5. Crystal Physics

Syllabus

Crystal Bonding – Ionic – covalent – metallic and van der Wall's molecular bonding - Introduction to Crystal systems (unit cell, Bravais lattices, Miller indices) - Crystal structures - atomic packing density of BCC, FCC and HCP structures - crystal imperfections - point defects - edge and screw dislocations – grain boundaries. X-ray diffractometer.

5.1. Introduction

There are four important mechanisms by which atoms are bonded in engineered materials. These are:

(1)metallic bond; (2)covalent bond;(3)Ionic bond; and (4) **van der Waals bond.**

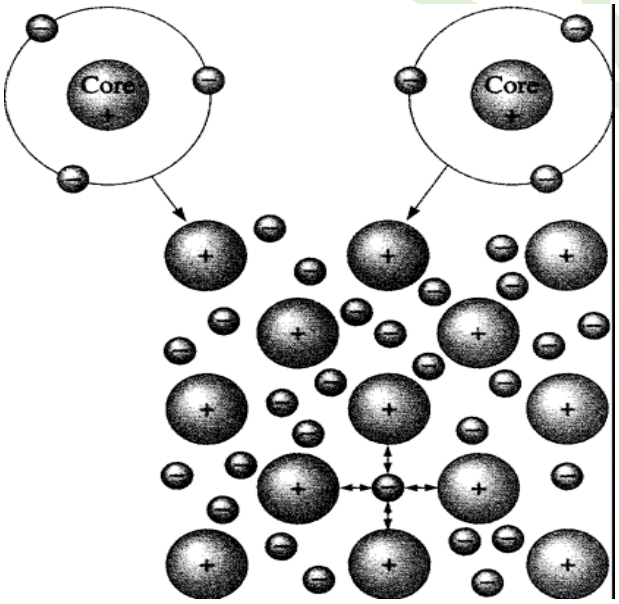
In the first three of these mechanisms, bonding is achieved when the atoms fill their outer *s* and *p* levels. These bonds are relatively strong and are known as **primary bonds** (relatively strong bonds between adjacent atoms resulting from the transfer or sharing of outer orbital electrons). The van der Waals bonds are secondary bonds and originate from a different mechanism and are relatively weaker. Let's look at each of these types of bonds.

The Metallic Bond The metallic elements have more electropositive atoms that donate their valence electrons to form a "sea" of electrons surrounding the atoms. Aluminum, for example, gives up its three valence electrons, leaving behind a core consisting of the nucleus and inner electrons. Since three negatively charged electrons are missing from this core, it has a positive charge of three. The valence electrons move freely within the electron sea and become associated with several atom cores. The positively charged ion cores are held together by mutual attraction to the electron, thus producing a strong metallic bond.

Because their valence electrons are not fixed in any one position, most pure metals are good electrical conductors of electricity at relatively low temperatures (~T < 300

K). Under the influence of an applied voltage, the valence electrons move, causing a current to flow if the circuit is complete.

Materials with metallic bonding exhibit relatively high Young's modulus since the bonds are strong. Metals also show good ductility since the metallic bonds are non-directional. There are other important reasons related to microstructure that can explain why metals actually exhibit *lower strengths* and *higher ductility* than what we may anticipate from their bonding. **Ductility** refers to the ability of materials to be stretched or bent without breaking. We will discuss these concepts in greater detail in Chapter 6. In general, the melting points of metals are relatively high. From an optical properties viewpoint, metals make good reflectors of visible radiation. Owing to their electro-positive character, many metals such as iron tend to undergo corrosion or oxidation. Many pure metals are good conductors of heat and are effectively used in many heat transfer applications. We emphasize that metallic bonding is *one of the factors* in our efforts to rationalize the trends in observed properties of metallic materials. As we will see in some of the following chapters, there are other factors related to microstructure that also play a crucial role in determining the properties of metallic materials.

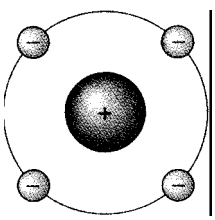


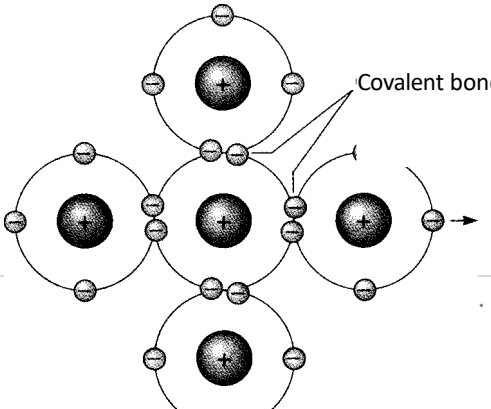
The Covalent Bond Materials with **covalent bonding** are characterized by bonds that are formed by sharing of valence electrons among two or more atoms. For example, a silicon atom, which has a valence of four, obtains eight electrons in its outer energy shell by sharing its electrons with four surrounding silicon atoms. Each

instance of sharing represents one covalent bond; thus, each silicon atom is bonded to four neighboring atoms by four covalent bonds. In order for the covalent bonds to be formed, the silicon atoms must be arranged so the bonds have a fixed **directional relationship** with one another. A directional relationship is formed when the bonds between atoms in a covalently bonded material form specific angles, depending on the material. In the case of silicon, this arrangement produces a tetrahedron, with angles of 109.5° between the covalent bonds.

Covalent bonds are very strong. As a result, covalently bonded materials are very strong and hard. For example, diamond (C), silicon carbide (SiC), silicon nitride (Si3N4), and boron nitride **(BN)** all exhibit covalency. These materials also exhibit very high melting points, which means they could be useful for high-temperature applications. On the other hand, the temperature resistance of these materials present challenges in their processing. The materials bonded in this manner typically have limited ductility because the bonds tend to be directional. The electrical conductivity of many covalently bonded materials (i.e., silicon, diamond, and many ceramics) is not high since the valence electrons are locked in bonds between atoms and are not readily available for conduction. With some of these materials, such as Si, we can get useful and controlled levels of electrical conductivity by deliberately introducing small levels of other elements known as dopants. Conductive polymers are also a good example of covalently bonded materials that can be turned into semiconducting materials. The development of conducting polymers that are lightweight has captured the attention of many scientists and engineers for developing flexible electronic components.

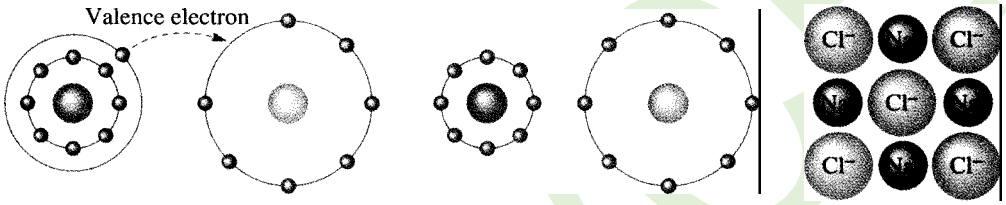
We cannot simply predict whether or not a material will be high or low strength, ductile or brittle, simply based on the nature of bonding! We need additional informa- tion on the atomic, microstructure, and macrostructure of the material. However, the nature of bonding does point to a trend for materials with certain types of bonding and chemical compositions.





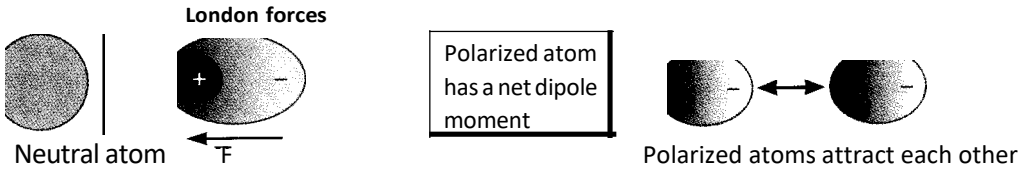
Silicon atom

The Ionic Bond When more than one type of atom is present in a material, one atom may donate its valence electrons to a different atom, filling the outer energy shell of the second atom. Both atoms now have filled (or emptied) outer energy levels, but both have acquired an electrical charge and behave as ions. The atom that contributes the electrons is left with a net positive charge and i5 called a **cation,** while the atom that accepts the electrons acquires a net negative charge and is called an **anion.** The oppositely charged ions are then attracted to one another and produce the **ionic bond.** For example, the attraction between sodium and chloride ions produces sodium chloride (NaCl), or table salt.



Na atom Cl atom Na^+ ion Cl^- ion

If two electrical charges +*q* and -*q* are separated by a distanced, the dipole moment is defined as *q* x *d.* Atoms are electrically neutral. Also, the centers of the positive charge (nucleus) and negative charge (electron cloud) coincide. Therefore, a neutral atom has no dipole moment. When a neutral atom is exposed to an internal or external electric field the atom gets polarized (i.e., the centers of positive and negative charges separate). This creates or induces a dipole moment. In some molecules, the dipole moment does not have to be induced- it exists by virtue of the direction of bonds and the nature of atoms. These molecules are known as **polar molecules.** An example of such a molecule that has a permanently built-in dipole moment is water.

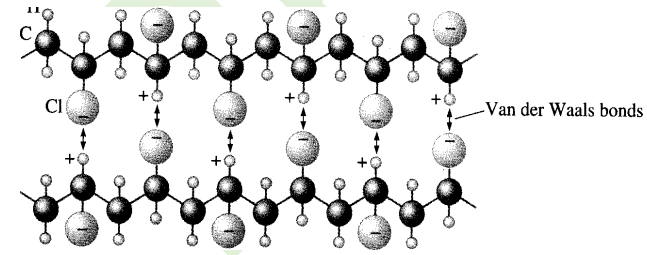


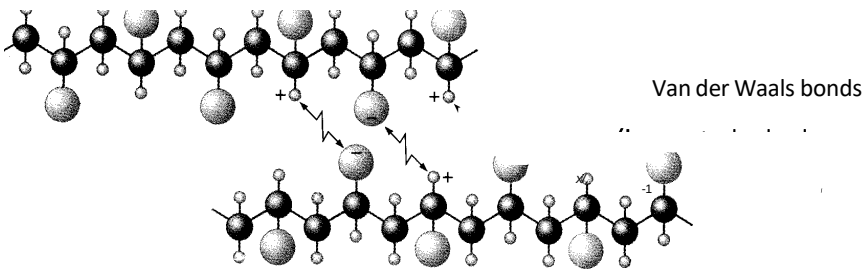
There are three types of **van der Waals** interactions, namely London forces, Keesom forces, and Debye forces. If the interactions are between two dipoles that are induced

in atoms or molecules, we refer to them as **London forces** (e.g., carbon tetrachloride) (Figure 2-16). When an induced dipole (that is, a dipole that is induced in what is otherwise a non-polar atom or molecule) interacts with a molecule that has a permanent dipole moment, we refer to this interaction as a **Debye interaction.** An example of Debye interaction would be forces between water molecules and those of carbon tetrachloride. If the interactions are between molecules that are permanently polarized (e.g., water molecules attracting other water molecules or other polar molecules), we refer to these as **Keesom interactions.** The attraction between the positively charged regions of one water molecule and the negatively charged regions of a second water molecule provides an attractive bond between the two water molecules.

The bonding between molecules that have a permanent dipole moment, known as the Keesom force, is often referred to as the **hydrogen bond,** where hydrogen atoms represent one of the polarized regions. Thus, hydrogen bonding is essentially a Keesom force and is a type of van der Waals force.

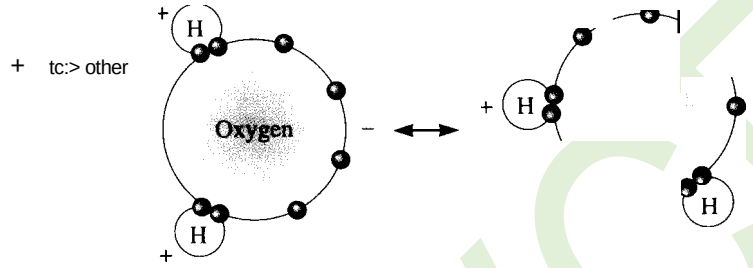
Note that van der Waals bonds are **secondary bonds,** but the atoms within the molecule or group of atoms are joined by strong covalent or ionic bonds. Heating water to the boiling point breaks the van der Waals bonds and changes water to steam, but much higher temperatures are required to break the covalent bonds joining oxygen and hydrogen atoms.





Although termed "secondary", based on the bond energies, van der Waals forces play a very important role in many areas of engineering. Van der Waals forces between atoms and molecules play a vital role in determining the surface tension and boiling points of liquids.

Van der Waals bonds can change dramatically the properties of certain materials. For example, graphite and diamond have very different mechanical properties. In many plastic materials, molecules contain polar parts or side groups (e.g., cotton or cellulose, PVC, Teflon). Van der Waals forces provide an extra binding force between the chains of these polymers



5.1 INTRODUCTION

The study of geometric form and other properties of crystalline solids by using X-rays or electron beams or neutron beams is known as crystallography.

Based on the internal atomic structure, the solids can be classified into two categories namely (i) Crystalline (ii) Non-crystalline (iii) Amorphous solids.

5.1.1 Crystalline Solids (or) Crystals

Crystalline Solids (or) Crystals are those in which the constituent atoms (or) molecules are arranged in an orderly fashion throughout, in a three dimensional pattern.

The crystalline solids have directional properties and therefore they are called **anisotropic substances.**

A crystalline material can be in two forms

(i) **Single crystal,** in which the solid contains only one crystal. These single crystals are produced artificially from their vapour (or) liquid state.

(ii) **Poly crystal,** which has an aggregate of many small crystals (or) grains separated by well defined grain boundaries. These crystals will have a sharp melting point.

Examples for crystalline solids: Diamond, Copper.

5.1.2 Amorphous Solids (or) Non-crystalline Solids

"Amorphous" means "without form".

In amorphous solids the constituent particles i.e., atoms (or) molecules are not arranged in an orderly fashion. In other way we can say that in amorphous solids the same atomic groups are arranged randomly in all directions.

These solids have no directional properties and therefore they are called **isotropic substances.**

Examples for amorphous solids: Plastics, Rubber.

5.1.3 Difference between Crystalline And Non-Crystalline Material

S.No	Crystalline material	Non-crystalline material
1.	They have definite and regular geometrical shapes which extend throughout the crystal.	They do not have definite geometrical shape.
2.	They are anisotropic.	They are isotropic.
3.	They are most stable.	They are less stable.
4.	They have sharp melting point.	They do not have sharp melting point.
5.	Examples : Diamond, NaCl, KCl, Copper, Iron, etc.	Examples : Glasses, Plastics, Rubber etc.

1.3. Basic crystallographic terms

Crystals

Crystal is a regular polyhedral form bounded by smooth surfaces, which is formed by chemical compound under the action of its interatomic forces, when passing from the state of liquid (or) gas to that of a solid, under suitable conditions.

The phase change from liquid (or) gas to solid is called crystallization.

Lattice

Lattice is defined as an array of points. fig.1.1 (a) which are imaginarily kept to represent the position of atoms in the crystal such that every lattice point has got the same environment as that of the other and hence one lattice point cannot be distinguished from the other lattice point. It is an imaginary concept.

Space lattice (or) crystal lattice

A three dimensional collection of points in space are called space lattice (or) crystal lattice. The environment about any particular point is in every way the same.

Lattice points

Lattice points denote the position of atoms (or) molecules in the crystal.

Lattice Planes

A set of parallel and equally spaced planes in a space lattice, which are formed with respect to the lattice points are called lattice planes.

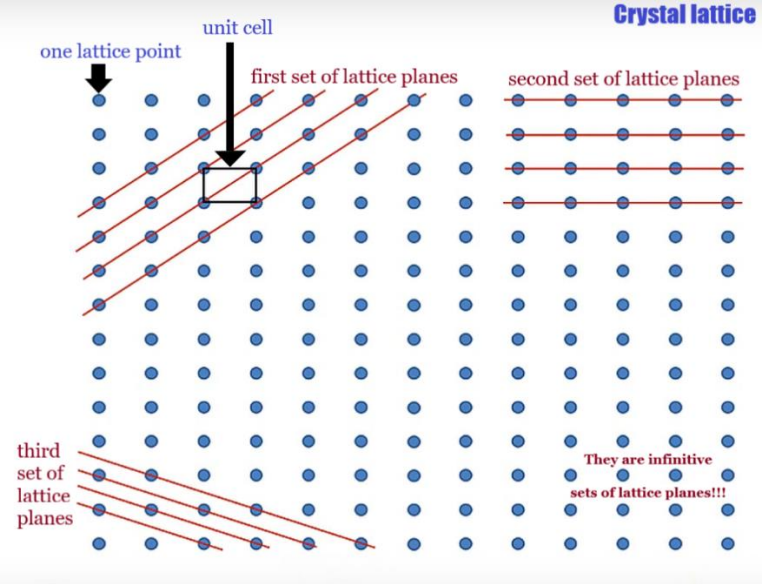


Fig 1.1 (a)

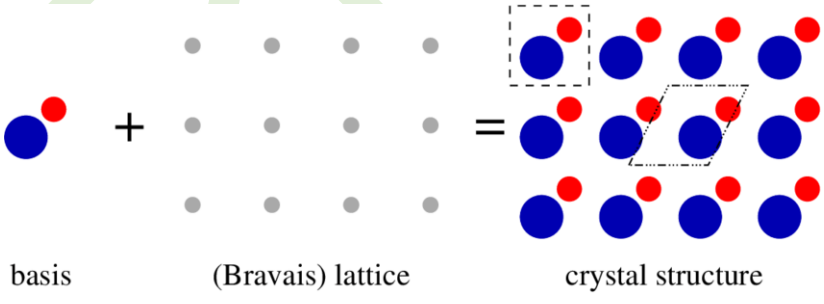
Basis (or) Motif

Basis (or) Motif is an unit assembly of atoms (or) molecules which are identified with respect to the position of lattice points, identical in composition, arrangement and orientation.

Crystal Structure

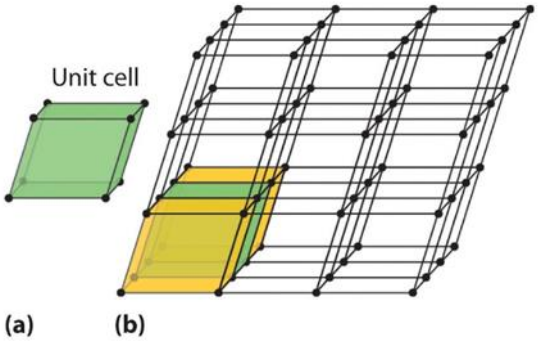
The crystal structure is formed by the addition of basis to every lattice point of the lattice

i.e., Space lattice + Basis => Crystal structure



Unit cell

The unit cell is defined as the smallest geometric figure, the translational repetition of which in all over the three dimensions gives actual crystal structure. Fig 1.2 (a) & (b).



Lattice parameters (or) Unit cell parameters

The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.

The intercepts a, b and c are nothing but the edges of the unit cell, (i.e., the distance between two lattice points) which defines the dimensions of a unit cell. These intercepts are known as its primitives (or) characteristic intercepts on the axes.

These three quantities a, b and c are also called the fundamental translational vectors (or) axial lengths. The angles between (a, b), (b, c) and (c, a) are denoted by γ, α and β respectively. These three angles (γ, α and β) are called interfacial angles (fig. 1.3a).

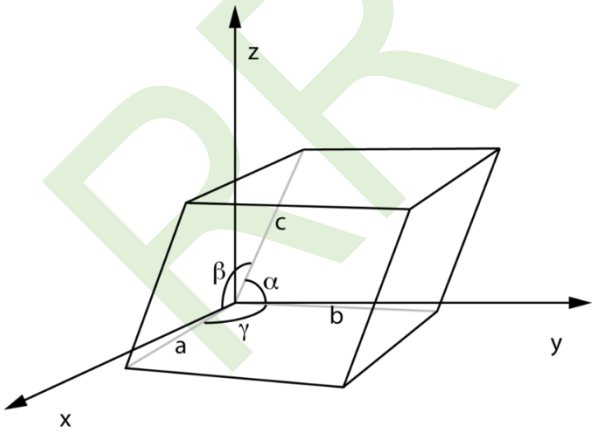


Fig 1.3 (a)

Both the intercepts (a, b, c) and interfacial angles (α, β, γ) constitute the lattice parameters (or) cell parameters of the unit cell.

Primitive cell

A Primitive cell is the simplest type of unit cell which contains only one lattice point per unit cell (contains lattice points at its corner only).

Example: Simple Cubic (SC)

Non-primitive cell

It there are more than one lattice points in a unit cell, it is called a non-primitive cell.

Example: BCC and FCC contain more than one lattice points per unit cell. Fig. 1.3 (b)

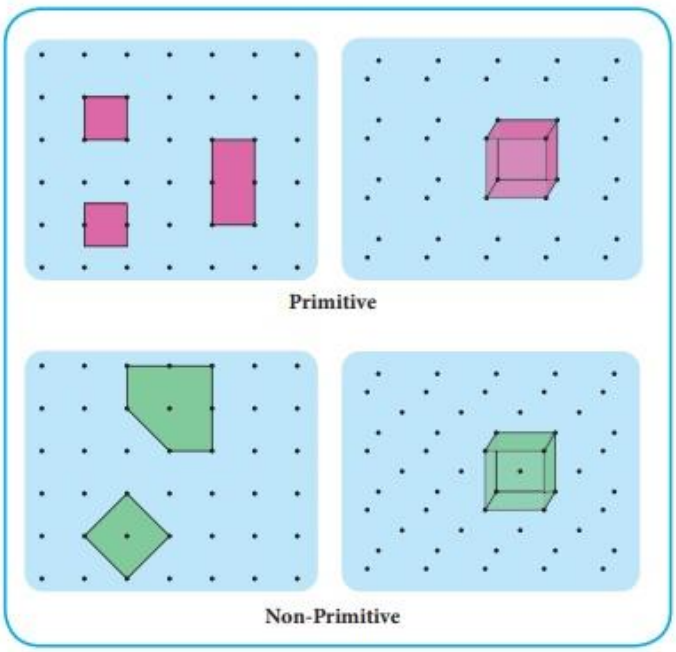
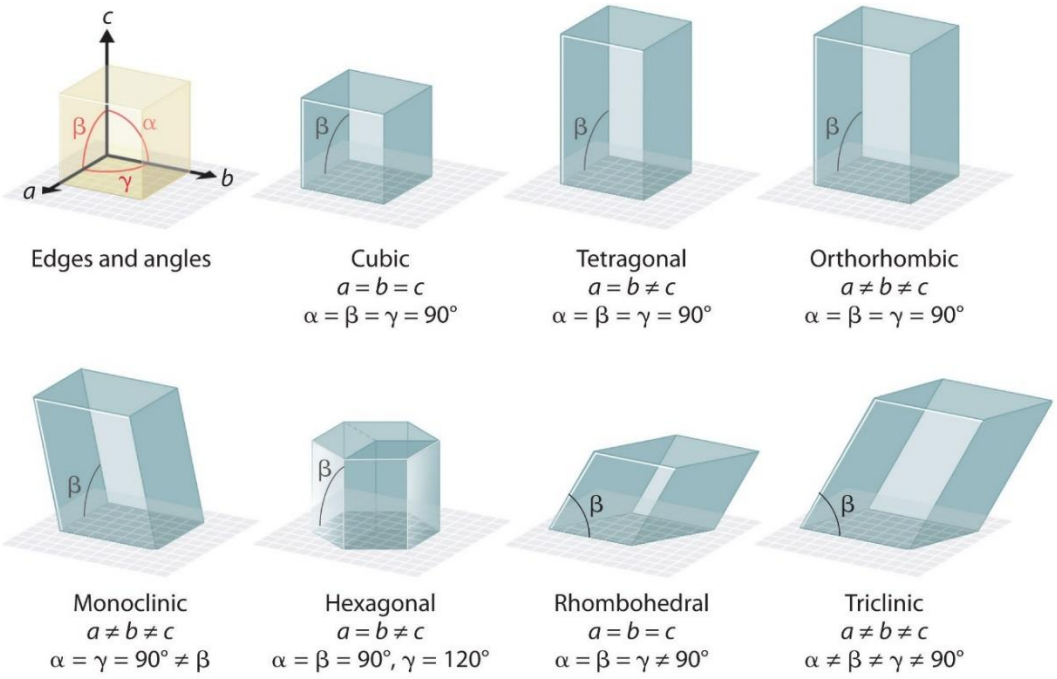


Fig 1.3(b)

1.4. Crystal systems

There are seven crystal systems namely cubic, tetragonal, orthorhombic, monoclinic, triclinic, rhombohedral and hexagonal.

Fig 1.4



1. Cubic system

Here, all the three axial lengths of the unit cell are equal and they are perpendicular to each other i.e., a = b = c and α= β= γ = 90°.

Example: Iron, Copper, NaCl, CaF_2.

2. Tetragonal system

In this system, two axial lengths of the unit cell are equal and third axial length is either longer or shorter. Al the three axis are perpendicular to eachother. a = b ≠ c and α= β= γ = 90°.

Example: White tin, Indium

3. Orthorhombic system

Here, three axial lengths of the unit cell are not equal but they are perpendicular to eachother. a ≠ b ≠ c and α= β= γ = 90°.

Example: Sulphur, Topaz

4. Monoclinic system

Here, three axial lengths of unit cell are not equal. Two axes are perpendicular to each other and third axis is obliquely inclined. a ≠ b ≠ c and α= β = 90°; γ ≠ 90°

Example: Sodium sulphide, Ferrous sulphate

5. Hexagonal system

Here, two axial lengths of unit cell are equal and lying in one plane at angle 120° with each other. The third axial length (vertical) is either longer or shorter than other two and it is perpendicular to this plane. $a = b \neq c$ and $\alpha = \beta = 90°$ $\gamma = 120°$

Example: quartz, Tourmaline

6. Rhombohedral system (Trigonal)

Here, three axial lengths of the unit cell are equal. They are equally inclined to each other at an angle other than 90°. $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$.

Example: calcite

7. Triclinic system

Here, three axial lengths of unit cell are not equal and all the three axes are inclined obliquely to each other. $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$

Example: Copper sulphate, Potassium dichromate

1.5. Bravais Lattice

Bravais introduces the concept of space lattice. He showed that there are only 14 ways of arranging points in space such that the environment looks same from each point.

Hence, there are only 14 types of space lattices which can be possibly developed from out '7' crystal systems as shown in table. We can understand that simple (P) is related to primitive cell which means, lattice points are at all 8 corners of the unit cell. Body centred (I) has lattice points at all 8 corners of the unit cell and one lattice point at the body centre. Face centred (F) has lattice points at all 8 corners of the unit cell and one lattice point at each face centre of 6 faces of the cube. Base centred (C) has lattice points at all 8 corners of the unit cell and 2 lattice points each at the centre of two faces opposite to each other.

These 14 types of space lattice are known as Bravais lattices.

BRAVAIS LATTICE

S.No	Crystal System	Bravais Lattice	Unit cell Parameters	Examples
1.	Cubic	Simple (P) Body centered (I) Face centered (F)	a = b = c α = β = γ = 90°	NaCl, CaF_2 $NaClO_3$
2.	Tetragonal	Simple (P) Body centered (I)	a = b ≠ c α = β = γ = 90°	$NiSO_4$, SnO_2 Indium, White tin
3.	Orthorhombic	Simple (P) Base centered(C) Body centered (I) Face centered (F)	a ≠ b ≠ c α = β = γ = 90°	KNO_3, $BaSO_4$ $MgSO_4$, Sulphur Topaz
4.	Monoclinic	Simple (P) Base centered (C)	a ≠ b ≠ c α = β = 90° : γ ≠ 90°	Na_2So_4, $FeSo_4$ NO_2SO_3
5.	Triclinic	Simple (P)	a ≠ b ≠ c α ≠ β ≠ γ ≠ 90°	$CuSo_4$', $K_2Cr_2O_7$
6.	Trigonal (Rhombohedral)	Simple (P)	a = b = c α = β = γ ≠ 90°	$CaSo_4$, Bi, Sb Calcite
7.	Hexagonal	Simple (P)	a = b ≠ c	Tourmaline

			α = β = 90° γ = 120°	Quartz
Total Bravais lattice		14		

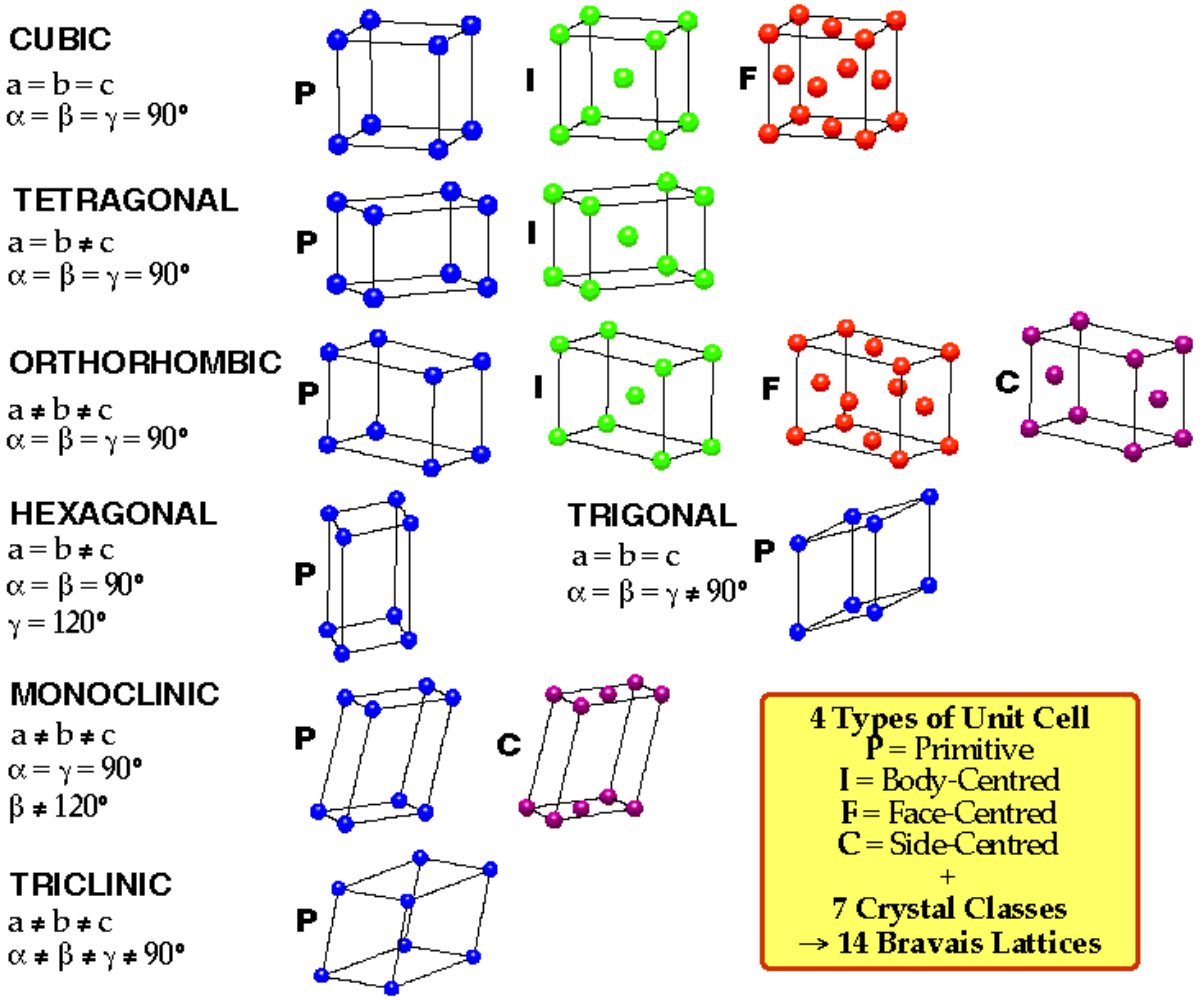


Fig. 1.5

1.6. Characteristics of unit cell

Assuming one atom to one lattice point, the unit cell is characterized by the following parameters:

i. **Number of atoms per unit cell**

ii. **Coordination number**

iii. **Nearest neighbouring distance**

iv. **Atomic radius**

v. **Packing factor**

(i) Number of atoms per unit cell (or) effective number

The total number of atoms present in (or) shared by a unit cell is known as number of atoms per unit cell.

(ii) Coordination number

It is the number of nearest atoms directly surrounding a particular atom in a crystal. The coordination number gives the information about the packing of atoms in a structure. It tells whether the crystal structure is closely packed or loosely packed. If the coordination number is high, then the structure is more closely packed. If it is low, then the structure is loosely packed.

(iii) Nearest neighbouring distance (2r)

It is the distance between the centres of two nearest neighbouring atoms. It is expressed in terms of the length of edge of the unit cell 'a' and it is *2r* in simple cubic

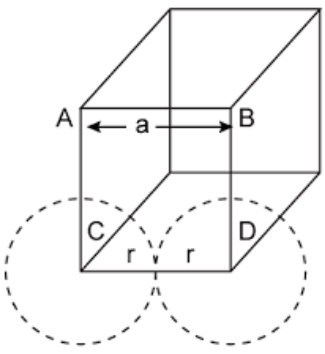


Fig. 1.6

(iv)Atomic radius (r)

It is half of the distance between two nearest neighbouring atoms in the crystal. It is denoted by *'r'*. It is usually expressed in terms of cube edge *'a'* (lattice parameter). For a simple cubic unit cell, the atomic radius is $r = \frac{a}{2}$

(v) Packing factor

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total volume of the unit cell (V)

i.e., Packing Factor $= \dfrac{\text{Volume occupied by the total number of atoms per unit cell} = v}{\text{Total Volume of the unit cell} \quad V}$

i.e., PF = $\dfrac{\text{Number of atoms per unit cell x Volume of one atom}}{\text{Total volume of the unit cell}}$

It is also known as *density of packing*

The packing factor tells us how closely the atoms are stacked in the unit cell. A high packing factor indicates that atoms are very closely packed and therefore there is very little unoccupied space.

On the other hand, a low packing factor indicates loose packing of atoms and hence there is relatively more unoccupied space.

1.7. Crystal structures – BCC, FCC and HCP

BODY CENTRED CUBIC STRUSTURE (BCC)

In this type of crystal structure the unit cell has one atom at each corner of the cube and one at body center of the cube which gives its total contribution to the unit cell. Fig .1.7. shows the arrangement of lattice points in a BCC unit cell

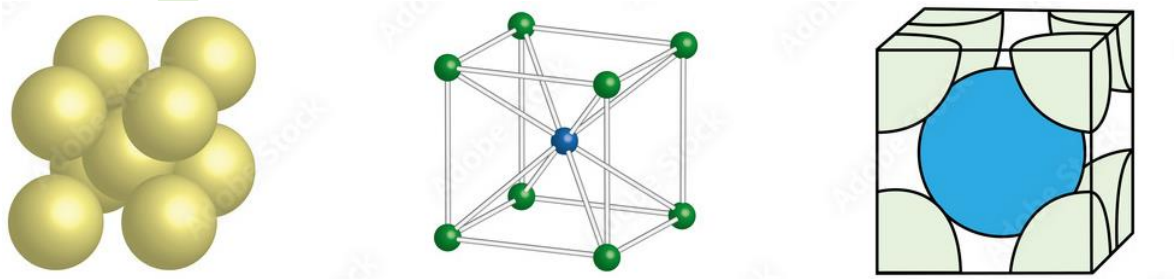


Fig. 1.7

Let us determine the characteristics of the BCC structure:

Number of atoms per unit cell (or) Effective Number

The total number of atoms present in (or) shared by an unit cell is known as number of atoms per unit cell

Number of atoms per unit cell:

Each and every corner atom is shared by 8 adjacent unit cells.

∴ The total number of corner atoms per unit cell = $\frac{1}{8}\times 8 = 1$

Number of body centered atoms per unit cell:

The body centered atom is shared by that particular unit cell alone and is not shared by any other unit cell.

∴ The number of body centered atoms per unit cell = $\frac{1}{1}\times 1 = 1$

∴ Total number of atoms = Total Number of corner atoms +

Per unit cell in BCC = Total number of body centered atoms = 1 +1 = 2

Atomic radius

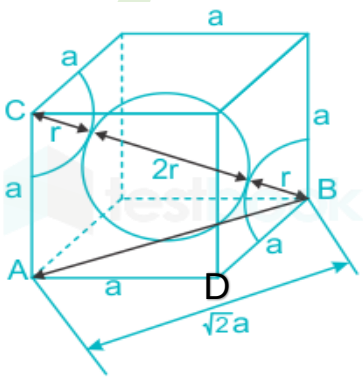


Fig.1.8.

In BCC structure, the corner atoms do not touch each other. But each corner atom touches the body centered atom along the body diagonal as shown in fig

1.7. Therefore the two corner atoms (B&C) situated at the opposite ends can be joined by drawing a diagonal as shown in figure 1.8. From the geometry of the fig.1.8, we can write

$(BC)^2 = (BA)^2 + (AC)^2$

$= (BD)^2 + (DA)^2 + (AC)^2$ (or)

$(BC)^2 = a^2 + a^2 + a^2 = 3a^2$

$BC = a\sqrt{3}$ (1)

From fig. 5.11 the diagonal of the cube BC = 4r (2)

$\therefore$ **From equations (1) & (2) , we can write** $4r = a\sqrt{3}$

(or) Atomic radius $r = \frac{a\sqrt{3}}{4}$

Co-ordination number

Co-ordination number is the number of nearest neighbouring atoms to a particular atom.

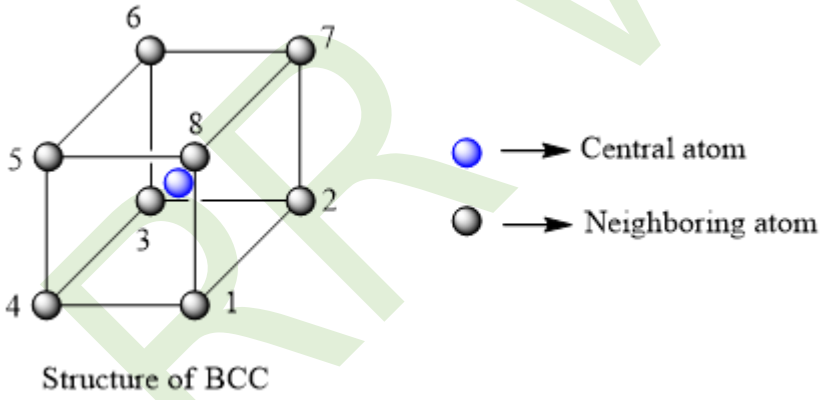


Fig. 1.9.

In BCC structure, there will be one body centered atom at the center of the unit cell and eight atoms at the 8 corners of the unit cell as shown in fig.1.9. The corner atoms do not touch each other. But each corner atom touches the body centered atom along

the body diagonal. Thus, for an atom X at the body centre obviously, there are 8 nearest neighbors (corner atoms).

Hence the coordination number for body centered cubic is 8.

Atomic Packing Factor (APF)

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total number of the unit cell (V).

In body centered cubic structure,

The number of atoms per unit cell = 2

$\therefore$ Volume of 2 atoms (Spherical) = $2 \times \frac{4}{3}\pi r^3$

We know the radius of atom in BCC is $r = \frac{a\sqrt{3}}{4}$

$\therefore$ Volume occupied by the atoms per unit cell (v) $= \frac{8\pi}{3}\left[\frac{a\sqrt{3}}{4}\right]^3 = \pi a^3 \frac{\sqrt{3}}{8}$

Volume of the unit cell for a cubic system (V) $= a^3$

$\therefore$ Atomic Packing Factor (APF) $= \frac{\pi a^3 \frac{\sqrt{3}}{8}}{a^3}$

(or) $APF = \pi \frac{\sqrt{3}}{8} = 0.68$

Therefore, we can say that 68% volume of the unit cell of BCC is occupied by atoms and remaining 32% volume is vacant.

Thus the packing density is 68%

Since the packing density is greater than simple cubic, it has tightly packed structured, when compared to SC.

Examples: Tungsten, Chromium and Molybdenum

Face Centred Cubic Structure (FCC)

In this type of crystal structure, the unit cell has one atom at each corner of the cube and one atom at the centre of each face. This structure is closely-packed because each atom has 12 nearest neighbours. This type of structure is more common in metals.

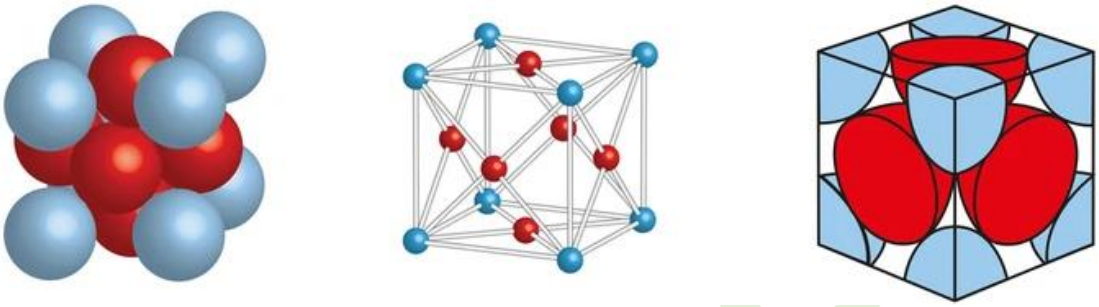


Fig. 1.10

Number of atoms per unit cell (or) Effective number

The total number of atoms present in (or) shared by a unit cell is known as number of atoms per unit cell.

Number of corner atoms per unit cell:

Each and every corner atom is shared by 8 adjacent unit cells.

$\therefore$ The total number of corner atoms per unit cell $= \frac{1}{8} \times 8 = 1$

Number of face centered atoms per unit cell:

Each face centered atom is shared by only two unit cells, which lie on either side of the atom. Similarly we have six face centered atoms in a unit cell.

$\therefore$ The total number of face centered atoms per unit cell $= \frac{1}{2} \times 6 = 3$

$\therefore$ Total number of atoms per unit cell in FCC = Total Number of corner atoms + Total number of face centered atoms = 1 +3 = 4

Atomic radius

In FCC structure, the corner atoms do not touch each other. But each corner atom touches the face centered atoms along the diagonal of the face of the cube as shown in fig. 1.11. Therefore, the two corner atoms (A and C) situated at the opposite ends of the same face can be joined by drawing a diagonal as shown in fig.1.11.

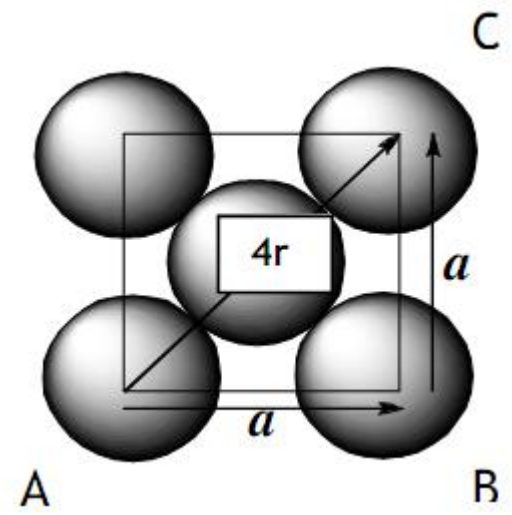


Fig. 1.11

From the geometry of the fig.5.13. We can write

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

$= a^2 + a^2$

$(AC)^2 = 2a^2$

$\therefore AC = a\sqrt{2}$ (1)

But from fig.5.14 the diagonal of the cube

$AC = 4r$ (2)

$\therefore$ From equations (1) and (2) we can write $4r = a\sqrt{2}$

∴ Atomic radius $r = \frac{a\sqrt{2}}{4}$

Co-ordination Number

Co-ordination number is the number of nearest neighbouring atoms to a particular atom.

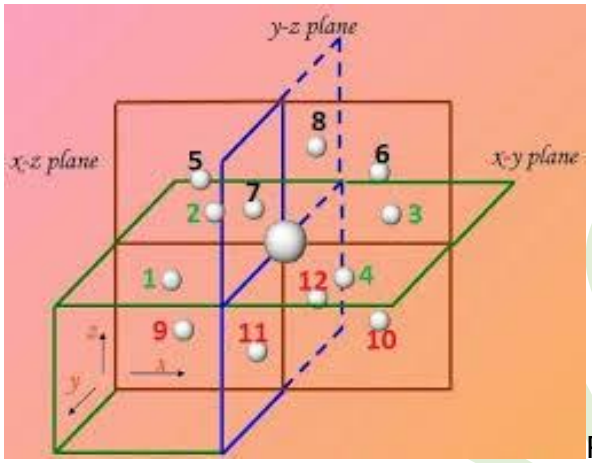


Fig 1.12

In this system, there are 8 corner atoms, and six face centered atoms one at the center of each face. To calculate the coordination number, for FCC, let us consider a XY plane as shown in fig. 1.12. in XY plane it has 4 face centered atoms (1,2,3,4) as nearest neighbours.

In a YZ plane which lie just above this corner atom, it has 4 more face centered atoms (5,6,7,8) as nearest neighbours and similarly in a XZ plane which lie just below this corner atom it has 4 more face centered atoms, (9,10,11,12) as nearest neighbours. The total number of nearest atoms to any corner atom is 4+4+4=12.

Hence the coordination number for face centered cubic is 12.

Atomic Packing Factor (APF)

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total volume of the unit cell (V).

In face centered cubic structure,

The number of atoms per unit cell =4

We know the radius of the atom in FCC $r = \frac{a\sqrt{2}}{4}$

∴ Volume occupied by the atoms per unit cell (v) = $4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi\left[a\frac{\sqrt{2}}{4}\right]^3 = \frac{\pi a^3\sqrt{2}}{6}$

Volume of the unit cell for a cubic system (V) = a^3

∴ Atomic packing factor (APF) $= \frac{\frac{\pi a^3\sqrt{2}}{6}}{a^3} = \pi\frac{\sqrt{2}}{6}$

APF = 0.74

Therefore, we can say that 74% volume of the unit cell of FCC is occupied by atoms and remaining 26% volume is vacant.

Thus, the packing density is 74%

Since the packing density is very high, the FCC structure has closely (or) tightly packed structure.

Examples: Copper, aluminium, nickel, gold, led and platinum.

Packing fraction of FCC = $\sqrt{2}$ x Packing fraction of SC

Hexagonal Closed Packed Structure

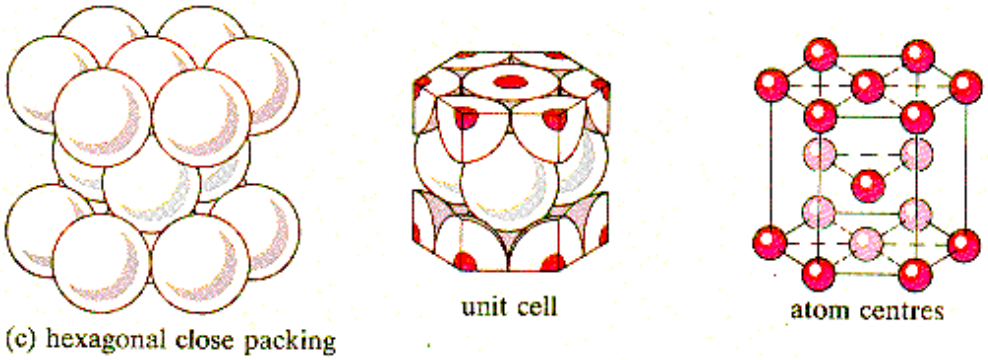


Fig. 1.13

In this type of crystal structure, the unit cell has one atom at each of the twelve corners of the hexagonal crystal, one atom at the center of the two hexagonal faces and three atoms symmetrically arranged in the body of the cell.

This structure is called close packed structure. Each atom has twelve nearest neighbours, six in its plane, and three in the plane above and three in the plane below. Metallic crystals usually have closed packed structure.

The unit cell of hexagonal close packed structure is shown in Fig.1.14. There are three layers of atoms in it. At the bottom layer (B_L) the central atom has six nearest neighbouring atoms in the same plane. Further the middle layer (M_L) which is at a distance c/2 from the bottom layer has three atoms as shown in Fig.1.16. Top layer (T_L) is similar to the bottom layer in the arrangement of atom and it is at a distance from the bottom layer.

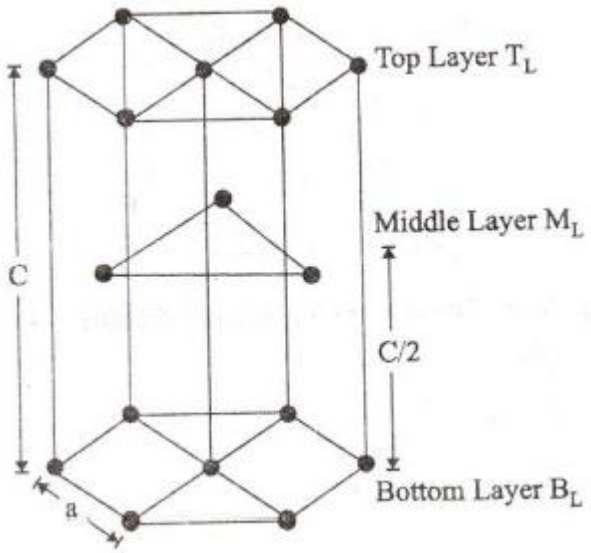


Fig. 1.14

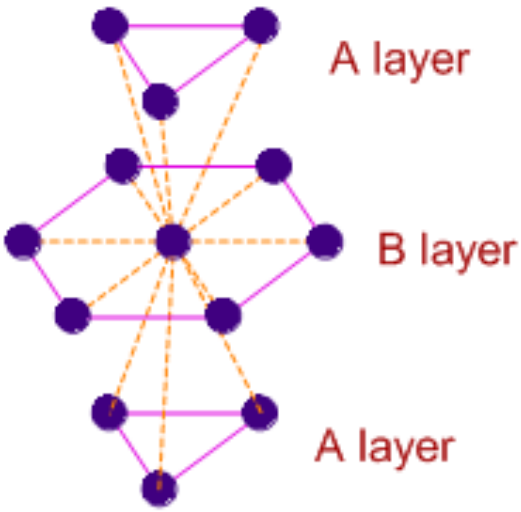


Fig. 1.15

Number of atoms per unit cell

$\therefore$ The number of corner atoms per unit cell = $\frac{1}{6}\times 12 = 2$

Number of base centered atoms per unit cell:

Each base atom is shared by two unit cells as shown in figure 1.14. Similarly we have two base centered atoms in an unit cell.

$\therefore$ The number of base centered atoms per unit cell = $\frac{1}{2}\times 2 = 1$

Number of middle layer atoms per unit cell:

The 3 atoms situated at the middle layer, within the body of the unit cell are fully contributing to that particular unit cell alone i.e., they are not shared by any other unit cells.

$\therefore$ The total number of middle layer atoms per unit cell = 3

$\therefore$ The total number of atoms per unit cell in HCP structure (N) = Number of corner atoms +

Number of Base atoms +

Number of middle layer atoms

i.e., N = 3+2+1 = 6 atoms

Atomic radius

Consider any two corner atoms in a hexagon closed packed structure. It has to be noted that each and every corner atom touches each other, therefore they are the nearest neighbours. From the below figure 1.18, we can write we can write a = 2r (or) r = a/2

Calculation of c/a ratio:

We know that ‘c’ is the height of the unit cell of HCP structure and ‘a’ is the distance between two neighbouring atoms. Now, consider a triangle ABO in the bottom layer (Fig 1.16.)

Here A, B & O are the lattice points and exactly above these atoms at a perpendicular distance ‘c’/2 the next layer atoms lies at C,

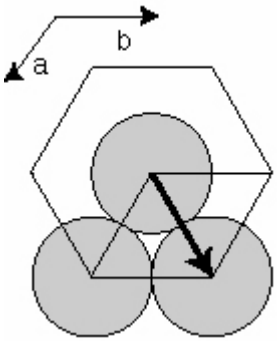


Fig. 1.16

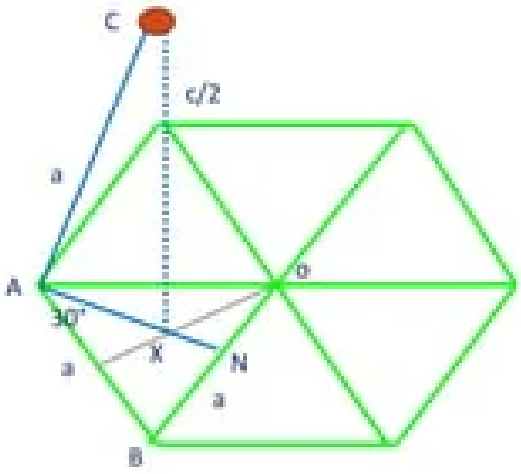


Fig. 1.17

In Δ ABN, cos 30° = AN / AB

$\therefore$ AN = AB cos 30° = $\frac{a\sqrt{3}}{2}$

i.e., AN = $\frac{a\sqrt{3}}{2}$ $\left[\because AB = a; \cos 30° = \frac{\sqrt{3}}{2}\right]$ (1)

But from Fig 5.18. (b), AX = $\frac{2}{3}AN$ (2)

$\therefore AX = \frac{2}{3} \times \frac{a\sqrt{3}}{2}$ = $\frac{2}{\sqrt{3 \times \sqrt{3}}} \times \frac{a\sqrt{3}}{2}$

AX = $\frac{a}{\sqrt{3}}$ (3)

In Δ AXC, $AC^2 = AX^2 + CX^2$ (4)

Substituting the values for AC =*a*; AX = $\frac{a}{\sqrt{3}}$ and CX = $\frac{C}{2}$ in equation (4), we get

$a^2 = \left[\frac{a}{\sqrt{3}}\right]^2 + \left[\frac{c}{2}\right]^2$ (5)

(or) $a^2 = \frac{a^2}{3} + \frac{c^2}{4}$ (or) $\frac{c^2}{4} = a^2 + \frac{a^2}{3}$

(or) $\frac{c^2}{4} = \frac{2a^2}{3}$ (or) $\frac{c^2}{a^2} = \frac{8}{3}$ (or) $\frac{c}{a} = \sqrt{\frac{8}{3}}$ = 1.633 (6)

Packing Factor

Volume of all atoms in a unit cell (*v*)

Nearest neighbouring distance , 2r = a

Atomic radius r = a/2

Number of atoms per unit cell , *n* = 6

Volume of all 6 atoms in the unit cell *v* = $6 \times \frac{4}{3}\pi r^3$

(or) *v* = $6 \times \frac{4}{3}\pi\left[\frac{a}{2}\right]^3$ = πa^3

Volume of the unit cell (V)

Area of the base = 6 x Area of triangle AOB

Area of triangle AOB = $\frac{1}{2}$ (BO)(AN)

Substituting for BO = *a* and AY = $\frac{a\sqrt{3}}{2}$ we have

Area of traingle AOB = $\frac{1}{2} \times \frac{a^2\sqrt{3}}{4} = \frac{a^2 3\sqrt{3}}{2}$

Volume of the unit cell of HCP = Base area x Height

$\therefore V = \frac{a^2 c 3\sqrt{3}}{2}$

Now, Packing Factor = $\frac{v}{V} = \frac{\frac{\pi a^3}{a^2 c 3\sqrt{3}}}{2} = \frac{2\pi}{3\sqrt{3}}\left[\frac{a}{c}\right] = \frac{2\pi}{3\sqrt{3}}\left[\frac{a}{c}\right] = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$

74% of the volume is occupied by the atoms and the remaining 26% volume is vacant.

Here the packing fraction of FCC and HCP are same and they are known as closely packed structures.

Examples: Magnesium, Zinc, Titanium, Zirconium, beryllium and cadmium.

Properties	BCC	FCC	HCP
Volume of unit cell	a^3	a^3	$\frac{3\sqrt{3}a^2c}{2}$
No. of atoms per unit cell	2	4	6
Co-ordination number	8	12	12
Atomic radius (r)	$\frac{\sqrt{3}a}{4}$	$\frac{\sqrt{2}a}{4}$	$\frac{a}{2}$
Packing factor	0.68	0.74	0.74
Examples	Iron, Barium, Tungsten	Copper, Aluminium, Nickel	Magnesium, Zinc, Titanium

1.5 Direction in Crystal

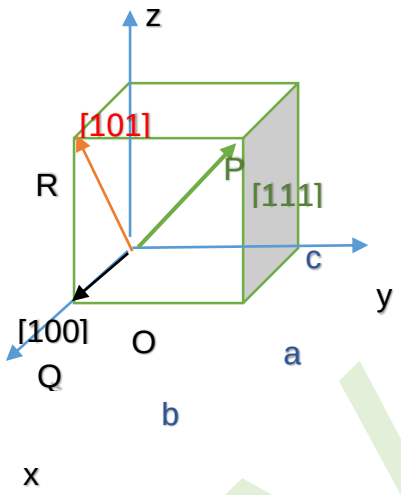
It is always useful to have a convention or standardized procedure to specify the directions in a crystal. The procedure of finding the directions inside the crystal is explained below

1. Consider any lattice point that lies on the line as origin.
2. Write down the position vector of the next nearest point on the line in terms of the fundamental translation vector $\vec{a}$, $\vec{b}$ and $\vec{c}$ of the unit cell of the crystal, say,

$$\vec{r} = r_1 \times \vec{a} + r_2 \times \vec{b} + r_3 \times \vec{c}$$

3. Now the components of position vector $\vec{r}$ along the three directions of *a, b, c* are r_1, r_2, r_3 respectively. Then the crystal direction is denoted by [r_1, r_2, r_3]. Let us apply this procedure to find the directions of OP, OQ and OR of an orthorhombic unit cell (*a ≠ b≠ c;* α = β = γ = 90°) as shown in figure 1.18 taking O as origin.

Fig. 1.18



Direction of OP

Position vector of *OP* = $\overrightarrow{OP}$ = 1 x $\vec{a}$ + 1 x $\vec{b}$ + 1 x $\vec{c}$

Therefore, r_1 = 1; r_2 = 1; r_3= 1

Hence, direction of OP is represented as [111]

Direction of OQ

Position vector of *OQ* = $\overrightarrow{OQ}$ = 1 x $\vec{a}$ + 0 x $\vec{b}$ + 0 x $\vec{c}$

Therefore, r_1 = 1; r_2 = 0; r_3= 0

Hence, direction of OP is represented as [100]

Direction of OR

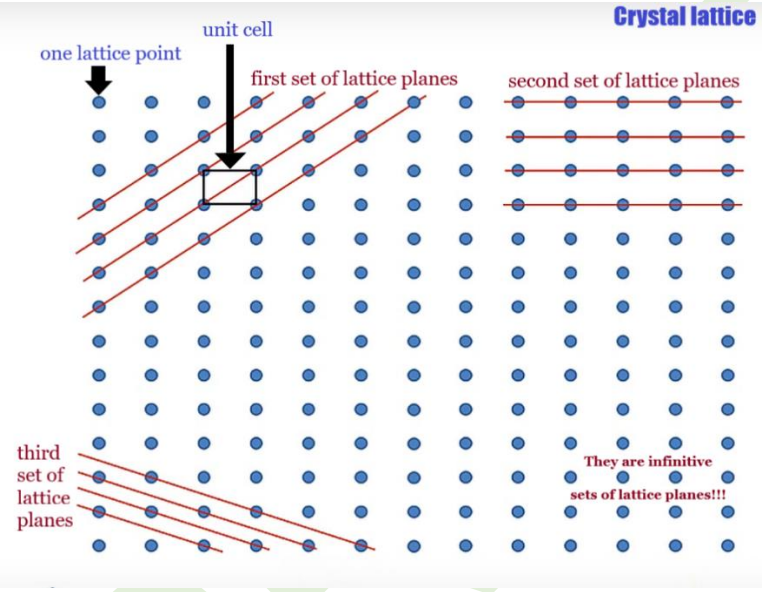
Position vector of *OR* = $\overrightarrow{OR}$ = 1 x $\vec{a}$ + 0 x $\vec{b}$ + 1 x $\vec{c}$

Therefore, $r_1 = 1$; $r_2 = 0$; $r_3 = 1$

Hence, direction of OP is represented as [101]

It should be understand that the direction of [222], [333], [444]… will all coincide with [111]. In such cases the lowest combination of integers i.e., [111] is used to specify the direction. If any of the integer is negative for example -3, it should be written as $\bar{3}$ which is read as 3 bar. Given three integers of direction, a family of directions with different possible combinations of them, both positive and negative, is represented with brackets of the type < >..

1.6. Planes in crystal



A crystal lattice is considered as a collection of a set of parallel equidistant plane passing through lattice points. These planes are known as lattice planes. These set of planes may be chosen in many different ways as shown in the above figure.

Miller indices

Definition: Miller indices are three possible integers that have the same ratio as the reciprocals of the intercepts of the plane concerned on the three axes.

Procedure: consider a crystal plane. Let us find its Miller indices as follows:

(1) Find the intercepts of the plane along the coordinate axes *X, Y, Z.* The intercepts are measured as the multiples of axial lengths.

(2) Take the reciprocal of these intercepts.

(3) Reduce the reciprocals in to whole numbers. This can be done by multiplying each reciprocal by the number obtain from LCM of the denominators.

(4) Write these integers within parentheses to get Miller indices.

Features:

(1) If a plane is parallel to any one of the coordinate axes, then its intercept will be infinity. Hence the miller indices for that particular axis is zero.

(2) The plane passing through the origin has non-zero intercepts

(3) All equally spaced parallel planes have the same Miller indices (*h k l*)

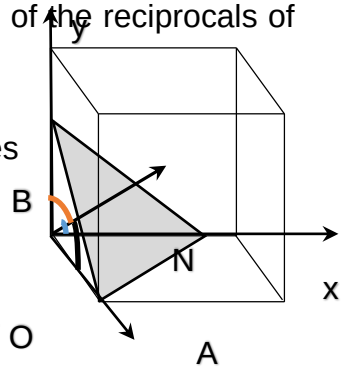
(4) This (*h k l)* indices define a set of parallel plane than a particular plane

(5) Miller indices is not only the ratio of indices but the notation to find all such planes

(6) If a plane cuts the axis on the negative side, then a bar is put just above the particular miller index.

Consider a cubic crystal of 'a' as side of a cube and a plane ABC as shown in figure. Let this plane belong to a family of planes whose miller indices are [*h k l*]. A normal ON is drawn ⊥r from the origin of the cube to the plane ABC. Let ON represents the interplanar spacing (d) of this family of plane.

The plane ABC makes OA, OB & OC as intercepts on crystallographic axes OX, OY & OZ respectively. α', β' and γ' are the angles between the crystallographic axes. We know that the miller indices of a plane are the smallest integers of the reciprocals of the intercepts.



But here, Intercepts are expressed as reciprocals of miller indices

Of the plane. $i.e.,$ OA: OB: OC = $\frac{1}{h} : \frac{1}{k} : \frac{1}{l} = \frac{a}{h} : \frac{a}{k} : \frac{a}{l}$

$\therefore \quad OA = \frac{a}{h} ; OB = \frac{a}{k} ; OC = \frac{a}{l}$ [Multiply by lattice constant 'a')

From the Geometry of right angles OAN, OBN & OCN, we have

$$cos\acute{\alpha} = \frac{ON}{OA} = \frac{\frac{d}{a}}{\frac{}{h}} = \frac{dh}{a}$$

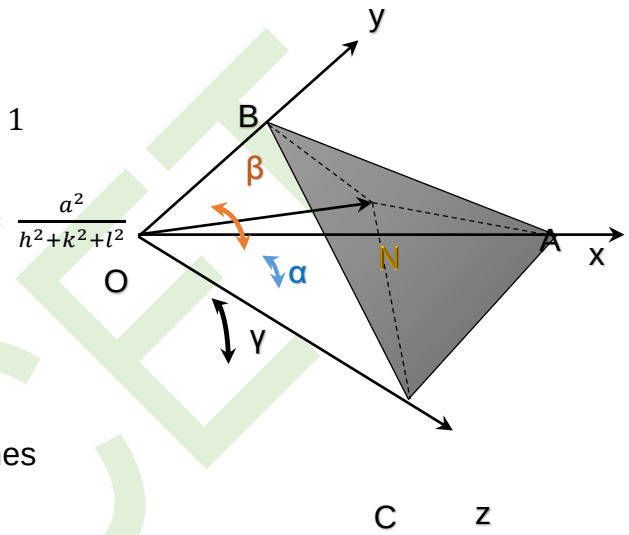
III^{rly} $cos\acute{\beta} = \frac{ON}{OB} = \frac{\frac{d}{a}}{\frac{}{k}} = \frac{dk}{a}$ & $cos\acute{\gamma} = \frac{ON}{OC} = \frac{\frac{d}{a}}{\frac{}{l}} = \frac{dl}{a}$ (blue - α', Red - β' and Black - γ')

The law of direction cosines is $cos^2\acute{\alpha} + cos^2\acute{\beta} + cos^2\acute{\gamma} = 1$

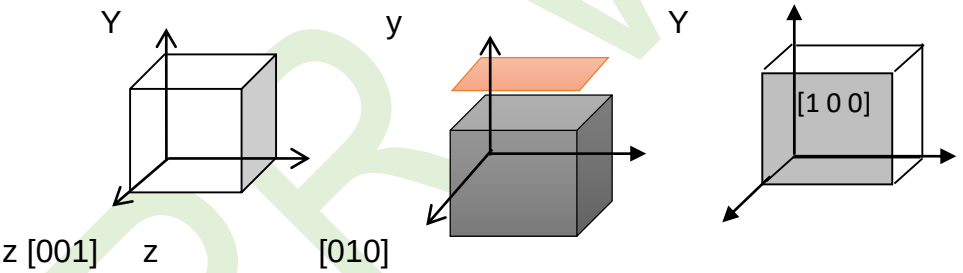
Substituting the values, $\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$

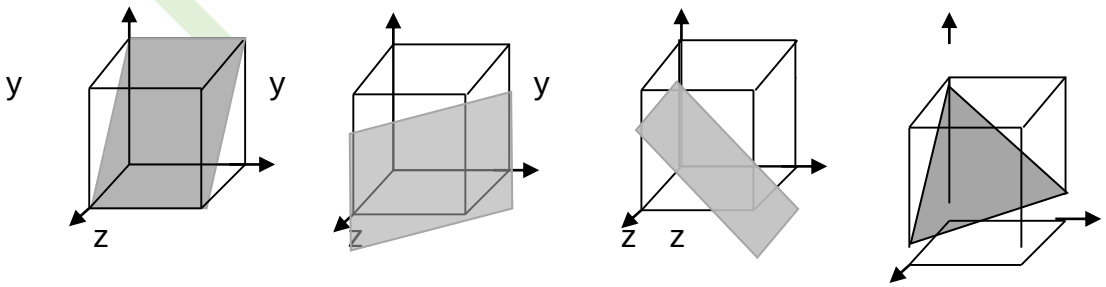
i.e., $\frac{d^2}{a^2}(h^2 + k^2 + l^2) = 1$ (or) $d^2 = \frac{a^2}{h^2+k^2+l^2}$

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



Some of the Miller indices with cubic crystal planes





Density of crystal

$$\text{Density of the crystal } (\rho) = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\text{Mass of the unit cell (M)} = \frac{\text{Atomic mass}}{\text{Avogardo number}} \times \text{Number of atoms per unit cell}$$

(or) $\frac{M}{N_A} \times n$; (or) $\rho = \frac{nM}{a^3 N_A}$

Linear density and planar density

Linear density is defined as number of atoms per unit length whose centers on the direction vector for specific crystallographic direction.

This is defined as the number of atoms per unit length along a specific crystal direction.

$$\frac{\text{Number of atoms centred on direction vector}}{\text{Length of direction vector}}$$

The unit of linear density is m^{-1}, nm^{-1}.

The planar density of a crystal is the density of atoms in a crystal plane. This is defined as the number of atoms per unit area on a crystal plane. This effects significantly the rate of plastic deformation.

It is defined as the number of atoms per unit area

$$\frac{\text{Number of atoms in a plane}}{\text{The area of the plane}}$$

The unit of planar density is m^{-2}, nm^{-2}.

1.8. Crystal imperfections

In an ideal crystal (perfect crystal), the atomic arrangement is perfectly regular and continuous throughout. But in real crystals due to some reasons the regular orientation of atoms may be distributed at a point, along a line or in a region.

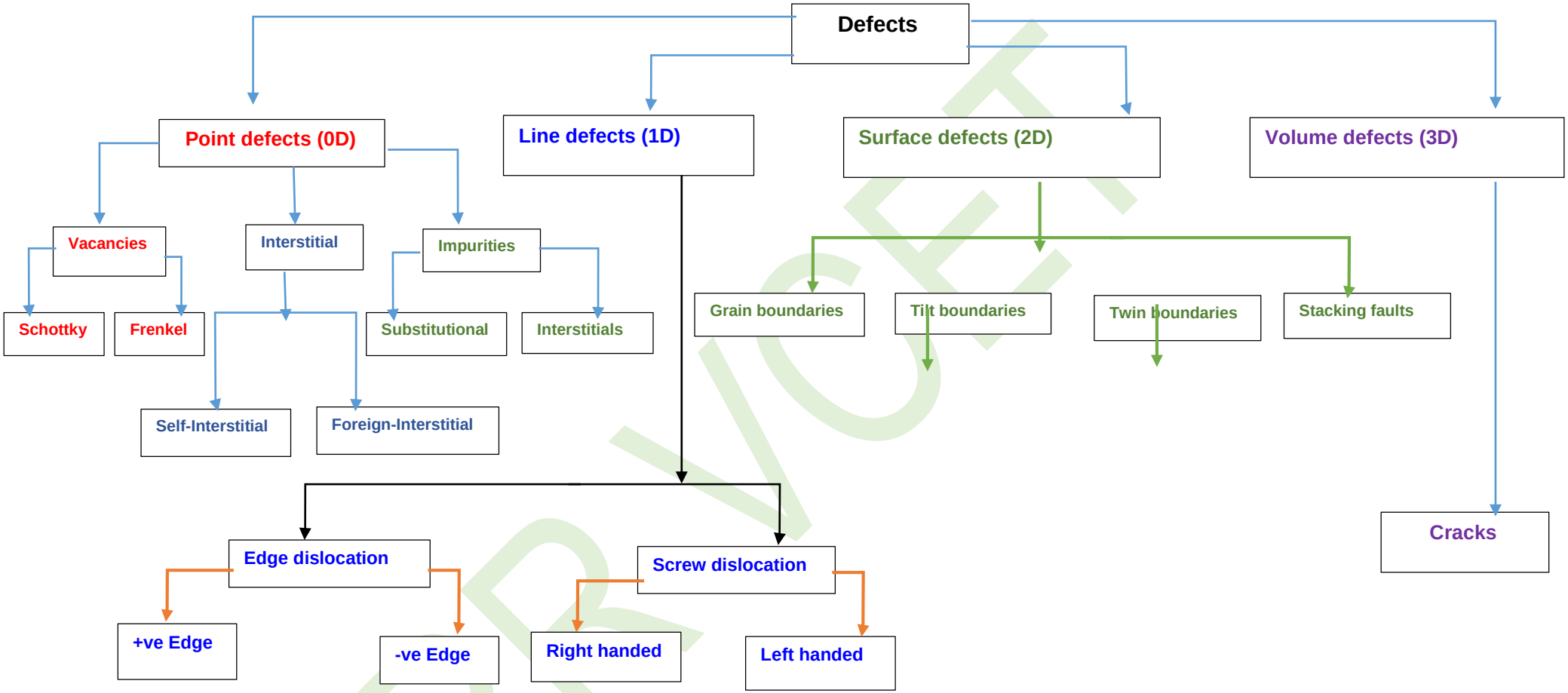
Definition

The disturbance occurred in the regular orientation of atoms is called crystal defect or imperfection.

The imperfections or defects are always present in the actual crystal and their effects are often very important in understanding the properties of crystal.

Some properties of crystal defects are structure sensitive i.e., properties such as mechanical strength, ductility, crystal growth, magnetic hysteresis, dielectric strength are greatly affected by the relatively minor changes in crystal structure caused by the imperfections.

Some other properties of crystals are structure-insensitive i.e., properties such as stiffness and density are not affected by the presence of impurities


Defects
Point defects (0D)
Line defects (1D)
Surface defects (2D)
Volume defects (3D)
Vacancies
Interstitial
Impurities
Schottky
Frenkel
Substitutional
Interstitials
Self-Interstitial
Foreign-Interstitial
Grain boundaries
Tilt boundaries
Twin boundaries
Stacking faults
Cracks
Edge dislocation
Screw dislocation
+ve Edge
-ve Edge
Right handed
Left handed

1.9. Point defects

Point defects are crystalline irregularities of atomic dimensions. They are imperfect points like regions in the crystal. One or two atomic diameter is the typical size of a point imperfection.

- Point defect takes place due to imperfect packing of atoms during crystallization
- They produce distortion inside the crystal structures.
- They produce strain only in its surroundings but they do not affect the regularity in other parts of the crystal.

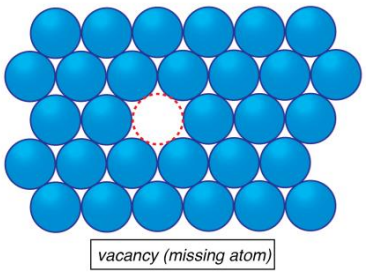
Types of crystal

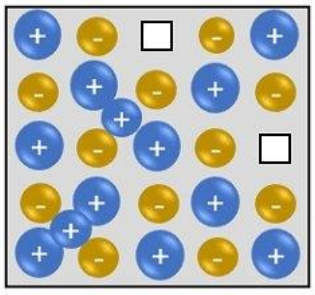
(a) Vacancies

A vacancy is the simplest point defect in a crystal. It refers to a missing atom or vacant atomic site. Whenever on or more atoms are missing from a normally occupied position as shown in figure, the defect caused is known as vacancy.

Vacancies may be single as shown in figure or two or more of them. These defects may arise due to imperfect packing during original crystallisation and thermal vibrations of the atoms at high temperatures.

The atoms surrounding the vacancies are displaced inwards thereby distorting the regularity of arrangement. These are different kinds of vacancies like Frenkel defect, Schottky defect, Colour defect, etc.,





Schottky defect

It refers to the missing of a pair of positive and negative ions in a crystal. Here, two oppositely charges ions are missing from an ionic crystal, therefore a cation-anion divacancy is created. This is known as Schottky defect or Schottky imperfection or Iron pair imperfection. Since a pair is missing, electrical neutrality is maintained.

Frenkel defect

A vacancy associated with interstitial impurity is called Frenkel defect. Here a missing atom occupy interstitial position. This defect always occurs in ionic crystal. If a positive ion moves into an interstitial site in an ionic crystal, a cation vacancy is created in normal ion site, this vacancy interstitial pair is known as Frenkel defect. Frenkel defect does not change the overall electrical neutrality of the crystal. The presence of these defects in ionic crystals causes an increase in electrical conductivity.

(b) Interstitial defect

When an extra atom occupies interstitial space (i.e. voids) within the crystal structure without removing parent atom, the defect is called interstitial defect.

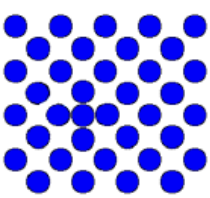
An atom can enter into interstitial space or void only if it is smaller than the parent atom otherwise, it will produce atomic distortion or strain because interstitial atom tends to push the surrounding atoms further apart. Interstitial defect has two types

(i) Self-interstitial

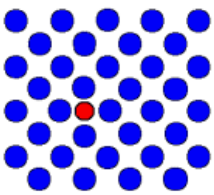
If an atom from same crystal occupies interstitial site, then it is called self-interstitial.

(ii) Foreign interstitial

If an impurity atom (foreign atom) occupies interstitial site, then it is called foreign-interstitial.



Self-interstitial



Interstitial
foreign atom

(c) Impurities

When the foreign atoms (impurities) are added to crystal lattices, they are known as impurities. The defect is called impurity defects. They are

(i) Substitutional impurity defect

A substitutional impurity refers to a foreign atom that replaces a parent atom in the lattice. Substitutional impurities change the electrical properties enormously.

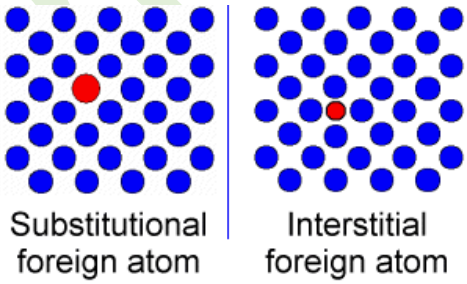
Example: *n*-type and *p*-type semiconductors have substitutional impurities from V group and III group elements. A controlled addition of impurity to a very pure semiconductor is the basis of producing many electronic devices like diode and transistors.

During the production of brass alloy, zinc atoms are doped in copper lattice. Here, zinc atoms are called as substitutional impurities.

(ii) Interstitial impurity

An interstitial impurity is a small size atom occupying the empty space (interstitial) in the parent crystal, without dislodging any of the parent atoms from other sites. An atom can enter into interstitial or empty space only when it is substantially smaller than parent atom.

Example: In FCC iron, the atomic radius of iron atom is 0.225 nm. The carbon atoms with atomic radius 0.078 nm can occupy empty spaces in FCC lattice as interstitial impurities.



1.10 Line defects or dislocations (1D effect)

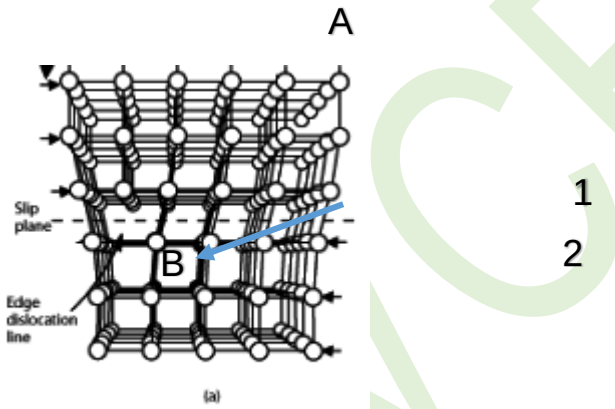
The defects due to dislocation or distortion of atoms along a line are known as line defects. These defects are also called dislocations. In the geometrical sense, they are

one dimensional defects. In line defects, a portion of a line of atoms is missing or displaced from its regular site.

Types of line defects

(a) Edge dislocation

An edge dislocation arises when one of the atomic planes forms only partially and does not extend through the entire crystal. The atomic plane AB abruptly terminates at B. It is viewed as an extra plane inserted in between a set of parallel planes. The edge of such a plane forms a line defect and it is called an edge dislocation. The atomic row 1 passing through point B has one atom more than row 2 adjacent to it.



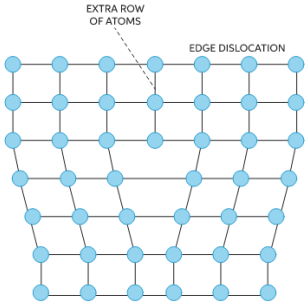
There are two configurations in dislocations:

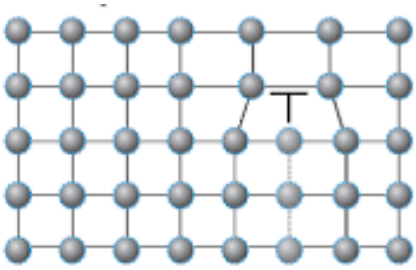
(i) Positive edge dislocation

If the extra plane of atoms is above the slip plane of the crystal than the edge dislocation is called positive as shown in figure. It is denoted by ⊥.

(ii) Negative edge dislocation

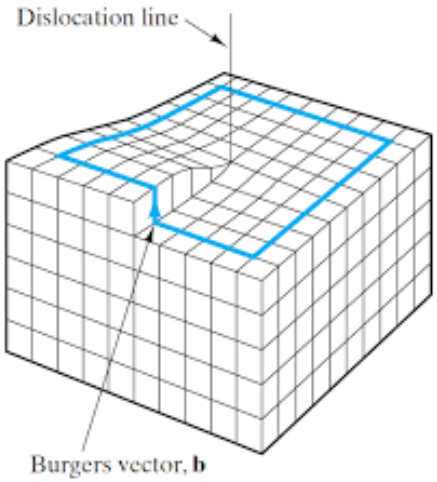
If the extra plane of atoms is below the slip plane than the edge dislocation is called negative. It is denoted by ┬.





(b) Screw dislocation

Screw dislocation is due to a displacement of atoms in one part of a crystal relative to rest of the crystal. The displacement terminates within crystal. This dislocation forms a spiral ramp around dislocation line. In a screw dislocation, there is a line of atoms about which crystal planes are wrapped to give an effect similar to threads of a screw. The row of atoms marking the termination of the displacement is the screw dislocation. The term screw represents that one part of the crystal is moving in spiral manner about dislocation line. If spiral motion of one part of the crystal is in clockwise direction then dislocation is right handed, on the other hand spiral motion is in anti-clockwise direction then, dislocation is left handed.

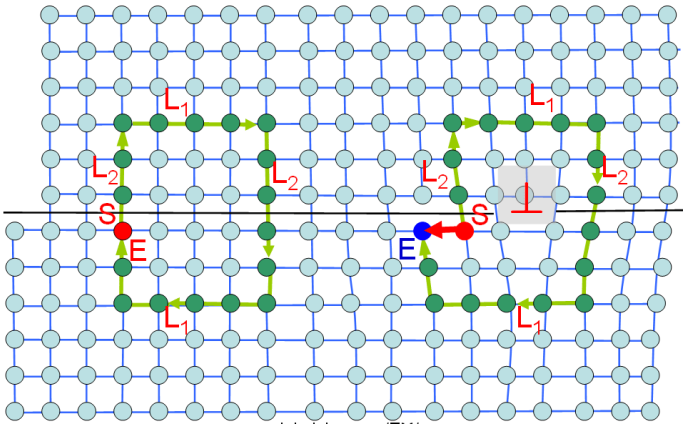


S.No	Edge dislocation	Screw dislocation
1	In edge dislocation, an edge of atomic plane is formed internal to the crystal	In screw dislocation, only distraction the lattice cell in the immediate vicinity is produced.
2	It is perpendicular to Burger's vector	It is parallel to Burger's vector
3	It moves in the direction of the Burger's vector	It moves in a direction perpendicular to the Burger's vector
4	If incomplete plane is above the slip plane then it is known as positive edge dislocation. It is represented by ⊥	If the spiral motion of the dislocation is in clock-wise direction then it is known as right handed screw dislocation
5	If incomplete plane is below the slip plane then it is known as negative edge dislocation. It is represented by ⊤	If the spiral motion of the dislocation is in anti-clockwise direction then it is known as left handed screw dislocation.
6	The amount of force required to form and move an edge dislocation is less	The amount of force required to form and move a screw dislocation is more.

1.11. Burger's vector

The dislocation lines are expressed by a Burger vector $\vec{b}$. It indicates the amount and direction of shift in lattice on slip plane. The following figure shows a perfect crystal and a crystal with positive edge dislocation. Consider a point starting from E moves in a particular direction as shown (Left side of figure) and it completes atomic distances in the form of circuit called *Burger circuit* or *Burger loop*. If the same circuit is drawn starting from E (as shown in right side) will not complete the circuit due to the presence of dislocation. Hence, if we wish to arrive at starting point E from S. then we must

move an extra distance $\vec{b}$ as shown in figure. The vector $\vec{b} = \vec{ES}$ connects end point with starting point is called burger's vector of the dislocation.

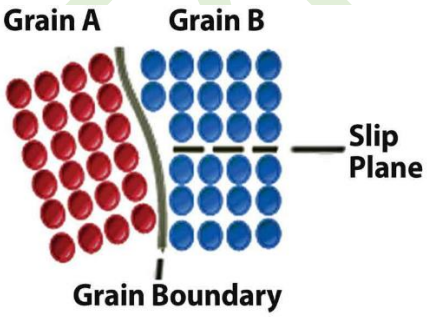


1.12. Surface defects (Plane defects -2D)

The defects on the surface of material are called surface defects or plane defects. They are also known as two dimensional imperfections. Surface defects are due to a change in the stacking of atomic planes on or across a boundary.

Some important internal surface defects are discussed below

(i) Grain boundaries



Whenever the grains of different orientations separate the general pattern of atoms and exhibits a boundary, the defect caused is called grain boundary. A grain boundary is formed when two growing grain surfaces meet. The shape of

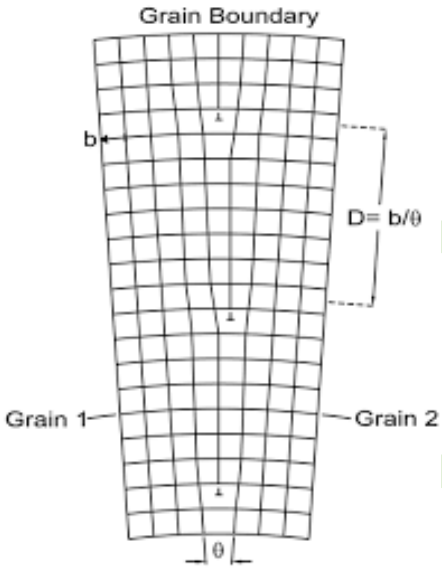
the grain is usually influenced by the presence of surrounding grains. This type of defect generally takes place during the solidification of liquid metal.

(ii) Tilt and twist boundaries

Tilt boundary is another surface imperfection. It is an array of parallel edge dislocation of same sign (i.e., either ⊤ or ⊥) arranged one above other in an array or series. Tilt angle is a type of low angle boundary (less than 10°). By rotation of an axis in the boundary, it is possible to bring the axis of two bordering grains into coincidence, then

Angle of tilt, $\tan\theta = \frac{b}{D}$, D – Dislocation spacing; b – Length of Burger's Vector.

When θ is small, then tan θ = θ & hence, $\theta = \frac{b}{D}$

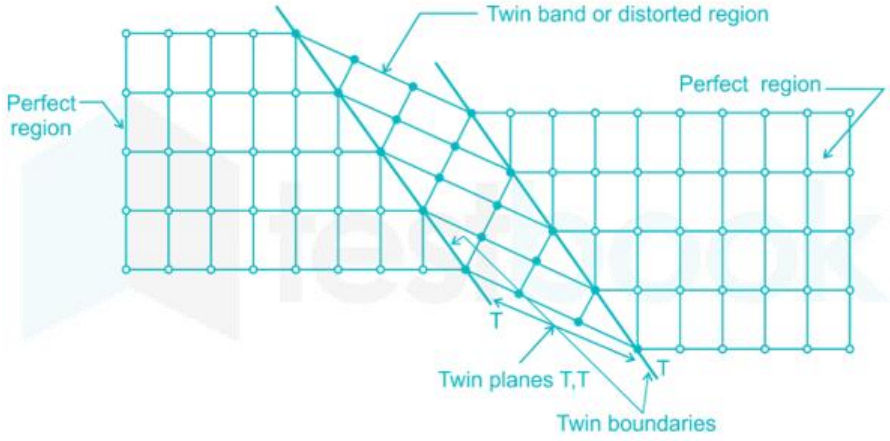


Twist boundaries

Twist boundaries are another type of low angle boundaries. It consists of atleast two sets of parallel screw dislocations lying in the boundary. In twist boundary, the rotation is about an axis normal to boundary.

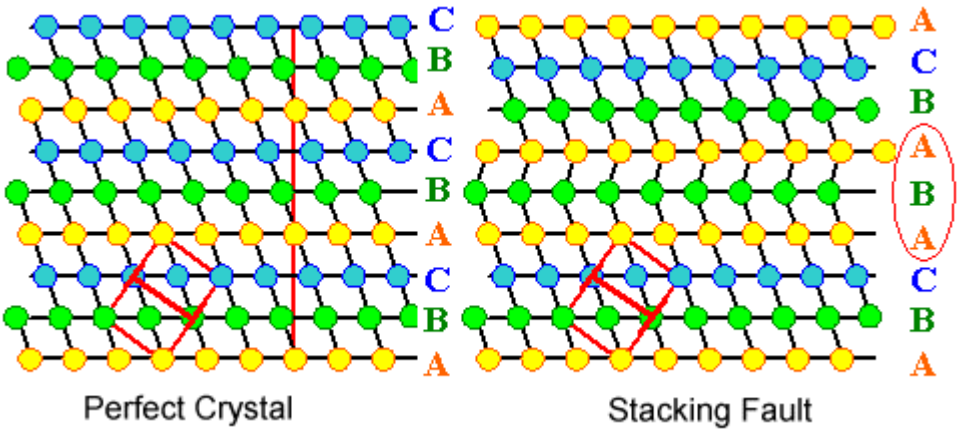
(iii) Twin boundaries

Twin boundaries are another surface imperfections. If the boundaries in which the atomic arrangement on one side of the boundary is somewhat a mirror image **of the** arrangement of atoms of the other side. The defect caused is called twin boundary.



Stacking faults

It is a kind surface imperfection. Whenever the stacking of atoms is not in proper sequence throughout the crystal, defect caused is called stacking fault



Explanation

The above figure shows the proper and improper sequence of atomic planes. Perfect crystal has a sequence C-B-A-C-B-A while the encircle part of the sequence is change on right side which forms a thin region of a hexagonal close packing in a FCC crystal.

. Bragg's law of X-Ray Diffraction

When electrons moving at high speeds are directed to a metal target, a small percentage of their kinetic energy is converted into x-rays. The x-rays emitted by the target consist of a continuous range of wavelengths, called white radiation, by analogy with white light consisting of a range of wavelengths. The **minimum wavelength in**

the continuous spectrum is inversely proportional to the applied voltage which accelerates the electrons towards the target. If the applied voltage is sufficiently high, in addition to the white radiation, a characteristic radiation of a specific wavelength and high intensity is also emitted by the target. The radiation emitted by a molybdenum target at 35 kV includes both types of radiation. In spectroscopic notation, the characteristic radiations are named K_α, K_β, L_α, etc. K_α radiation has a high intensity and is commonly used in diffraction studies. The wavelengths of this radiation for typical target metals are given below:

Target Metal	Mo	Cu	Co	Fe	Cr
K_α (wavelengths)	0.71 Å	1.54 Å	1.79 Å	1.94 Å	2.29 Å

A beam of x-rays directed at a crystal interacts with the electrons of the atoms in the crystal. The electrons oscillate under the impact and become a new source of electromagnetic radiation. The waves emitted by the electrons have the same frequency as the incident x-rays. The emission is in all directions. As there are millions of atoms in a crystal, the emission in a particular direction is the combined effect of the oscillations of electrons of all the atoms. The emissions will be in phase and reinforce one another only in certain specific directions, which depend on the direction of the incident x-rays, their wavelength as well as the spacing between atoms in the crystal. In other directions, there is destructive interference of the emissions from different sources. The easiest way to visualize the diffraction effects produced by the three-dimensional grating provided by the crystal is to consider the Bragg law.

In the following Figure, a set of parallel planes in a crystal is shown. A beam of x-rays of wavelength λ is directed towards the crystal at an angle θ to the atomic planes. In Bragg law, the interaction described above between x-rays and the electrons of the atoms is visualized as a process of reflection of x-rays by the atomic planes. This is an equivalent description of the diffraction effects produced by a three-dimensional grating. The atomic planes are considered to be semi-transparent, that is, they allow a part of the x-rays to pass through and reflect the other part, the incident angle θ (called the Bragg angle) being equal to the reflected angle. Referring to above figure,

there is a path difference between rays reflected from plane 1 and the adjacent plane 2 in the crystal. The two reflected rays will reinforce each other, only when this path difference is equal to an integral multiple of the wavelength. If d is the interplanar spacing, the path difference is twice the distance d sin θ, as indicated in the above figure. The Bragg condition for reflection can therefore be written as

$$2 d \sin \theta = n \lambda \quad (1)$$

Where *n* is an integer and θ is the wavelength of the x-rays used. A first order reflection is obtained, if *n* = l; a second order reflection occurs if *n* = 2, and so on.

As sin θ has a maximum value of 1, for a typical value of interplanar spacing of 2 Å, Eq. (1) gives the upper limit of λ for obtaining a first order reflection as 4 Å. There will be no reflection if λ is greater than 4 Å. λ can be reduced indefinitely, obtaining reflections from other sets of planes that have spacing less than 2 Å as well as an increasing number of higher order reflections. A very small wavelength of the order of 0.1 Å is not necessarily an advantage as it tends to produce other effects such as knocking off electrons from the atoms of the crystal and getting absorbed in the process. The wavelengths of the K_α radiation given in the above table for typical target metals lie in the right range. The Bragg equation can be used for determining the lattice parameters of cubic crystals. Let us first consider the value that n should be assigned. A second order reflection from (100) planes should satisfy the following Bragg condition:

$$2 \lambda = 2 d_{100} \sin \theta$$

$$\text{(or) } \lambda = d_{100} \sin \theta \quad (2)$$

Similarly, a first order reflection from (200) planes should satisfy the following condition:

$$\lambda = 2 d_{200} \sin \theta \quad \textbf{(3)}$$

We have earlier noted that the interplanar spacing of (100) planes is twice that for (200) planes. So, Eqs. (2) and (3) are identical. For any incident beam of x-rays, the Bragg angle θ would be the same, as the two sets of planes in question are parallel.

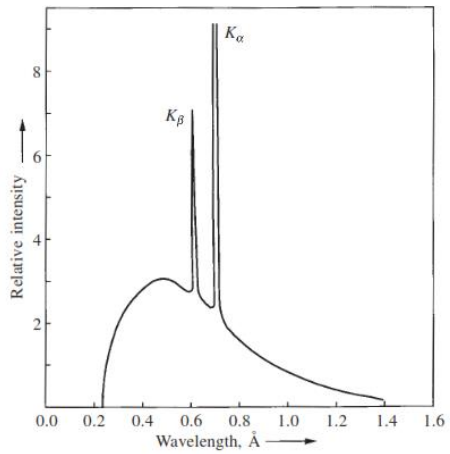
As Eqs. (2) and (3) are identical, the two reflections ill superimpose on each other and cannot be distinguished. By a similar argument, it can be shown that the third order reflection from (100) planes will superimpose on the first order reflection from (300) planes. In view of such superimposition, there is no need to consider the variations in n separately; instead, we take n to be unity for all reflections from parallel sets of planes such as (100), (200), (300), (400), etc. In a crystal, it may turn out, for example, that there is no (200) plane with atoms on it. Then, what is designated as a (200) reflection actually refers to the second order reflection from (100) planes.

In diffraction studies, in order to increase the probability that crystals with the right orientation for Bragg reflection are available, one of the following procedures is adopted:

(i) A monochromatic x-ray beam of a specific wavelength is combined with numerous possible θ values so that reflection occurs at the right combination that satisfies the Bragg law. This is done by placing thousands of crystals of random orientation in the path of the beam. The crystals are usually in powder form.

(ii) A single crystal is held stationary in the path of the beam so that θ is kept constant. A white radiation is then directed at the crystal so that numerous values of the wavelength are available, and again the right combination will lead to the diffraction condition. This method is called the Laue technique.

(iii) A single crystal is held in the beam of a monochromatic radiation and is rotated such that at some position of the crystal, the diffraction condition is satisfied. This method is known as the rotating crystal method. Even though this is not the most widely used method, it provides greater certainty in identification, as well as more accurate measurement of the intensities of the reflected beam.



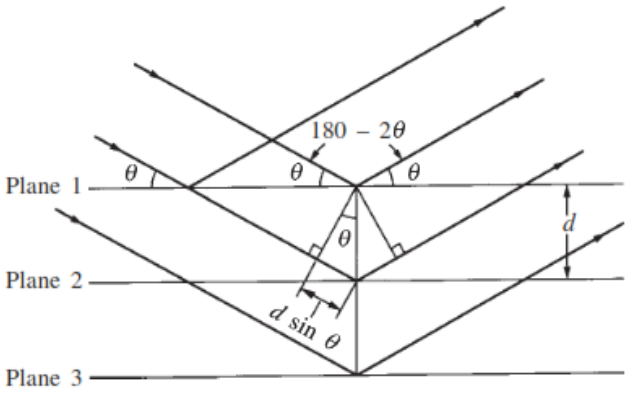


Illustration of the Bragg law.

The spectrum of x-rays emitted from a molybdenum target at 35 kV.

The powder method

The powder method is a widely used experimental technique for the routine determination of crystal structures. It is highly suitable for identification and for determination of the structures of crystals of high symmetry. Here, a monochromatic x-ray beam, usually of K_α radiation, is incident on thousands of randomly oriented crystals in powder form. The powder camera, called the Debye-Scherrer camera, consists of a cylindrical cassette, with a strip of photographic film positioned around the circular periphery of the cassette. The powder specimen is placed at the centre of the cassette in a capillary tube or pasted on a thin wire. The tube, the wire and the paste material must be of some non-diffracting substance such as glass or glue. The x-ray beam enters through a small hole, passes through the powder specimen and the unused part of the beam leaves through a hole at the opposite end. The geometry of the powder method is illustrated in the below figure.

Consider a set of parallel crystal planes making an angle θ with the incident direction. When this angle satisfies the Bragg equation, there is reflection. By virtue of the large number of randomly oriented crystals in the powder, there are a number of possible orientations of this set of planes in space for the same angle θ with the incident direction. So the reflected radiation is not just a pencil beam like the incident one; instead, it lies on the surface of a cone whose apex is at the point of contact of the incident radiation with the specimen. Also, the interplanar spacing d being the same for all members of a family of crystal planes, they all reflect at the same Bragg angle

θ, all reflections from a family lying on the same cone. After taking n = 1 in the Bragg equation, there are still a number of combinations of d and θ that would satisfy the Bragg law. For each combination of d and θ, one cone of reflection must result and, therefore, many cones of reflection are emitted by the powder specimen. If the reflected cones were recorded on a flat film placed normal to the exit beam, they will be in the form of concentric circles. In the powder camera, however, only a part of each reflected cone is recorded by the film strip positioned at the periphery of the cylindrical cassette. The recorded lines from any cone are a pair of arcs that form part of the circle of intersection. When the film strip is taken out of the cassette and spread out, it looks like the figure given below.

Note that the angle between a reflected line lying on the surface of the cone and the exit beam is 2θ. Therefore, the angle included at the apex of the cone is twice this value, 4θ, When the Bragg angle is 45°, the cone opens out into a circle and reflection at this angle will make a straight line intersection with the film strip at the midpoint between the incident and the exit points in the below figure. When the Bragg angle is greater than 45°, back reflection is obtained, that is, the reflected cones are directed towards the incident beam. Bragg angles up to the maximum value of 90° can be recorded by the film of the powder camera, which is not possible on a flat film placed in front of the exit beam. The exposure in a powder camera must be sufficiently long to give reflected lines of good intensity. The exposure time is usually a few hours. After the film is exposed and developed, it is indexed to determine the crystal structure. It is easily seen that the first arc on either side of the exit point corresponds to the smallest angle of reflection. The pairs of arcs beyond this pair have larger Bragg angles and are from planes of smaller spacings, recall that $d = \lambda / (2 \sin \theta)$.

The distance between any two corresponding arcs on the spread out film is termed S, Fig. 4. S is related to the radius of the powder camera R:

$$S = 4R\theta \qquad (4)$$

where θ is the Bragg angle expressed in radians. For easy conversion of the distance S measured in mm to Bragg angle in degrees, the camera radius is often chosen to be 57.3 mm, as 1 rad = 57.3°. In the powder method, the intensity of the reflected beam can also be recorded in a diffractometer, which uses a counter in place of the

film to measure intensities. The counter moves along the periphery of the cylinder and records the reflected intensities against 2θ. Peaks in the diffractometer recording (Fig. 4) correspond to positions where the Bragg condition is satisfied.