



Introduction of Solid

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الفرقة الثالثة انجليزي

شعبة الفيزياء

تربية عام

الجزء الأول

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CHAPTER (1) : Crystal Structure

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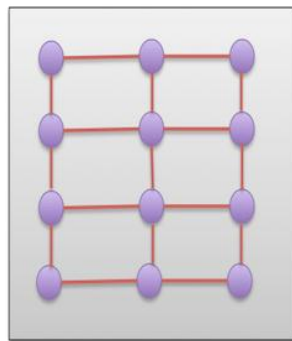
CHAPTER (1)

Crystal Structure

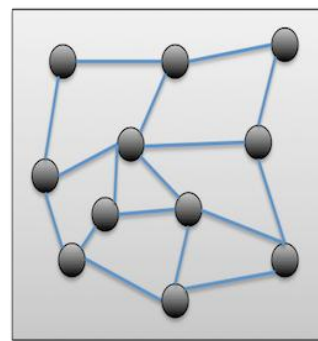
Types of Solids

On the basis of the arrangement of constituent particles, the solids are classified into two categories, namely:

- Amorphous Solids
- Crystalline Solids



Crystalline Solid



Amorphous Solid

Image 1: Arrangement of Atoms

Amorphous Solids

The solids in which the constituent particles of matter are arranged in a random manner are called amorphous solids. It is a non-crystalline solid with no proper arrangement of atoms in the solid lattice. In other words, we can define amorphous solids as materials which don't have certain organized arrangement of atoms and molecules. Most solids are amorphous in nature and are utilized in many sectors as well. One of the

most common examples of amorphous solids is glass, which is used widely in the manufacturing sector.

Characteristics of Amorphous Solids

An Amorphous Solid depicts following properties, which are as follows:

- The constituent particles of matter inside solid are arranged in a random manner, that is, the position of atoms and molecules is not fixed and varies from one solid to another
- Amorphous Solids don't have definite shape or geometry due to random arrangement of atoms and molecules inside the solid lattice
- Short-range order is found in amorphous solids
- Amorphous Solids are also called **Pseudo-solids** or **Supercooled Liquids** because they don't form crystalline structure and has the ability to flow
- The nature of amorphous solids is isotropic in nature that is, the properties measured in all directions come out to be same, example refractive index of amorphous solids is same
- Amorphous solids don't show sharp melting point, this is because of irregular packing of amorphous solids
- When we cut an amorphous solid, we find the broken constituent particles to be irregular in shape and geometry

- Amorphous solids are unsymmetrical in nature, due to irregular packing of atoms and molecules inside the solid lattice
- Amorphous solids don't have fixed heat of fusion because of absence of sharp melting point

Examples: Plastics, Glass, Rubber, Metallic Glass, Polymers, Gel etc.

Uses of Amorphous Solids

There are many applications of amorphous solids, some of them are:

- The glass is widely used in packaging (food jars, cosmetics box, and soft-drink bottles), making tableware (utensils), in the construction of buildings (windows, lighting, and shelves) etc.
- Rubber is mainly used in manufacturing of tires, footwear, ropes, camp cloth and as a raw material for several industries
- Use of polymer can be seen in manufacturing of pipes, medicines and as a raw ingredient for many factories
- Amorphous silicon is considered as the best photovoltaic material to convert sunlight into electricity

- **Crystalline Solids**

The solids in which the constituent particles of matter are arranged and organized in a specific manner are called **Crystalline Solids**. These

solids contain crystals in their structure and each crystal has definite geometry. Adding further, as crystalline solids have low potential energy, they are the most stable form of solids. Almost all solids fall in the category of crystalline solids including metallic elements (iron, silver, and copper) and non-metallic elements (Phosphorus, Sulphur, and iodine). Also several compounds like sodium chloride, zinc sulphide and naphthalene build crystalline solids.

Crystalline Solid

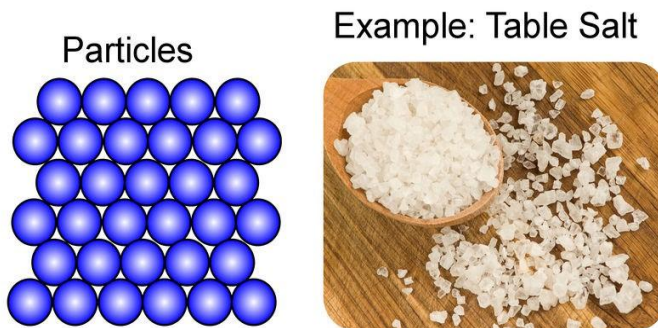


Image 2: Example of Crystalline Solids

Characteristics of Crystalline Solids

The main characteristics of crystalline solids are mentioned as below:

- Crystalline solids show regular structure and have definite geometrical shape
- The sharp freezing point is found in crystalline solids. This is because the distance between same atoms/molecules or ions is same and remains constant, unlikely from amorphous solids

- The heat of fusion is definite and fixed as the regularity in crystal lattice remains same and is ideal
- Crystalline Solids are also known as **True Solids** as they don't tend to flow like pseudo solids
- When we cut a crystal solids with a knife, we obtain a flat and smooth surface
- The nature of crystalline solid is anisotropic; that is, the properties turn out to be different in different direction
- Crystalline solids depict both long range and short range order

Examples: Quartz, Calcite, Sugar, Mica, Diamonds etc.

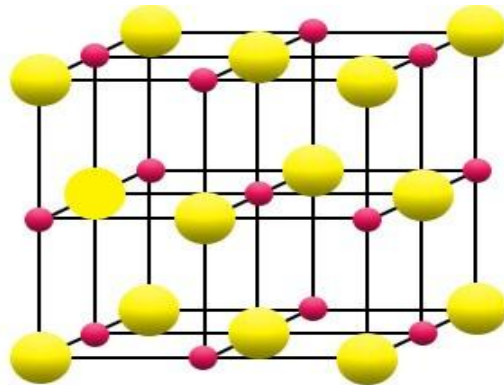


Image 3: Lattice Structure of Crystalline Solids

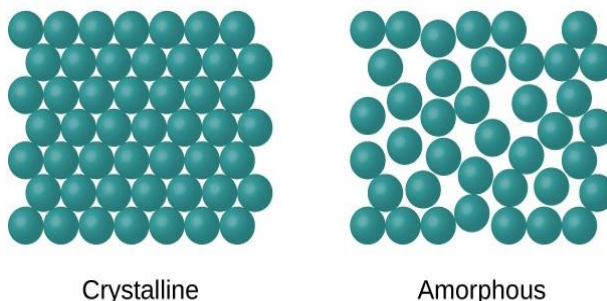
Uses of Crystalline Solids

There are many applications of crystalline solids, some are:

- Diamond is the most decent example of crystalline solids and is widely used in making beautiful jewelry items

- Quartz is extensively used in manufacturing of watches and clocks
- Many crystalline solids are used as a raw material in many industries

Difference between Crystalline and Amorphous Solids



In crystalline solids, constituent particles (atoms, molecules or ions) arrange in a three-dimensional periodic manner. Non-crystalline solids do not have a consistent arrangement of particles. So, non-crystalline solids are amorphous solids. With regard to the geometry of these solids, crystalline solids have a well-defined geometrical shape due to the regular arrangement of unit cells, unlike Non-crystalline solids that do not have well-defined geometrical shape. Furthermore, crystalline solids have a long range order while non-crystalline solids have a short range order.

Crystalline solids have a high fixed value for the heat of fusion and a definite melting point. However, non-crystalline solids do not have a fixed value for the heat of fusion and they melt over a range. Moreover, crystalline solids are true solids. They show all the properties of solids. On the contrary, Non-crystalline solids do not show all the properties of

solids. Therefore, they are called “pseudo solids”. Energy in crystalline solids is lower than that of non-crystalline solids.

Crystalline vs Noncrystalline Solids		
More Information Online WWW.DIFFERENCEBETWEEN.COM		
	Crystalline Solids	Noncrystalline Solids
DEFINITION	In crystalline solids, constituent particles (atoms, molecules or ions) arrange in a three-dimensional periodic manner.	Non-crystalline solids do not have a consistent arrangement of particles.
GEOMETRY	Have a well-defined geometrical shape due to the regular arrangement of unit cells.	Do not have well-defined geometrical shape.
RANGE OF ORDER	Have a long-range order.	Have a short range order.
MELTING POINT	Have a definite melting point.	Melt over a range
HEAT OF FUSION	Have a high fixed value for the heat of fusion.	Do not have a fixed value for the heat of fusion.
PROPERTIES	These solids are true solids, so they show all the properties of solids.	These solids do not show all the properties of solids. Therefore, they are called “pseudo solids”.
ENERGY	Energy in crystalline solids is lower than that of non-crystalline solids.	Energy in non-crystalline solids is higher than that of crystalline solids.

Crystal structure

Crystals Because a crystalline solid consists of repeating patterns of its components in three dimensions (a crystal lattice), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cell. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

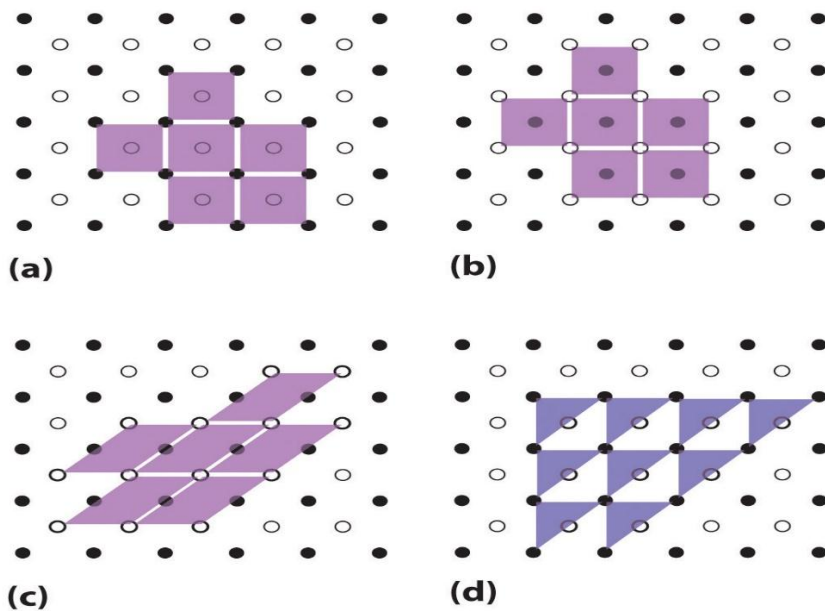


Figure 1

Unit Cells in Two Dimensions. (a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall

pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.

Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure 1. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in Figure 1. d is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure 2.

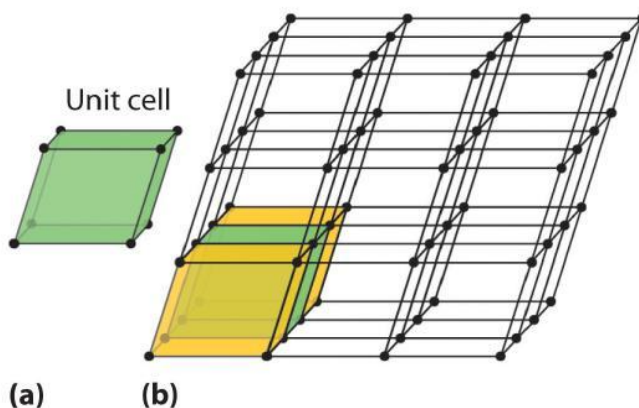


Figure 2

In crystallography, **crystal structure** is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material. Ordered structures occur from the intrinsic nature of the

constituent particles to form symmetric patterns that repeat along the principal directions of three-dimensional space in matter.

The smallest group of particles in the material that constitutes this repeating pattern is the unit cell of the structure. The unit cell completely reflects the symmetry and structure of the entire crystal, which is built up by repetitive translation of the unit cell along its principal axes. The translation vectors define the nodes of the Bravais lattice.

The lengths of the principal axes, or edges, of the unit cell and the angles between them are the lattice constants, also called lattice parameters or cell parameters.

The geometry of the unit cell is defined as a parallelepiped, providing six lattice parameters taken as the lengths of the cell edges (a, b, c) and the angles between them (α, β, γ).

The symmetry properties of the crystal are described by the concept of space groups. All possible symmetric arrangements of particles in three-dimensional space may be described by the 230 space groups.

The crystal structure and symmetry play a critical role in determining many physical properties, such as cleavage, electronic band structure, and optical transparency.

Lattice systems

Lattice systems are a grouping of crystal structures according to the axial system used to describe their lattice. Each lattice system consists of a set of three axes in a particular geometric arrangement. All crystals fall into one of seven lattice systems. They are similar to, but not quite the same as the seven crystal systems

Crystal System

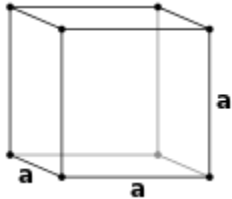
- 1- triclinic
- 2- monoclinic
- 3- rhombohedral
- 4- hexagonal
- 5- orthorhombic
- 6- tetragonal
- 7- cubic

1-The cubic Lattice.

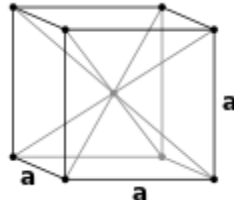
The most symmetrical of the systems. All the angles are equal to 90° , and all the sides are of the same length ($a = b = c$). Only the length of one of the sides (a) is required to describe this system completely. In addition to simple cubic, the cubic lattice also includes body-centered cubic and face-centered cubic

Body-centered cubic results from the presence of an atom (or ion) in the center of a cube, in addition to the atoms (ions) positioned at the vertices

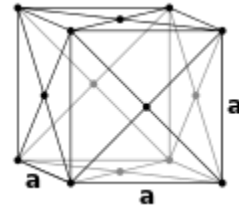
of the cube. In a similar manner, a face-centered cubic requires, in addition to the atoms (ions) positioned at the vertices of the cube, the presence of atoms (ions) in the center of each of the cubes face.



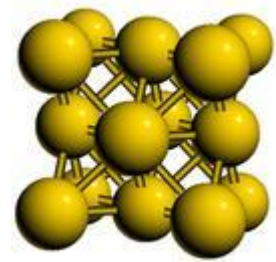
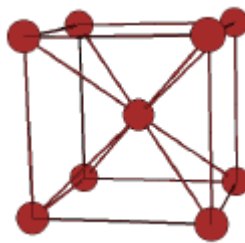
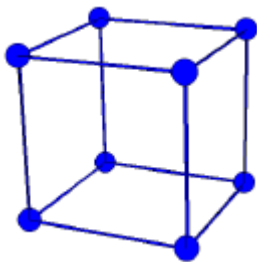
Simple cubic (P)



Body-centered cubic (I)



Face-centered cubic (F)



2 -The tetragonal Lattice.

All of its angles equal to 90° , and has two out of the three sides of equal length ($a = b$). The system also includes body-centered tetragonal

3- Orthorhombic Lattice .

All of the angles are equal to 90° , while all of its sides are of unequal length. The system needs only to be described by three lattice parameters. This system also includes body-centered orthorhombic, base-centered orthorhombic, and face-centered orthorhombic

(Figure 3). A base-centered lattice has, in addition to the atoms (ions) positioned at the vertices of the orthorhombic lattice, atoms (ions) positioned on just two opposing faces.

4- The rhombohedral Lattice .

Is also known as trigonal, and has no angles equal to 90° , but all sides are of equal length ($a = b = c$), thus requiring only by one lattice parameter, and all three angles are equal ($\alpha = \beta = \gamma$).

5- A hexagonal Lattice .

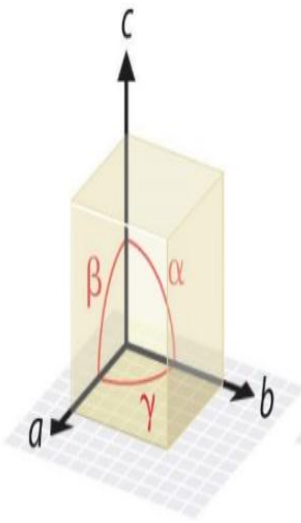
A hexagonal crystal structure has two angles equal to 90° , with the other angle (γ) equal to 120° . For this to happen, the two sides surrounding the 120° angle must be equal ($a = b$), while the third side (c) is at 90° to the other sides and can be of any length.

6-The monoclinic lattice .

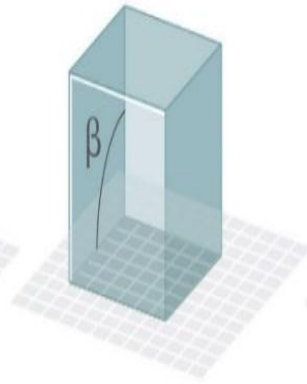
Has no sides of equal length, but two of the angles are equal to 90° , with the other angle (usually defined as β) being something other than 90° . It is a tilted parallelogram prism with rectangular bases. This system also includes base-centered monoclinic

7- The triclinic lattice

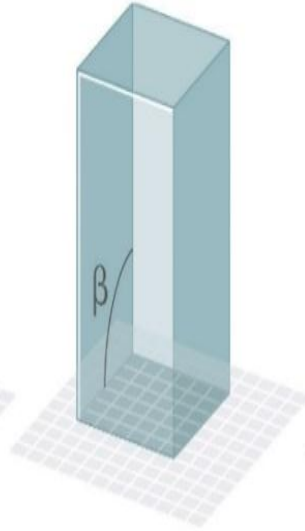
In the triclinic lattice none of the sides of the unit cell are equal, and none of the angles within the unit cell are equal to 90° . The triclinic lattice is chosen such that all the internal angles are either acute or obtuse. This crystal system has the lowest symmetry and must be described by 3 lattice parameters (a , b , and c) and the 3 angles (α , β , and γ).



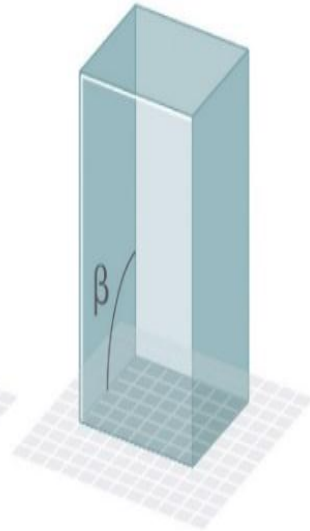
Edges and angles



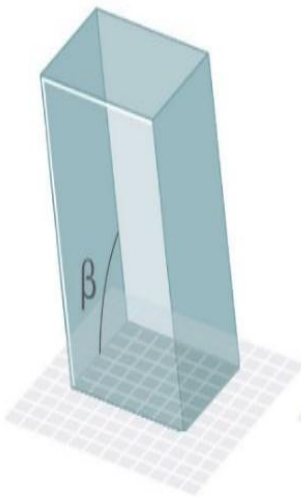
Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



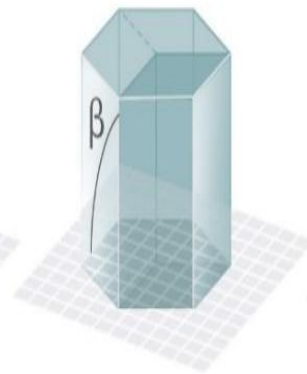
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



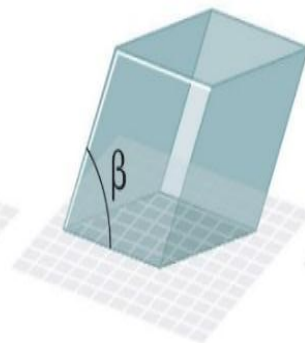
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



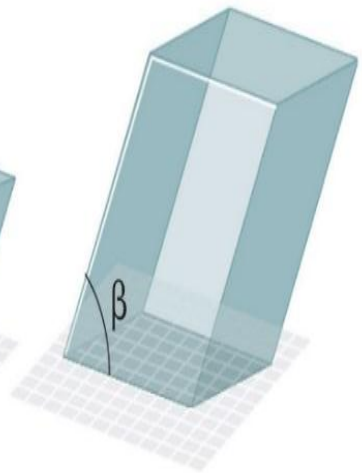
Monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ \neq \beta$



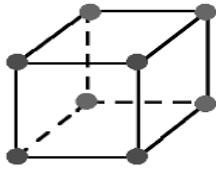
Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



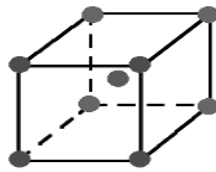
Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



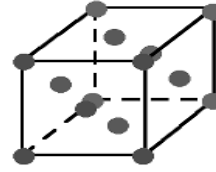
Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



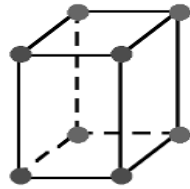
simple cubic



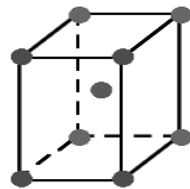
body-centered
cubic



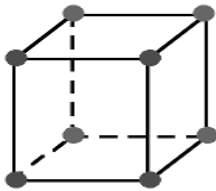
face-centered
cubic



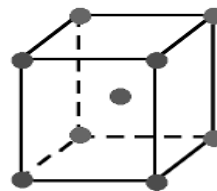
simple
tetragonal



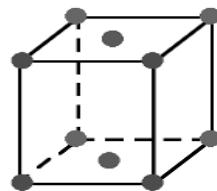
body-centered
tetragonal



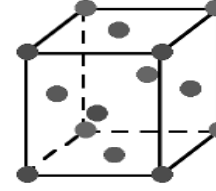
simple
orthorhombic



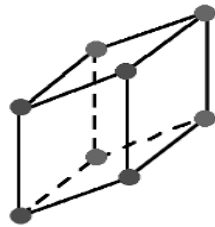
body-centered
orthorhombic



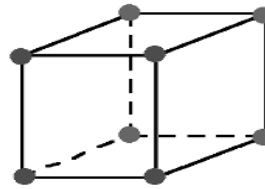
base-centered
orthorhombic



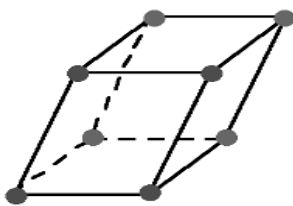
face-centered
orthorhombic



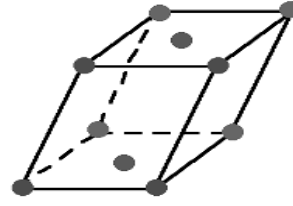
rhombohedral



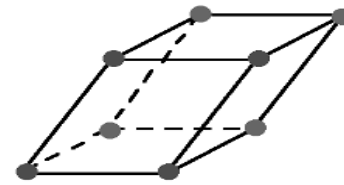
hexagonal



simple
monoclinic



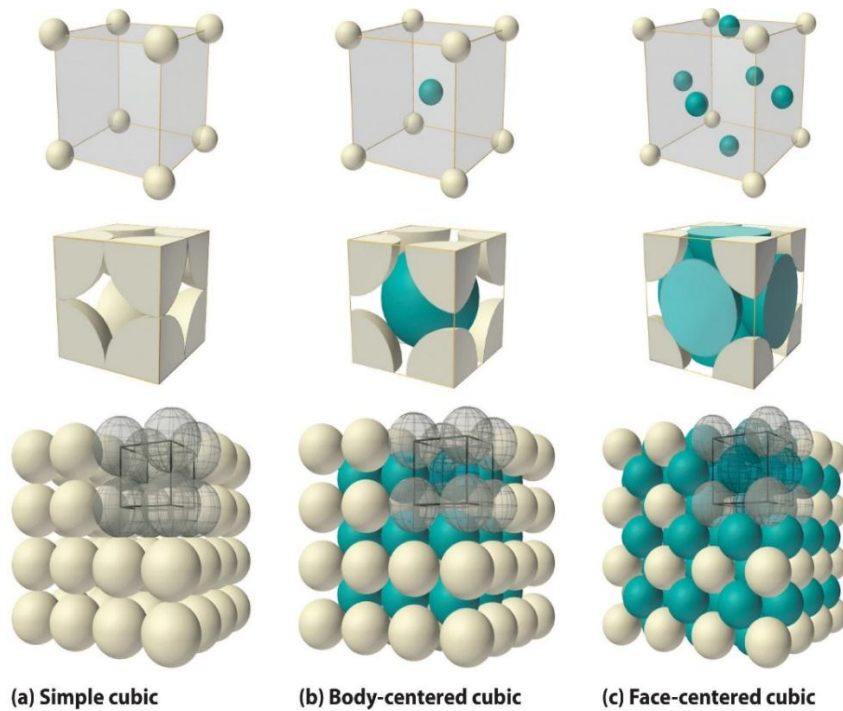
base-centered
monoclinic



triclinic

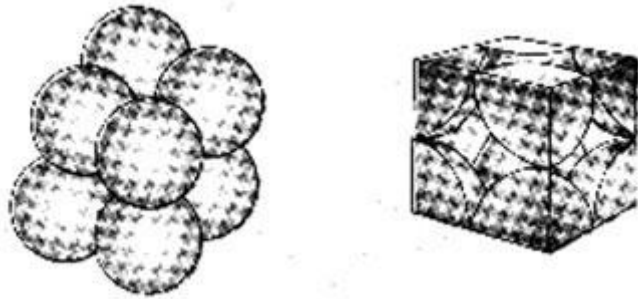
The number of atoms per unit cell

In different types of unit cells, the number of atoms per unit cell can be calculated as follows :



The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells .

(a) In Primitive or Simple cubic unit cell .(SC)



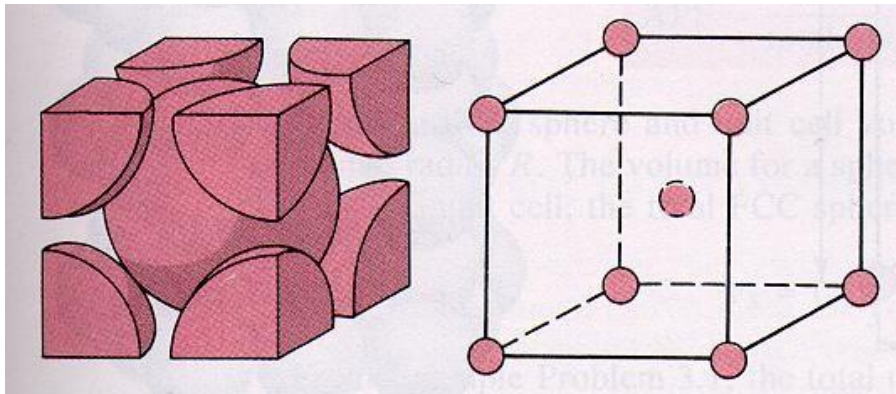
from the above figure it is clear that here eight atoms which are present at 8 corners are shared by 8 unit cells. Hence, contribution of each atom present at the corner = Thus, total no. of atoms present per unit cell

$$= 8 \times \frac{1}{8} = 1 \text{ atom .}$$

$$a = 2r$$

(b) In body centred cubic unit (BCC)

Atoms are arranged at the corners of the cube with another atom at the cube center.

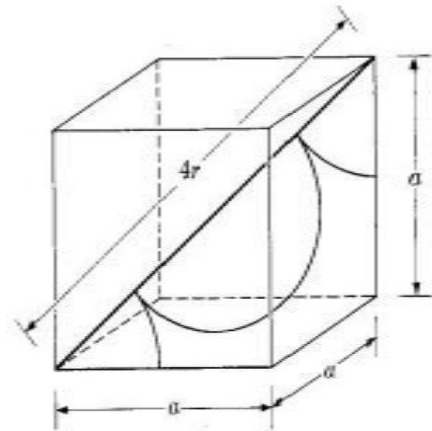


from the above figure it is clear that this unit cell has 1 complete atom additional to that present in simple cubic unit . Hence, the total no. of atom present = 1+1=2 atoms per unit cell.

atom

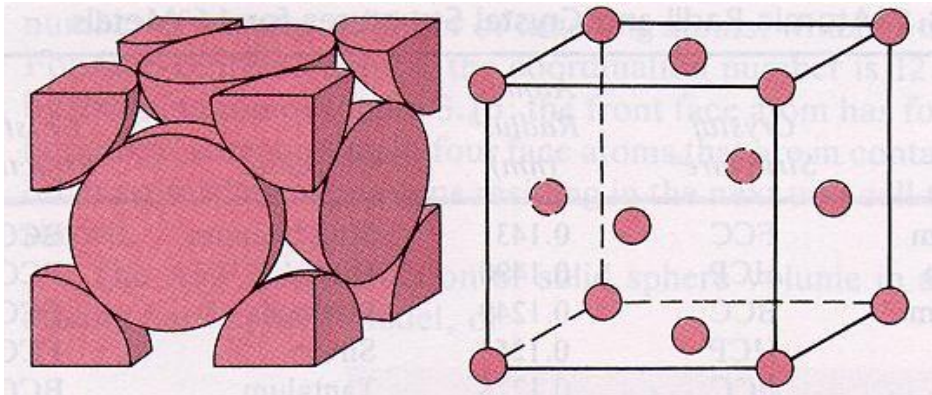
$$(4r)^2 = a^2 + a^2 + a^2 = 3a^2$$

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



(c) In face centred cubic unit cell .(FCC)

Atoms are arranged at the corners and center of each cube face of the cell.



From the above figure it is clear that here -

(i) 8 corner atoms x atoms per unit cell = 1 atom

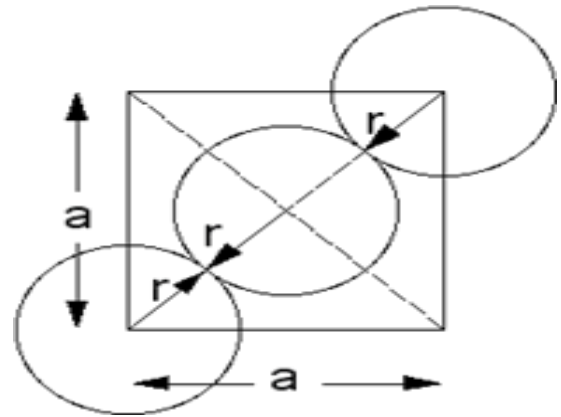
(ii) 6 face atoms with representation of 1/2 atom per face per unit cell,

thus - $6 \times \frac{1}{2} = 3$ atoms

Total atoms present per unit cell = $1 + 3 = 4$
atoms

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

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



Atomic Packing Factor :

Atomic Packing Factor is : The ratio of atomic sphere volume to unit cell volume

$$F = \frac{n \times V}{a^3}$$

$$F_{bcc} = \frac{n \times V}{a^3} = \frac{2 \times 4\pi r^3}{3(4r\sqrt{3})^3} = 68\%$$

Close-Packed Structures :

The most efficient way for equal sized spheres to be packed in three dimensions is to stack close packed layers on top of each other to give a close packed structure. There are two simple ways in which this can be done, resulting in either a hexagonal or cubic close packed structures.

There are two types of Close-Packed Structures

1- Hexagonal Close-Packed

2- Cubic Close-Packed Structures

1- Hexagonal Close Packed

If two close packed layers A and B are placed in contact with each other so as to maximize the density, then the spheres of layer B will rest in the hollow (vacancy) between three of the spheres in layer A. This is demonstrated in Figure 7.. Atoms in the second layer, B (shaded light gray), may occupy one of two possible positions (Figure 7 a or b) but not both together or a mixture of each. If a third layer is placed on top of layer B such that it exactly covers layer A, subsequent placement of layers will result in the following sequence ...ABABAB.... This is known as hexagonal close packing or hcp.

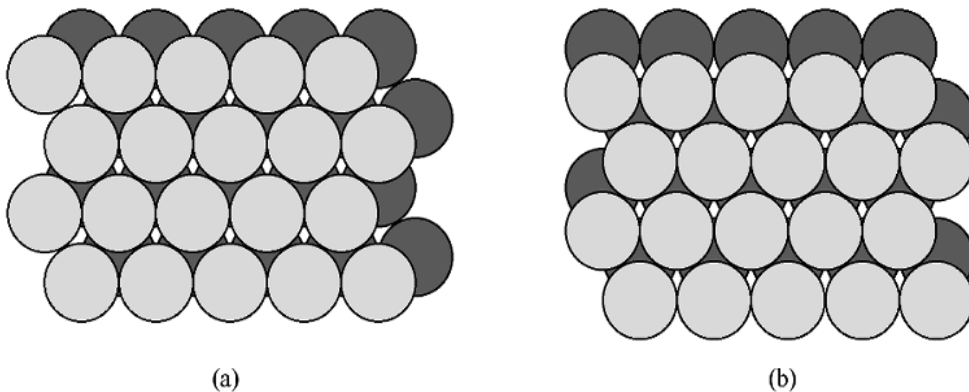


Figure 7. Schematic representation of two close packed layers arranged in A (dark grey) and B (light grey) positions. The alternative stacking of the B layer is shown in (a) and (b).

2- Cubic Close Packed: Face-centered Cubic

In a similar manner to the generation of the hexagonal close packed structure, two close packed layers are stacked (Figure 8) however, the third layer (C) is placed such that it does not exactly cover layer A, while sitting in a set of troughs in layer B (Figure 8), then upon repetition the packing sequence will be ...ABCABCABC.... This is known as cubic close packing or ccp.

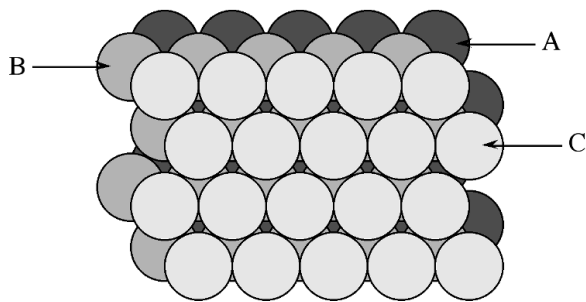
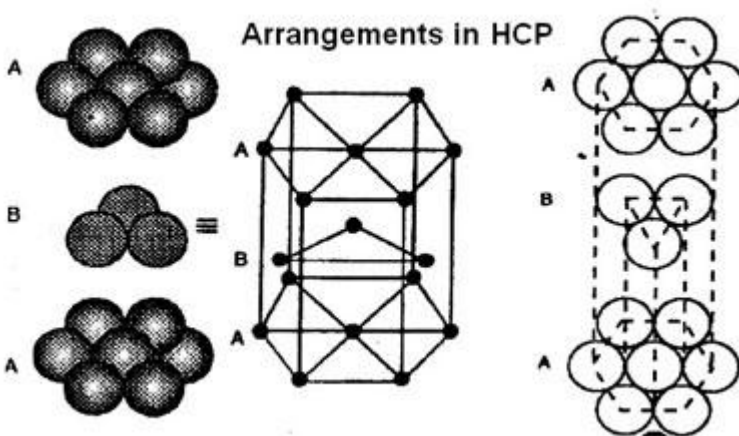
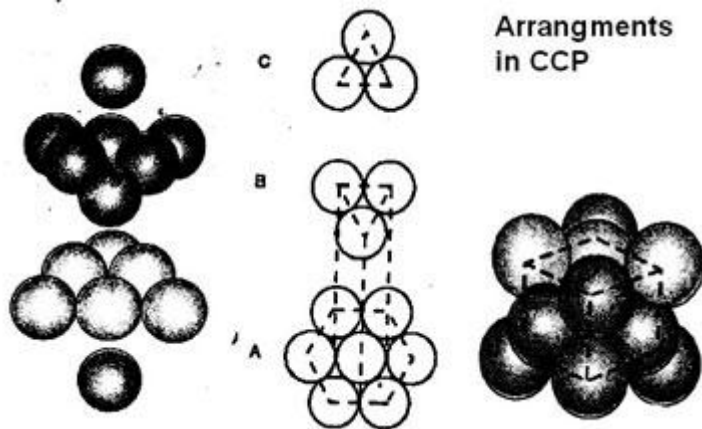


Figure 8 Schematic representation of the three close packed layers in a cubic close packed arrangement: A (dark grey), B (medium grey), and C (light grey).





The Packing Fraction

The Packing Fraction (F) is defined as The ratio of atomic sphere volume to the total volume of unit cell also referred to as the Packing Factor or packing efficiency of the unit cell.

$$\text{The Packing Fraction} = \frac{\text{Volume of ions present in unit cell}}{\text{Volume of the unit cell}}$$

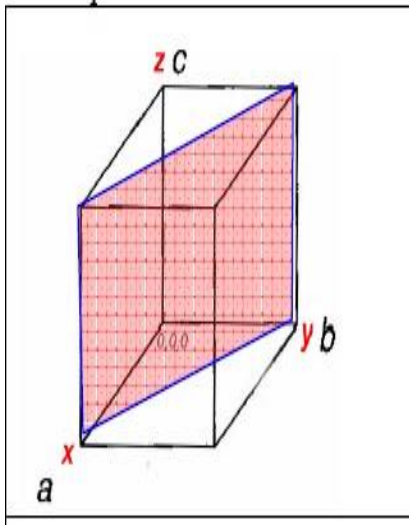
$$F_{bcc} = \frac{nxV}{a^3} = \frac{2 \times 4\pi r^3}{3(4r\sqrt{3})^3} = 68\% \quad F_{hcp} = 74\%$$

Crystal Planes

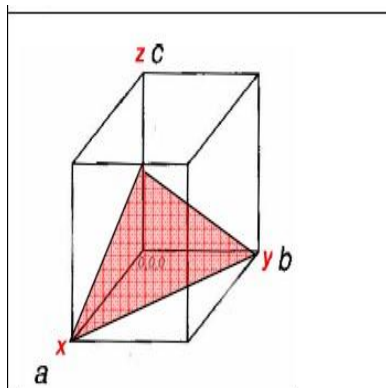
Planes in a crystal can be specified using a notation called Miller indices. The Miller index is indicated by the notation (hkl) where h , k , and l are reciprocals of the plane with the x , y , and z axes. To obtain the Miller indices of a given plane requires the following steps:

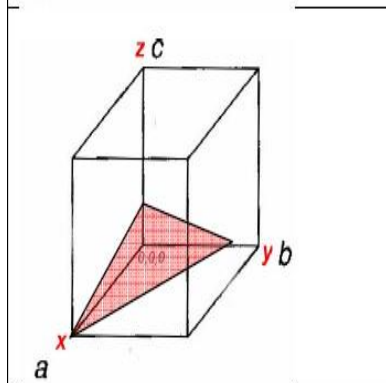
1. The plane in question is placed on a unit cell.

- Its intercepts with each of the crystal axes are then found.
- The reciprocal of the intercepts are taken.
- These are multiplied by a scalar to insure that is in the simple ratio

		x (a)	y (b)	z (c)
	Intercept on axes	1	1	∞
	Reciprocal	1/1	1/1	$1/\infty = 0$
	Integer Clear	1	1	0
	Miller Indices	(110)		

of whole numbers.

		x (a)	y (b)	z (c)
	Intercept on axes	1	1	$\frac{1}{2}$
	Reciprocal	1	1	2
	Integer Clear	1	1	2
	Miller Indices	(112)		

		x (a)	y (b)	z (c)
	Intercept on axes	1	$\frac{3}{4}$	$\frac{1}{4}$
	Reciprocal	1	$\frac{4}{3}$	4
	Integer Clear	3	4	12
	Miller Indices	(3 4 12)		



For example, the face of a lattice that does not intersect the y or z axis would be (100), while a plane along the body diagonal would be the (111) plane. An illustration of this along with the (111) and (110) planes is given in Figure 9

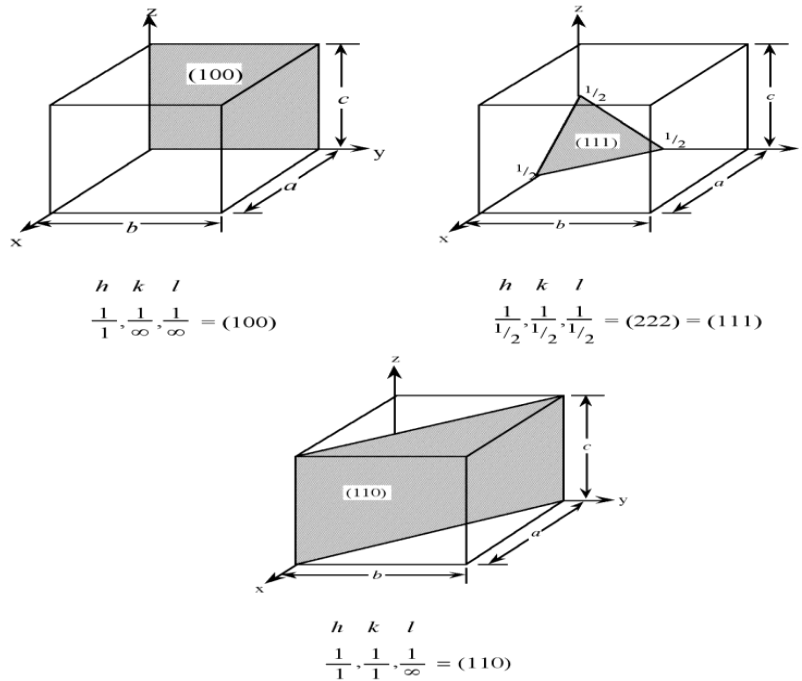
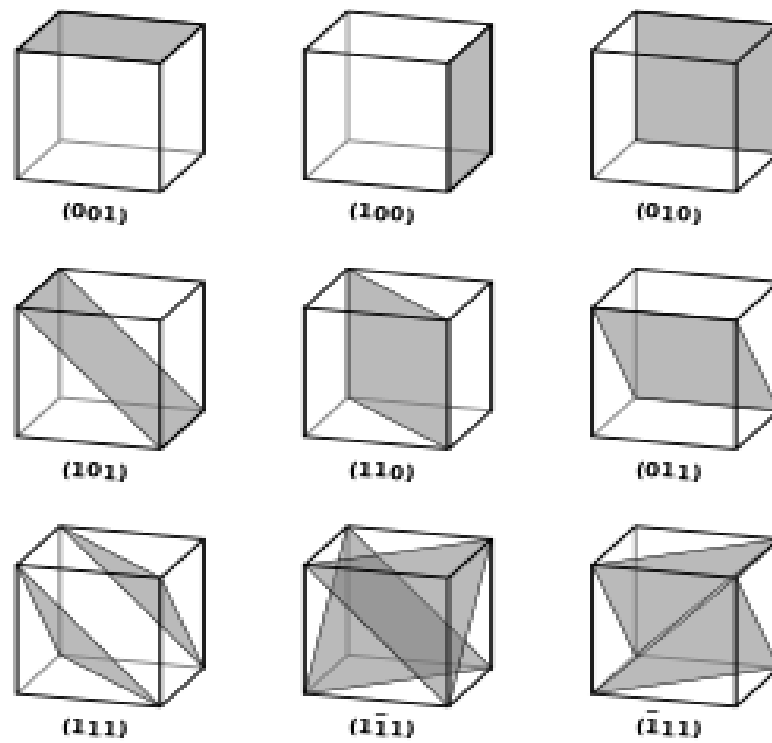
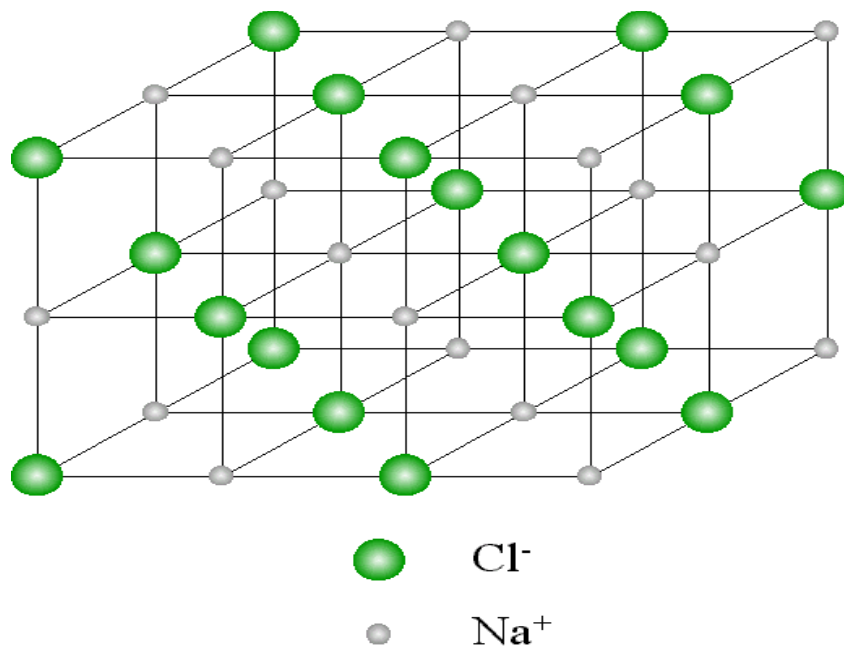


Figure 9 Examples of Miller indices notation for crystal planes.

As with crystal directions, Miller indices directions may be grouped in families. Individual Miller indices are given in parentheses (hkl), while braces {hkl} are placed around the indices of a family of planes. For example, (001), (100), and (010) are all in the {100} family of planes, for a cubic lattice.



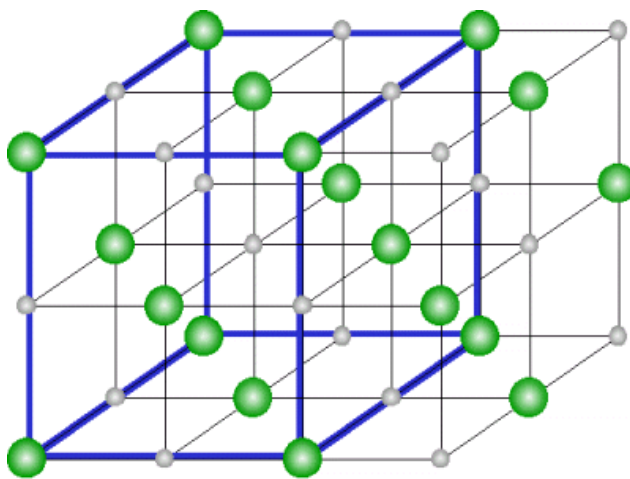
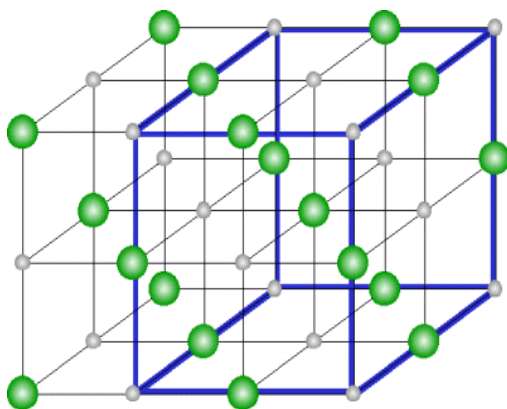
The crystal structure of sodium chloride



The unit cell of sodium chloride is cubic, and this is reflected in the shape of NaCl crystals

The unit cell can be drawn with either the Na^+ ions at the corners, or with the Cl^- ions at the corners.

- If the unit cell is drawn with the Na^+ ions at the corners, then Na^+ ions are also present in the *center of each face of the unit cell*
- If the unit cell is drawn with the Cl^- ions at the corners, then Cl^- ions are also present in the *center of each face of the unit cell*



Within the unit cell there must be an equal number of Na^+ and Cl^- ions.

For example, for the unit cell with the Cl^- ions at the center of the faces

- The top layer has $(1/8+1/8+1/8+1/8+1/2)=1 \text{ Cl}^-$ ion, and $(1/4+1/4+1/4+1/4)=1 \text{ Na}^+$ ion
- The middle layer has $(1/2+1/2+1/2+1/2)=2 \text{ Cl}^-$ ions and $(1/4+1/4+1/4+1/4+1)=2 \text{ Na}^+$ ions
- The bottom layer will contain the same as the top or 1 each Cl^- and Na^+ ions
- The unit cell has a total of 4 Cl^- and 4 Na^+ ions in it. *This equals the empirical formula NaCl.*

CHAPTER (2)

Symmetry Operations and Elements

A Symmetry operation is an operation that can be performed either physically or imaginatively that results in no change in the appearance of an object. Again it is emphasized that in crystals, the symmetry is internal, that is it is an ordered geometrical arrangement of atoms and molecules on the crystal lattice. But, since the internal symmetry is reflected in the external form of perfect crystals, we are going to concentrate on external symmetry, because this is what we can observe. There are 3 types of symmetry operations: rotation, reflection, and inversion. We will look at each of these in turn.

Rotation Definition

Rotation means the circular movement of an object around a centre. It is possible to rotate different shapes by an angle around the centre point. Mathematically, a rotation means a map. All the rotations around a fixed point that make a group under a structure are called the rotation group of a unique space. When coming to the three-dimensional shapes, we can turn or rotate the objects about an infinite number of imaginary lines known as rotational axes. Now one might have the question of what the **rotation of axes** is? Here is the answer. The rotations around X, Y and Z axes are known as the principal rotations. The rotations around

any axis can be performed by taking the rotation around the X-axis, followed by the Y-axis and then finally the z-axis.

Center of Rotation

For a figure or object that has rotational symmetry, the fixed point around which the rotation occurs is called the centre of rotation.

Example: the centre of rotation of a windmill in the centre of the windmill from which its blades originate.

Angle of Rotational Symmetry

For a figure or object that has rotational symmetry, the angle of turning during rotation is called the angle of rotation. Example: when a square is rotated by 90 degrees, it appears the same after rotation. So, the angle of rotation for a square is 90 degrees.

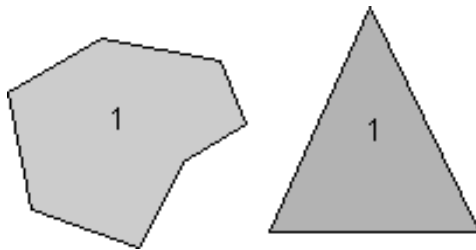
In the same way, a regular hexagon has an angle of symmetry as 60 degrees, a regular pentagon has 72 degrees, and so on.

Rotational Symmetry

If an object can be rotated about an axis and repeats itself every 90° of rotation then it is said to have an axis of 4-fold rotational symmetry. The axis along which the rotation is performed is an element of symmetry referred to as a rotation axis. The following types of rotational symmetry axes are possible in crystals

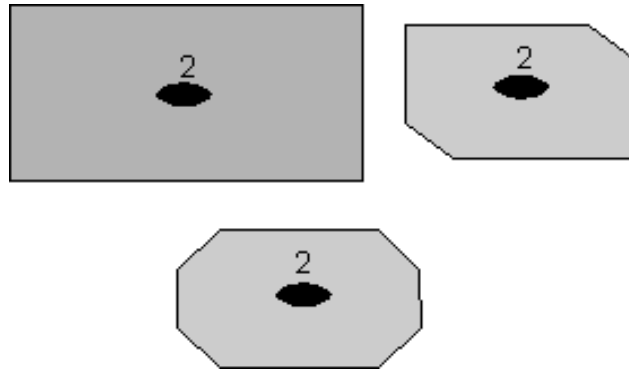
1-Fold Rotation Axis

An object that requires rotation of a full 360° in order to restore it to its original appearance has no rotational symmetry. Since it repeats itself 1 time every 360° it is said to have a 1-fold axis of rotational symmetry.



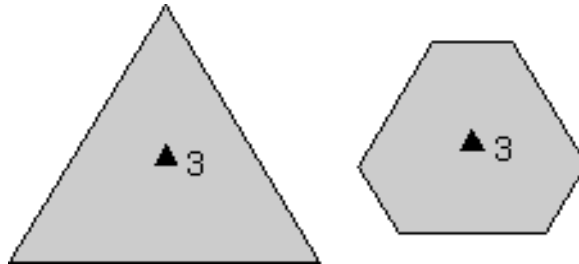
2-fold Rotation Axis

If an object appears identical after a rotation of 180° , that is twice in a 360° rotation, then it is said to have a 2-fold rotation axis ($360/180 = 2$). Note that in these examples the axes we are referring to are imaginary lines that extend toward you perpendicular to the page or blackboard. A filled oval shape represents the point where the 2-fold rotation axis intersects the page. This symbolism will be used for a 2-fold rotation axis throughout the lectures and in your text



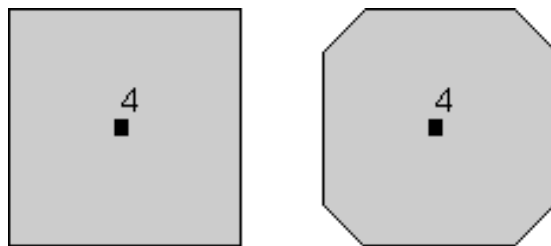
3-Fold Rotation Axis

Objects that repeat themselves upon rotation of 120° are said to have a 3-fold axis of rotational symmetry ($360/120 = 3$), and they will repeat 3 times in a 360° rotation. A filled triangle is used to symbolize the location of 3-fold rotation axis.



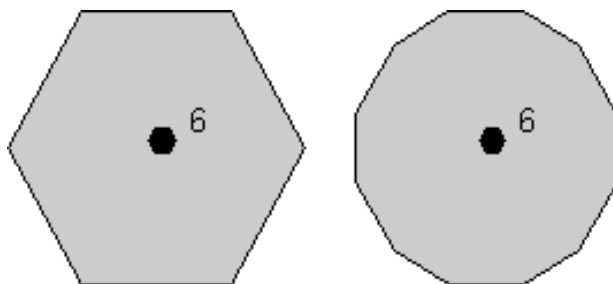
4-Fold Rotation Axis

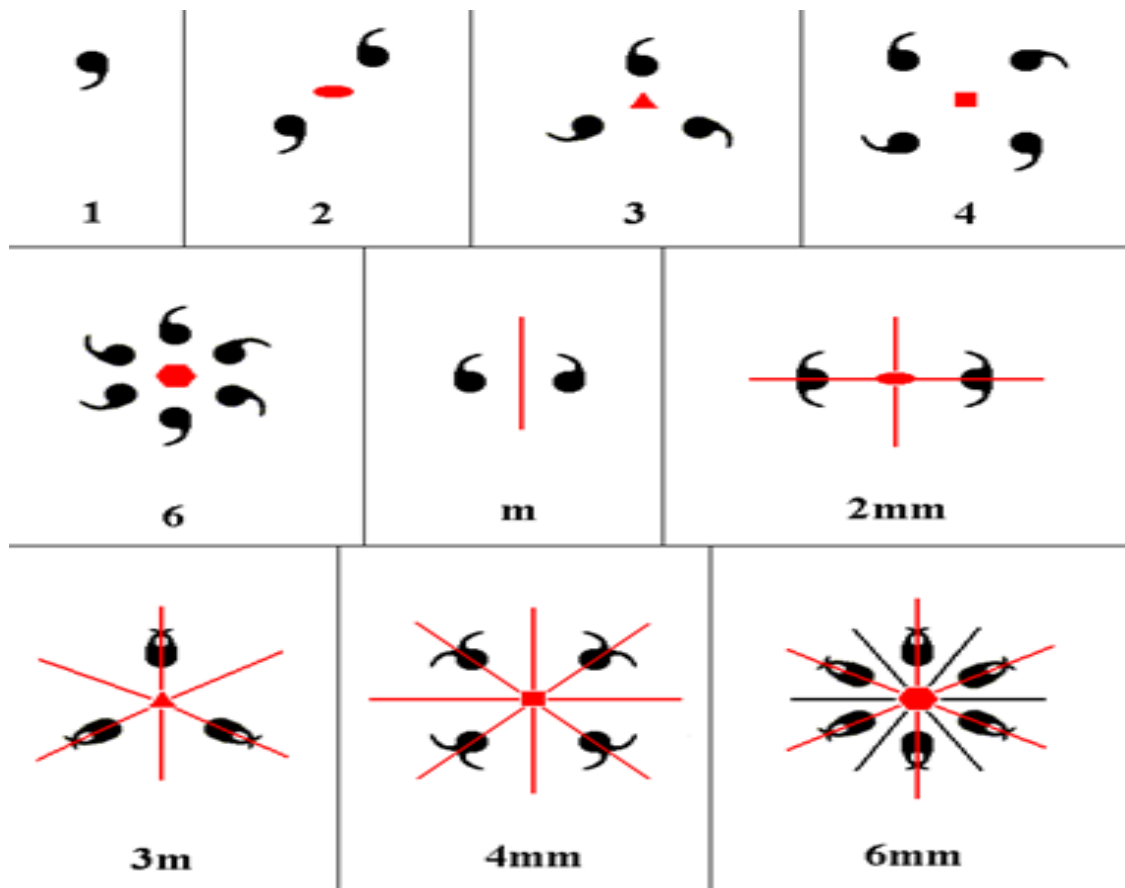
If an object repeats itself after 90° of rotation, it will repeat 4 times in a 360° rotation, as illustrated previously. A filled square is used to symbolize the location of 4-fold axis of rotational symmetry.



6-Fold Rotation Axis

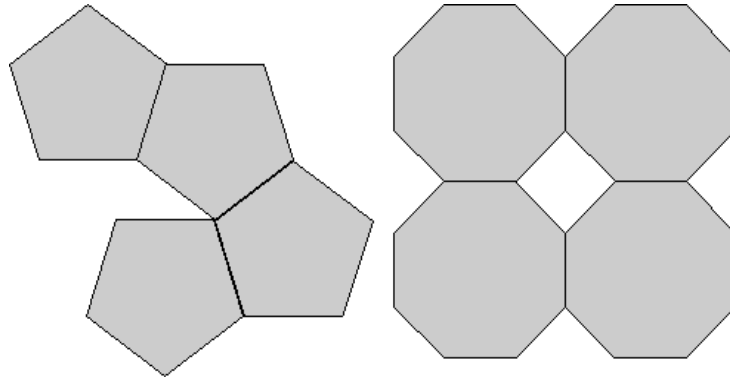
If rotation of 60° about an axis causes the object to repeat itself, then it has 6-fold axis of rotational symmetry ($360/60=6$). A filled hexagon is used as the symbol for a 6-fold rotation axis.





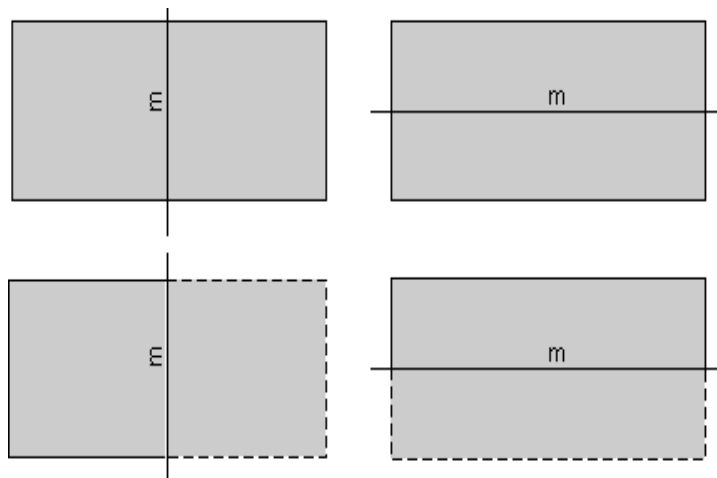
The Ten Planar Point Groups

Although objects themselves may appear to have 5-fold, 7-fold, 8-fold, or higher-fold rotation axes, these are not possible in crystals. The reason is that the external shape of a crystal is based on a geometric arrangement of atoms. Note that if we try to combine objects with 5-fold and 8-fold apparent symmetry, that we cannot combine them in such a way that they completely fill space, as illustrated below.



Mirror Symmetry (Plane of Symmetry)

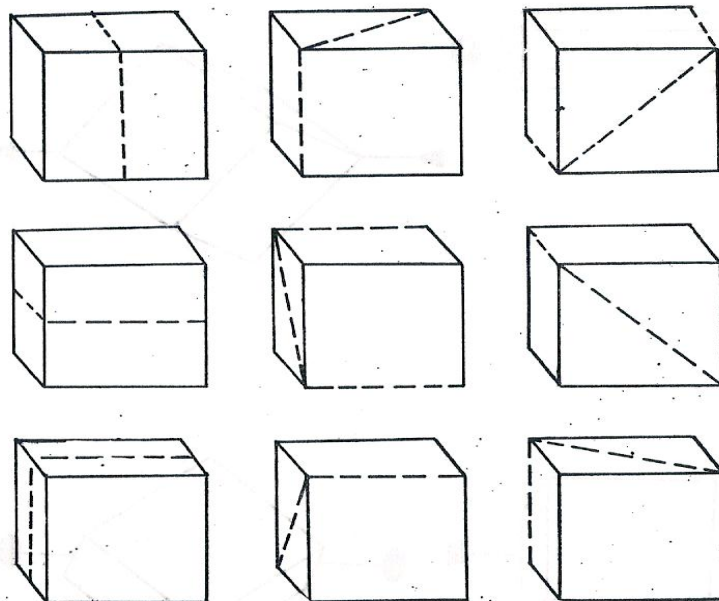
A mirror symmetry operation is an imaginary operation that can be performed to reproduce an object. The operation is done by imagining that you cut the object in half, then place a mirror next to one of the halves of the object along the cut. If the reflection in the mirror reproduces the other half of the object, then the object is said to have mirror symmetry. The plane of the mirror is an element of symmetry referred to as a *mirror plane*, and is symbolized with the letter *m*.

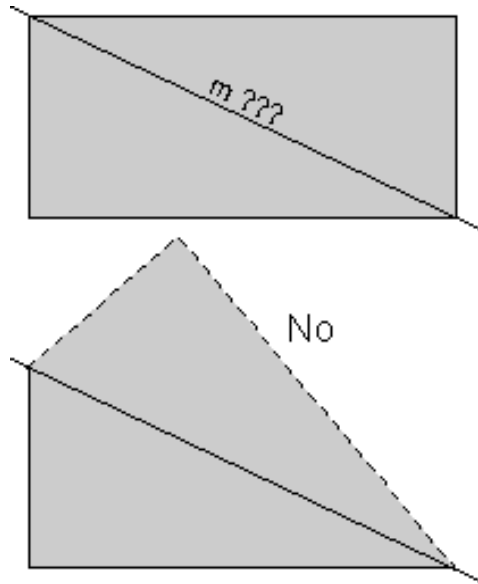


The rectangles shown here have two planes of mirror symmetry.

The rectangle on the left has a mirror plane that runs vertically on the page and is perpendicular to the page. The rectangle on the right has a mirror plane that runs horizontally and is perpendicular to the page. The dashed parts of the rectangles below show the part the rectangles that would be seen as a reflection in the mirror.

The rectangles shown above have two planes of mirror symmetry. Three dimensional and more complex objects could have more. For example, the hexagon shown above, not only has a 6-fold rotation axis, but has 6 mirror planes.



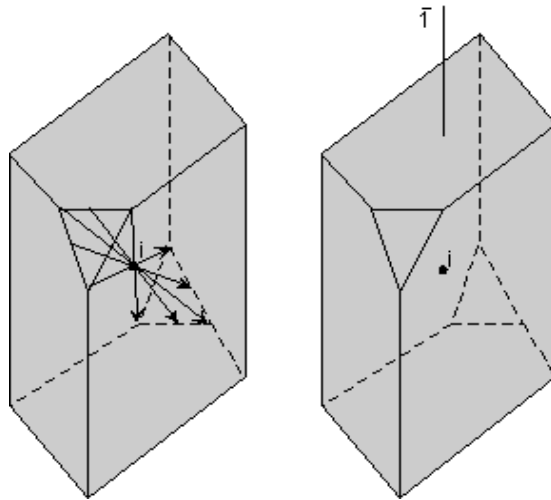


Note that a rectangle does not have mirror symmetry along the diagonal lines. If we cut the rectangle along a diagonal such as that labeled "m ???", as shown in the upper diagram, reflected the lower half in the mirror, then we would see what is shown by the dashed lines in lower diagram. Since this does not reproduce the original rectangle, the line "m???" does not represent a mirror plane.

Center of Symmetry (Inversion)

Another operation that can be performed is inversion through a point. In this operation lines are drawn from all points on the object through a point in the center of the object, called a symmetry center (symbolized with the letter "i"). The lines each have lengths that are equidistant from the original points. When the ends of the lines are connected, the original object is reproduced inverted from its original appearance. In the diagram shown here, only a few such lines are drawn for the small

triangular face. The right hand diagram shows the object without the imaginary lines that reproduced the object.



If an object has only a center of symmetry, we say that it has a 1 fold rotoinversion axis. Such an axis has the symbol $\bar{1}$, as shown in the right hand diagram above. Note that crystals that have a center of symmetry will exhibit the property that if you place it on a table there will be a face on the top of the crystal that will be parallel to the surface of the table and identical to the face resting on the table.

CHAPTER (3)

Crystalline Defects

The ideal crystal has an infinite 3D repetition of identical units, which may be atoms or molecules.

Real crystals are limited in size, and they have some disorder in stacking which are called *defects*.

1- Point Defects

Point defects are defects which are not extended in space in any dimension. There is not strict limit for how small a "point" defect should be, but typically the term is used to mean defects which involve at most a few extra or missing atoms without an ordered structure of the defective positions.

A Point Defect involves a single atom change to the normal crystal array.

There are three major types of point defect: Vacancies, Interstitials and Impurities.

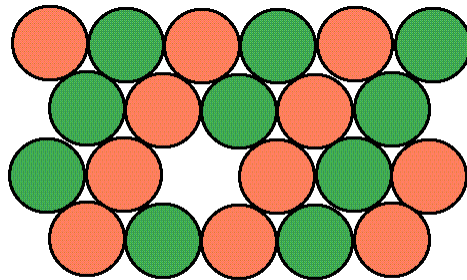
They may be built-in with the original crystal growth, or activated by heat.

They may be the result of radiation, or electric current etc, etc.

Vacancies

Vacancies are sites which are usually occupied by an atom but which are unoccupied. If a neighboring atom moves to occupy the vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. The stability of the surrounding crystal structure guarantees that the neighboring atoms will not simply collapse around the vacancy. In some materials, neighboring atoms actually move away from a vacancy, because they can better form bonds with atoms in the other directions. A vacancy (or pair of vacancies in an ionic solid) is sometimes called a [Schottky defect](#).

A Vacancy is the absence of an atom from a site normally occupied in the lattice.



An empty lattice site is a vacancy

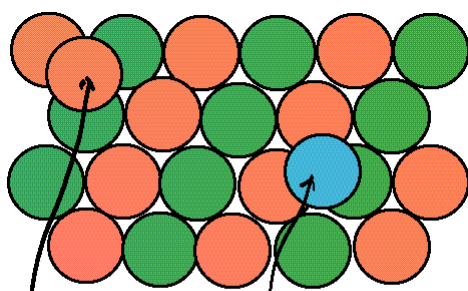
Interstitials

[Interstitials](#) are atoms which occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy

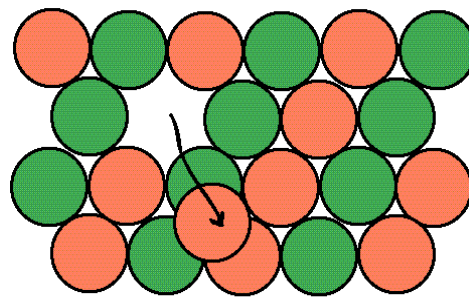
configurations. Small atoms in some crystals can occupy interstices without high energy, such as [hydrogen](#) in [palladium](#).

An Interstitial is an atom on a non-lattice site.

There needs to be enough room for it, so this type of defect occurs in open covalent structures, or metallic structures with large atoms.



An interstitial is an off-lattice atom which may be a foreign atom or a regular atom



An interstitial may form by an atom moving to an off-lattice site and create a vacancy at the same time

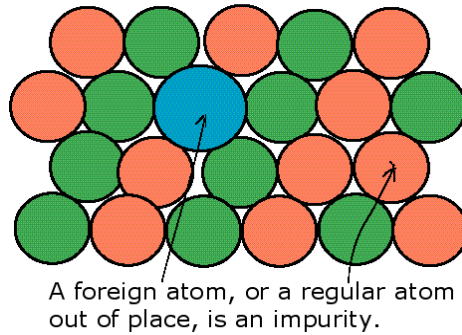
A nearby pair of a vacancy and an interstitial is often called a [Frenkel defect](#) or Frenkel pair

Impurities

Impurities occur because materials are never 100% pure. In the case of an impurity, the atom is often incorporated at a regular atomic site in the crystal structure. This is neither a vacant site nor is the atom on an interstitial site and it is called a *substitutional* defect. The atom is not supposed to be anywhere in the crystal, and is thus an impurity.

An Impurity is the substitution of a regular lattice atom with an atom that does not normally occupy that site.

The atom may come from within the crystal, (e.g. a Chlorine atom on a Sodium site in a NaCl crystal) or from the addition of impurities.



The concentration of point defects in a crystal is typically between 0.1% and 1% of the atomic sites, however extremely pure materials can now be grown.

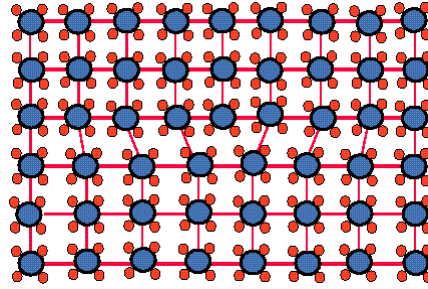
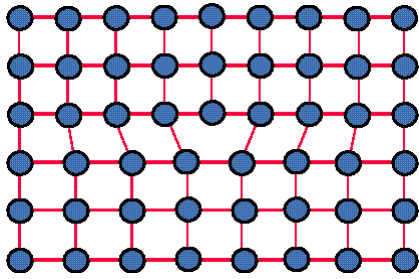
The concentrations and movement of point defects in a solid are very important in controlling colour and deformation.

2- Line Defects (Dislocation)

A Dislocation is a line discontinuity in the regular crystal structure. There are two basic types: Edge dislocations, and Screw dislocations.

An Edge dislocation :

In a Metal may be regarded as the insertion (or removal) of an extra half plane of atoms in the crystal structure.

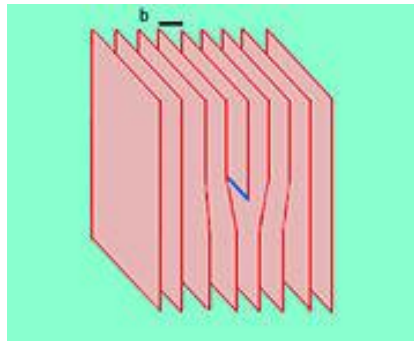


In Ionic and Covalent solids edge dislocations involve extra half planes of *unit cells*.

The regions surrounding the dislocation line are made of essentially perfect crystal.

The only severe disruption to the crystal structure occurs along the dislocation line (perpendicular to the page).

Note that perpendicular to the page, the line may step up or down. These steps are known as *jogs*.



An *edge dislocation* is shown. The dislocation line is presented in blue, the Burgers vector b in black.

Edge dislocations are caused by the termination of a plane of atoms in the middle of a crystal. In such a case, the adjacent planes are not straight, but instead bend around the edge of the terminating plane so that the crystal structure is perfectly ordered on either side. The analogy with a stack of paper is apt: if a half a piece of paper is inserted in a stack of paper, the defect in the stack is only noticeable at the edge of the half sheet.

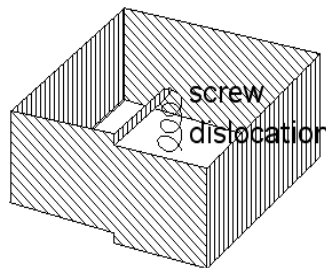
A Screw Dislocation :

Changes the character of the atom planes.

The atom planes no longer exist separately from each other.

They form a single surface, like a screw thread, which "spirals" from one end of the crystal to the other.

(It is actually a *helical* structure because it winds up in 3D, not like a spiral that is flat.)



In the average crystal structure, there are $\sim 10^{12}$ m of dislocation lines per m^3 of crystal.

The screw dislocation is more difficult to visualise, but basically comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the atomic planes of atoms in the crystal lattice.

Combinations of edge and screw dislocations are often formed as edge dislocations can be formed by branching off a screw dislocation.

The presence of dislocation results in lattice strain (distortion). The direction and magnitude of such distortion is expressed in terms of a [Burgers vector](#) (b). For an edge type, b is perpendicular to the dislocation line, whereas in the cases of the screw type it is parallel. In metallic materials, b is aligned with close-packed crystallographic directions and its magnitude is equivalent to one interatomic spacing.

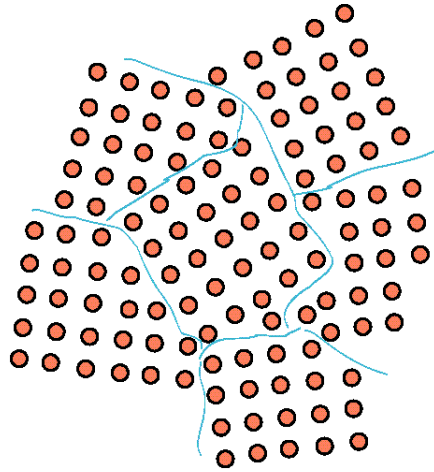
3- Planar Defects

A Planar Defect is a discontinuity of the perfect crystal structure across a plane.

Grain Boundaries

Grain boundaries occur where the crystallographic direction of the lattice abruptly changes. This usually occurs when two crystals begin growing separately and then meet.

A Grain Boundary is a general planar defect that separates regions of different crystalline orientation (i.e. *grains*) within a polycrystalline solid.



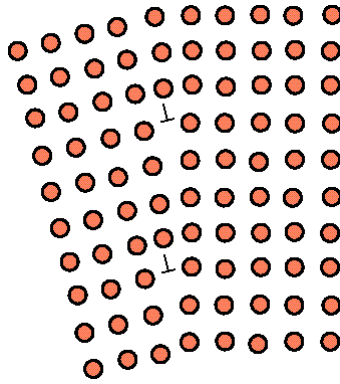
The atoms in the grain boundary will not be in perfect crystalline arrangement.

Grain boundaries are usually the result of uneven growth when the solid is crystallising.

Grain sizes vary from $1\ \mu\text{m}$ to $1\ \text{mm}$.

Tilt Boundaries

A Tilt Boundary, between two slightly mis-aligned grains appears as an array of edge dislocations.

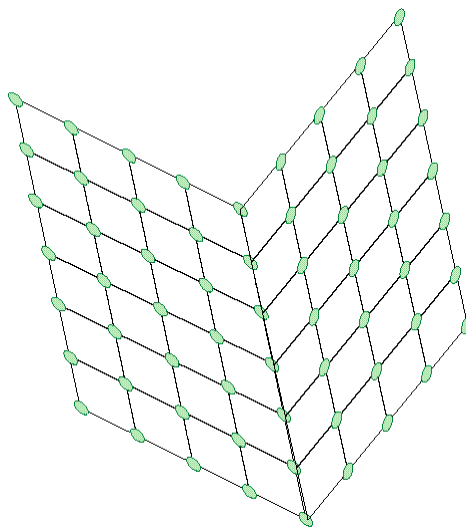


Twin Boundaries

A Twin Boundary happens when the crystals on either side of a plane are mirror images of each other.

The boundary between the twinned crystals will be a single plane of atoms.

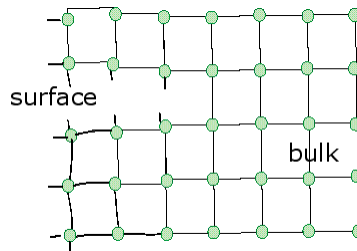
There is no region of disorder and the boundary atoms can be viewed as belonging to the crystal structures of both twins



Twins are either grown-in during crystallisation, or the result of mechanical or thermal work.

Microcracks

A Microcrack occurs where internal broken bonds create new surfaces.



They are about $10 \mu\text{m}$ in size and there is a tendency to form on the surface of a solid rather than in the bulk.

They also form at grain boundaries and other regions of disorder.

The region across which the bonds are broken is known as the *separation plane*.

Microcracks are formed when there is abrasion (or impacts) with dust particles.

They are important in determining how, and where, a solid may fracture.

When a crystal has more than one type of atom, there will be *Chemical* as well as *Physical* disorder in the grain-boundaries.

Volume Defects

Volume defects are *Voids*, i.e. the absence of a number of atoms to form internal surfaces in the crystal.

They have similar properties to microcracks because of the broken bonds at the surface.

CHAPTER (4)

X-ray crystallography is the experimental science determining the atomic and molecular structure of a crystal, in which the crystalline structure causes a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their crystallographic disorder, and various other information.

Since many materials can form crystals—such as salts, metals, minerals, semiconductors, as well as various inorganic, organic, and biological molecules—X-ray crystallography has been fundamental in the development of many scientific fields. In its first decades of use, this method determined the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. The method also revealed the structure and function of many biological molecules, including vitamins,

X-ray crystallography is still the primary method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments. X-ray crystal structures can also account

for unusual electronic or elastic properties of a material, shed light on chemical interactions and processes .

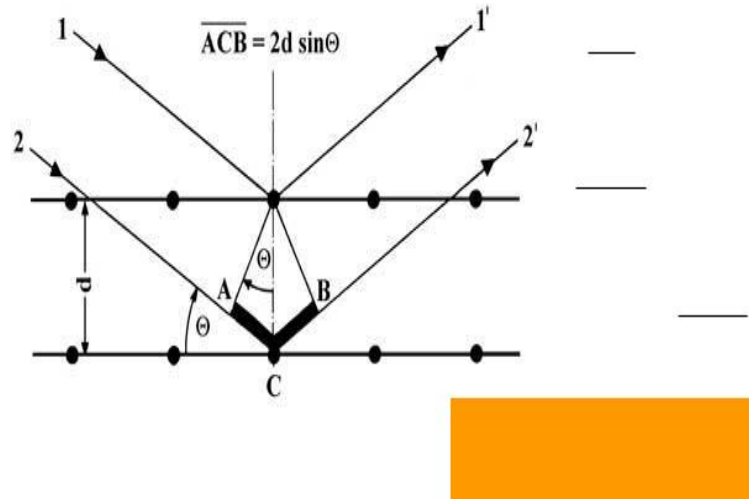
X-ray crystallography is related to several other methods for determining atomic structures. Similar diffraction patterns can be produced by scattering electrons or neutrons, which are likewise interpreted by Fourier transformation. If single crystals of sufficient size cannot be obtained, various other X-ray methods can be applied to obtain less detailed information; such methods include fiber diffraction, powder diffraction and (if the sample is not crystallized) small-angle X-ray scattering (SAXS)

Diffraction refers to the apparent bending of waves around small objects and the spreading out of waves past small apertures. In our context, diffraction is the scattering of a coherent wave by the atoms in a crystal. A diffraction pattern results from interference of the scattered waves.

Refraction is the change in the direction of a wave due to a change in its speed.

BRAGG'S LAW OF DIFFRACTION

No peak is observed unless the condition for constructive interference ($\delta = n\lambda$, with n an integer) is precisely met:



$$AC \sin \theta = d$$

$$ACB = 2d \sin \theta$$

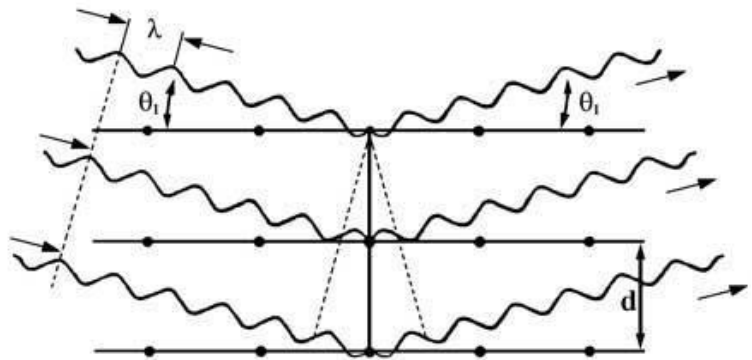
$$n\lambda = ACB$$

$$\text{Bragg's Law: } n\lambda = 2d \sin \theta$$

When Bragg's Law is satisfied, "reflected" beams are in phase and interfere constructively. Specular "reflections" can occur only at these angles

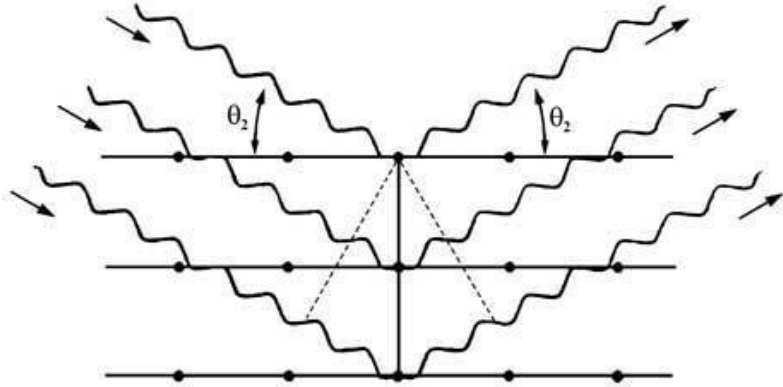
1st order:

$$2d \sin \theta_1$$



2nd order:

$$2d \sin \theta$$



By convention, we set the diffraction order = 1 for XRD.

For instance, when $n=2$ (as above), we just halve the d -spacing to make $n=1$.

$$2d \sin \theta \quad \rightarrow \quad 2(d/2) \sin \theta$$

e.g. the 2nd order reflection of d_{100} occurs at same θ as 1st order reflection of d_{200}

XRD TECHNIQUES AND APPLICATIONS

1- POWDER X-RAY DIFFRACTION

is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of unknown materials. This data is represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities (I/I_0), mineral name and chemical formulae

The XRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units - 10^{-8} cm). The intensity(I) is measured to discriminate (using I ratios) the various D spacings and the results are compared to this table to identify possible matches. Note: 2 theta angle calculated from the Bragg Equation .

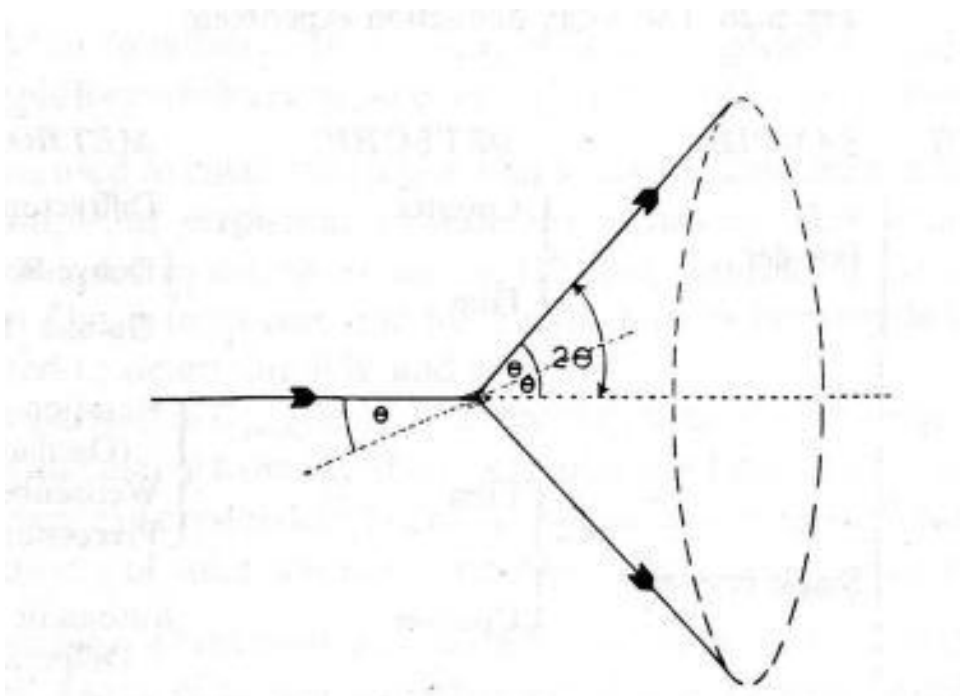
1-uses monochromatic radiation, scans angle

2-sample is powder → all orientations simultaneously presented to beam

3- some crystals will always be oriented at the various Bragg angles

4-this results in cones of diffracted radiation

5- cones will be spotty in coarse samples (those w/ few crystallites)

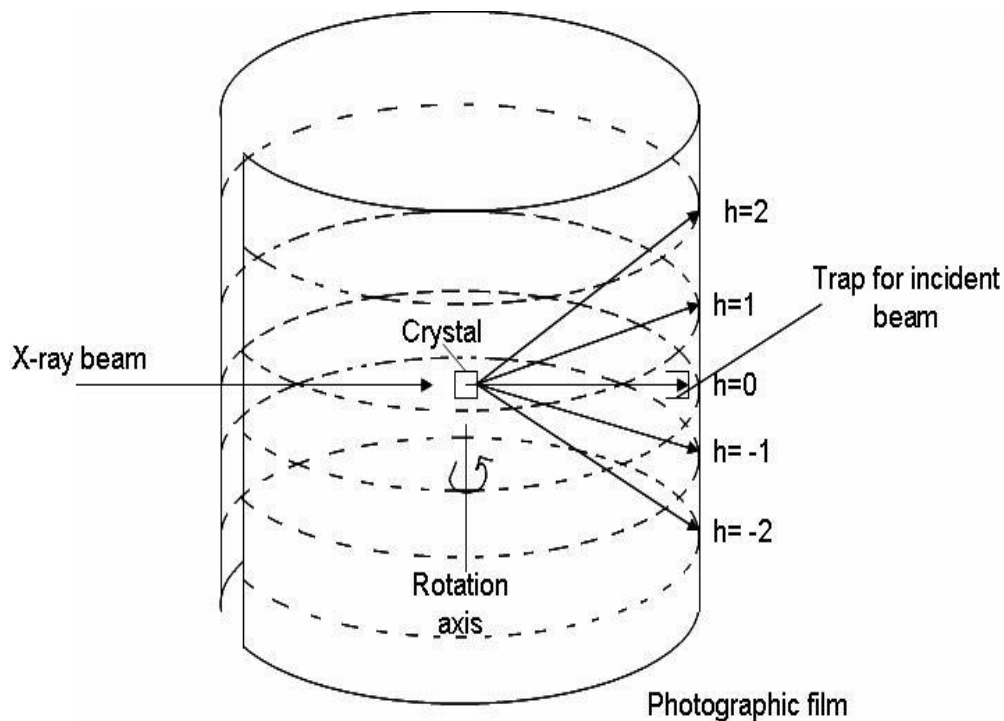


2-X-ray : Rotating Crystal Method

To describe the periodic, three dimensional nature of crystals, the Laue equations are employed: where a , b , and c are the three axes of the unit cell, θ_0 , ϕ_0 , ψ_0 are the angles of incident radiation, and θ , ϕ , ψ are the angles of the diffracted radiation. A diffraction signal (constructive interference) will arise when h , k , and l are integer values. The rotating crystal method employs these equations.

X-ray radiation is shown onto a crystal as it rotates around one of its unit cell axis. The beam strikes the crystal at a 90 degree angle. Using equation 1 above, we see that if θ_0 is 90 degrees, then $\cos\theta_0=0$. For the equation to hold true, we can set $h=0$, granted that $\theta_0=90$. The above

three equations will be satisfied at various points as the crystal rotates. This gives rise to a diffraction pattern (shown in the image below as multiple h values). The cylindrical film is then unwrapped and developed. The following equation can be used to determine the length of the axis around which the crystal was rotated: where a is the length of the axis, y is the distance from $h=0$ to the h of interest, r is the radius of the film, and λ is the wavelength of the x-ray radiation used. The first length can be determined with ease, but the other two require far more work, including remounting the crystal so that it rotates around that particular axis.



3- Laue Method

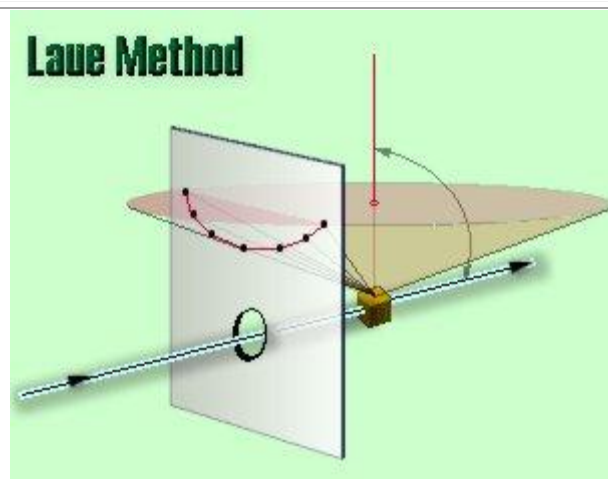
The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal. The diffracted beams form arrays of spots, that lie on curves on the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and q involved. Each curve therefore corresponds to a different wavelength. The spots lying on any one curve are reflections from planes belonging to one [zone](#). Laue reflections from planes of the same zone all lie on the surface of an imaginary cone whose axis is the zone axis.

Experimental

There are two practical variants of the Laue method, the back-reflection and the transmission Laue method. You can study these below:

Back-reflection Laue

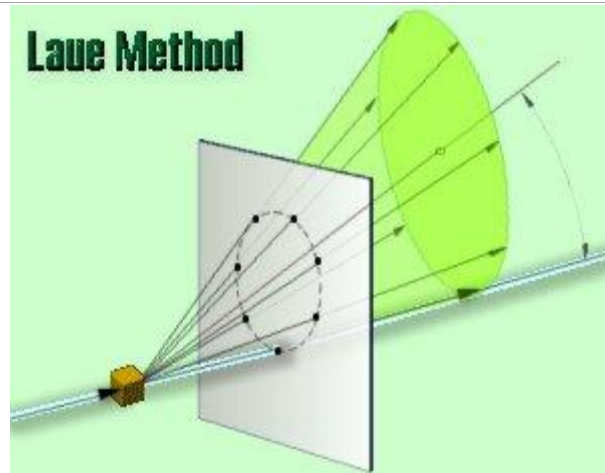
In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded. One side of the cone of Laue reflections is defined by the transmitted



beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.

Transmission Laue

In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal. One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



Crystal orientation is determined from the position of the spots. Each spot can be indexed, i.e. attributed to a particular plane, using special charts. The Greninger chart is used for back-reflection patterns and the Leonhardt chart for transmission patterns. The Laue technique can also be used to assess crystal perfection from the size and shape of the spots. If the crystal has been bent or twisted in anyway, the spots become distorted and smeared out.

Electron and neutron diffraction

Other particles, such as electrons and neutrons, may be used to produce a diffraction pattern. Although electron, neutron, and X-ray scattering

are based on different physical processes, the resulting diffraction patterns are analyzed using the same coherent diffraction imaging techniques.

As derived below, the electron density within the crystal and the diffraction patterns are related by a simple mathematical method, the Fourier transform, which allows the density to be calculated relatively easily from the patterns. However, this works only if the scattering is *weak*, i.e., if the scattered beams are much less intense than the incoming beam. Weakly scattered beams pass through the remainder of the crystal without undergoing a second scattering event. Such re-scattered waves are called "secondary scattering" and hinder the analysis. Any sufficiently thick crystal will produce secondary scattering, but since X-rays interact relatively weakly with the electrons, this is generally not a significant concern. By contrast, electron beams may produce strong secondary scattering even for relatively thin crystals (>100 nm). Since this thickness corresponds to the diameter of many viruses, a promising direction is the electron diffraction of isolated macromolecular assemblies, such as viral capsids and molecular machines, which may be carried out with a cryo-electron microscope. Moreover, the strong interaction of electrons with matter (about 1000 times stronger than for X-rays) allows determination of the atomic structure of extremely small volumes . The field of applications for electron crystallography ranges from bio molecules like membrane

proteins over organic thin films to the complex structures of (nano crystalline) intermetallic compounds and zeolites.

Neutron diffraction is an excellent method for structure determination, although it has been difficult to obtain intense, monochromatic beams of neutrons in sufficient quantities. Traditionally, nuclear reactors have been used, although sources producing neutrons by spallation are becoming increasingly available. Being uncharged, neutrons scatter much more readily from the atomic nuclei rather than from the electrons. Therefore, neutron scattering is very useful for observing the positions of light atoms with few electrons, especially hydrogen, which is essentially invisible in the X-ray diffraction. Neutron scattering also has the remarkable property that the solvent can be made invisible by adjusting the ratio of normal water, H_2O , and heavy water, D_2O .

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