dimensions) i.e. it fills up all of space without overlapping or leaving gaps.

A *crystalline structure* consists of identical copies of the *basis* located at all the points of the Bravais lattice.

A *primitive unit cell* is the box which contains the basis. A unit cell may be chosen to contain more than one copy of the basis, this is known as a *non – primitive unit cell*.



The area of the unit cell made using a' and b' is four times greater than that of the unit cell constructed with a and b ; $|\vec{a}' \times \vec{b}'| = 4 |\vec{a} \times \vec{b}|$

Lattice vectors a and b are primitive and define a primitive unit cell. Lattice vectors a' and b' are non - primitive.

The non – primitive unit cell contains four copies of the basis.

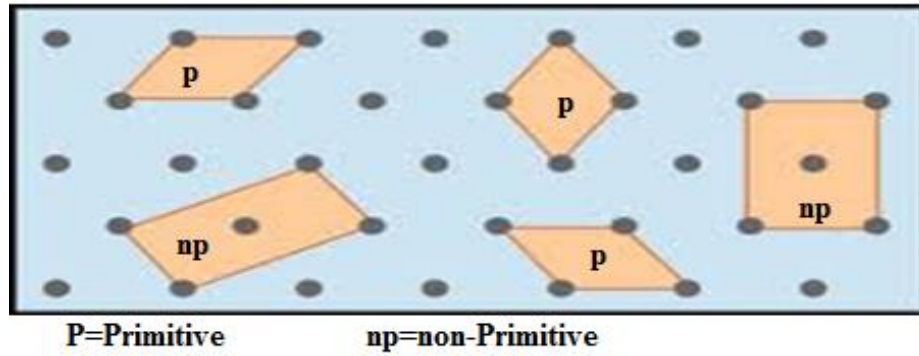
The choice of unit cell and lattice vectors is inseparable. A non – primitive choice is usually made to reflect some symmetry in the structure which may not be apparent in the primitive unit cell.

A unit cell is a region that fills all of space, without either overlapping or leaving voids, when translated through some subset of the vectors of a Bravais lattice. A unit cell is primitive if the same is true for all the vectors of a Bravais Lattice.

A *conventional unit cell* may be chosen which is non – primitive, usually to preserve some symmetry (or Orthogonality) of the lattice vectors.

Primitive Cell: A cell that contains points in its corners only and its axes are as short as possible and subject to equation (3).

Non-Primitive Cell: A cell that contains other points of interest in addition to the pillars, and the length of its axes is not as short as possible, and the equation (3)



$$\text{primitive unit cell volume} = \frac{\text{crystal volume}}{N}$$

Unit cell: It is the smallest unit in the space grid, a unit that is repeated in the three directions resulting in a large crystallization of the solid material and has the same symmetry as the unit cell.

The unit size of the 3D unit is given by the relationship:

$$\mathbf{V} = |\vec{a} \cdot \vec{b} \times \vec{c}| \quad \text{or} \quad \mathbf{V} = |\vec{a} \times \vec{b} \cdot \vec{c}|$$

It is important here to conduct the process of cross-directional (cross) first and then multiplying the dot and uses this law to calculate the size of primary and non-primary cells.

Example: A unit cell in the crystallization of its basic vector is given as follows:

$$\vec{c} = a(\hat{i} + \hat{j} + \hat{n}) \quad , \quad \vec{b} = a\hat{j} \quad , \quad \vec{a} = a\hat{i}$$

Calculate the size of this cell and row it.

Crystal Symmetry:

Crystal Symmetry: Is a repetition or matching of parts of a shape around a plane or straight or point. The circle is symmetrical around any diameter. If a particular position of a body can be described with more than one direction, so can not distinguish between these surfaces it is said that this body is symmetrical. The ball is symmetrical around its largest circular plane. The cube has many similarities. It is diametrically symmetrical, cylindrical, round, and around its center. When the 32 point groups for the basis are incorporated into the 14 Bravais lattice, there are 230 space groups.

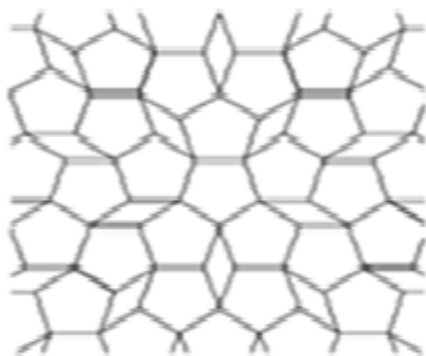
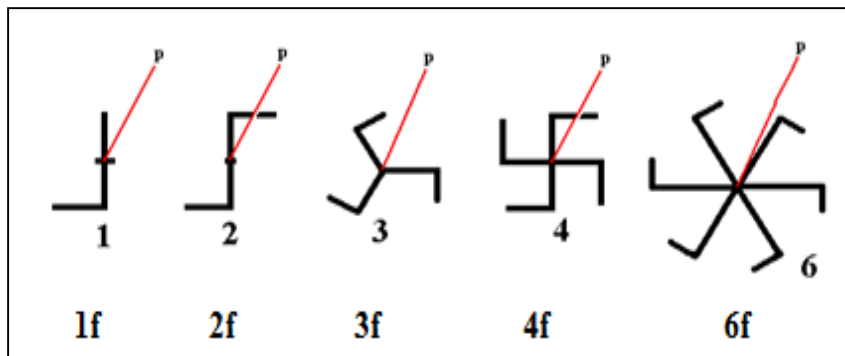
Crystal Asymmetry: It is a form that does not have repetition and has no match in parts such as the right hand or the left hand of the human.

The symmetry in the crystal is a process or effects that can be imagined to occur on the crystal and after the completion of the crystal appears as the origin of any repetition or return parts to the positions that were occupied before the occurrence of those processes.

The symmetry or basic elements of symmetry are:

1 - suitable rotational axis: is a false line passes through the center of the crystal, so that if a full cycle (360°) without any offset to repeat during that session and the positions of the crystal a number of times and must be the angle of rotation (θ) one of the equal parts obtained from the division of the full cycle on the integer numbers n is called Fold.

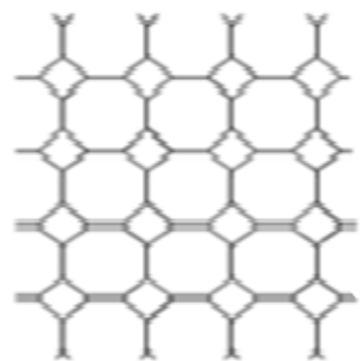
Where these numbers correspond to the permissible degrees of symmetry $n = 1, 2, 3, 4, 6$ and $\theta = 360^\circ / n$ where 5, 7, 8 are not allowed because they either leave a vacuum or The four units of the unit are four-dimensional and the simplest example of the appropriate rotational axis is the rotation of the fan with three blades (3 folds) $\theta = 120^\circ$ and four blades (4 folds) $\theta = 90^\circ$.



5f



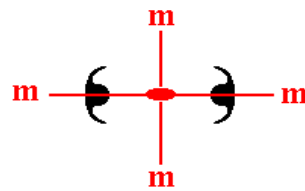
7f



8f

2-Non suitable rotational axis: It is a process of rotation followed by a reflection process to repeat the body itself, ie it is a hybrid process (rotation + reflection) and there are five axes rotational reflective symbolizes: ($\tilde{1}$, $\tilde{2}$, $\tilde{3}$, $\tilde{4}$, $\tilde{6}$) one tild $\tilde{1}$.

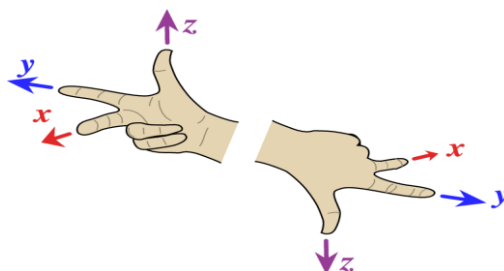
3-The plane of symmetry: an imaginary level that divides the body or crystal into two similar halves so that one of the halves can be a picture of the other, such as the human body if divided into two halves equal lengthwise. This symbolizes the process (m) (mirror)) and if the body section to several symmetrical sections, for example, two symmetrical up and down and two symmetrical to the right and to the left like the rectangle, the mirror is double (mm) (double mirror).



2 m m

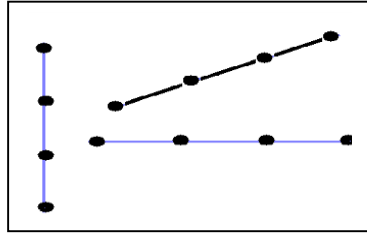
4-The center of symmetry: The center of symmetry is a center of inversion because this center has the property of the heart of all the space through one point of intersection and the simplest example of our position the left hand thumb to touch the right hand thumb and one hands fingers down and inside us towards us the other hand and fingers to the top and the back of the hand we have got A symmetry center symbolizes: $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$

one bar $\bar{1}$.



Plain lattices and their symmetries:

The lattice, as previously passed, is a set of points arranged by a specific system, and it repeats itself periodically. The one-way rewind is called linear, two-dimensional or three -dimensional space lattice. The linear lattice consists of similar points of equal proportions .There is one basic type of linear lattice because there is only one way of arranging points and the only difference is the distance between points.

**Classifying lattices: symmetry in 2D****Two Dimensional Lattice Types**

All of the possible two dimensional lattices fall into one of these 5 categories;

1- Square; $|\vec{a}| = |\vec{b}|$: $\gamma = 90^\circ$ 4 fold - 4 mirror planes.

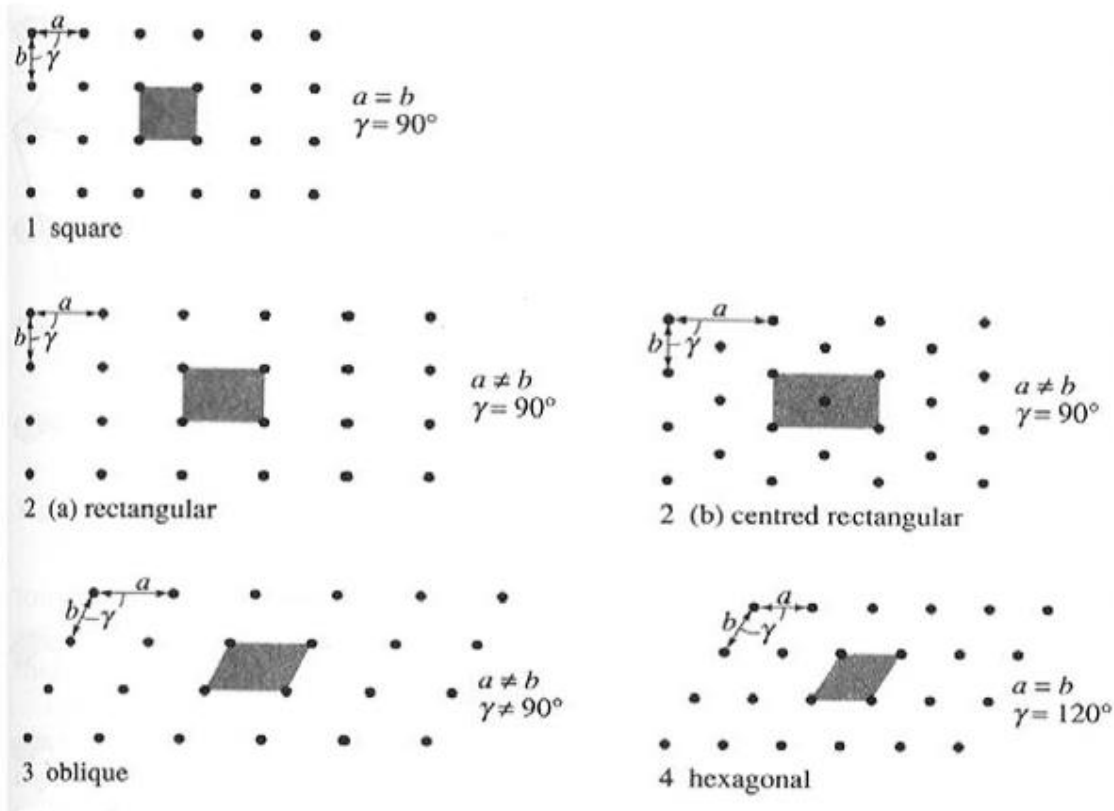
2- Rectangular ; $|\vec{a}| \neq |\vec{b}|$: $\gamma = 90^\circ$ 2 fold - 2 mirror planes.

3- Hexagonal; $|\vec{a}| = |\vec{b}|$: $\gamma = 120^\circ$ 6 fold - 6 mirror planes

A special case of rectangular lattice is centered when its initial cell is characterized by the characteristics of $\vec{a} = \vec{b}$ and $\gamma \neq 60^\circ \text{ or } 120^\circ$

4- Centred Rectangular ; $|\vec{a}| \neq |\vec{b}|$: $\gamma \neq 90$ $\gamma = \left(\cos^{-1} \frac{a}{2b}\right)$.

5- Oblique $|\vec{a}| \neq |\vec{b}|$: $\gamma \neq 90$



Space Lattice (3D) and Crystal Systems:

There are five basic types of **Bravais lattices** (in three dimensions)

1-Primitive Lattice (P)

Where each unit cell contains $1/8$ points in each of its eight corners, so that each initial cell contains one syllable point (point $8 * 1/8 = 1$).

2-Face Centered Lattice

It is marked with the symbol F and contains $1/8$ points in its eight corners, plus $1/2$ point of the six faces, ie, the total of these elements is 4 points ($8 * 1/8 + 6 * 1/2 = 4$ points).

3-Body Centered Lattice

It is symbolized by the symbol (I) and contains $1/8$ points in its eight corners plus one point of the center of the body, ie, the total number of these bars is two points ($8 * 1/8 + 1 = 2$ points).

4-Base or Side Centered Lattice

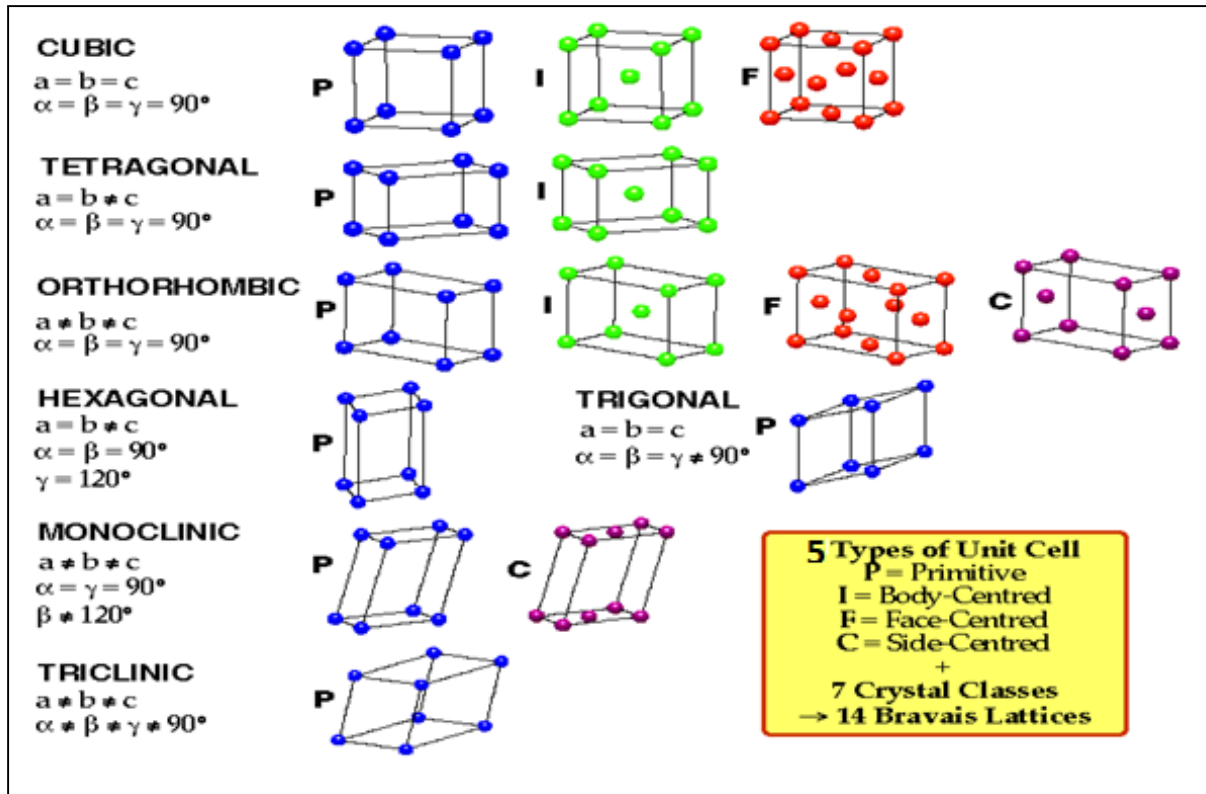
This type is characterized by having $1/8$ points in its eight corners plus $1/2$ point of spike in two opposite faces of its six faces and therefore the sum of its contents are two points ($8 * 1/8 + 2 * 1/2 = 2$ points). These symbols are denoted by the symbol A, B or C by the location of the two points on the sides of the cell.

5-Rhombohedral Lattice

It is a special case of primary alloys and is symbolized by the symbol R. The shape of the cell is the object of the faces but the three axes are not perpendicular i.e. that $a \neq b \neq c$ and $\alpha = \beta = \gamma \neq 90^\circ$.

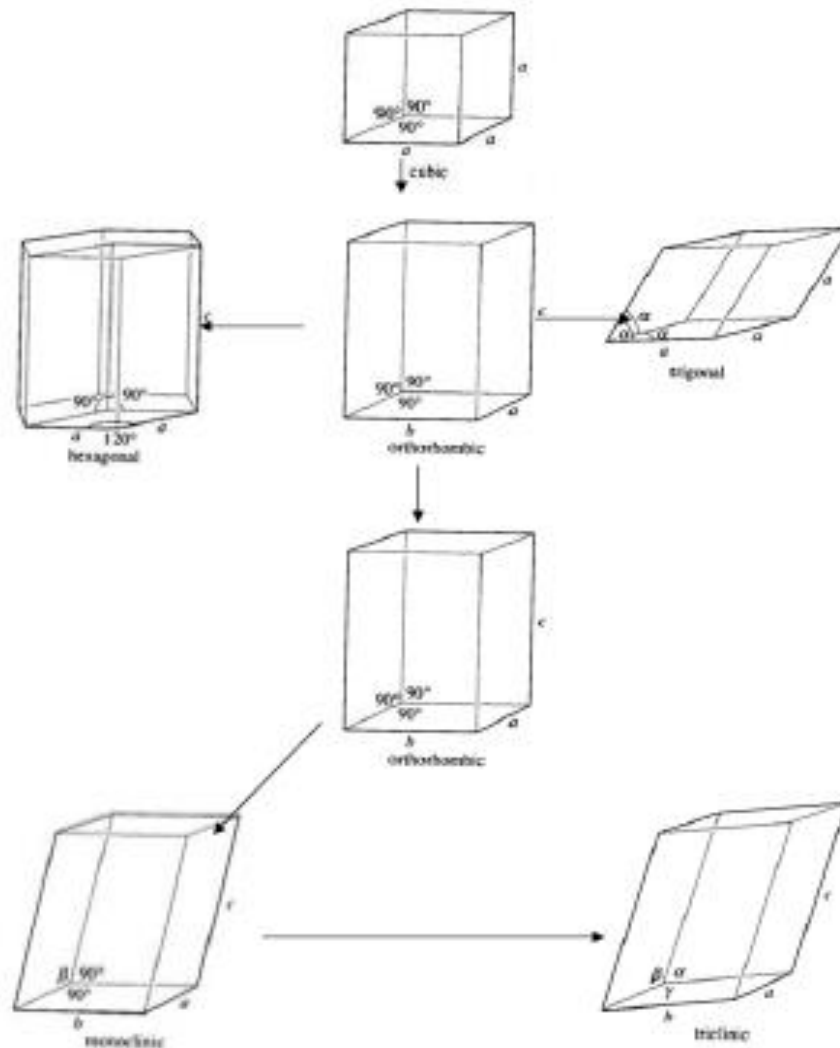
The 5 types of basic alloys are distributed on 7 crystalline systems, of which 14 are Bravais lattices.

The following are the seven crystalline systems and the **14 Bravais lattices** alloys:



The **seven** crystalline systems can be arranged from **high symmetry (cubic)** to their **lowest symmetry (triclinic)**.

	Cubic P (sc), I (bcc), F (fcc)	
Hexagonal P	Tetragonal P, I	Trigonal R
	Orthorhombic P, C, I, F	
	Monoclinic P, C	
	Triclinic P	



We can observe that the Hexagonal system and Trigonal system have the same degree of symmetry.

The simple cubic lattice(sc) or (SC)

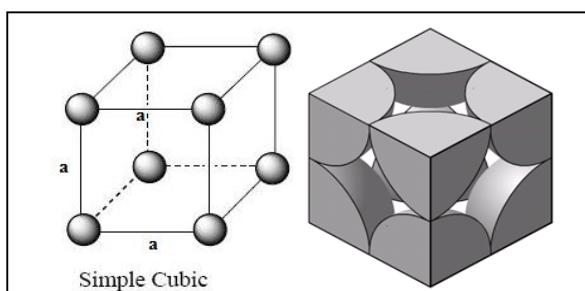
The simple cubic lattice has basis vectors and the unit cell is a simple cube. The simplest crystal based on this lattice has single atoms at the lattice points. Each atom has six identical nearest neighbors.

Features of Cubic Cubes:

The cube system includes three types of lattices:

Simple Cubic lattice (sc or SC):

It contains a single point of $1/8$ points in each of the eight corners and its vectors: \vec{a} , \vec{b} , \vec{c} , which are primary vectors of length L.



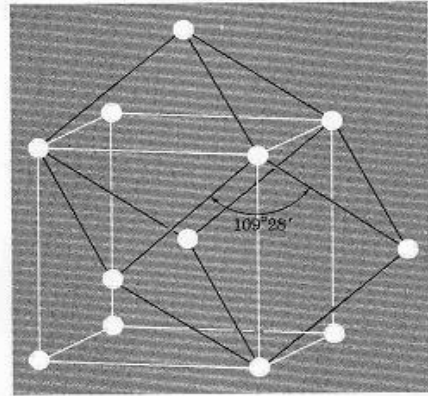
$$\frac{1}{8} \times 8 = 1 \text{ point}$$

Body Centered Cubic (bcc or BCC):

It contains two points in one of the pillars and one in the center of the cell, which is a non-primary cells because the unit cell is not initial and can calculate the primary vectors and then the cell unity of the initial as follows:

We draw three vectors from the spike point in the center of the cube and consider it the point of origin, ending with three points at the corners of the cube as in the figure and completing the shape of the facets to obtain the primary vector cell with the primary vectors: \vec{c} , \vec{b} , \vec{a} .

$$\left. \begin{aligned} \vec{a} &= \frac{a}{2} \begin{pmatrix} \hat{i} + \hat{j} - \hat{k} \end{pmatrix} \\ \vec{b} &= \frac{a}{2} \begin{pmatrix} -\hat{i} + \hat{j} + \hat{k} \end{pmatrix} \\ \vec{c} &= \frac{a}{2} \begin{pmatrix} \hat{i} - \hat{j} + \hat{k} \end{pmatrix} \end{aligned} \right\} \text{ for primitive cc}$$



$$\frac{1}{8} \times 8 + 1 = 2 \text{ points}$$

The primary unit cell is the Rhombohedral side length $\left(\frac{\sqrt{3}}{2}L\right)$ and its axes \vec{a} , \vec{b} , \vec{c} , and each of them has an angle of approximately 109° and the location of the two points: 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Q / Prove that the primitive unit cell size of the bcc cube is equal to 1/2 the size of the normal unit cell of the same lattice.

$$V = |\vec{a} \times \vec{b} \cdot \vec{c}| \quad \text{or} \quad V = |\vec{a} \cdot \vec{b} \times \vec{c}|$$

Q / Prove that the volume of a primitive lattice of the bcc is 1/2 volume of the normal lattice.

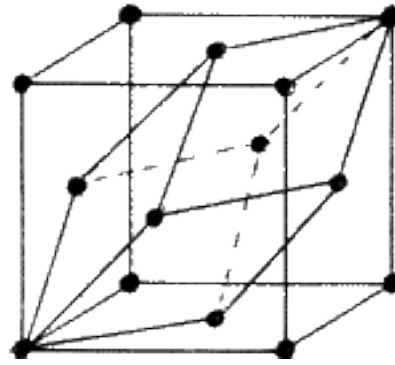
Face Centered Cubic (fcc or FCC):

It contains four points, a point of the hips and a half point in each of the six faces. It is not an initial complication because the unit cell is not prime. To get the primary vector, we draw three vectors from the point of the spike in one of the corners of the cube and consider it the point of origin, ending with the

splicing points located in the centers of the sides close to the point of origin as in the adjacent shape. We complete the two facets to obtain the initial unit cell with primary vectors:

$$\left. \begin{aligned} \vec{a} &= \frac{a}{2} \begin{pmatrix} \hat{i} + \hat{j} \end{pmatrix} \\ \vec{b} &= \frac{a}{2} \begin{pmatrix} \hat{j} + \hat{k} \end{pmatrix} \\ \vec{c} &= \frac{a}{2} \begin{pmatrix} \hat{i} + \hat{k} \end{pmatrix} \end{aligned} \right\} \text{للشبكة الأولية}$$

$$\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4 \text{ points}$$



Point's position: 000 , $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$

Q / Prove that the volume of a primitive lattice of the fcc is 1/4 volume of the normal lattice.

Filling Factor or Packing Factor:

The ratio of the size of the atoms in a unit cell to the size of that unit cell is different. In order to calculate the **Filling Factor**, we assume that the adjacent atoms are very contact, that is, the shortest distance between two points of the diameter of the atom (nearest neighbor = $2r$) The percentage is calculated as follows:

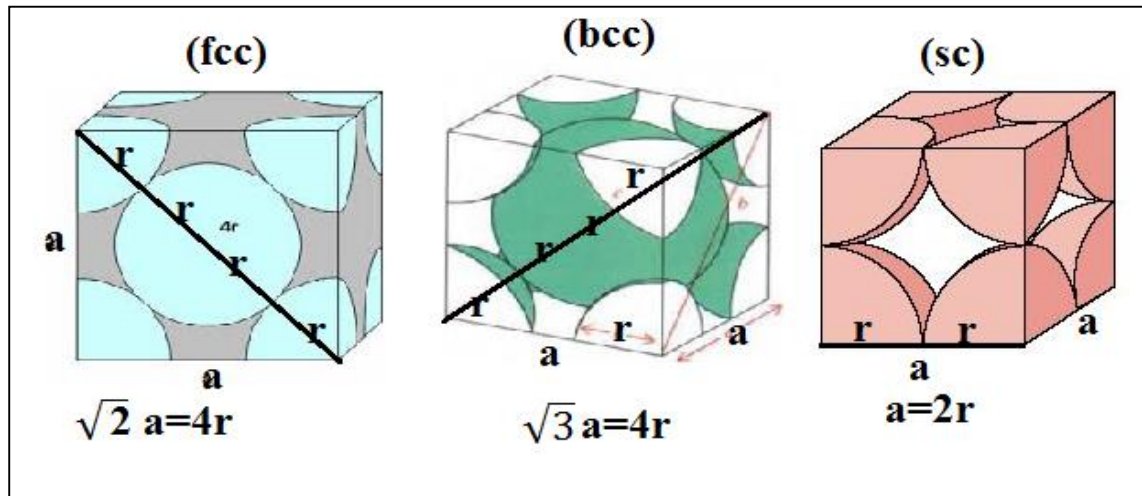
$$(\text{Unit cell in atoms number} * \text{per atom size}) / (\text{unit cell size}) * 100\%$$

The size of one atom

$$\text{Filling Factor} = \frac{\text{The volume of one atom} \times \text{The number of atoms in the unit cell}}{\text{The volume of unit cell}} \%100$$

$$P.F = \frac{\frac{4}{3} \pi r^3 * N}{V} * 100\% = \frac{4}{3} \pi r^3 * \frac{N}{V} * 100\%$$

Where r : atom's radius, $2r$: The diameter of the atom represents the nearest neighbor.



The table below that represents some of the specifications of the cubic system, where ($a = L$)

	sc	bcc	fcc
Volume of normal cell	L^3	L^3	L^3
Number of points for each normal cell	1	2	4
Number of points per unit size (N / V)	$1/L^3$	$2/L^3$	$4/L^3$
Number of nearest neighborhood	6	8	12
The distance of the nearest neighbor	L	$L \frac{\sqrt{3}}{2}$	$L \frac{1}{\sqrt{2}}$
The distance of the second neighbor	12	6	6
Second Neighborhood distance	$\sqrt{2}L$	L	L
Packing Factor	0.52	0.68	0.74

Theoretical Density Computation for Crystal

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density and compare the answer with its measured density.

$$\begin{aligned}\rho &= \frac{nA_{\text{Cu}}}{V_{\text{C}}N_{\text{A}}} = \frac{nA_{\text{Cu}}}{(16R^3\sqrt{2})N_{\text{A}}} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.023 \times 10^{23} \text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3\end{aligned}$$

The literature value for the density of copper is 8.94 g/cm³, which is in very close agreement with the foregoing result.

Miller Indices

These are indices for crystal planes: X-rays in X-ray crystallography are scattered by sets of parallel crystal planes.

Any plane is specified by 3 non-colinear points, such as the intercepts on the a₁; a₂; a₃ axes. That is, the translation vectors of the unit cell (or Bravais lattice).

So, to form the Miller indices:

General Principles of Miller Indices

1. If a Miller index is zero, the plane is parallel to that axis.
2. The smaller a Miller index, the more nearly parallel the plane is to the axis.
3. The larger a Miller index, the more nearly perpendicular a plane is to that axis.
4. Multiplying or dividing a Miller index by a constant has no effect on the Orientation of the plane
5. Miller indices are almost always small.

So, for example, if we have a plane which intercepts the axes at (2; 3 ;2), its reciprocal is (1/2 ; 1/3 ; 1/2), and scaling (multiply by 6 in this case) results in (3 2 3). These are the Miller indices.

If the intercept is negative, put a bar over the index. For example, for intercepts (-3; 2; 2), we will have indices ($\bar{2}$ 3 3).

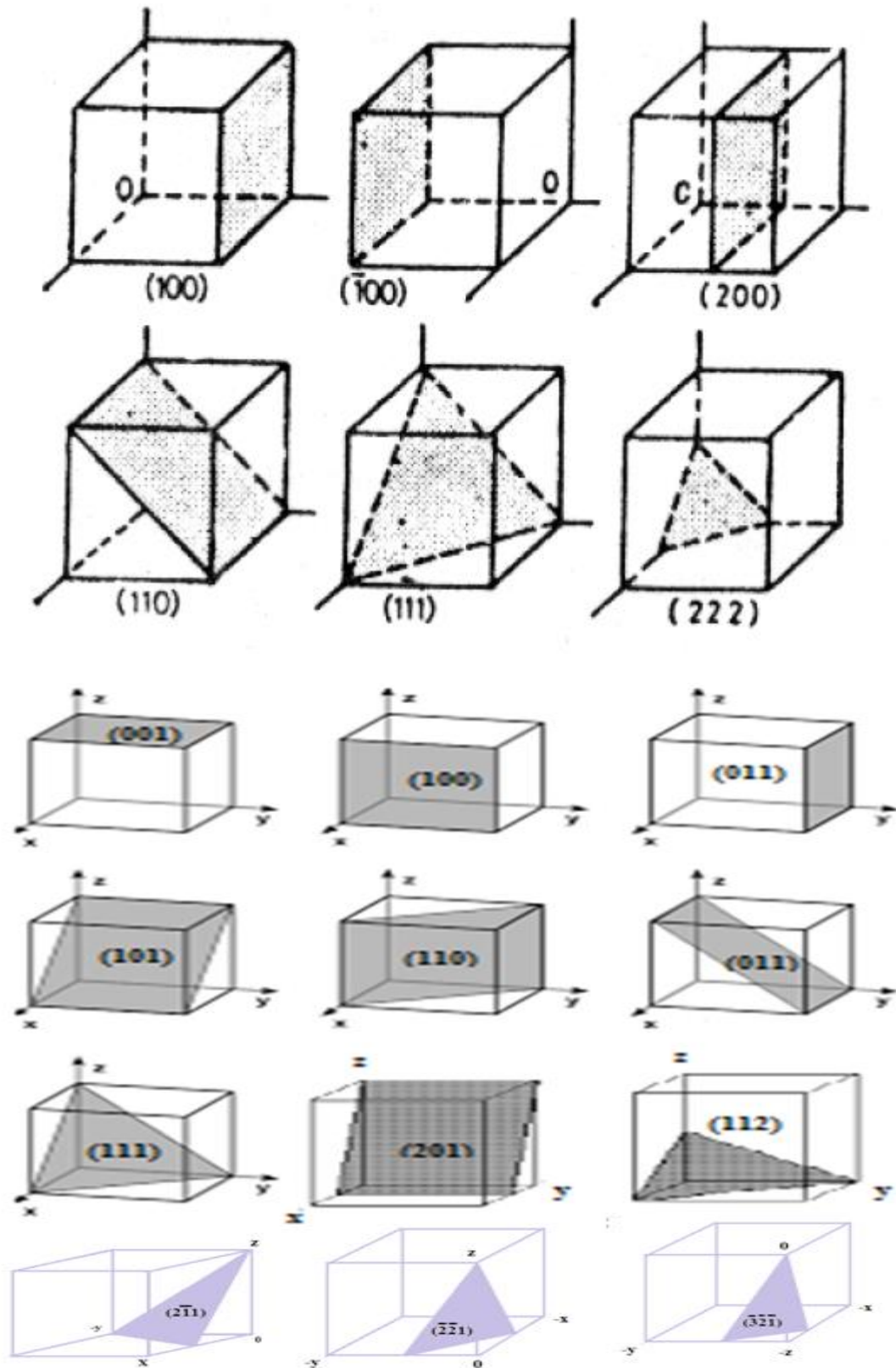
If the plane is parallel to an axis, its intercept will be at infinity, hence its index will be 0.

Planes with Miller indices (h; k; l) are parallel to those with (nh; nk; nl), for any integer n.

The axes are defined differently in each case. The axes for

- (a) Has intercepts at (∞ ; 1; ∞) and therefore Miller indices (0; 1; 0).
- (b) Has intercepts at (1; 1; ∞), and indices (1; 1; 0).
- (c) Has intercepts at (1; 1; -1), and therefore indices (1; 1; $\bar{1}$).

Q/If x, y and z axes intercept 3, 4, and 2, calculate the Miller indices.



Q / Draw the following crystalline surfaces of the cube system:

(200), (004), (023), (120), ($0\bar{1}0$), (001), (010), (222), (011),

$(331), (420), (2\bar{1}1), (\bar{1}31), (110), (\bar{1}10), (111), (020)$

The six cubic faces can be expressed as follows:

$(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1}) = \{100\}$

$\{333\}$: Means all planes equivalent to:

$\{333\} = (333), (\bar{3}33), (3\bar{3}3), (33\bar{3}), (\bar{3}\bar{3}3), (3\bar{3}\bar{3}), (\bar{3}3\bar{3}), (\bar{3}\bar{3}\bar{3})$

If all planes values are different for $\{h k l\}$ we obtain 48 different equal planes such as $\{423\}$, $\{253\}$, $\{134\}$ and others}. If two similar values of $\{h k l\}$ were obtained, 24 equal planes were found: $\{115\}$, $\{224\}$, $\{133\}$

Q/ Try to find the 24 equivalent surfaces

Hexagonal structure

The crystalline planes of the hexagonal form represent four Miller indices instead of three and write $(h k i l)$.

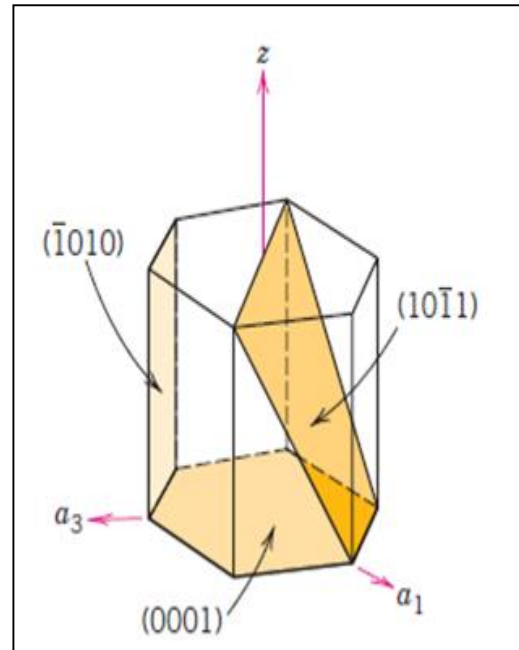
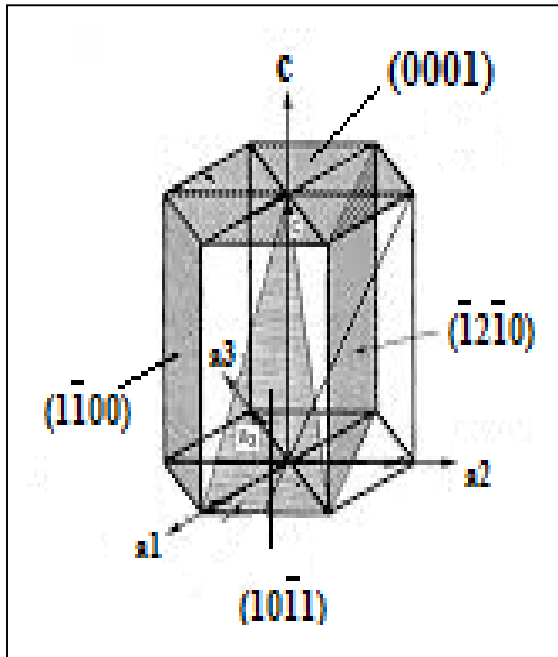
Example: Calculate Miller's indices in the hexagonal structure of its intersections.

$a_1 = 1$	$a_2 = -1$	$a_3 = \infty$	$c = \infty$	
1	- 1	∞	∞	<i>Intersections</i>
1	- 1	0	0	<i>Reciprocal</i>

Miller indices $(1 \bar{1} 0 0)$

The upper base (0001) and the lower base (0001). The axes of this lattice are called the axes of Baravis and are subject to the directional relation:

$$\vec{a_1} + \vec{a_2} = -\vec{a_3}$$



Direction of a Vector

To set any direction in the crystal, we use three parameters, u v w , and are written in $[uvw]$, which are integer numbers that do not have a common factor greater than one. There are equivalent directions in the crystal and to denote them are written in $\langle uvw \rangle$. When writing :

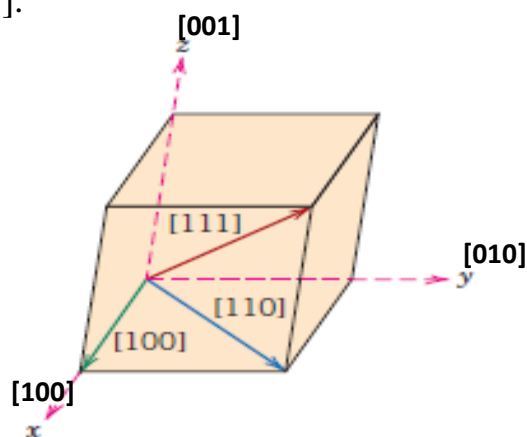
$\langle 110 \rangle = [110], [101], [011], [1\bar{0}1], [\bar{1}01], [01\bar{1}], [0\bar{1}1], [0\bar{1}\bar{1}], [\bar{1}\bar{1}\bar{1}] \dots$

We use square brackets to denote vectors, and round brackets for directions.

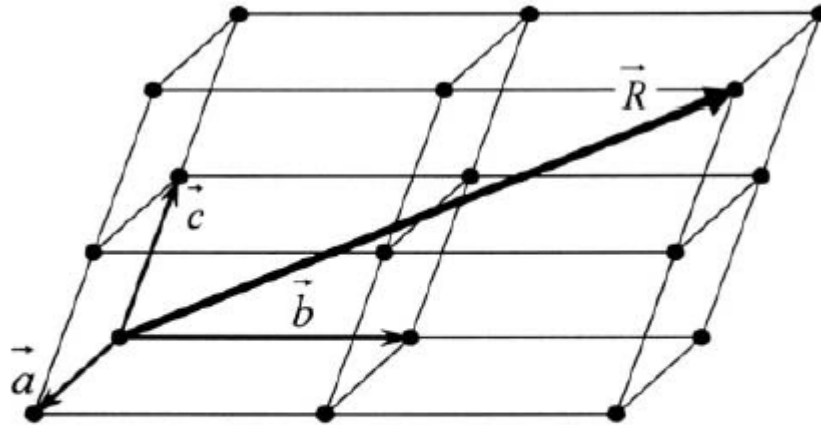
So, the indices are the smallest integers whose ratios are in the ratios of the components of the vector, referred to the crystal axes. So, for example, if:

$$\mathbf{v} = \frac{1}{3} \mathbf{a} + \frac{1}{3} \mathbf{b} + \frac{1}{6} \mathbf{c}$$

Then it has indices $[2\ 2\ 1]$.



Q: Determine the direction index for the lattice vector shown below.



A: We can decompose the vector \vec{R} as: $\vec{R} = 1\vec{a} + 2\vec{b} + 2\vec{c}$.
This corresponds to $u=1$, $v=2$, $w=2$, and the direction is thus $[122]$.

In general, direction $[h\ k\ l]$ is perpendicular to the plane of Miller indices $(h\ k\ l)$.

The Miller indices $(h\ k\ l)$ of the plane of the $[uvw]$ bound range of indices must be subject to the algebraic relationship:

$$hu + kv + lw = 0 \dots\dots\dots (1)$$

The range axis coefficients $[uvw]$ can be calculated for intersected planes such as:

$$u = k_1l_2 - k_2l_1$$

$$v = l_1h_2 - l_2h_1 \dots\dots\dots (2)$$

$$w = h_1k_2 - h_2k_1$$

To find Miller indices (hkl) for the plane consist of the two directions $[u_1\ v_1\ w_1]$ and $[u_2\ v_2\ w_2]$:

$$h = v_1w_2 - v_2w_1$$

$$k = w_1u_2 - w_2u_1 \dots\dots\dots (3)$$

$$l = u_1 v_2 - u_2 v_1$$

Find the plane (h k l) containing the two directions [110] and [211] using equations 3 and then find the direction of [uvw] to which planes (011) and (111) belong using equations (2).

How to calculate the angle \emptyset enclosed between two planes \emptyset :

The angle \emptyset between $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$ can be calculated in a cubic crystal and represents the angle between the two perpendiculars on these two planes as follows:

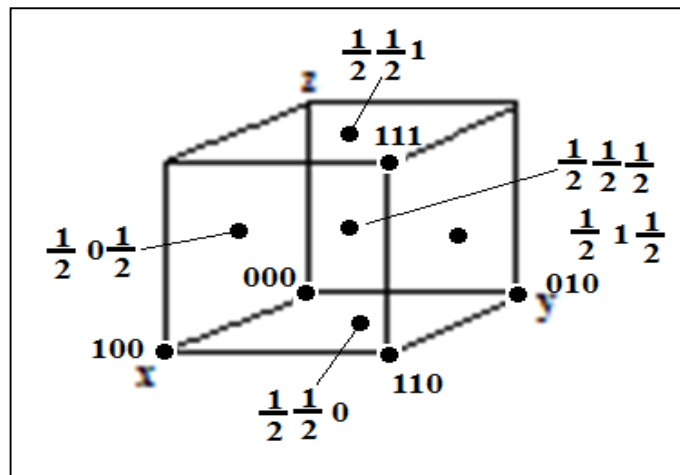
$$\emptyset = \cos^{-1} \left(\frac{(h_1 h_2 + k_1 k_2 + l_1 l_2)}{[(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)]^{\frac{1}{2}}} \right)$$

H.W: Find the angle \emptyset enclosed between the two planes:

(111) and (212), (312) and $(4\bar{2}1)$, $[12\bar{3}]$ and $[\bar{2}01]$ in a cubic crystal.

Positions of atoms in unit cell

Positions of atoms represent a point location in the unit cell with three uvw atomic coordinates where all the coordinates represent the distance of the origin point in units of a, b, c and uvw **without brackets and without commas**. The positions of the atoms within the unit cell are represented by fractional units less than one and the value of uvw does not always exceed one at all.



Notation	Designation
(hkl)	Plane
$\{hkl\}$	Equivalent plane
$[uvw]$	Direction
$\langle uvw \rangle$	Equivalent direction
$(hkil)$	Plane in hexagonal systems
$[uvtw]$	Direction in hexagonal systems

It represents the vertical distance between any two successive surfaces of a parallel set of planes in a cubic and d_{hkl} is given to any set of parallel surfaces in the crystallization of a cube whose length of ordinary L or a with the following relationship:

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

We note from the relationship that d_{hkl} depends on the numerical value of Miller's indices and does not depend on the signs of those coefficients. There are different groups of parallel planes with different Miller indices, but equal d_{hkl} , such as (333), (511) and planes (600), (422).

Here is a table of $1 / d^2$ values for some crystalline systems:

<i>Crystal system</i>	<i>Volume of normal Unit cell</i>	$\frac{1}{d^2}$
<i>Cubic</i>	L^3 or a^3	$\frac{h^2 + k^2 + l^2}{a^2}$
<i>Tetragonal</i>	a^2c	$\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
<i>Orthorhombic</i>	abc	$\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
<i>Hexagonal</i>	$\frac{\sqrt{3}}{2}a^2c$	$\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) \frac{l^2}{c^2}$

f

Q / Show that the perpendicular distance between two adjacent planes of a set (hkl) in a cubic lattice of lattice constant a is:

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad \text{for cubic structure}$$

In $\triangle ONA$.

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

ON represents the perpendicular distance between the ABC plane and the origin point O, which represents d_{hkl} .

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

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

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

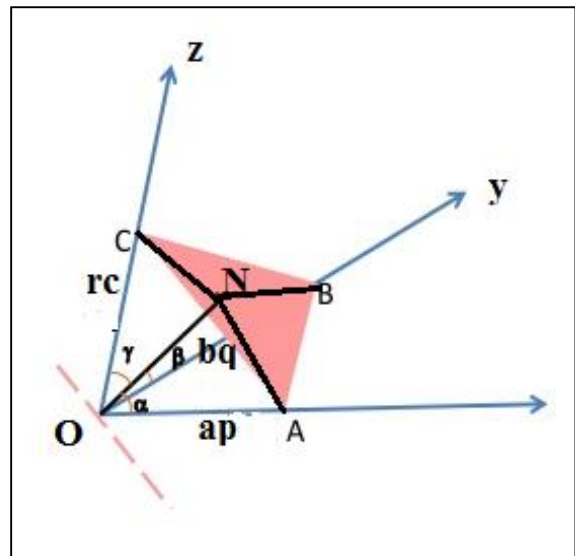
$$\triangle ONB : \cos B = \frac{ON}{OB} = \frac{d_{hkl}}{\frac{b}{k}} = \frac{k}{b} d_{hkl}$$

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

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

We have identical triangles: $\therefore \cos^2 \gamma = \left(\frac{l}{c} \right)^2 d_{hkl}^2 \dots \dots \dots (3)$

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



It can substitute (1), (2) and (3) in (4) produce:

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

In cubic system ($a = b = c$) ; so that leads to:

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

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

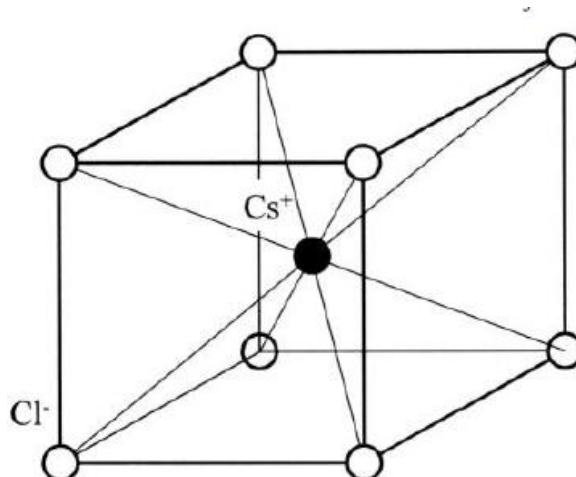
Simple Crystal Structures

Cesium Chloride Structure (CsCl)

The cesium chloride structure has a body-centered cubic (**bcc**) lattice and the corresponding Bravais lattice is simple cubic. The basis consists of **two** atoms located at the corners Cl^- (**000**) and center positions Cs^+ ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) of the cubic unit cell. Each atom may be viewed as at the center of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is **eight**.

Cl^- : (000)

Cs^+ : ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$)

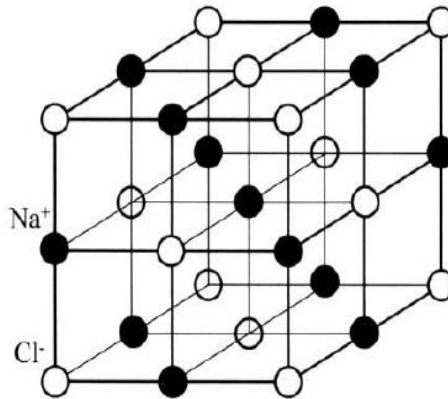


Sodium chloride structure

The structure of sodium chloride, NaCl, is shown in Fig. below. The Bravais lattice is **face-centered cubic (fcc)** and the basis consists of **one Na atom** and **one Cl atom** separated by one-half the body diagonal of the cubic unit cell. The standard unit cell contains **four sodium ions** and **four chlorine ions, four molecules** of sodium chloride with ions in the positions:

Cl⁻: (000); ($\frac{1}{2}\frac{1}{2}0$); ($\frac{1}{2}0\frac{1}{2}$); ($0\frac{1}{2}\frac{1}{2}$)

Na⁺: ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$); ($00\frac{1}{2}$); ($0\frac{1}{2}0$); ($\frac{1}{2}00$)



There are similar structures for sodium chloride such as: KCl, KBr, AgBr ... etc.

Diamond structure

Elements from the column IV in the periodic table, such as carbon (the diamond form), germanium, silicon and gray tin, crystallize in the diamond structure. The Bravais lattice of diamond is **face-centered cubic (fcc)**. The basis has two identical atoms located at (000) and ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) in the cubic unit cell, for each point of the fcc lattice.

The conventional cubic unit cell thus contains eight atoms. There is no way to choose a primitive unit cell such that the basis of diamond contains only **one** atom.

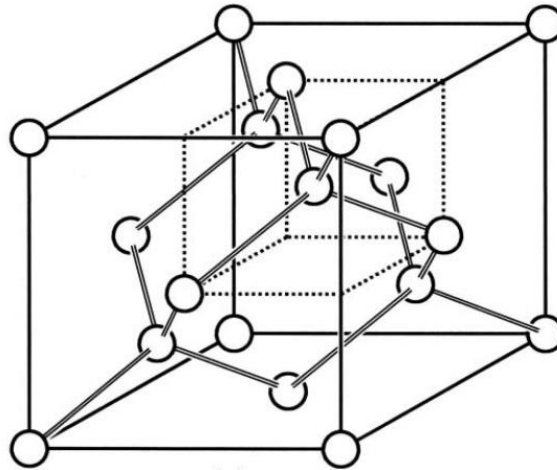
The atoms which are at least partially in the conventional cubic unit cell are located at the following coordinates:

$$C : 000, \quad 0\frac{1}{2}\frac{1}{2}, \quad \frac{1}{2}0\frac{1}{2}, \quad \frac{1}{2}\frac{1}{2}0$$

$$C : \frac{1}{4}\frac{1}{4}\frac{1}{4}, \quad \frac{1}{4}\frac{3}{4}\frac{3}{4}, \quad \frac{3}{4}\frac{1}{4}\frac{3}{4}, \quad \frac{3}{4}\frac{3}{4}\frac{1}{4}$$

The tetrahedral bonding characteristic of the diamond structure is shown in Fig. below. Each atom has 4 nearest neighbors and 12 second nearest neighbors.

(Number of atoms) $n = 4 + 6/2 + 8/8 = 8$



Each carbon atom is connected to four neighboring atoms (first neighborhood) in a covalent bond and is surrounded by twelve atoms as a second neighbor. Despite the high diamond hardness, the filling ratio is not more than 34%.

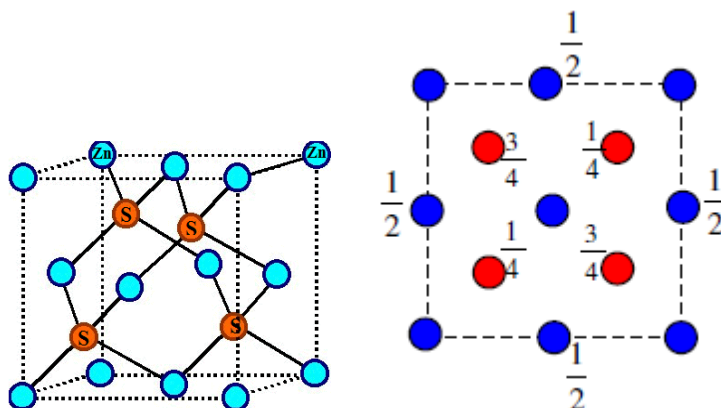
H.W / Calculate the packing factor (P.F) of diamonds. Hint: Take the plane (110).

Cubic Zinc Structure (Zinc Blend) ZnS

The cubic structure of zinc sulfide is called zinc blend. The ZnS base is composed of two atoms, Zn and S, instead of the two carbon atoms that are similar in diamonds. Zn and S atoms are arranged to occupy the following atomic positions:

$$\text{Zn} : 000, \quad 0\frac{1}{2}\frac{1}{2}, \quad \frac{1}{2}0\frac{1}{2}, \quad \frac{1}{2}\frac{1}{2}0$$

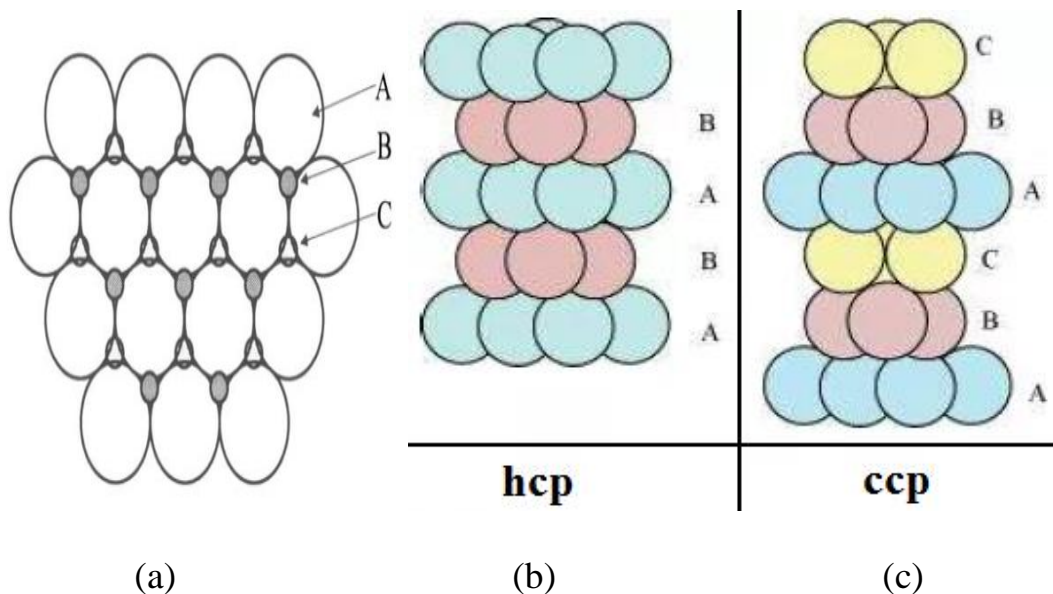
$$\text{S} : \frac{1}{4}\frac{1}{4}\frac{1}{4}, \quad \frac{1}{4}\frac{3}{4}\frac{3}{4}, \quad \frac{3}{4}\frac{1}{4}\frac{3}{4}, \quad \frac{3}{4}\frac{3}{4}\frac{1}{4}$$



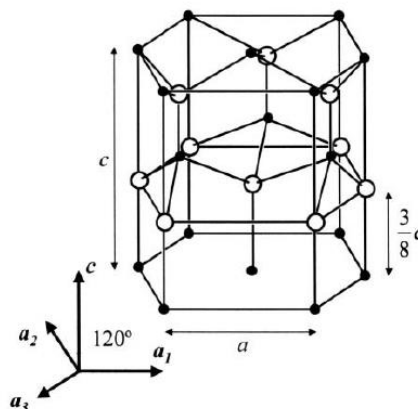
Hexagonal close-packed (hcp) structure and Cubic closed packed (ccp)

The simplest way to stack layers of spheres is to place centers of spheres (atoms) directly above one another. The resulting structure is called simple hexagonal structure. There is, in fact, no example of crystals with this structure

because it is unstable. However, spheres can be arranged in a single hexagonal close-packed layer A (Fig. 1.32) by placing each sphere in contact with six others. A second similar layer B may be added by placing each sphere of B in contact with three spheres of the bottom layer, at positions B in Fig. (a). This arrangement has the lowest energy and is therefore stable. A third layer may be added in two different ways. We obtain the cubic structure if the spheres of the third layer C are added over the holes in the first layer A that are not occupied by B, as in Fig. (c). We obtain the hexagonal close-packed structure Fig. 1(b) when the spheres in the third layer are placed directly over the centers of the spheres in the first layer, thus replicating layer A. The packing factor is 0.74 for both structures and it is the largest value of packing factor can be obtained for any crystal structure.



Q/Show that the c/a ratio for an ideal hexagonal closed-packed structure is:
 $(8/3)^{1/2} = 1.633$.

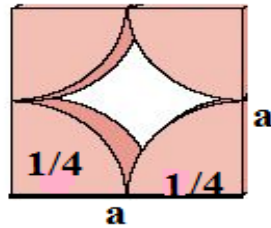


The density of plane (ρ)

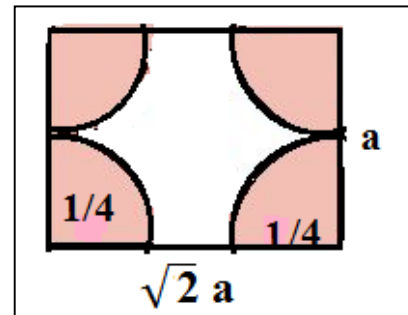
$$\rho = \frac{\text{No. of atoms}}{\text{Area}}$$

(SC)*1- For planes $\{100\}$

$$\rho = \frac{\frac{1}{4} * 4}{a^2} = \frac{1}{a^2}$$

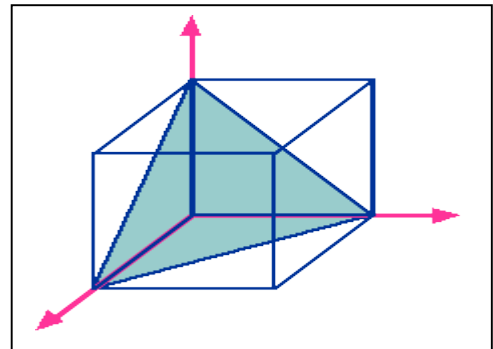
2- For planes $\{100\}$

$$\rho = \frac{1}{a * \sqrt{2}a} = \frac{\frac{1}{4} * 4}{\sqrt{2}a^2} = \frac{1}{\sqrt{2}a^2}$$

3- For planes $\{111\}$

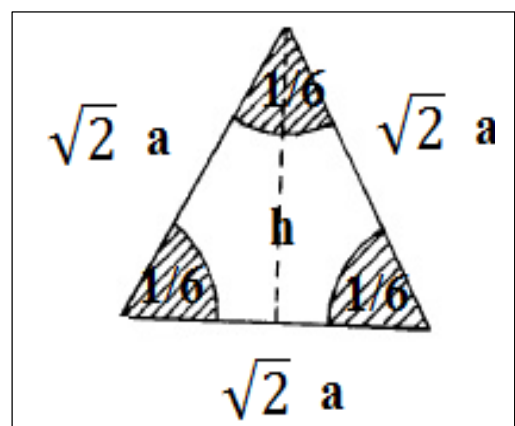
$$h = \sqrt{(\sqrt{2}a)^2 - \left(\frac{\sqrt{2}}{2}a\right)^2}$$

$$h = \left(2a^2 - \frac{1}{2}a^2\right)^{\frac{1}{2}} = \sqrt{\frac{3}{2}}a$$



$$\text{area} = \frac{1}{2} \sqrt{2}a * h$$

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

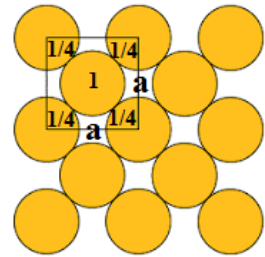


$$\rho = \frac{\frac{1}{6} * 3}{\frac{\sqrt{3}}{2} a^2} = \frac{1}{\sqrt{3} a^2}$$

(FCC) **

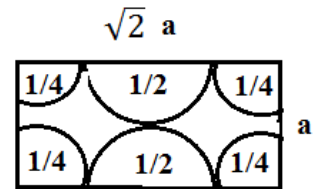
1- For the planes {100}

$$\rho = \frac{\frac{1}{4} * 4 + 1}{a^2} = \frac{2}{a^2}$$



2- For the planes {110}

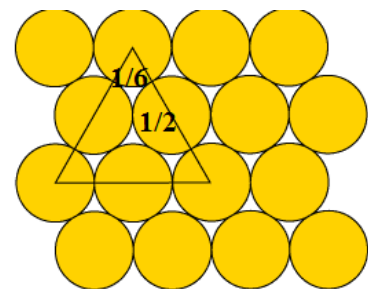
$$\rho = \frac{\frac{1}{4} * 4 + \frac{1}{2} * 2}{\sqrt{2} a^2} = \frac{2}{\sqrt{2} a^2} = \frac{\sqrt{2}}{a^2}$$



3- For the planes {111}

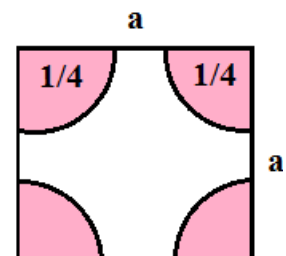
$$\rho = \frac{\frac{1}{6} * 3 + \frac{1}{2} * 3}{\frac{\sqrt{3}}{2} a^2}$$

$$\rho = \frac{\frac{1}{2} + \frac{3}{2}}{\frac{\sqrt{3}}{2} a^2} = \frac{2}{\frac{\sqrt{3}}{2} a^2} = \frac{4}{\sqrt{3} a^2}$$



(BCC) ***

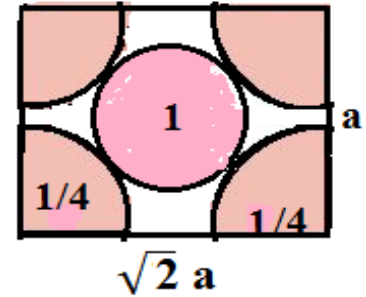
1- For the planes {100}



$$\rho = \frac{1}{a^2}$$

2- For the planes {110}

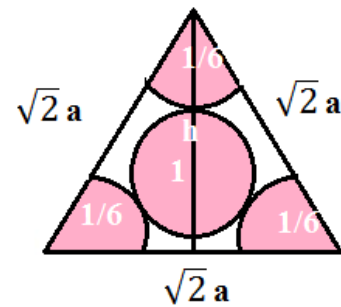
$$\rho = \frac{\frac{1}{4} * 4 + 1}{\sqrt{2}a^2} = \frac{2}{\sqrt{2}a^2}$$



3- For the planes {111}

$$\rho = \frac{\frac{1}{6} * 3 + 1}{\frac{\sqrt{3}}{2}a^2}$$

$$\rho = \frac{\frac{3}{2}}{\frac{\sqrt{3}}{2}a^2} = \frac{\sqrt{3}}{a^2}$$

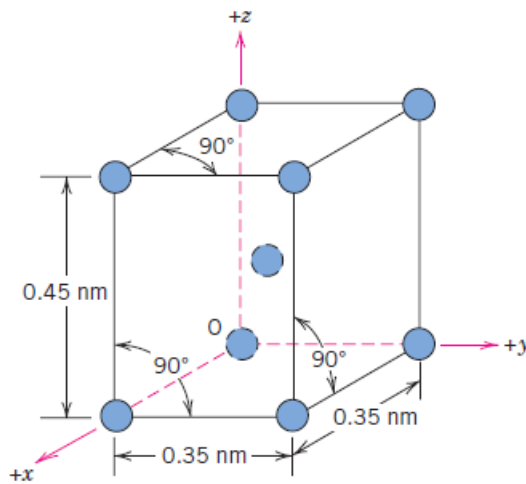


- 1- Calculate the volume of an FCC unit cell in terms of the atomic radius r .
- 2- Show that the atomic packing factor for the hcp crystal structure is 0.74.
- 3- If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters.
- 4- Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius (r) are related through $a=4r/\sqrt{3}$.
- 5- Titanium has an HCP crystal structure and a density of 4.51 g/cm³.
 - (a) What is the volume of its unit cell in cubic meters?
 - (b) If the c/a ratio is 1.58, compute the values of c and a .
- 6- Niobium has an atomic radius of 0.1430 nm and a density of 8.57 g/cm³. Determine whether it has an FCC or BCC crystal structure.

- 7- Some hypothetical metal has the simple cubic crystal structure, if its atomic weight is 74.5 g/ mol and the atomic radius is 0.145 nm, compute its density.
- 8- Below are listed the atomic weight, density, and atomic radius for three hypothetical alloys. For each determine whether its crystal structure is FCC, BCC, or simple cubic.

<i>Alloy</i>	<i>Atomic Weight (g/mol)</i>	<i>Density (g/cm³)</i>	<i>Atomic Radius (nm)</i>
A	43.1	6.40	0.122
B	184.4	12.30	0.146
C	91.6	9.60	0.137

- 9- Some hypothetical metal has the simple cubic crystal structure. If its atomic weight is 74.5 g/ mol and the atomic radius is 0.145 nm, compute its density.
- 10- Below is a unit cell for a hypothetical metal.
- (a) To which crystal system does this unit cell belong?
- (b) What would this crystal structure be called?
- (c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



- 11- Show that the packing factor for the diamond structure is 34 % .

Methods of determining crystal structure

The following methods are widely used for determining crystal structure

(i) X-ray diffraction:

1. Measure the average spacing between layers or rows of atoms
2. Determine the orientation of a single crystal or grain
3. Find the crystal structure of an unknown material
4. Measure the size, shape and internal stress of small crystalline regions

Experimental Diffraction Methods

(a) Bragg's spectrometer method (b) Laue's method (c) Powder method

(ii) Electron diffraction and (iii) Neutron diffraction

We have already discussed Bragg's method. Now, we will discuss other methods.

Laue's Method

This is one of the principal method to study X-ray diffraction and to determine crystal structure. In this method, a single crystal is placed in the path of X-rays beam and the glancing angle θ is kept constant. A white radiation having wide range of wavelengths is allowed to fall on the crystal. Each set of crystal plane selects appropriate value of wavelength, satisfying Bragg's law. Obviously, each set of plane will produce a spot which fulfils Bragg's law.

A beam of polychromatic X-rays strike at 90° on the plane of the crystal. The rays, while passing through the crystal meet Bragg's planes having different interplanar spacing's d . These different sets of planes make different angles θ with the direction of X-rays beam. We can see that certain combinations of θ and d satisfy the Bragg's condition, with the result that the intensity of diffracted X-rays increase.

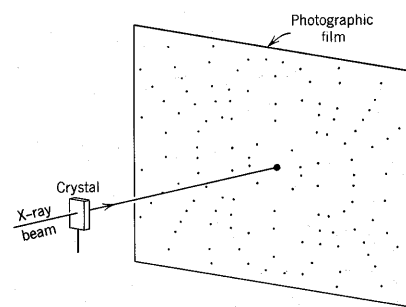
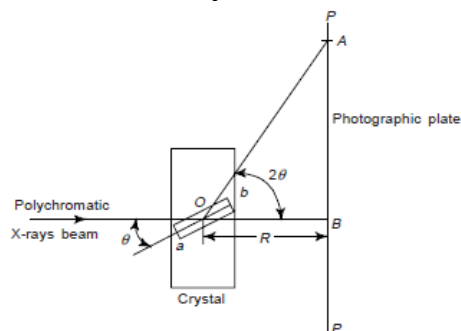


Fig. 7.8. Obtaining a Laue photograph with a stationary

When primary rays are allowed to pass through the crystal, they produce a black spot at B on photographic plate PP . Different wavelengths are included

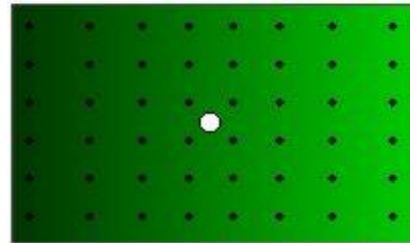
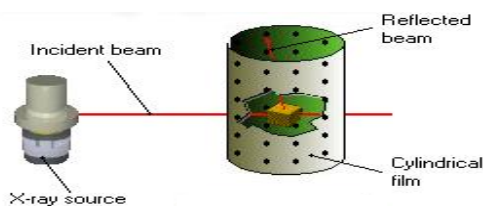
in the primary X-rays and hence they will produce spots around this central spot, which are less pronounced.

Let ab represent the position of one of the possible Bragg's plane, θ the corresponding angle and A any

spot (other than central spot) on PP . From $\triangle AOB$, one finds $AB = R \tan 2\theta$. Knowing AB and R , one can find θ for the corresponding plane. Laue's method is quite useful for single large size crystal.

Rotating Crystal Method:

In this method, a single crystal is rotated about the fixed axis in a beam of monochromatic X-rays or neutrons. The angle θ is variable while the wavelength is kept constant. The variation of angle θ due to rotation of the crystal brings different atomic planes in the crystal into position for which Bragg's reflection holds good. To record such reflections a film is mounted on a cylindrical holder that is concentric with a rotating spindle.



Powder Method

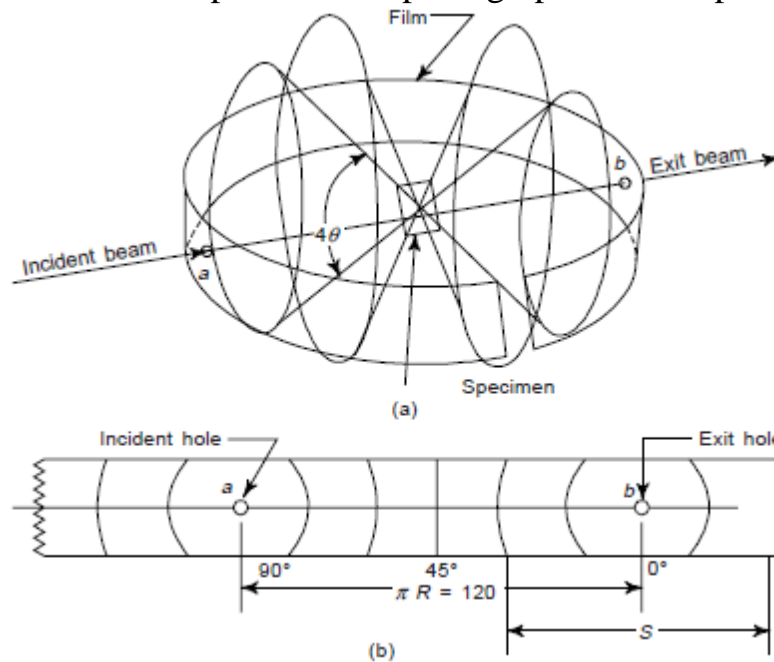
If a powdered specimen is used, instead of a single crystal, then there is *no need to rotate* the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.

This method is useful for samples that are difficult to obtain in single crystal form. The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors a , b and c which define the unit cell for the crystal.

For every set of crystal planes, by chance, *one or more crystals* will be in the **correct orientation** to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

This method is quite useful when single crystals of large size are not available. Method is used to determine the structure of crystalline solids. The sample used is in the form of a fine powder containing a large number of tiny crystallites with random orientations. It is prepared by crushing the commonly available polycrystalline material, thus eliminating the tedious process of growing the single crystals.

The powder is placed in a capillary tube or pasted on a thin wire or pressed and cemented into a thin spindle. This powder specimen is mounted at the center around which a strip of circular photographic film is positioned.



A collimated beam of monochromatic X-rays is produced by passing the X-ray through a filter and a collimator. This is allowed to strike the specimen (in capillary tube or wire or spindle) through a small hole.

The specimen is slowly revolved inside the specially constructed powder camera. The X-ray beam enters through hole 'a', passes through the specimen and the unused part of beam exit through hole 'b'.

Let us consider that the incident beam make an angle θ with a set of parallel crystal plane. If Bragg condition is satisfied, then there will be reflection. Since there are a large number of randomly oriented crystals in the powder sample and hence there are several possible orientations of this set of planes of same angle θ . Consequently, the reflected rays will not be in the form of parallel beam but they will lie on the surface of a cone with its apex at the sample and the semivertical angle 2θ .

Different cones are observed for different sets of d and θ for a particular value of n , and also for different combinations of θ and n for a particular value of d . As the film is of narrow width only a part of each.

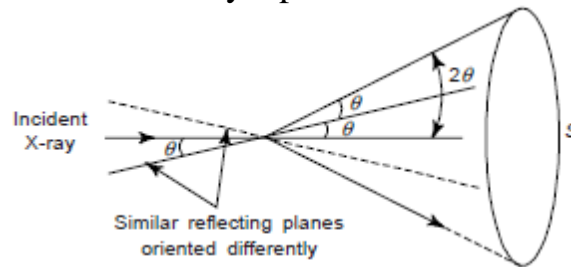


Figure shows the diffraction pattern of tungsten metal. The numbers on the peak are the indices of the planes which produce that peak. One can compute the interplanar spacings by measuring the value of θ and using Bragg's law.

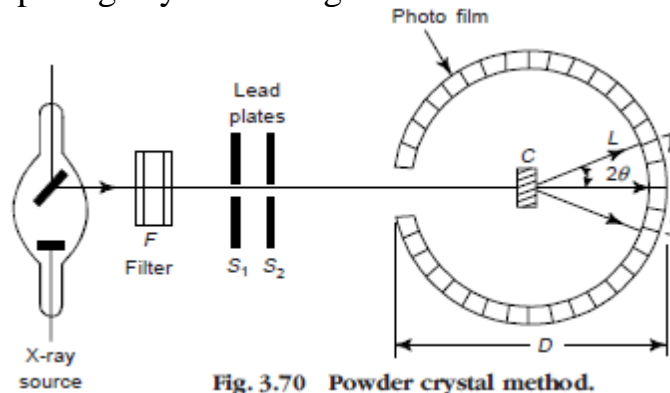
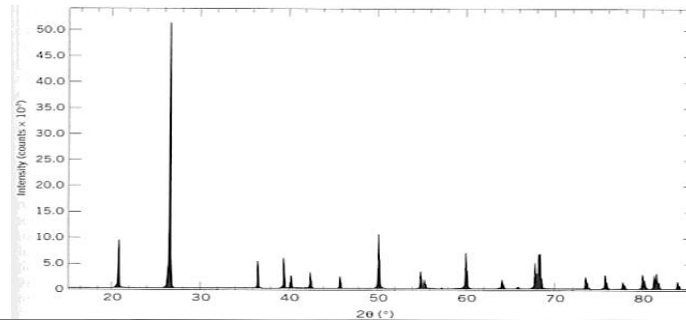


Fig. 3.70 Powder crystal method.



#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	4.2570	22.0	1	0	0	20.850	10.425	0.1175	21	1.2285	1.0	2	2	0	77.660	38.830	0.4070
2	3.3420	100.0	1	0	1	26.651	13.326	0.1495	22	1.1999	2.0	2	1	3	79.875	39.938	0.4167
3	2.4570	8.0	1	1	0	36.541	18.271	0.2035	23	1.1978	1.0	2	2	1	80.044	40.022	0.4174
4	2.2820	8.0	1	0	2	39.455	19.727	0.2191	24	1.1843	3.0	1	1	4	81.145	40.572	0.4222
5	2.2370	4.0	1	1	1	40.283	20.141	0.2235	25	1.1804	3.0	3	1	0	81.470	40.735	0.4236
6	2.1270	6.0	2	0	0	42.464	21.232	0.2351	26	1.1532	1.0	3	1	1	83.818	41.909	0.4336
7	1.9792	4.0	2	0	1	45.808	22.904	0.2526	27	1.1405	1.0	2	0	4	84.969	42.484	0.4384
8	1.8179	14.0	1	1	2	50.139	25.070	0.2750	28	1.1143	1.0	3	0	3	87.461	43.731	0.4487
9	1.8021	1.0	0	0	3	50.610	25.305	0.2775	29	1.0813	2.0	3	1	2	90.855	45.428	0.4624
10	1.6719	4.0	2	0	2	54.867	27.434	0.2991	30	1.0635	1.0	4	0	0	92.819	46.410	0.4701
11	1.6591	2.0	1	0	3	55.327	27.663	0.3014	31	1.0476	1.0	1	0	5	94.662	47.331	0.4773
12	1.6082	1.0	2	1	0	57.236	28.618	0.3109	32	1.0438	1.0	4	0	1	95.115	47.558	0.4790
13	1.5418	9.0	2	1	1	59.947	29.973	0.3243	33	1.0347	1.0	2	1	4	96.223	48.112	0.4832
14	1.4536	1.0	1	1	3	63.999	32.000	0.3440	34	1.0150	1.0	2	2	3	98.734	49.367	0.4926
15	1.4189	1.0	3	0	0	65.759	32.879	0.3524	35	0.9898	1.0	4	0	2	102.195	51.098	0.5052
16	1.3820	6.0	2	1	2	67.748	33.874	0.3618	36	0.9873	1.0	3	1	3	102.556	51.278	0.5064
17	1.3752	7.0	2	0	3	68.128	34.064	0.3636	37	0.9783	1.0	3	0	4	103.880	51.940	0.5111
18	1.3718	8.0	3	0	1	68.321	34.160	0.3645	38	0.9762	1.0	3	2	0	104.195	52.098	0.5122
19	1.2880	2.0	1	0	4	73.460	36.730	0.3882	39	0.9636	1.0	2	0	5	106.141	53.071	0.5189
20	1.2558	2.0	3	0	2	75.668	37.834	0.3982									

The Method	λ	θ	d
Laue Method	changing	constant	constant
Rotating Method	constant	Partial changing	constant
Powder Method	constant	changing	constant

$$E = h\nu = \frac{hc}{\lambda} \quad \text{for X-ray}$$

$$h = 6.626 \times 10^{-34} \text{ J.s} \quad \text{Planck's constant}$$

$$c = 3 \times 10^8 \frac{m}{sec} \quad \text{Velocity of Light}$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$\lambda(\text{\AA}) = \frac{12.4}{E(\text{keV})}$$

(ii) Neutrons Diffraction

Since waves are diffracted by a crystal, we can also use electrons and neutrons instead of X-rays, provided the wavelengths of matter wave's associates with these particles are in the range of 1 to 10 Å.

Wavelength for neutron

The neutron possesses a neutral charge but possesses a magnetic charge for the mismatch of positive and negative charge centers. It is therefore used in:

- 1- The study of magnetic crystals
- 2- Study the structures of some light elements such as hydrogen
- 3- The differentiation of isotopes for one element because of its interaction with atomic nuclei.

$$\lambda(\text{\AA}) = \frac{h}{p} = \frac{h}{\sqrt{2m_n E}} = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} E}}$$

$$\lambda(\text{\AA}) = \frac{0.28}{\sqrt{E(\text{eV})}}$$

Where λ is in (Å) and E in eV. Thus the energy of a neutron of wavelength of 1 Å is $\approx 0.08 \text{ eV}$.

The thermal neutrons in an atomic reactor have the energy $\approx 0.08 \text{ eV}$ and hence can be used for the study of crystal diffraction.

iii. Electrons Diffraction

The phenomenon of electronic diffraction is essentially proof of the presence of waves associated with electrons under the theory of de Broglie, but what distinguishes the electrons from the photon or neutron has a charge and react strongly with the material and penetrate into relatively small distances up to a few hundred of the angstroms before suffering from flexible or inflexible scattering therefore, the electron does not play a similar role to x-ray in the study of crystalline structure, but the use is limited to two main goals:

- 1- Study of the surfaces of crystals
- 2- Study thin films.

Wavelength for electron

$$\lambda(\text{\AA}) = \frac{h}{\sqrt{2m_e E}} = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} E}} = \frac{4.91 \times 10^{-19}}{\sqrt{E}}$$

$$\lambda(\text{\AA}) = \frac{1.2}{\sqrt{E(\text{keV})}} \quad \text{Where } \lambda \text{ is in } \text{\AA} \text{ and } E \text{ is in keV.}$$

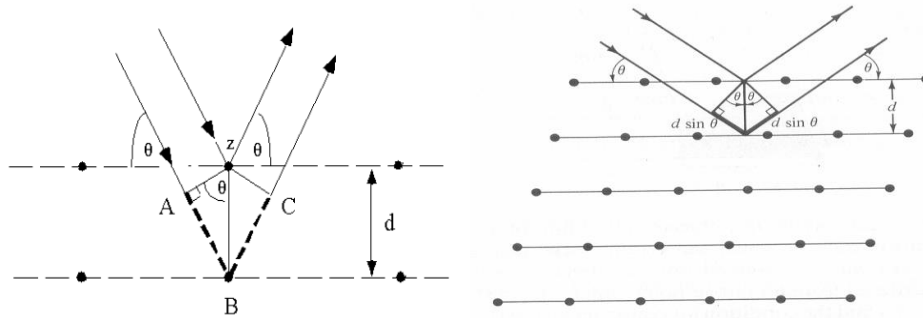
The thermal neutrons from the nuclear reactors have a large spread in energy and therefore we have to monochromatize them. These neutrons are allowed to fall on a crystal and a particular reflected beam is selected. This is allowed to fall on the test sample under examination. The intensity of the scattered beam is measured through a counter.

We must note that though the neutron diffraction studies are very similar to those of X-rays, there are many differences. X-rays are scattered by electrons, whereas neutrons are scattered by nuclei. Using this property of neutrons, one can study many low atomic weight elements by neutron diffraction where X-rays are incapable of giving precise results. We know that a neutron possesses a magnetic moment and hence has an additional scattering due to magnetic ordering. Obviously, neutron diffraction studies have become important in magnetic structure determinations, X-ray or electron diffraction studies do not reveal this structure. One can also study lattice vibrations using neutron diffraction technique.

Bragg's Law

Bragg's Law can easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z. The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance AB + BC if the two beams are to continue

traveling adjacent and parallel. This extra distance must be an integral (n) multiple of the wavelength (λ) for the phases of the two beams to be the same:



$$n \lambda = AB + BC \dots\dots\dots (1)$$

Recognizing d as the hypotenuse of the right triangle ABZ , we can use trigonometry to relate d and θ to the distance $(AB + BC)$. The distance AB is opposite θ so,

$$AB = d \sin \theta \dots\dots\dots (2) \quad \text{Because } AB = BC \text{ eq. (2) becomes,}$$

$$n \lambda = 2AB \dots\dots\dots (3) \quad \text{Substituting eq. (2) in eq. (3) we have,}$$

$$n \lambda = 2 d_{(hkl)} \sin \theta \dots\dots\dots (4)$$

And Bragg's Law has been derived. The location of the surface does not change the derivation of Bragg's Law. In general Bragg's reflection can only occur for wavelength $\lambda \leq 2d$. This explains why visible light is not used. Visible light have much longer wavelengths.

For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.14, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$, since we are considering the (220) planes. Therefore,

$$\begin{aligned} d_{hkl} &= \frac{a}{\sqrt{h^2 + k^2 + l^2}} \\ &= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm} \end{aligned}$$

(b) The value of θ may now be computed using Equation 3.13, with $n = 1$, since this is a first-order reflection:

$$\sin \theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790 \text{ nm})}{(2)(0.1013 \text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13^\circ$$

The diffraction angle is 2θ , or

$$2\theta = (2)(62.13^\circ) = 124.26^\circ$$

Problems:

1-Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC Chromium when monochromatic radiation of wavelength 0.711 \AA is used when the atomic radius is 1.249 \AA .

2-The metal niobium has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for the niobium atom.

3- For which set of crystallographic planes will a first order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel when monochromatic radiation having a wavelength of 0.1542 nm is used when $r_{\text{Ni}} = 0.1246 \text{ nm}$?

4-Carbon crystallization is made up of two structures: diamond and graphite. The diamond is fcc. The lattice constant is 3.57 \AA and the graphite has a hexagonal crystalline system in which $a = 2.46 \text{ \AA}$ and $C = 6.7 \text{ \AA}$. If you know that the diamond density is 3.51 g / cm^3 and the density of the graphite is 2.25 g / cm^3 , calculate the number of carbon atoms in the unit cell for diamonds and graphite, with the carbon weight being (12.01) .

5- The copper crystallizes with the fcc structure. If the atomic mass is 63.54 atomic mass units and the density is 8.96 g / cm^3 , calculate the nearest distance between the two copper atoms.

6-X-rays with wavelength 1.54 \AA are reflected from the (1 1 0) planes of a cubic crystal with unit cell $a = 6 \text{ \AA}$. Calculate the Bragg angle, θ , for orders of reflection, $n = 1-5$.

Reciprocal lattice

There are two types of lattice are of a great importance: 1. Reciprocal lattice 2. Direct lattice (which is the Bravais lattice that determines a given reciprocal lattice).

What is a reciprocal lattice?

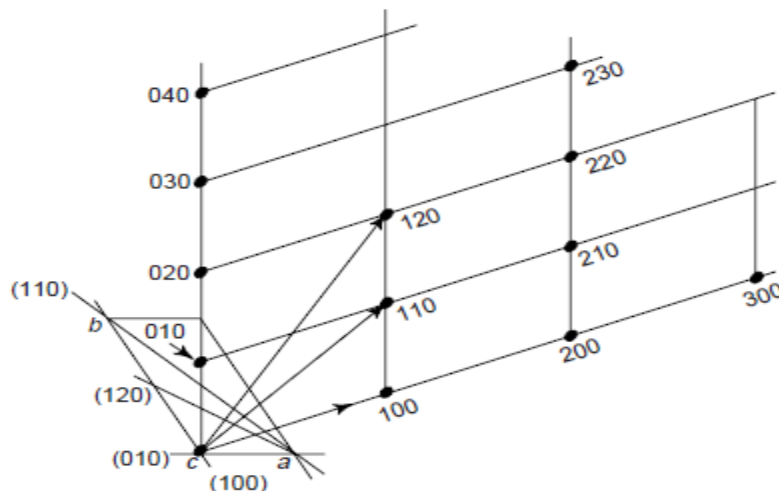
A reciprocal lattice is regarded as a geometrical abstraction. It is essentially identical to a "wave vector" k -space. Definition: Since we know that \vec{R} may construct a set of points of a Bravais lattice, thus a reciprocal lattice can be defined as: - The collection of all wave vectors that yield plane waves with a period of the Bravais lattice.

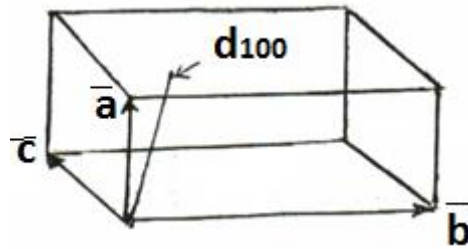
Reciprocal lattice: can be defined as an undetermined number of points are connected to a periodic system in a three-dimensional space so that the space between these points is inversely proportional to the diffraction of the different groups of planes in a conventional or direct lattice. The lengths of the vectors are measured in the Reciprocal lattice by inverted vector units in the conventional lattice cm^{-1} , \AA^{-1} , cm^{-1} . The space of the Reciprocal lattice is called the Reciprocal space or the Fourier space.

Reciprocal Lattice System:

This concept of the Reciprocal form came as a result of X-ray diffraction experiments since the knowledge of the different directions in which the crystal is diffracted is not sufficient to know the behavior of the crystalline planes. Therefore, it is necessary to know (d) because it assigns the reflection angles to the grooves of the planes.

If the normals were plotted for each plane of a common origin point and their lengths were proportional to the special spaces of each plane, the points at the ends of these columns form a reciprocal system.



Reciprocal lattice Vectors:

For the reciprocal lattice there is a relationship between the length of the normal (perpendicular) on the plane (hkl) and the crystalline axes \vec{a} , \vec{b} , \vec{c} in real space.

Size of unit cell = Base area x Height

If the height is d_{100} , as in the previous figure

$$V = (d_{100})(bc \sin\theta) = (d_{100})(\vec{b} \times \vec{c})$$

$$1/d_{100} = \frac{\text{area}}{\text{volume}} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

The normal on the plane represents the vector unit \vec{n} , so the reciprocal vector can be written \vec{G}_{hkl}

$$\vec{G}_{hkl} = K \frac{1}{d_{100}} \vec{n} \dots \dots \dots 1$$

$$K = 2\pi \dots \dots \dots 2$$

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

According the plane (100)

$$\vec{G}_{100} = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

\vec{G}_{100} represents:

$$\vec{G}_{100} = a^*$$

$$\vec{G}_{010} = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

By the same method:

$$\vec{G}_{010} = b^* \quad \text{also:}$$

$$\vec{G}_{011} = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

$$\vec{G}_{011} = c^*$$

The relationship of the axes of the reciprocal lattice with the normal lattice is

$$: \vec{a}^* \cdot \vec{b} = 0, \vec{b}^* \cdot \vec{c} = 0, \vec{c}^* \cdot \vec{a} = 0$$

$$\vec{a}^* \cdot \vec{c} = 0, \vec{b}^* \cdot \vec{a} = 0, \vec{c}^* \cdot \vec{b} = 0$$

$$\vec{a}^* \cdot \vec{a} = \vec{b}^* \cdot \vec{b} = \vec{c}^* \cdot \vec{c} = 2\pi$$

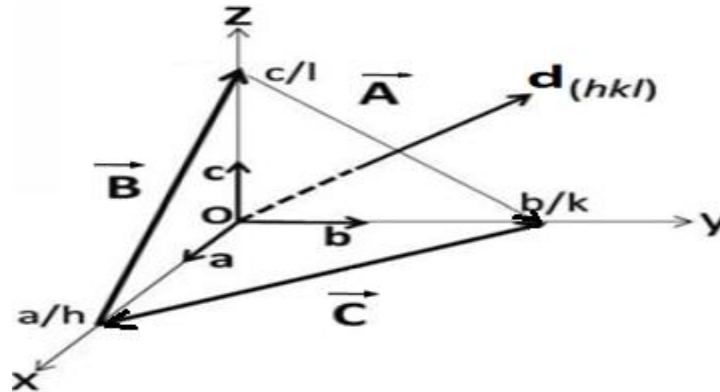
The reciprocal lattice vector from the origin point of the hkl point is :

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$\vec{G}_{hkl} = \frac{2\pi}{d_{hkl}} \hat{n}, \quad \hat{n} : \text{is the unit vector normal to the (hkl) plane.}$$

To prove that the vector of the reciprocal lattice \vec{G}_{hkl} is normal on the crystal plane (hkl) is to show that the scalar multiplication of the vector \vec{G}_{hkl} and any vectors within the v (hkl) will be zero.

The plane (hkl) shown in the figure below intercepts \vec{a} at point \vec{a}/h and \vec{b} at point \vec{b}/k and \vec{c} at point \vec{c}/l .



Assume vector \vec{c} located within this surface:

$$\vec{c} = \frac{\vec{a}}{h} - \frac{\vec{b}}{k}$$

$$\vec{c} \cdot \vec{G}_{hkl} = \left(\frac{\vec{a}}{h} - \frac{\vec{b}}{k}\right) \cdot (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)$$

$$= \frac{\vec{a}}{h} \cdot (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) - \frac{\vec{b}}{k} \cdot (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)$$

$$\vec{c} \cdot \vec{G}_{hkl} = 2\pi \quad h/h + 0 + 0 - 2\pi k/k - 0$$

$$\vec{C} \cdot \vec{G}_{hkl} = 0$$

In the same way, scalar multiplication of vector \vec{A} and \vec{G}_{hkl}

$$\vec{A} \cdot \vec{G}_{hkl} = 0 \quad \text{and} \quad \vec{B} \cdot \vec{G}_{hkl} = 0$$

The \vec{G}_{hkl} vector is normal on the \vec{C} and \vec{A} so it is perpendicular to the plane that contains them, that means the plane (hkl).

• It can also be proved that:

$$(a^*)^* = a \quad \& \quad (b^*)^* = b \quad \& \quad (c^*)^* = c$$

$$a \cdot a^* = 2\pi \dots \dots \dots 1$$

$$(a^*)^* = 2\pi \frac{b^* \times c^*}{a^* \cdot b^* \times c^*} \dots \dots \dots 2$$

To substitute for the value of 2π in equation 2 we get the:

$$(a^*)^* = a \cdot \frac{a^* \cdot b^* \times c^*}{a^* \cdot b^* \times c^*}$$

$(a^*)^* = a$ So, in the same way we prove the rest.

Find intrplaner space using the concepts of reciprocal lattice: (d_{hkl})

d_{hkl} can be found using the concepts of reciprocal lattice such as equations:

$$\vec{G}_{hkl} = \left(\frac{2\pi}{d_{hkl}}\right) \vec{n} \dots \dots \dots 1$$

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \dots \dots \dots 2$$

Equation (2) represents any vector in the reciprocal lattice from the point of origin to the point (hkl) where we represented the plane (hkl) with a point.

Equation (1) represents the reciprocal vector, where \vec{n} is a unit vector, the normal on the plane.

Using scalar multiplication of Equation (2) i.e \vec{G}_{hkl} vector by itself.

$$\begin{aligned}
 \vec{G}_{hkl} \cdot \vec{G}_{hkl} &= (ha^* + kb^* + lc^*) \cdot (ha^* + kb^* + lc^*) \\
 &= hh a^* \cdot a^* + hk a^* b^* + hl a^* \cdot c^* + \dots \dots \dots 3 \\
 &\quad Kh b^* \cdot a^* + kk b^* \cdot b^* + kl b^* \cdot c^* + \\
 &\quad Lh c^* \cdot a^* + lk c^* \cdot b^* + ll c^* \cdot c^*
 \end{aligned}$$

By using the relations:

$$\left. \begin{aligned}
 a^* \cdot b^* &= a^* b^* \cos \gamma^* \\
 b^* \cdot c^* &= b^* c^* \cos \alpha^* \\
 c^* \cdot a^* &= c^* a^* \cos \beta^*
 \end{aligned} \right\} \dots \dots \dots 4$$

We arrange equation (3) and use equation (4) to get:

$$\left. \begin{aligned}
 G_{hke}^2 &= h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^* b^* \cos \gamma^* \\
 &\quad + 2klb^* c^* \cos \alpha^* + 2lh c^* a^* \cos \beta^*
 \end{aligned} \right\} \dots \dots \dots 5$$

Equation (5) represents an expression of the triclinic crystalline system in which the lattices constant and angles are not equal and is the lowest system for symmetry.

When squaring equation 1 and substituting it in equation 5 and apply the results to the cubic crystal system in it.

$$a = b = c \text{ and } 90^\circ = \alpha = \beta = \gamma$$

$$4\pi^2/d_{hkl}^2 = (h^2 + k^2 + l^2) a^{*2}$$

$$a^* = \frac{2\pi}{a}$$

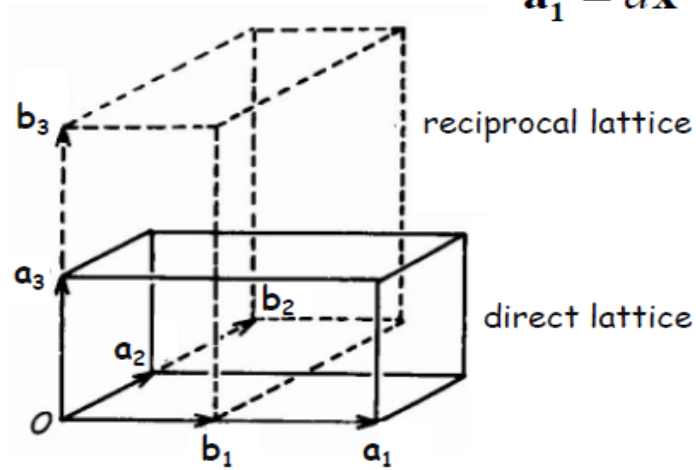
$$4\pi^2/d_{hkl}^2 = (h^2 + k^2 + l^2) \left(\frac{2\pi}{a}\right)^2$$

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

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

b_1, b_2, b_3 are parallel to a_1, a_2, a_3 , respectively.

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \quad \mathbf{a}_2 = b\hat{\mathbf{y}} \quad \mathbf{a}_3 = c\hat{\mathbf{z}}$$

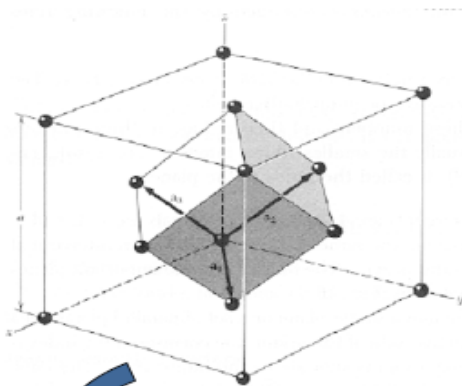


$$\mathbf{b}_1 = \frac{2\pi}{a} \hat{\mathbf{x}}$$

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

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

RECIPROCAL LATTICE OF FCC IS BCC



FCC primitive vectors:

$$\mathbf{a}_1 = \frac{a}{2} (\hat{\mathbf{y}} + \hat{\mathbf{z}}),$$

$$\mathbf{a}_2 = \frac{a}{2} (\hat{\mathbf{z}} + \hat{\mathbf{x}}),$$

$$\mathbf{a}_3 = \frac{a}{2} (\hat{\mathbf{x}} + \hat{\mathbf{y}}).$$

Note: not orthogonal

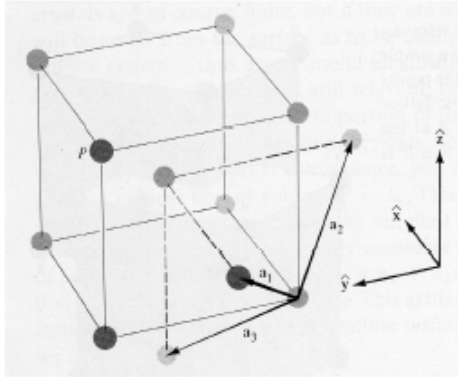


$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = 2\pi \frac{\frac{a^2}{4} (\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})}{\frac{a^3}{8} (2)} = \frac{4\pi}{a} \frac{1}{2} (\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$$

$$\mathbf{b}_2 = \frac{4\pi}{a} \frac{1}{2} (\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}) \quad \mathbf{b}_3 = \frac{4\pi}{a} \frac{1}{2} (\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

→ BCC reciprocal lattice with lattice constant $4\pi/a$

RECIPROCAL LATTICE OF BCC IS FCC



BCC primitive vectors (not orthogonal)

$$\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}),$$

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



$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = 2\pi \frac{\frac{a^2}{4}(2\hat{y} + 2\hat{z})}{\frac{a^3}{8}(4)} = \frac{4\pi}{a} \frac{1}{2}(\hat{y} + \hat{z})$$

$$\mathbf{b}_2 = \frac{4\pi}{a} \frac{1}{2}(\hat{z} + \hat{x}) \quad \mathbf{b}_3 = \frac{4\pi}{a} \frac{1}{2}(\hat{x} + \hat{y})$$

→ FCC reciprocal lattice with lattice constant $4\pi/a$

Diffraction condition to maximum intensity: -

For the purpose of obtaining the maximum intensity of the wave from a plane in the crystal of what must be achieved the three equations of Laue, which is formulated in terms of the wave vector variable.

$$\vec{a} \cdot \Delta \vec{K} = 2\pi q$$

$$\vec{b} \cdot \Delta \vec{K} = 2\pi r$$

$$\vec{c} \cdot \Delta \vec{K} = 2\pi s$$

Where: s, r, q , and $\Delta \vec{K}$

These three equations are realized simultaneously if the change in wave vector $\Delta \vec{K}$ is equal to the vector of reciprocal lattice \vec{G}_{hkl} and thus the intensity is increased.

$$\Delta \vec{K} = \vec{G}_{hkl} \dots \dots \dots 1$$

$$\vec{k} - \vec{k}_0 = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The equation above means that vectors are equal in value and direction (their lengths are equal and one is parallel to the other and both are perpendicular to the plane of the crystal).

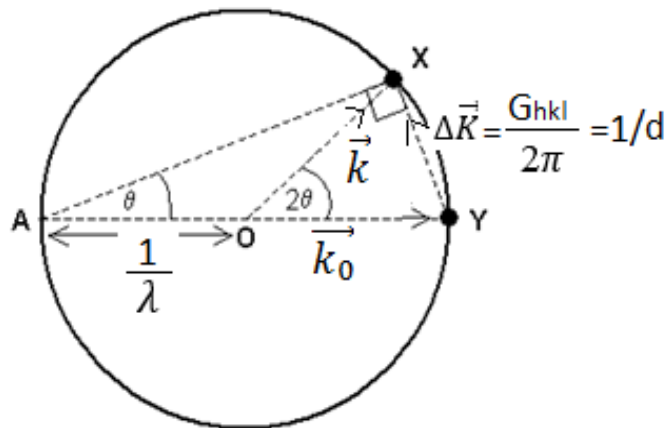
In order to obtain the equation above, we make to equivalence the Bragg and Laue conditions. This can be proved as follows:

\vec{k}_0 : is the wave's vector of the incident beam .

\vec{k} : is the wave's vector of reflected beam angle θ is made with the crystal plane (hkl).

$$|\vec{k} - \vec{k}_0| = |\Delta \vec{K}| = |\vec{G}_{hkl}| \dots\dots\dots 2$$

Graphical representation of Bragg's law:



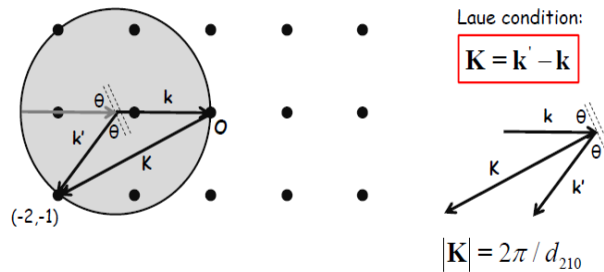
$$2d \sin \theta = \lambda$$

$$2d_{hkl} \sin \theta_{hkl} = \lambda$$

$$\sin \theta_{hkl} = \frac{\lambda/2}{d_{hkl}} = \frac{(1/d_{hkl})}{(2/\lambda)}$$

Ewald Sphere construction

Diffraction occurs only when a reciprocal lattice point lies on the surface of the Ewald sphere.



In this case, $hkl = -2, -1, 0$ so diffraction occurs from the $(\bar{2}\bar{1}0)$ planes and the diffracted beam moves off along k' .

$$\vec{k} - \vec{k}_0 = \vec{G}_{hkl}$$

$$|\vec{k} - \vec{k}_0| = |\Delta \vec{K}| = |\vec{G}_{hkl}|$$

$$\vec{k} = \vec{G}_{hkl} + \vec{k}_0 \dots\dots\dots 1$$

By quadrature the two equations and the elastic scattering do not change

$$\text{energy} |\vec{k}| = |\vec{k}_0|$$

$$K^2 = (\vec{k})^2 = (\vec{G}_{hkl} + \vec{k}_0)^2 = G_{hkl}^2 + \vec{G}_{hkl} \cdot \vec{k}_0 + K_0^2$$

$$\therefore G_{hkl} + 2\vec{G}_{hkl} \cdot \vec{k}_0 = 0 \quad \text{Laue Condition for diffraction}$$

Brillouin Zones

The region around the point of reciprocal lattice (reciprocal space = wave vector space = Fourier space) is called the Brillouin zone, which is defined as the smallest size of the rounded space or is centered around one of the points of the reciprocal lattice and defined by a set of planes that divide it in the middle and vertical on the vectors of the reciprocal lattice.

Which links that point to the adjacent points as shown in the figure below:

To determine the Brillouin zone around any point as follows: -

- 1 - Connect the point with all the neighboring points by vectors.
- 2 - Draw vertical (planes) vertical on each of these vectors at their middle.
- 3 - The smallest area bound by the vectors (planes) is called the Brillouin zone.

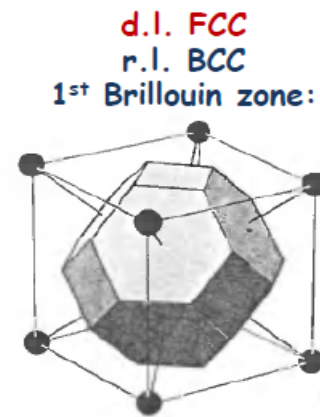
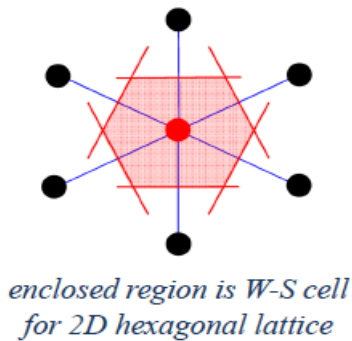
The size of each Brillouin zone is the unit cell of the inverse volume

$$V_{\text{BZ}} = \left(\frac{2\pi}{V}\right)^3$$

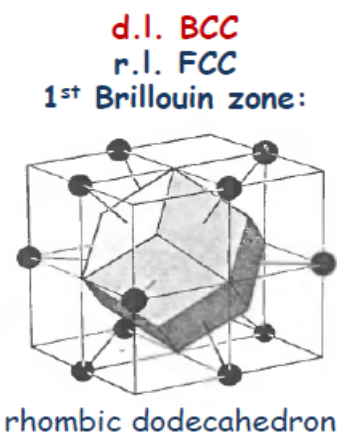
FIRST BRILLOUIN ZONES

The Wigner-Seitz cell of the reciprocal lattice is called the first Brillouin zone (FBZ).

Wigner-Seitz cell: primitive cell with lattice point at its center



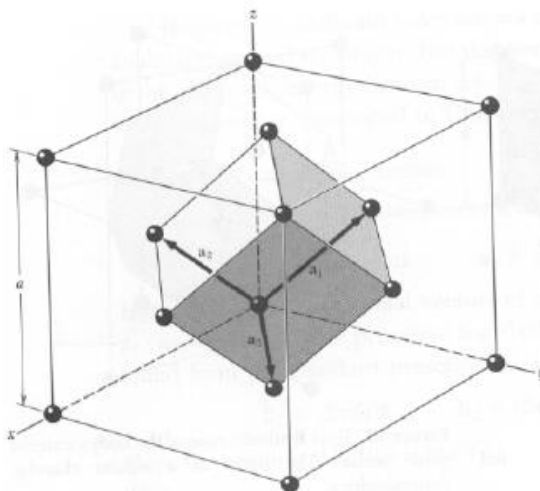
truncated octahedron



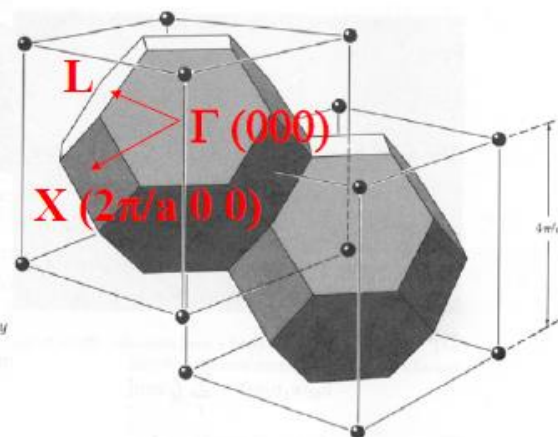
rhombic dodecahedron

Examples for Brillouin zones

face-centered cubic



d.l.: centered and primitive cell



r.l.: 1st Brillouin zone

Structure Factor (F_{hkl})

- Describes how atomic arrangement (uvw) influences the intensity of the scattered beam.
- It tells us which reflections (i.e., peaks, hkl) to expect in a diffraction pattern.

$$F_{hkl} = \sum_{n=1}^{n=N} f_n e^{i\Phi_n} \dots\dots\dots 1$$

Φ_n : Represents the phase difference between the atomic beam of the atom (n) and that beam of the first atom located at the point of origin of the unit cell.

$$\Phi_n = 2\pi (u_n h + v_n k + w_n l) \dots\dots\dots 2$$

Where (hkl) Miller indices, U_n, v_n, w_n coordinates of atoms, so the structure factor equation can be written to n number of atoms.

$$F_{hkl} = f_1 + f_2 e^{i\Phi_2} + f_3 e^{i\Phi_3} + \dots\dots\dots f_n e^{i\Phi_n} \dots\dots\dots 3$$

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

$$F_{hkl} = \sum_{n=1}^{n=N} f_n \cos \Phi_n + \sum_{n=1}^{n=N} f_n i \sin \Phi$$

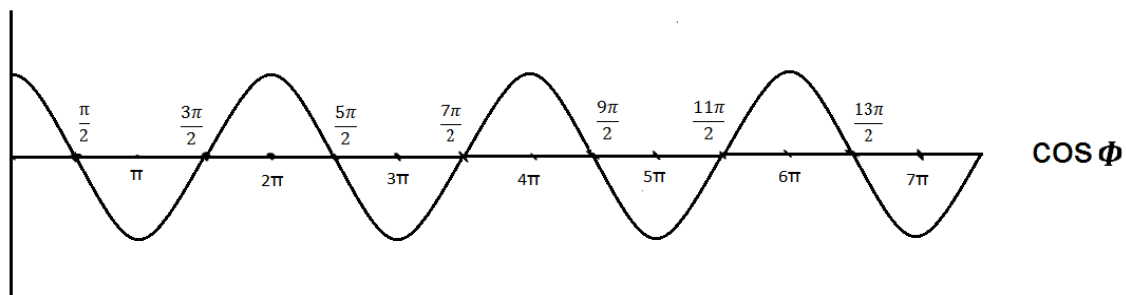
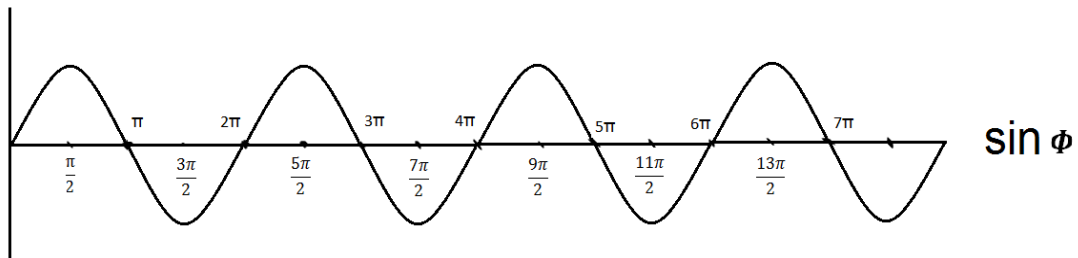
$$F_{hkl} = \sum_{i=1}^{n=N} f_i e^{2\pi i(uh + vk + wl)} \dots\dots\dots 4$$

The intensity of the amplitude of the wave scattered by one electron diffracted wave is proportional to $|F_{hkl}|^2$. $I \propto |F_{hkl}|^2$

Structure Factor (F_{hkl}) depends on some factors:

- 1- Number of lattice points in the unit cell.
- 2 - Specification of the basis; the number of atoms, their sites and whether the atoms are similar or different.
- 3 - Miller's indices to the surface to be calculated.
- 4 - The ability of scattering of each atom.

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



The amplitude of the resultant wave is given by a ratio of amplitudes:

$$|F_{hkl}| = \frac{\text{amplitude of the wave scattered by all atoms of a UC}}{\text{amplitude of the wave scattered by one electron}}$$

Some Useful Relations

$$e^{\pi i} = e^{3\pi i} = e^{5\pi i} = \dots = -1$$

$$e^{2\pi i} = e^{4\pi i} = e^{6\pi i} = \dots = +1$$

$$e^{n\pi i} = (-1)^n, \text{ where } n \text{ is any integer}$$

$$e^{n\pi i} = e^{-n\pi i}, \text{ where } n \text{ is any integer}$$

$$e^{ix} + e^{-ix} = 2 \cos x$$

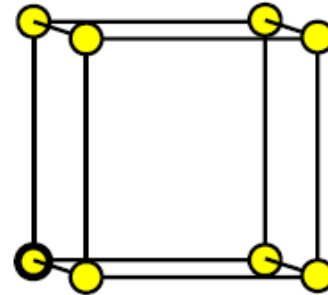
Needed for structure factor calculations

F_{hkl} for Simple Cubic

- Atom coordinate(s) u, v, w :
 - 0,0,0

$$F_{hkl} = \sum_{i=1}^N f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$

$$F_{hkl} = f e^{2\pi i(0 \cdot h + 0 \cdot k + 0 \cdot l)} = f$$



No matter what atom coordinates or plane indices you substitute into the structure factor equation for simple cubic crystals, the solution is always non-zero.

Thus, all reflections are allowed for simple cubic (primitive) structures.

F_{hkl} for Body Centered Cubic

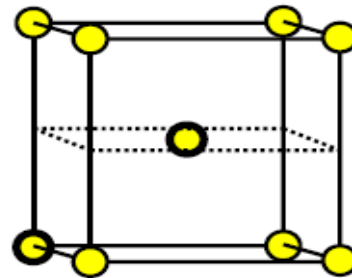
- Atom coordinate(s) u, v, w :
 - 0,0,0;
 - $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

$$F_{hkl} = \sum_{i=1}^N f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$

$$F_{hkl} = f e^{2\pi i(0)} + f e^{2\pi i\left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}\right)}$$

$$\therefore$$

$$F_{hkl} = f \left(1 + e^{\pi i(h+k+l)} \right)$$



When $h+k+l$ is even $F_{hkl} = \text{non-zero} \rightarrow \text{reflection}$.

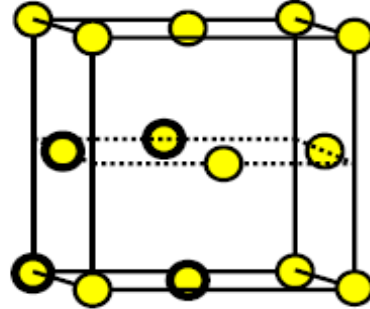
When $h+k+l$ is odd $F_{hkl} = 0 \rightarrow \text{no reflection}$.

F_{hkl} for Face Centered Cubic

- Atom coordinate(s) u, v, w :

- $0, 0, 0$;
- $\frac{1}{2}, \frac{1}{2}, 0$;
- $\frac{1}{2}, 0, \frac{1}{2}$;
- $0, \frac{1}{2}, \frac{1}{2}$.

$$F_{hkl} = \sum_{i=1}^N f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$



$$F_{hkl} = f e^{2\pi i(0)} + f e^{2\pi i\left(\frac{h}{2} + \frac{k}{2}\right)} + f e^{2\pi i\left(\frac{h}{2} + \frac{l}{2}\right)} + f e^{2\pi i\left(\frac{k}{2} + \frac{l}{2}\right)}$$

\therefore

$$F_{hkl} = f \left(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \right)$$

7

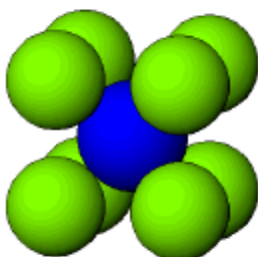
- Substitute in a few values of hkl and you will find the following:
 - When h, k, l are unmixed (i.e. all even or all odd), then $F_{hkl} = 4f$. [NOTE: zero is considered even]
 - $F_{hkl} = 0$ for mixed indices (i.e., a combination of odd and even).

CsCl STRUCTURE

Cesium Chloride is primitive cubic

Cs (0,0,0)

Cl (1/2,1/2,1/2)



$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{d}_j}$$

$$\Phi_{\mathbf{K}} = f_{\text{Cs}} + f_{\text{Cl}} e^{i\pi(h+k+l)}$$

$$\Phi = f_{\text{Cs}} + f_{\text{Cl}} \text{ when } h + k + l \text{ even}$$

$$\Phi = f_{\text{Cs}} - f_{\text{Cl}} \text{ when } h + k + l \text{ odd}$$

Cs⁺ and Cl⁻ are not isoelectronic
→ systematic absences unlikely

but what about CsI? ~~~

SIMPLE ANALYSIS OF SIMPLE PATTERNS

What will we see in XRD patterns of SC, BCC, FCC?

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
		SC	FCC	BCC

$$h^2 + k^2 + l^2$$

SC: 1,2,3,4,5,6,8,9,10,11,12,...

BCC: 2,4,6,8,10,12,...

FCC: 3,4,8,11,12,16,24,...

Observable diffraction peaks for monoatomic crystals

We can take ratios of $(h^2 + k^2 + l^2)$ to determine structure.

PROCEDURE FOR INDEXING AN XRD PATTERN

The procedures are standard. They work for any crystal structure regardless of whether the material is a metal, a ceramic, a semiconductor, a zeolite, etc... There are two methods of analysis. You will do both. One I will refer to as the mathematical method. The second is known as the analytical method. The details are covered below.

Mathematical Method

Interplanar spacings in cubic crystals can be written in terms of lattice parameters using the plane spacing equation:

The term in parentheses $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any one pattern (because the X-ray wavelength λ and the lattice parameters a do not change). Thus $\sin^2 \theta$ is proportional to $h^2 + k^2 + l^2$. This proportionality shows that planes with higher Miller indices will diffract at higher values of θ .

Since $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{\left(\frac{\lambda^2}{4a^2}\right)(h_1^2 + k_1^2 + l_1^2)}{\left(\frac{\lambda^2}{4a^2}\right)(h_2^2 + k_2^2 + l_2^2)} \text{ or } \frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{(h_1^2 + k_1^2 + l_1^2)}{(h_2^2 + k_2^2 + l_2^2)}.$$

The ratio of $\sin^2 \theta$ values scales with the ratio of $h^2 + k^2 + l^2$ values.

If the ratio of : $\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{(h_1^2 + k_1^2 + l_1^2)}{(h_2^2 + k_2^2 + l_2^2)}$ $\left. \begin{array}{l} = 0.5, \text{ the structure is } \mathbf{BCC} \\ = 0.75, \text{ the structure is } \mathbf{FCC} \end{array} \right\}$

Primitive	$h^2 + k^2 + l^2 = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16 \dots$
Body-centered	$h^2 + k^2 + l^2 = 2, 4, 6, 8, 10, 12, 14, 16 \dots$
Face-centered	$h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32 \dots$
Diamond cubic	$h^2 + k^2 + l^2 = 3, 8, 11, 16, 19, 24, 27, 32 \dots$

The lattice parameters can be calculated from:

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

which can be re-written as:

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

Structure	Allowed Reflections
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed

Q/Determine of Crystal Structure (lattice type) from 2θ versus Intensity Data where $\lambda = 1.54 \text{ \AA}$.

#	2θ ($^\circ$)	θ ($^\circ$)	$\sin\theta$	$\sin^2\theta$	$h^2+k^2+l^2$	hkl	d(\AA)
1	38.3811						
2	44.5573						
3	64.6816						
4	77.6192						
5	81.757						
6	98.0552						

Problems:

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

1- Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium when monochromatic radiation of wavelength 0.0711 nm is used.

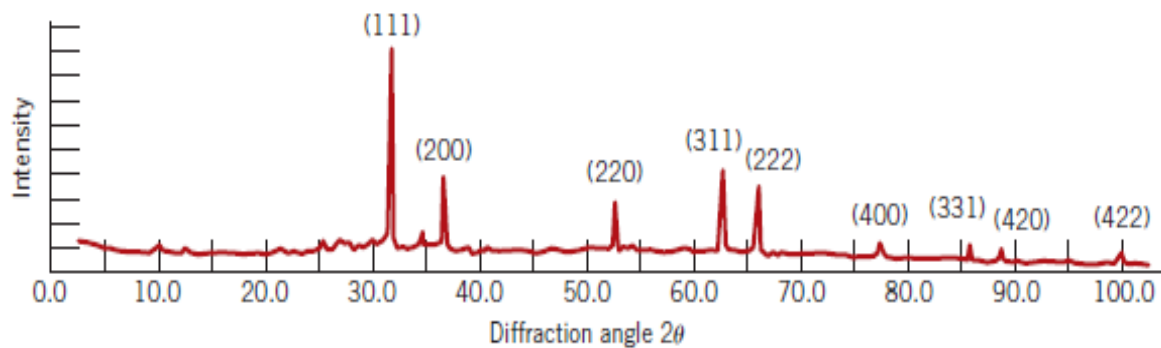
2- Using the data for α -iron, (in table above) compute the interplanar spacings for the (111) and (211) sets of planes.

3- The metal rhodium has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at 36.12° when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute **(a)** the interplanar spacing for this set of planes, and **(b)** the atomic radius for a rhodium atom.

4- The metal niobium has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for the niobium atom.

5- For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel when monochromatic radiation having a wavelength of 0.1542 nm is used?

6- Figure below shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also determine the lattice parameter of Pb for each of the peaks.



Introduction

The subject of lattice dynamics in the solid state physics is very important in the interpretation of the concepts of the physical properties of solids and is intended to lattice dynamics is the study of vibrations of the lattice atoms. Thus, we can describe the overall behavior of the solid matter through thermal, electrical or mechanical properties, and thus deepen our understanding of these properties.

The atoms within the crystalline structure are in the case of a vibration movement, i.e. they move a simple harmonic motion without moving from one location to another but this movement depends on the temperature. At absolute zero, the atoms within the chain settle in equilibrium positions in a state of stillness. When the temperature is raised, the atoms start to oscillate around the equilibrium positions with an offset depending on the temperature.

Vibrational modes of atoms within the crystalline structure are expressed by classical theory as elastic sound waves moving in a continuous medium in a certain pattern and extending through its crystallization is not defined. In modern theories, however, vibration patterns pass through a group of particles that can not be distinguished called phonons.

The thermal properties of the solids, thermal capacity, thermal conductivity, as well as the non-elasticity of the neutrons or X-rays by crystals and others are all explained by the vibration of the lattice resulting in phonons.

Inelastic scattering of photons by phonons

The Bragg law (elastic scattering) for x-ray diffracted by a crystal is subject to the law of vector conservation i.e.:

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

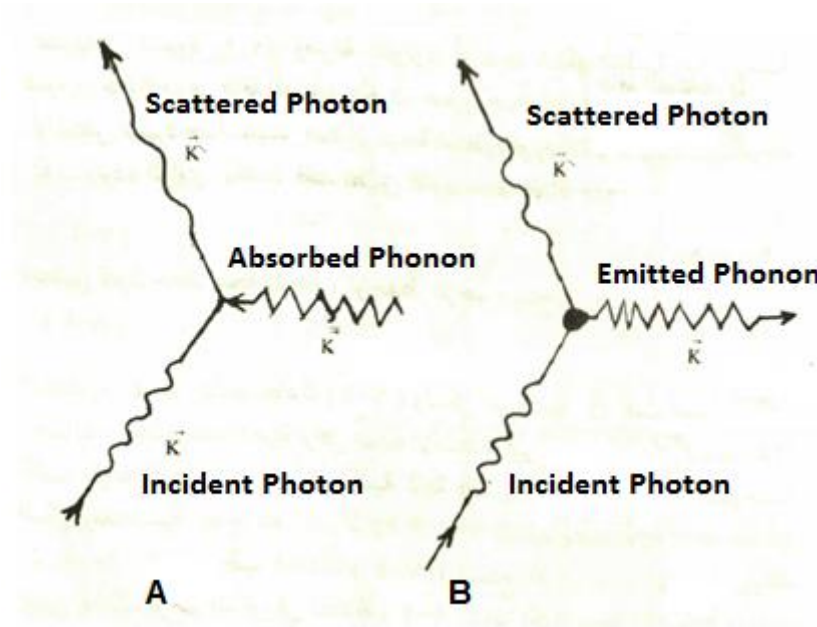
\vec{K} is the vector of the photon (incident wave)

\vec{K}' is the scattering photon vector

\vec{G} Reciprocal lattice vector

An inelastic scattering may occur between the photons incident on the crystal and the waves (phonons) resulting from the vibration of the crystal atoms, resulting in the emission or creation or annihilation of a phonon which has a vector \vec{k} . Using the vector conservation law, we obtain:

$$\vec{k}' - \vec{k} = \vec{G} \mp \vec{k}$$



Where the negative sign refers to the generation of the phonon and the positive sign to the annihilation or absorption of the phonon.

The electric field of the incident photon on the crystal generates mechanical stresses periodically inside the crystal, which causes the change of elastic properties of the crystal, so in this type of interaction can photon to generate or absorb the phonon and thus changes ω to ω' .

It is the change in the value and direction of the photon wave vector as well as its energy, as a result of the creation or annihilation of acoustic phonons. This is why this process is considered an inelastic process. This process is called Brillouin scattering, but because of the large difference between

velocity of acoustic wave and the velocity of light, the photon's velocity is very small, so the energy of the generated or absorbed phonon is very small. Assuming that the result of a photon's scattering was generating a phonon has wave vector \vec{k} , and angular frequency ω_o , when the energy conservation law is applied, it is produced:

$$\hbar\omega = \hbar\omega' + \hbar\omega_o \dots\dots (1)$$

By applying the law to conversation of the vector wave (or conversation momentum) produces:

$$\hbar\vec{K} = \hbar\vec{K}' + \hbar\vec{k} \dots\dots (2)$$

The speed of the acoustic wave v_s is fixed:

$$\vec{k}v_s = \omega_o$$

But for the electrical wave:

$$Kc = \omega$$

$$c \gg v_s$$

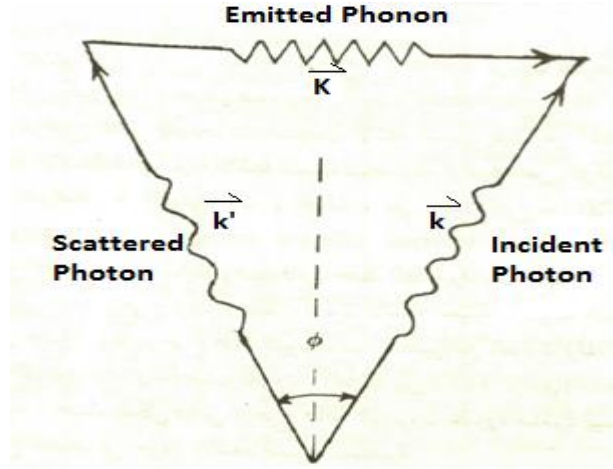
$$cK \gg v_s k$$

$$\omega \gg \omega_o$$

From equation (1) can obtain:

$$K = K' \quad , \quad \omega = \omega'$$

To graphically represent the momentum in (2) is:



An almost equilateral triangle

$$\vec{k} = 2K \sin \frac{\varphi}{2} \dots \dots (3)$$

A formula (3) can be written in terms of the refractive index of the crystal (n). The ratio between the speed of the photon in vacuum and its speed in crystal where:

$$n = \left(\frac{c}{\omega/K} \right) \dots \dots (4)$$

Thus, the equation "3" after multiplying two sides by v_s in crystal as follows:

$$v_s k = 2v_s \omega n c^{-1} \sin \frac{\varphi}{2} \dots \dots (5)$$

But ($v_s k$) is equivalent to the emitted photon frequency (ω_o). Therefore, equation (5) is written as follows:

$$\omega_o = 2v_s \omega n c^{-1} \sin \frac{\varphi}{2} \dots \dots (6)$$

Thus, we have obtained an approximate relation to the frequency of phonons generated by the crystal when the photons suffered an inelastic scattering

photon. The maximum relative change of the photon frequency (visible light) in this process:

$$\frac{\omega - \omega'}{\omega} = \frac{\omega_0}{\omega} \cong 2v_s n c^{-1} \dots \dots (7)$$

The shifting of the frequency of X-ray's photon due to its inelastic scattering is very small compared to the shifting of the photon when studying the phonon spectrum, where neutron energy can be measured directly while the small shifting in the x-ray is difficult to measure.

Inelastic scattering of neutrons by phonons

The thermal neutron can be defined as a neutron with thermal energy of about 0.025eV at 288K. The energy of the thermal neutron is an approach to the energy of the phonon.

Therefore, a significant change in neutron energy is expected during its inelastic scattering with the nuclei of the crystal atoms

If the velocity of the neutron \vec{v} and its mass M_n will be vector wave is:

$$\vec{K}_n = \frac{M_n \vec{v}}{\hbar} \dots \dots \dots (8)$$

And the kinetic energy:

$$E = \frac{\hbar^2 K_n^2}{2M_n} \dots \dots \dots (9)$$

When the inelastic scattering of the neutron is happened by absorption or generation of a phonon, its wave vector, and energy change to E' , K'_n respectively, as follows:

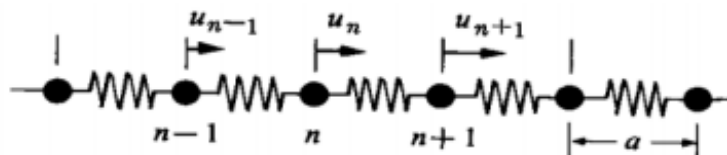
$$\left. \begin{aligned} \vec{K}_n - \vec{K}'_n &= \vec{G} + \vec{K} \\ E - E' &= \mp \hbar \omega_k \end{aligned} \right\} \dots\dots\dots (10)$$

Measuring the value of the acquired or lost energy of the scattered neutron as a function of the direction of the scattering. In practice, it can use relation (10) to find the dispersion relation between K , ω_k for the generated or absorbed phonon by inelastic scattering.

Vibrational modes of linear monoatomic lattice

Consider one-dimensional crystal lattice and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions.

This is known as the *harmonic approximation*, which holds well provided that the displacements are small. One might think about the atoms in the lattice as interconnected by elastic springs.



u_n : displacement
 α : elastic constant

$$F_R = c (u_{n+1} - u_n) \dots\dots\dots (11)$$

$$F_{(l)} = c (u_n - u_{n-1}) \dots\dots\dots (12)$$

$$F_n = F_{(R)} - F_{(l)}$$

$$F_n = c [u_{n+1} - u_n - u_n + u_{n-1}]$$

$$F_n = c [u_{n+1} + u_{n-1} - 2u_n] \quad \dots \dots \dots (13)$$

Equation (13) represents the equation of motion for any atom in the chain under the influence of the forces of the first neighbors only. Longitudinal wave propagation can be represented in a homogeneous solid in a particular direction such as x.

$$u = Ae^{i[Ex - \omega t]}$$

$$\text{or } u = Ae^{i[Kx - \omega t]} \quad \dots \dots \dots (14)$$

Where x represents the position of the stability of the vibrated atom from the point of origin. Since the displacement of the atom "n" from its point of origin from $na = x$ then equation (14) can be written as follows:

$$u = Ae^{i[Kna - \omega t]} \quad \dots \dots \dots (15)$$

By derivation the displacement twice according to the time, we get the acceleration of this atom as follows:

$$\frac{du_n}{dt} = Ai\omega e^{i[Kna - \omega t]} \quad \dots \dots \dots (16)$$

$$\frac{d^2u_n}{dt^2} = -\omega^2 A\omega e^{i[Kna - \omega t]} \quad \dots \dots \dots (17)$$

$$\ddot{u} = -\omega^2 u_n \quad \dots \dots \dots (18)$$

This means that the direction of acceleration or the direction of the force causing the acceleration is opposite to the displacement direction, That is, repeating force is affecting the n atom is:

$$F_n = -\omega^2 u_n \quad \dots\dots\dots (19)$$

By connect the eqs. (13) and (19):

$$-m\omega^2 u_n = c [u_{n+1} + u_{n-1} - 2u_n] \quad \dots\dots\dots (20)$$

$$-m\omega^2 = c \left[\frac{u_{n+1}}{u_n} + \frac{u_{n-1}}{u_n} - \frac{2u_n}{u_n} \right]$$

$$\omega^2 = \frac{c}{m} \left[2 - \frac{u_{n+1}}{u_n} - \frac{u_{n-1}}{u_n} \right] \quad \dots\dots\dots (21)$$

But:

$$\frac{u_{n+1}}{u_n} = \frac{A \exp[ik(n+1)a - i\omega t]}{A \exp[ik(na) - i\omega t]} = e^{ika}$$

This leads to:

$$\omega^2 = \frac{c}{m} [2 - e^{ika} - e^{-ika}]$$

$$= \frac{c}{m} [2 - (\cos ka + i \sin ka) - (\cos ka - i \sin ka)]$$

$$= \frac{c}{m} [2 - 2 \cos ka] = \frac{2c}{m} (1 - \cos ka)$$

$$(1 - \cos ka) = 2 \sin^2 \left(\frac{ka}{2} \right)$$

$$\omega^2 = 4 \frac{c}{m} \sin^2 \left(\frac{ka}{2} \right) \quad \dots\dots\dots (22)$$

$$\omega = \pm \left(\frac{c}{m}\right)^{\frac{1}{2}} \sin\left(\frac{ka}{2}\right) \dots \dots \dots (23)$$

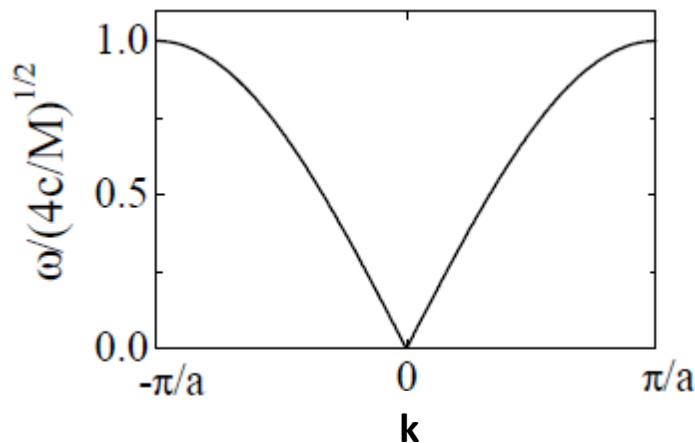
Equation (23) represents the **dispersive relation** between the angular frequency (ω) and the value of the wave vector [k] for the monoatomic chain.

Which is the relationship between the frequency of vibrations and the wavevector q . This dispersion relation have a number of important properties.

(i) *Reducing to the first Brillouin zone.* The frequency and the displacement of the atoms do not change when we change k by $k+2\pi/a$. This means that these solutions are physically identical. This allows us to set the range of independent values of q within the first Brillouin zone, i.e.

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}.$$

Within this range of q the frequency ω versus q is shown in following:



The maximum frequency is $4C/M$. The frequency is symmetric with respect to the sign change in k , i.e. $\omega(k) = \omega(-k)$. This is not surprising because a mode with positive k corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative q corresponds to the wave traveling

from the right to the left. Since these two directions are equivalent in the lattice the frequency does not change with the sign change in k .

At the boundaries of the Brillouin zone $k = \pm\pi/a$ the solution represents a standing wave: $u_n = A(-1)^n e^{-i\omega t}$ atoms oscillate in the opposite phases depending on whether n is even or odd. The wave moves neither right nor left.

(ii) *Phase and group velocity.* The phase velocity is defined by

$$V_p = \frac{\omega}{k} \quad \dots\dots (24)$$

and the group velocity by

$$V_g = \frac{d\omega}{dk} \quad \dots\dots (25)$$

The physical distinction between the two velocities is that v_p is the velocity of the propagation of the plane wave, whereas the v_g is the velocity of the propagation of the wave packet. The latter is the velocity for the propagation of energy in the medium.

For the particular dispersion relation (23) the group velocity is given by:

$$v_g = \sqrt{\frac{Ca^2}{m}} \cos \frac{ka}{2} \quad \dots\dots\dots (26)$$

As is seen from Eq.(26) the group velocity is zero at the edge of the zone where $k = \pm\pi/a$. Here the wave is standing and therefore the transmission velocity for the energy is zero.

(iii) *Long wavelength limit.* The long wavelength limit implies that $\lambda \gg a$. In this limit $ka \ll 1$. We can then expand the sine in Eq. (23) and obtain for the positive frequencies:

$$\omega = \sqrt{\frac{c}{m}} ka = v_o k \dots\dots\dots (27) \quad \sqrt{\frac{c}{m}} a = v_o$$

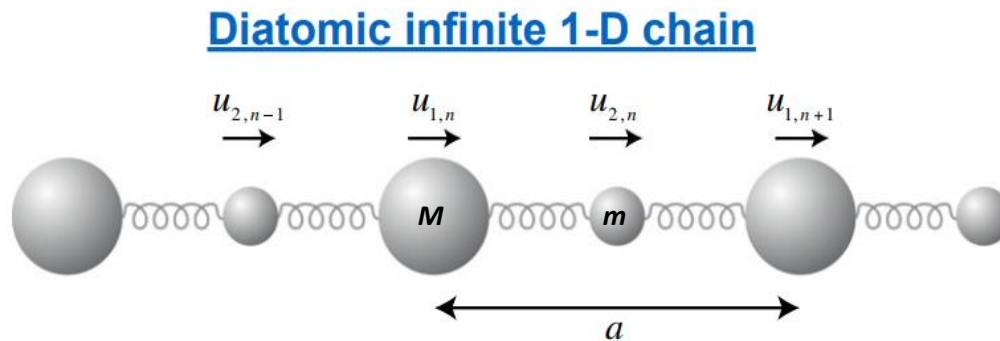
We see that the frequency of vibration is proportional to the wave vector. This is equivalent to the statement that velocity is independent of frequency. In this case:

$$V_p = \frac{\omega}{k} = \sqrt{\frac{c}{m}} a \quad \dots\dots\dots (28)$$

This is the velocity of sound for the one dimensional lattice which is consistent with the expression we obtained earlier for elastic waves.

Vibrational Modes of Linear Diatomic Lattice

Now we consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. It appears that the diatomic lattice exhibit important features different from the monoatomic case. Figure (1) shows a diatomic lattice with the unit cell composed of two atoms of masses M and m with the distance between two neighboring atoms a .



We can treat the motion of this lattice in a similar fashion as for monoatomic lattice. However, in this case because we have two different kinds of atoms, we should write two equations of motion:

$$\left. \begin{aligned} u_{2n} &= A \exp\{i[K(2n)a - \omega t]\} \\ u_{2n+1} &= B \exp\{i[K(2n+1)a - \omega t]\} \end{aligned} \right\} \dots (1)$$

Where B and A represent the vibration intensity of small and large atoms, respectively.

$$\left. \begin{aligned} m \left(\frac{d^2 u_{2n}}{dt^2} \right) &= m(-\omega^2 u_{2n}) = c[u_{2n+1} + u_{2n-1} - 2u_{2n}] \\ M \left(\frac{d^2 u_{2n+1}}{dt^2} \right) &= M(-\omega^2 u_{2n+1}) = c[u_{2n+2} + u_{2n} - 2u_{2n+1}] \end{aligned} \right\} \dots\dots (2)$$

$$\left. \begin{aligned} -M\omega^2 B &= cA[\exp(iKa) + \exp(-iKa)] - 2cB \\ -m\omega^2 A &= cB[\exp(iKa) + \exp(-iKa)] - 2cA \end{aligned} \right\} \dots\dots (3)$$

But

$$\exp(iKa) + \exp(-iKa) = 2 \cos Ka$$

So

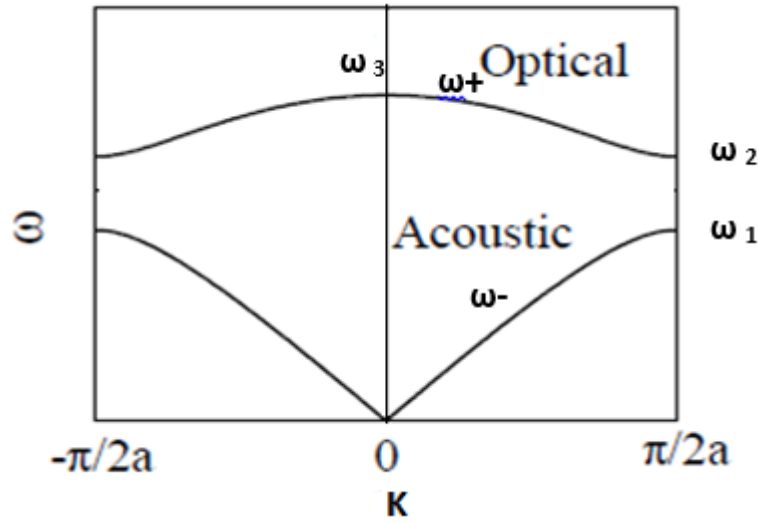
$$\left. \begin{aligned} (m\omega^2 - 2c)A + 2cB \cos Ka &= 0 \\ (M\omega^2 - 2c)B + 2cA \cos Ka &= 0 \end{aligned} \right\} \dots\dots\dots (4)$$

$$\therefore (2c - m\omega^2)(2c - M\omega^2) = 4c^2 \cos^2 Ka \dots\dots (5)$$

In order to solve this equation we obtain the relationship between the value of the wave vector and the angular frequency K and ω

$$\omega^2 = c \left[\frac{1}{m} + \frac{1}{M} \right] \mp c \left[\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2(Ka)}{mM} \right]^{1/2} \dots\dots (6)$$

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves, as is shown in Figure (2):



Acoustical branch for linear diatomic lattice:

The lower curve is called the *acoustic branch*, while the upper curve is called the *optical branch*. The optical branch begins at $k=0$ and $\omega=0$. Then with increasing k the frequency increases in a linear fashion. This is why this branch is called acoustic: it corresponds to elastic waves or sound. Eventually this curve saturates at the edge of the Brillouin zone .

$$\left(-\frac{\pi}{2a}\right) \leq K \leq \left(\frac{\pi}{2a}\right)$$

On the other hand, the optical branch has a nonzero frequency at zero k .

To substitute for the value of $\left(K = \mp \frac{\pi}{2a}\right)$ in equation (6) for the greatest possible value of the angular frequency, we see clearly that the maximum angular frequency of the sound pattern vibrations does not depend on the mass of the small atom (m) where:

$$\omega^2 = c \left[\frac{1}{m} + \frac{1}{M} \right] \mp c \left[\left(\frac{1}{m} - \frac{1}{M} \right)^2 \right]^{1/2} = c \left[\frac{1}{m} + \frac{1}{M} \right] \mp \left[\frac{c}{mM} - \frac{1}{mM} \right]^{1/2}$$

$$\therefore (\omega_{-mar}) = \omega_1 = \left(\frac{2c}{M} \right)^{1/2} \dots\dots\dots (7)$$

When the masses of the series atoms ($m = M$) are equal, the lattice becomes a monoatomic.

The ratio between the intensity of large atom (B) and small (A) is:

$$\frac{B}{A} = \left[\frac{2c - m\omega_-^2}{2c \cos(Ka)} \right] \dots\dots\dots (8)$$

Also

$$\frac{B}{A} = \frac{2c \cos(Ka)}{2c - M\omega_-^2}$$

In the low frequency zone or long wavelengths when K values are so small that:

$$\sin^2(Ka) \cong (K^2 a^2)$$

$$\omega_- \cong \left(\frac{2c}{m+M} \right)^{1/2} Ka \dots\dots\dots (9)$$

$$V_0 = \frac{\omega_-}{K} = \left(\frac{2c}{m+M} \right)^{1/2} a \dots\dots\dots (10)$$

$$\frac{B}{A} = \infty, \omega_- \rightarrow \omega_1 = \left(\frac{2c}{M} \right)^{1/2} \dots\dots\dots (11)$$

$$V_P = \frac{\omega}{K} = \left(\frac{8ca^2}{\pi^2 M} \right)^{1/2} \dots\dots\dots (12) \quad V_o = V_p$$

$$V_g = \frac{d\omega}{dK} = 0 \dots\dots\dots (13)$$

Optical branch for linear diatomic lattice

The optical branch includes all the angular frequencies (ω_+) in the previous figure, which comes from the positive choices of equation (6).

When $K = 0$ the angular frequency (ω_3) is as great as possible and the acoustic patterns = zero ie :

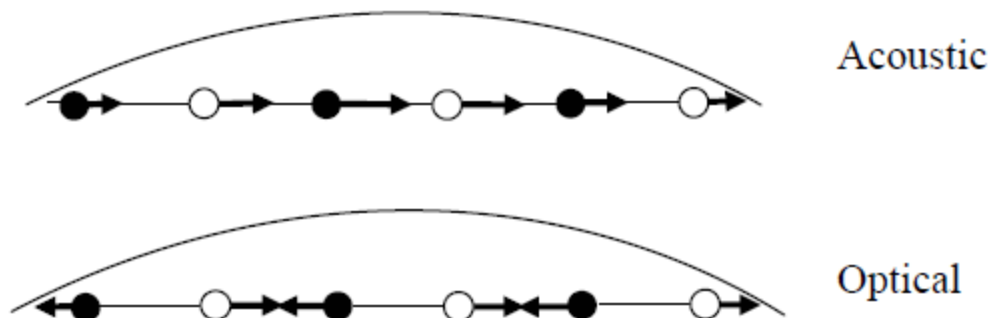
$$K \Rightarrow 0, \omega_+ \rightarrow \omega_3 = \omega_{\max} = \left[2c \left(\frac{1}{m} + \frac{1}{M} \right) \right]^{1/2} \dots (14)$$

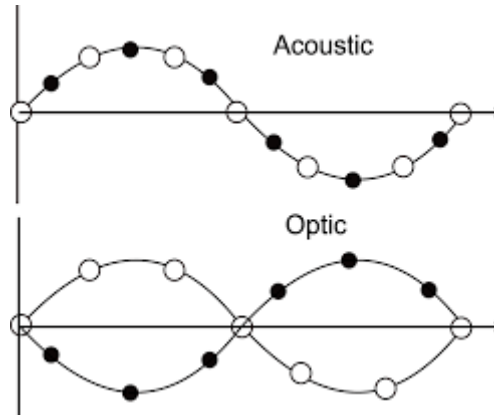
$$V_p = \frac{\omega}{K} \rightarrow \infty, \frac{d\omega}{dK} \Rightarrow 0, \frac{B}{A} \rightarrow -\frac{m}{M} \dots (15)$$

This means at the long wavelengths with optical vibration the neighboring atoms move in opposite directions or phase difference (π) so that the center of the mass of any neighboring two atoms remains intact, ie, the binary molecule in each cell vibrates independent of its molecular neighbors while the center of the cell remains fixed.

The distinction between the acoustic and optical branches of lattice vibrations can be seen most clearly by comparing them at $k=0$ (infinite wavelength). As follows from Eq. (8), for the acoustic branch $\omega = 0$ and $B=A$. So in this limit the two atoms in the cell have the same amplitude and the phase.

Therefore, the molecule oscillates as a rigid body, as shown in Figure (3) for the acoustic mode.



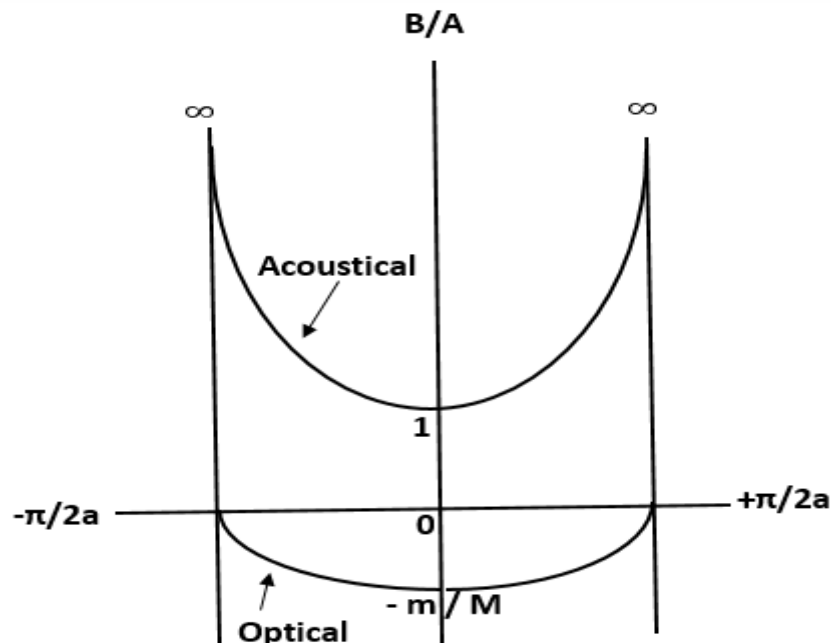


The ratio of the intensities (B / A) remains negative during the optical branch but approaches zero when the K value of the greatest value ($\pi/2a$) is closer to (ω_+) than the minimum angular frequency (ω_2) can be ($4a = \lambda$).

$$K = \frac{\pi}{2a}, \omega_+ = \omega_2 = \left(\frac{2c}{m} \right)^{1/2}, \frac{B}{A} = 0 \dots \dots \dots (16)$$

$$\frac{\omega}{K} = \left(\frac{8ca^2}{\pi^2 m} \right)^{1/2}, \frac{d\omega}{dk} = 0 \dots \dots \dots (17)$$

The amplitude of the large atom (B) is zero, regardless of the amplitude of the small atom (A). This means that the large atom has stopped moving and therefore depends on ω_2 only on the small atom mass (m) and force constant (c).

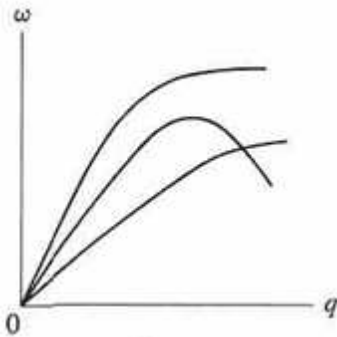


In this figure, we observe that the ratio of atoms masses of acoustic vibration patterns varies from 1 (for long wavelengths) to infinity (∞) (for the shortest wave possible $\cong 0$), while this ratio changes to the optical vibration patterns from $(-m/M)$ (for the shortest wave possible $\cong 0$) to 0 (for long wavelengths).

Monoatomic 3-D lattice

These considerations can be extended to the three-dimensional lattice. To avoid mathematical details we shall present only a qualitative discussion. Consider, first, the monatomic Bravais lattice, in which each unit cell has a single atom. The equation of motion of each atom can be written in a manner similar to that of monoatomic 1-D lattice. The solution of this equation in three dimensions can be represented in terms of *normal modes*.

$$\mathbf{u} = \mathbf{A} e^{i(\mathbf{k}\mathbf{r}-\omega t)}$$



The number of transverse patterns is always twice the number of longitudinal patterns.

In general, if the number of atoms to crystallize is P , the number of branches dispersive the phonon ($3P$) is the sum of the acoustic branches and $3P-3$ is the sum of the optical branches.

If we have a crystal containing N of the primitive cells, the total number of $3PN$ branches will be distributed as follows:

Number of longitudinal sound patterns: N

Number of transverse sound patterns: $2N$

Number of linear optical patterns ($P-1$): N

Number of Transverse optical patterns: $2(P-N)N$

3.4 Phonons

So far we discussed a classical approach to the lattice vibrations. As we know from quantum mechanics the energy levels of the harmonic oscillator are quantized. Similarly the energy levels of lattice vibrations are quantized. The quantum of vibration is called a *phonon* in analogy with the photon, which is the quantum of the electromagnetic wave.

We know that the allowed energy levels of the harmonic oscillator are given by:

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \quad \dots\dots\dots (8)$$

Where n is the quantum number. A normal vibration mode in a crystal of frequency ω . If the energy of this mode is given by Eq. (8) we can say that this mode is occupied by n *phonons* of energy $\hbar\omega$. The term $\frac{1}{2}\hbar\omega$ is the zero point energy of the mode.

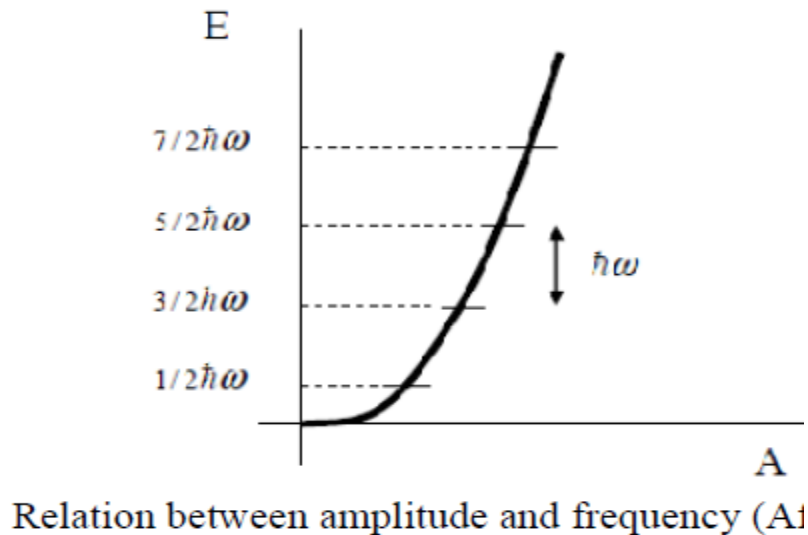
Let us now make a comparison between the classical and quantum solutions in one dimensional case. Consider a normal vibration

$$u = Ae^{i(qx - \omega t)} \quad \dots\dots\dots (9)$$

Where u is the displacement of an atom from its equilibrium position x and A is the amplitude. The energy of this vibrational mode averaged over time is:

$$E = \frac{1}{2} M\omega^2 A^2 = \left(n + \frac{1}{2}\right)\hbar\omega \quad \dots\dots\dots (10)$$

It is evident from Eq. (10) above that there is a relationship between the amplitude of vibration and the frequency and the phonon occupation of the mode. In classical mechanics any amplitude of vibration is possible, whereas in quantum mechanics only discrete values are allowed. This is shown in Figure below.



Linear Monoatomic Lattice

1-For Linear monoatomic Lattice prove that the dispersive relation between ω and k is: $\omega = \pm \left(\frac{c}{m}\right)^{\frac{1}{2}} \sin\left(\frac{ka}{2}\right)$

2-When the $V_p = V_g$? Prove that.

3- Prove that: $\omega_{\max} = \pm \left(\frac{c}{m}\right)^{\frac{1}{2}}$

Linear Diatomic Lattice

1-For Linear Diatomic Lattice prove that the dispersive relation between ω and k is:

$$\omega^2 = c \left[\frac{1}{m} + \frac{1}{M} \right] \pm c \left[\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2(Ka)}{mM} \right]^{\frac{1}{2}}$$

2-For an acoustical branch:

a- At $k=0$, c: $\omega_1=0$

b- At $k = \pm \frac{\pi}{2a}$, prove that: $\omega_- = \omega_1 = \left(\frac{2c}{M}\right)^{\frac{1}{2}}$

c- At low frequency zone or long wavelengths, prove that:

$$\omega_- \cong \left(\frac{2c}{m+M} \right)^{\frac{1}{2}} Ka$$

3-For an optical branch:

a- At $k=0$, prove that: $\omega_3 = \omega_{\max} = \left[2c \left(\frac{1}{m} + \frac{1}{M} \right) \right]^{\frac{1}{2}}$

b- At $k = \pm \frac{\pi}{2a}$, prove that: $\omega_+ = \omega_2 = \left(\frac{2c}{m}\right)^{\frac{1}{2}}$

c- At low frequency zone or long wavelengths, prove that:

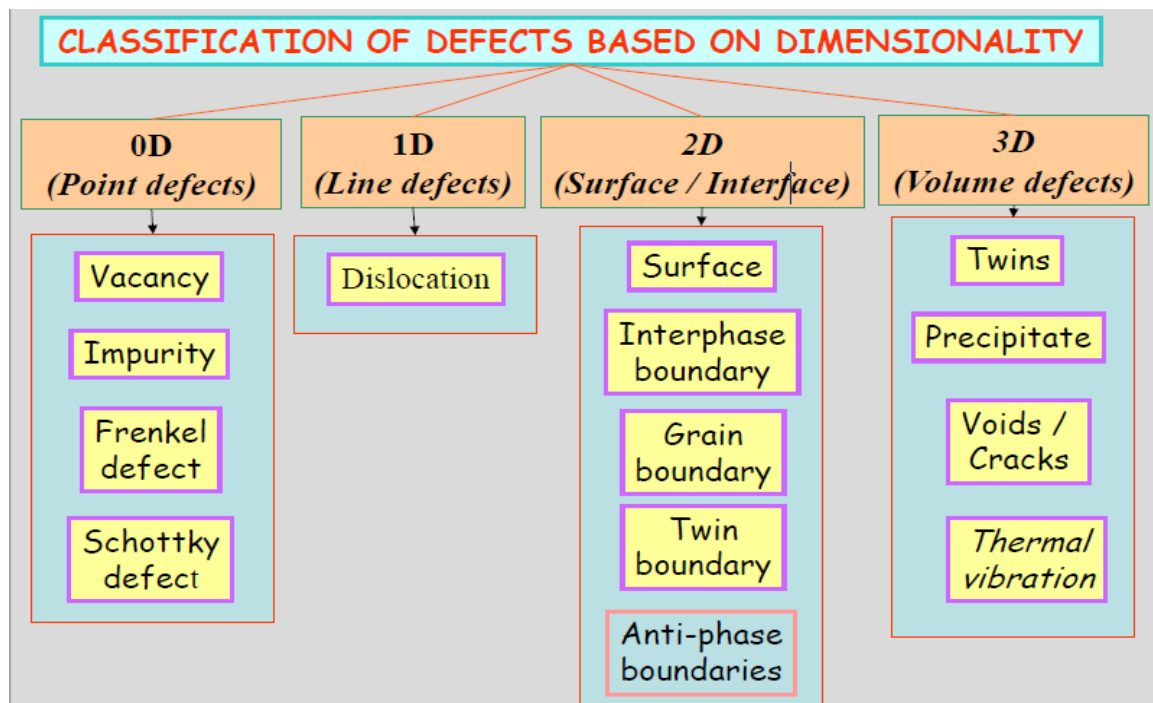
$$\omega_+ \cong \left(\frac{2c}{m+M} \right)^{\frac{1}{2}} Ka$$

Crystal Defects

Crystalline solids have a very regular atomic structure: that is, the local positions of atoms with respect to each other are repeated at the atomic scale. These arrangements are called perfect crystal structures. However, above 0°C all crystalline materials are not perfect: the regular pattern of atomic arrangement is interrupted by crystal defects. The defect types are classified according to their dimension:

Lattice defects can be sorted into four group:

1. Point defects (0-D) : vacancies, interstitial defects, substitution defects.
2. Line defects (1-D) : edge dislocation, screw dislocation.
3. Surface Imperfections (2-D) : material surface, grain boundaries.
4. Volume (Bulk) defects (3-D). precipitates, voids (vacancy agglomerates), bubbles, dislocation clusters



Why defect are important? There are a lot of properties that are controlled or affected by defects, for example:

- ❖ Electric and thermal conductivity in metals (strongly reduced by point defects).
- ❖ Electronic conductivity in semi-conductors (controlled by substitution defects).
- ❖ Diffusion (controlled by vacancies).
- ❖ Ionic conductivity (controlled by vacancies).
- ❖ Plastic deformation in crystalline materials (controlled by dislocation).
- ❖ Colors (affected by defects).
- ❖ Mechanical strength (strongly depended on defects).

Point defects (0-D)

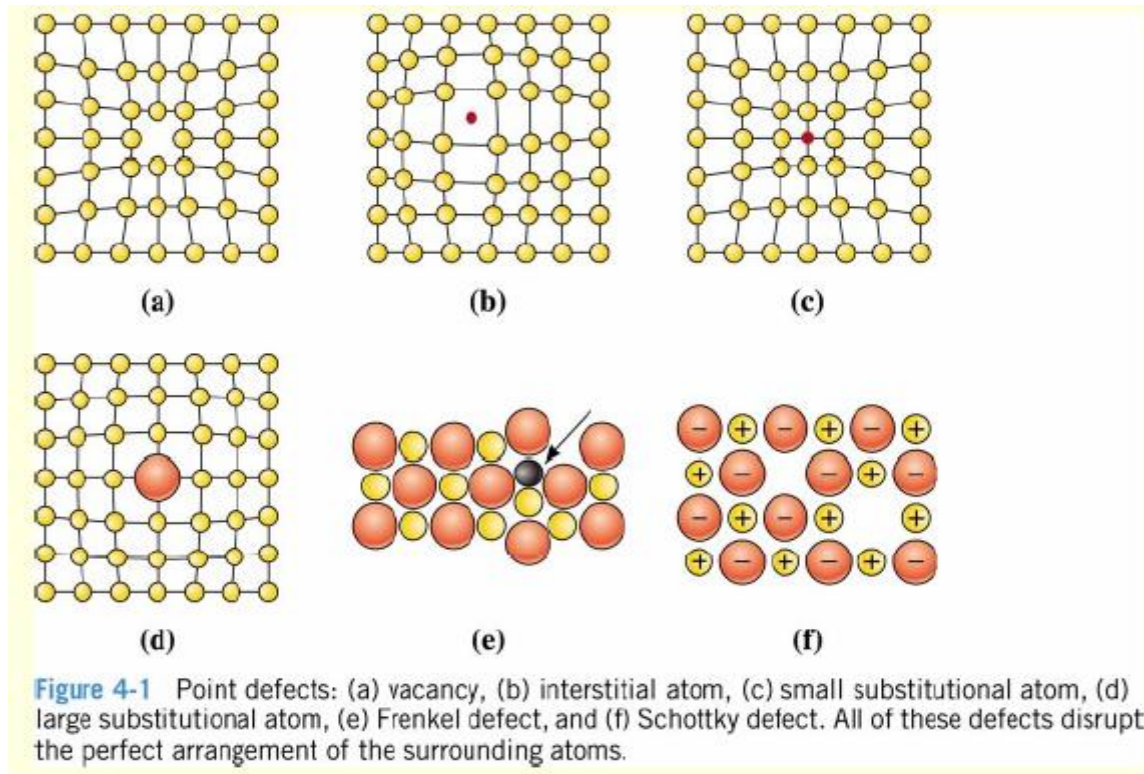
Self-interstitial – A self-interstitial is an atom from the crystal that is crowded into an interstitial site, a small void space that under ordinary circumstances is not occupied. The formation of this defect is not highly probable, and it exists in very small concentrations.

Vacancy - A vacancy is produced when an atom is missing from a normal site. Formed when atoms are removed from their lattice positions.

Impurities in solids - A pure metal consisting of only one type of atom just isn't possible. Impurity or foreign atoms will always be present, and some will exist as crystalline point defects. The addition of impurity atoms to a metal will result in the formation of a solid solution.

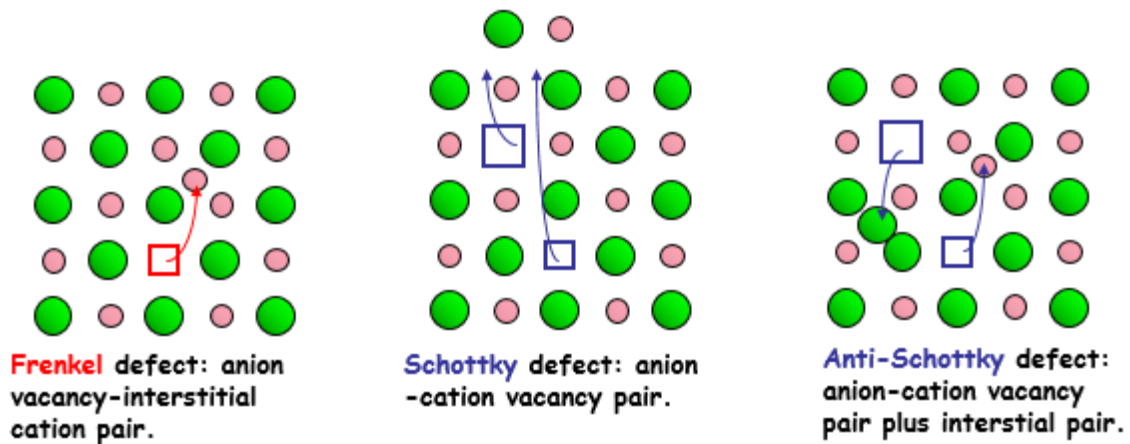
Impurity point defects are found in solid solutions, of which there are two types:

1. Substitutional – one atom is replaced by a different type of atom.
2. Interstitial – extra atom is inserted into the lattice structure at a normally unoccupied position



Other point's defects:

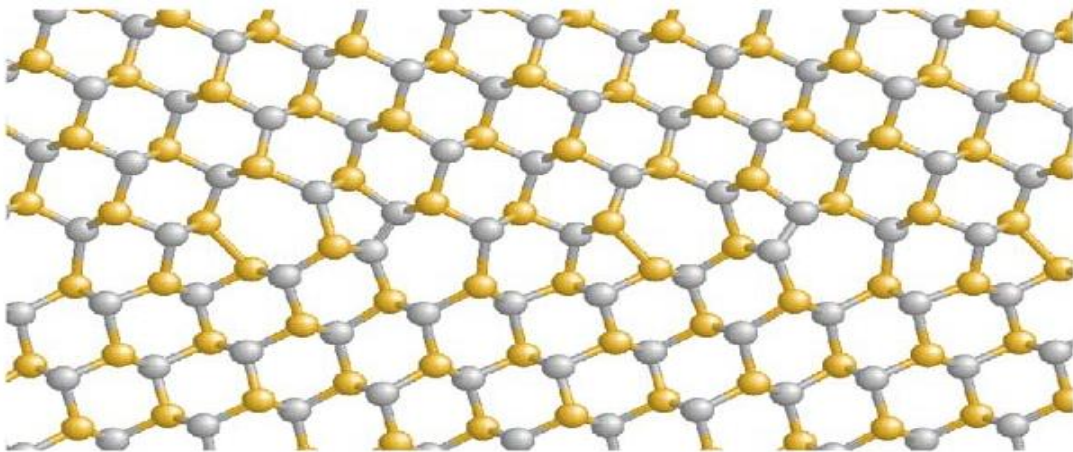
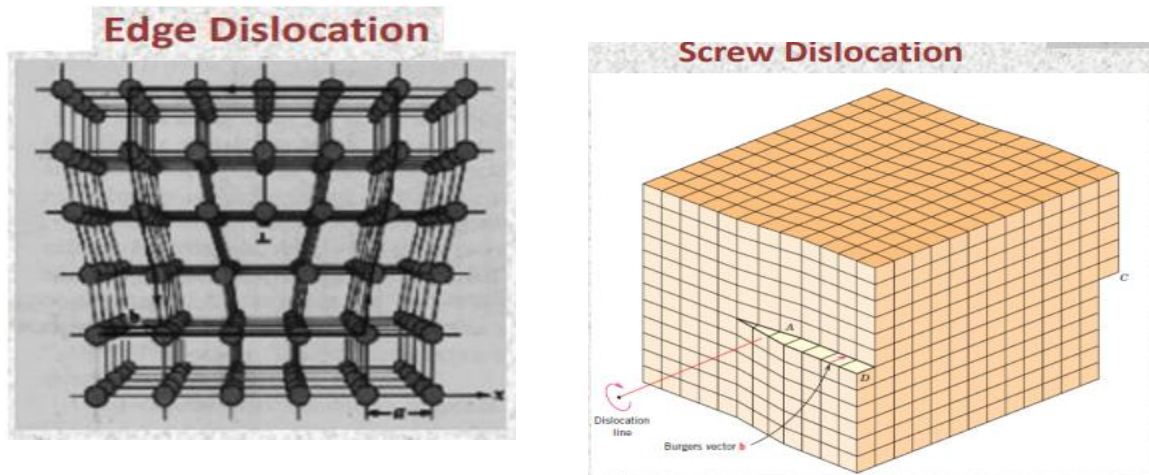
- **Frenkel defect** – ion jumps from a normal lattice point to an interstitial site, leaving behind a vacancy (vacancy-interstitial). A vacancy-interstitial pair.
- **Schottky defect** – pair of vacancies in ionically bonded material. Both anion and cation must be missing from the lattice to maintain the crystal neutral. Formed when atoms are removed from their lattice positions (typically to the surface) as a result of thermal fluctuations.



Line Defects

Dislocations: Boundary between two regions of a surface which are perfect themselves but are out of registry with each other. The resulting lattice distortion is centered along a line.

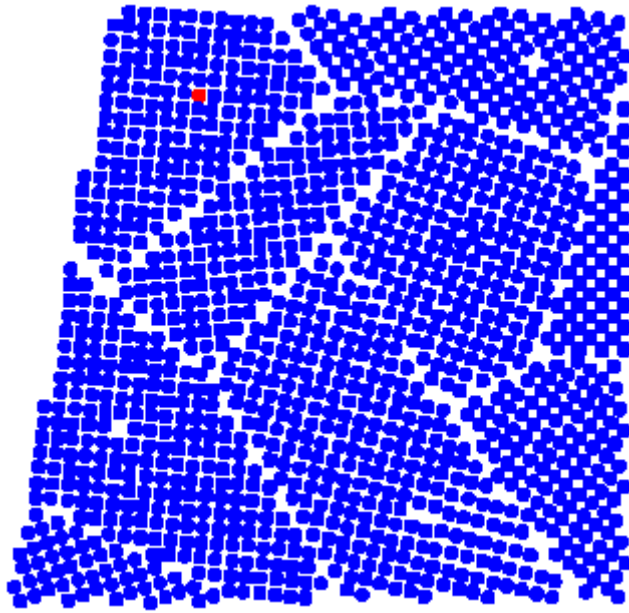
- Burgers Vector, b : A vector by which the lattice on one side of an internal surface containing the dislocation line is displaced relative to the lattice on the other side.
- There are two special cases of dislocations
 - ❖ Edge Dislocation: b and normal vector along the dislocation line l are perpendicular
 - ❖ Screw Dislocation: b and normal vector along the dislocation line l are parallel



Surface Imperfections (2-D)

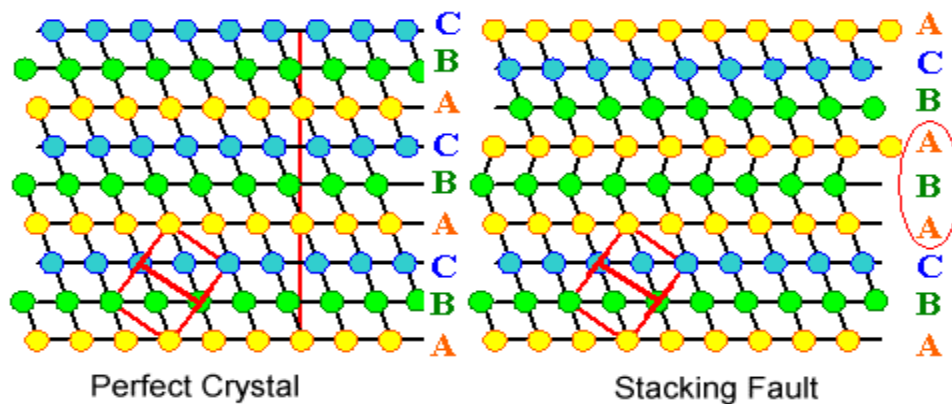
❖ Grain Boundaries in Poly crystals

Solids generally consist of a number of crystallites or grains. Grains can range in size from nanometers to millimeters across and their orientations are usually rotated with respect to neighboring grains. Where one grain stops and another begins is known as a grain boundary. Grain boundaries limit the lengths and motions of dislocations.

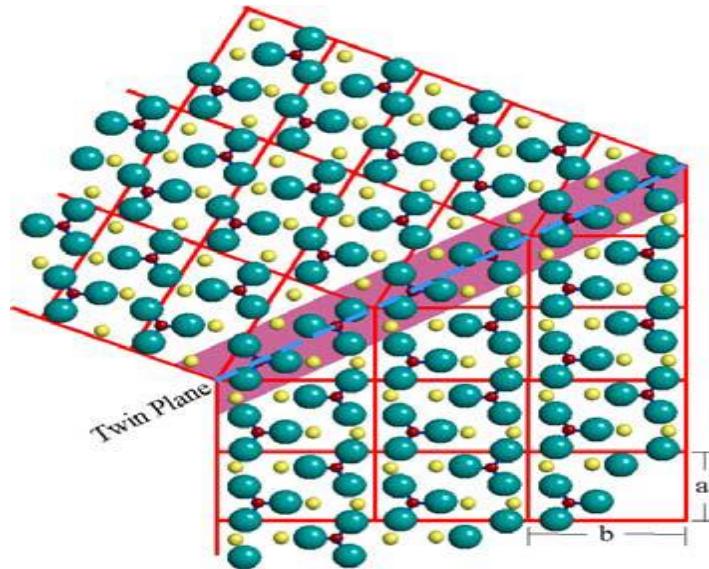


❖ Stacking Faults

A stacking fault is a one or two layer interruption in the stacking sequence of atom planes. Stacking faults occur in a number of crystal structures, but it is easiest to see how they occur in close packed structures. For example, it is known from a previous discussion that face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in their stacking order. In the fcc arrangement the pattern is ABCABCABC. A stacking fault in an fcc structure would appear as one of the C planes missing. In other words the pattern would become ABCABABCA or another order.



❖ **Twine boundaries**



The Number of Vacancies

The equilibrium number of vacancies **n** formed as a result of thermal vibrations may be calculated from thermodynamics:

$$N_v = (N_s - N_v) e^{-Q_v/K_B T} \dots\dots\dots (1)$$

when: $N_v \ll N_s$

$$\therefore N_v \cong N_s e^{-Q_v/K_B T} \dots\dots\dots (2)$$

Where **N** is the number of regular lattice sites, **K_B** is the Boltzmann constant, **Q_v** is the energy needed to form a vacant lattice site in a perfect crystal, and **T** the temperature in Kelvin.

Using this equation we can estimate that at room temperature in copper there is one vacancy per 10¹⁵ lattice atoms, whereas at high temperature, just below the melting point there is one vacancy for every 10,000 atoms.

Note, that the above equation gives the lower end estimation of the number of vacancies, a large numbers of additional (nonequilibrium) vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.)

Q1/ Suppose that a crystal contains number atoms 10^{29} atom/m³ at 27°C (room temperature) and the formation energy of the gap is 1 eV. Calculate the number of vacancies and the concentration of vacancies.

$$N_v \cong N_s e^{-Q_v/K_B T}$$

$$N_v = 10^{29} e^{-\frac{1 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times (300)}}$$

$$= 10^{29} e^{-\frac{1.6 \times 10^2}{4.04}}$$

$$= 10^{12} \text{ vacancy}$$

$$\text{Concentration of vacancies} = \frac{N_v}{N_s} = \frac{10^{12}}{10^{29}} = 10^{-17}$$

Q2/

Let's estimate the number of vacancies in Cu at room T

$$N_v = N_s \exp\left(-\frac{Q_v}{k_B T}\right)$$

The Boltzmann's constant $k_B = 1.38 \times 10^{-23} \text{ J/atom-K} = 8.62 \times 10^{-5} \text{ eV/atom-K}$

The temperature in Kelvin $T = 27^\circ \text{C} + 273 = 300 \text{ K}$.

$$k_B T = 300 \text{ K} \times 8.62 \times 10^{-5} \text{ eV/K} = 0.026 \text{ eV}$$

The energy for vacancy formation $Q_v = 0.9 \text{ eV/atom}$

The number of regular lattice sites $N_s = N_A \rho / A_{\text{Cu}}$

$$N_A = 6.023 \times 10^{23} \text{ atoms/mol}$$

$$\rho = 8.4 \text{ g/cm}^3$$

$$A_{\text{Cu}} = 63.5 \text{ g/mol}$$

$$N_s = \frac{(6.023 \times 10^{23} \text{ atoms/mol}) \times (8.4 \text{ g/cm}^3)}{63.5 \text{ g/mol}} = 8 \times 10^{22} \text{ atoms/cm}^3$$

$$N_v = 8 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3} \exp\left(-\frac{0.9 \text{ eV/atom}}{0.026 \text{ eV/atom}}\right) =$$

$$= 7.4 \times 10^7 \text{ vacancies/cm}^3$$

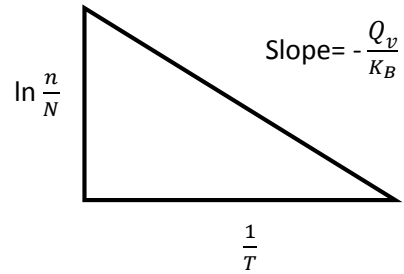
Note: The formation energy of vacancy can be calculated from the equation:

$$N_v = N_s e^{-Q_v/K_B T}$$

$$\left(\frac{N_v}{N_s}\right) = e^{-Q_v/K_B T}$$

$$\ln\left(\frac{N_v}{N_s}\right) = -\frac{Q_v}{K_B T} = \left(-\frac{Q_v}{K_B}\right) \frac{1}{T}$$

$$slope = -\frac{Q_v}{K_B}$$



The slope and K_B are known then can calculate Q_v .