

Module 1

Structure of Materials

Introduction

Materials science, also commonly known as materials science and engineering, is an interdisciplinary field which deals with the discovery and design of new materials. This relatively new scientific field involves studying materials through the materials paradigm (synthesis, structure, properties and performance). It incorporates elements of physics and chemistry, and is at the forefront of nano science and nanotechnology research. In recent years, materials science has become more widely known as a specific field of science and engineering.

Importance of Materials

A material is defined as a substance (most often a solid, but other condensed phases can be included) that is intended to be used for certain applications. There are a myriad of materials around us—they can be found in anything from buildings to spacecrafts. Materials can generally be divided into two classes: crystalline and non-crystalline. The traditional examples of materials are metals, ceramics and polymers. New and advanced materials that are being developed include semiconductors, nanomaterials, biomaterials etc.

The material of choice of a given era is often a defining point. Phrases such as Stone Age, Bronze Age, Iron Age, and Steel Age are great examples. Originally deriving from the manufacture of ceramics and its putative derivative metallurgy, materials science is one of the oldest forms of engineering and applied science. Modern materials science evolved directly from metallurgy, which itself evolved from mining and (likely) ceramics and the use of fire. A major breakthrough in the understanding of materials occurred in the late 19th century, when the American scientist Josiah Willard Gibbs demonstrated that the thermodynamic properties related to atomic structure in various phases are related to the physical properties of a material. Important elements of modern materials science are a product of the space race: the understanding and engineering of the metallic alloys, and silica and carbon materials, used in the construction of space vehicles enabling the exploration of space. Materials science has driven, and been driven by, the development of revolutionary technologies such as plastics, semiconductors, and biomaterials.

Before the 1960s (and in some cases decades after), many materials science departments were named metallurgy departments, reflecting the 19th and early 20th century emphasis on metals. The field has since broadened to include every class of materials, including ceramics, polymers, semiconductors, magnetic materials, medical implant materials, biological materials and nanomaterials (materomics).

Historical Perspective

Materials are so important in the development of civilization that we associate ages with them. In the origin of human life on earth, the Stone Age, people used only natural materials like stone, clay, skins, and wood. When people found copper and how to make it harder by alloying, the Bronze Age started about 3000 BC. The use of iron and steel, stronger materials that gave advantage in wars started at about 1200 BC. The next big step was the discovery of a cheap process to make steel around 1850, which enabled the railroads and the building of the modern infrastructure of the industrial world.

Why Study Materials Science?

- To be able to select a material for a given use based on considerations of cost and performance.
- To understand the limits of materials and the change of their properties with use.
- To be able to create a new material that will have some desirable properties.

All engineering disciplines need to know about materials. Even the most immaterial like software or system engineering depend on the development of new materials, which in turn alter the economics, like software-hardware trade-offs. Increasing applications of system engineering are in materials manufacturing (industrial engineering) and complex environmental systems.

Classification of Materials

Like many other things, materials are classified in groups, so that our brain can handle the complexity. One could classify them according to structure, or properties, or use. The one that we will use is according to the way the atoms are bound together:

Metals: The valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the ions together. Metals are usually strong, conduct electricity and heat well and are opaque to light (shiny if polished). Examples: aluminum, steel, brass, gold.

Semiconductors: The bonding is covalent (electrons are shared between atoms). Their electrical properties depend extremely strongly on minute proportions of contaminants. They are opaque to visible light but transparent to the infrared. Examples: Si, Ge, GaAs.

Ceramics: Atoms behave mostly like either positive or negative ions, and are bound by Coulomb forces between them. They are usually combinations of metals or semiconductors with oxygen, nitrogen or carbon (oxides, nitrides, and carbides). Examples: glass, porcelain, many minerals.

Polymers: are bound by covalent forces and also by weak van der Waals forces, and usually based on H, C and other non-metallic elements. They decompose at moderate temperatures (100–400 °C), and are lightweight. Other properties vary greatly. Examples: plastics (nylon, teflon, polyester) and rubber. Other categories are not based on bonding. A particular microstructure identifies

Composites: Composites made of different materials in intimate contact (example: fiberglass, concrete, wood) to achieve specific properties. **Biomaterials** can be any type of material that is biocompatible and used, for instance, to replace human body parts.

Advanced Materials

Materials used in "High-Tec" applications, usually designed for maximum performance, and normally expensive. Examples are titanium alloys for supersonic airplanes, magnetic alloys for computer disks, special ceramics for the heat shield of the space shuttle, etc.

Modern Material's Needs

- Engine efficiency increases at high temperatures: requires high temperature withstanding materials
- Use of nuclear energy requires solving problem with residues, or advances in nuclear waste processing.
- Hypersonic flight requires materials that are light, strong and resist high temperatures.
- Optical communications require optical fibers that absorb light negligibly.
- Civil construction – materials for unbreakable windows.
- Structures: materials that are strong like metals and resist corrosion like plastics.

Atomic Structure

Atoms are composed of electrons, protons, and neutrons. Electrons and protons are negative and positive charged particles respectively. The magnitude of each charged particle in an atom is 1.6×10^{-19} Coulombs.

The mass of the electron is negligible with respect to those of the proton and the neutron, which form the *nucleus* of the atom. The unit of mass is an atomic mass unit (*amu*) = 1.66×10^{-27} kg, and equals 1/12 the mass of a carbon atom. The Carbon nucleus has $Z=6$, and $A=6$, where Z is the number of protons, and A the number of neutrons. Neutrons and protons have very similar masses, roughly equal to 1 *amu* each. A neutral atom has the same number of electrons and protons, Z .

A *mol* is the amount of matter that has a mass in grams equal to the atomic mass in *amu* of the atoms. Thus, a mole of carbon has a mass of 12 *grams*. The number of atoms in a mole is called the Avogadro number, $N_{av} = 6.023 \times 10^{23}$. Note that $N_{av} = 1 \text{ gram}/1 \text{ amu}$.

Calculating n , the number of atoms per cm^3 of a material of density $\delta(\text{g}/\text{cm}^3)$:

$$n = N_{av} \frac{\delta}{M}$$

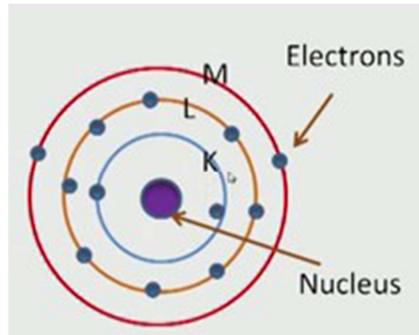
where M is the atomic mass in *amu* (*grams per mol*). Thus, for graphite (carbon) with a density $\delta = 1.8 \text{ g}/\text{cm}^3$, $M = 12$, we get $6 \times 10^{23} \text{ atoms/mol} \times 1.8 \text{ g}/\text{cm}^3 / 12 \text{ g/mol} = 9 \times 10^{22} \text{ C atoms}/\text{cm}^3$.

For a molecular solid like ice, one uses the molecular mass, $M_{(\text{H}_2\text{O})} = 18$. With a density of 1 g/cm^3 , one obtains $n = 3.3 \times 10^{22} \text{ H}_2\text{O molecules}/\text{cm}^3$. Note that since the water molecule contains 3 atoms, this is equivalent to $9.9 \times 10^{22} \text{ atoms}/\text{cm}^3$.

Most solids have atomic densities around $6 \times 10^{22} \text{ atoms}/\text{cm}^3$. The cube root of that number gives the number of atoms per centimeter, about 39 million. The mean distance between atoms is the inverse of that, or 0.25 nm. This is an important number that gives the scale of atomic structures in solids.

Atomic Models

Bohr's Atomic Model



Schematic representation of the Bohr atom.

In the year 1913, Niels Bohr proposed an atomic structure model, describing an atom as a small, positively charged nucleus surrounded by electrons that travel in circular orbits around the positively charged nucleus like planets around the sun in our solar system, with attraction provided by electrostatic forces, popularly known as Bohr's atomic model. It was basically an improved version of Rutherford's atomic model overcoming its limitations.

Silent features of Bohr atomic model:

- Electrons revolve around the nucleus in stable orbits without emission of radiant energy. Each orbit has a definite energy and is called an energy shell or energy level.
- An orbit or energy level is designated as K, L, M, N shells. When the electron is in the lowest energy level, it is said to be in the ground state.
- An electron emits or absorbs energy when it jumps from one orbit or energy level to another. When it jumps from a higher energy level to lower energy level it emits energy while it absorbs energy when it jumps from a lower energy level to a higher energy level.
- The energy absorbed or emitted is equal to the difference between the energies of the two energy levels (E_1, E_2) and is determined by Plank's equation.

$$\Delta E = E_2 - E_1 = hv$$

Where,

ΔE = energy absorbed or emitted

h = Plank's constant

v = frequency of electromagnetic radiation emitted or absorbed

- The angular momentum of an electron revolving in energy shells is given by:

$$m_e v r = nh/2\pi$$

Where,

n = number of corresponding energy shell; 1, 2, 3

m_e = mass of the electron

v = velocity

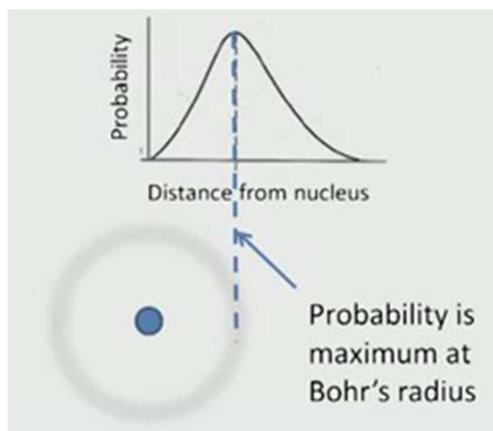
r =radius

h = Plank's constant

Limitations of Bohr Atomic Model Theory

- It violates the Heisenberg Uncertainty Principle. The Bohr atomic model theory considers electrons to have both a known radius and orbit i.e. known position and momentum at the same time, which is impossible according to Heisenberg.
- The Bohr atomic model theory made correct predictions for smaller sized atoms like hydrogen, but poor spectral predictions are obtained when larger atoms are considered.
- It failed to explain the Zeeman effect when the spectral line is split into several components in the presence of a magnetic field.
- It failed to explain the Stark effect when the spectral line gets split up into fine lines in the presence of an electric field.

Wave-mechanical model



Wave-mechanical model

In wave-mechanical model the electron is considered to exhibit both wave like and particle like characteristics. With this model, an electron is no longer treated as a particle moving in

a discrete orbital; rather, position is considered to be the probability of an electron being at various locations around the nucleus. In other words, position is described by a probability distribution or electron cloud. An atomic orbital may be defined as the three dimensional space around the nucleus within which the probability of finding an electron of given energy is maximum. So, wherever the probability is more you will have more chances of finding electron there. And actually it coincides with whatever the radius was predicted by Bohr model.

Bonding forces and energies

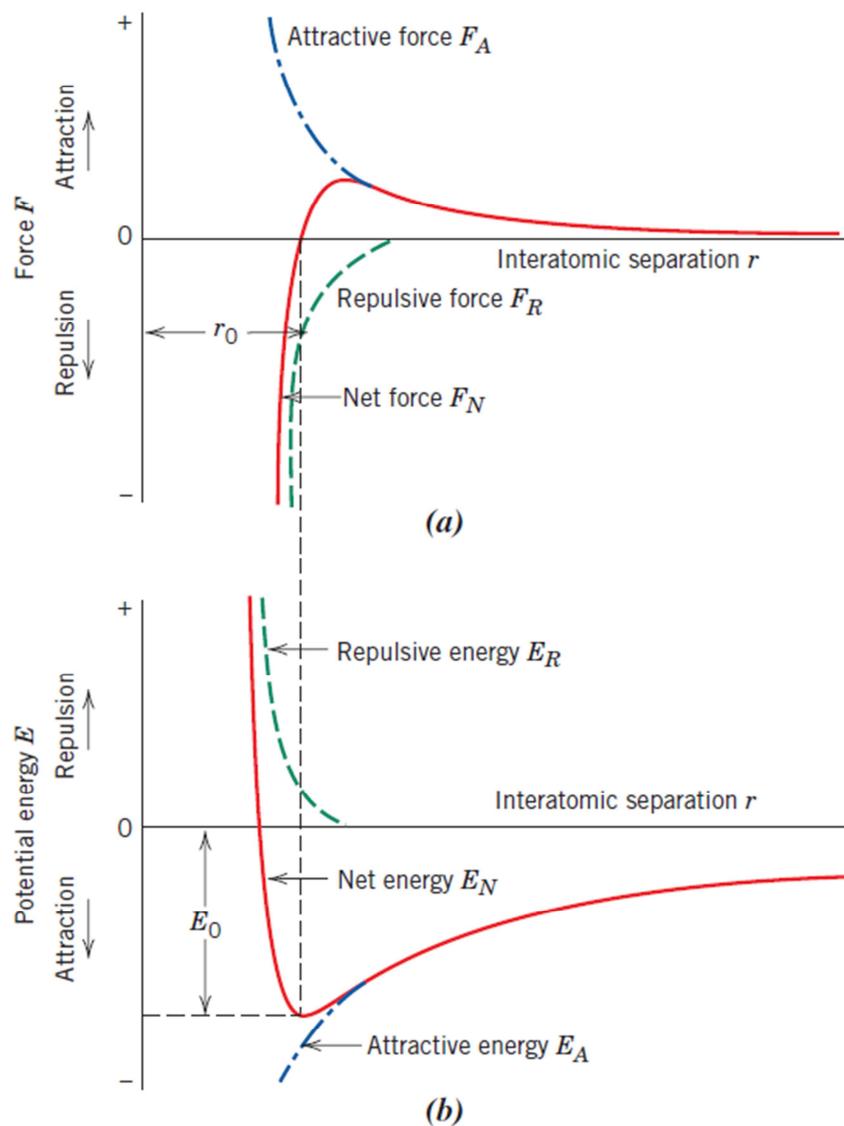


Figure (a) The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms. **(b)** The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms.

An understanding of many of the physical properties of materials is enhanced by knowledge of the interatomic forces that bind the atoms together. Perhaps the principles of atomic bonding are best illustrated by considering how two isolated atoms interact as they are brought close together from an infinite separation. At large distances, interactions are negligible because the atoms are too far apart to have an influence on each other; however, at small separation distances, each atom exerts forces on the others. These forces are of two types, attractive (F_A) and repulsive (F_R), and the magnitude of each depends on the separation or interatomic distance (r); Figure (a) is a schematic plot of F_A and F_R versus r . The origin of an attractive force F_A depends on the particular type of bonding that exists between the two atoms, as discussed shortly. Repulsive forces arise from interactions between the negatively charged electron clouds for the two atoms and are important only at small values of r as the outer electron shells of the two atoms begin to overlap (Figure a). The net force F_N between the two atoms is just the sum of both attractive and repulsive components; that is,

$$F_N = F_A + F_R \dots\dots\dots(1)$$

which is also a function of the interatomic separation, as also plotted in Figure (a). When F_A and F_R are equal in magnitude but opposite in sign, there is no net force—that is,

$$F_A + F_R = 0 \dots\dots\dots(2)$$

and a state of equilibrium exists. The centers of the two atoms remain separated by the equilibrium spacing r_0 , as indicated in Figure 2.10a. For many atoms, r_0 is approximately 0.3 nm. Once in this position, any attempt to move the two atoms farther apart is counteracted by the attractive force, while pushing them closer together is resisted by the increasing repulsive force.

Sometimes it is more convenient to work with the potential energies between two atoms instead of forces. Mathematically, energy (E) and force (F) are related as

$$E = \int F dr \dots\dots\dots(3)$$

And, for atomic systems

$$\begin{aligned} E_N &= \int_r^\infty F_N dr \\ &= \int_r^\infty F_A dr + \int_r^\infty F_R dr \\ &= E_A + E_R \end{aligned} \dots\dots\dots(4)$$

in which E_N , E_A , and E_R are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms.

Figure (b) plots attractive, repulsive, and net potential energies as a function of interatomic separation for two atoms. From Equation 4, the net curve is the sum of the attractive and repulsive curves. The minimum in the net energy curve corresponds to the equilibrium spacing, r_0 . Furthermore, the **bonding energy** for these two atoms, E_0 , corresponds to the energy at this minimum point (also shown in Figure b); it represents the energy required to separate these two atoms to an infinite separation.

Although the preceding treatment deals with an ideal situation involving only two atoms, a similar yet more complex condition exists for solid materials because force and energy interactions among atoms must be considered. Nevertheless, a bonding energy, analogous to E_0 above, may be associated with each atom. The magnitude of this bonding energy and the shape of the energy–versus–interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding. Furthermore, a number of material properties depend on E_0 , the curve shape, and bonding type

Force in Equation 3 may also be expressed as

$$\begin{aligned} F &= dE/dr \\ F_N &= F_A + F_R \\ &= \frac{dE_A}{dr} + \frac{dE_R}{dr} \end{aligned}$$

Chemical bonding

The nature of chemical bonds is classified as primary and secondary bonds based on bond strength and directionality. The interatomic bonds are known as primary bonds, whereas the intermolecular bonds are known as secondary bonds. The attractive forces in primary bonds are directly associated with the valence electrons. The electrons in the outermost orbit are in a state of high energy and are relatively unstable. The primary bonds are formed by borrowing, lending or sharing the valence electrons. Secondary bonds are significantly weaker than primary bonds.

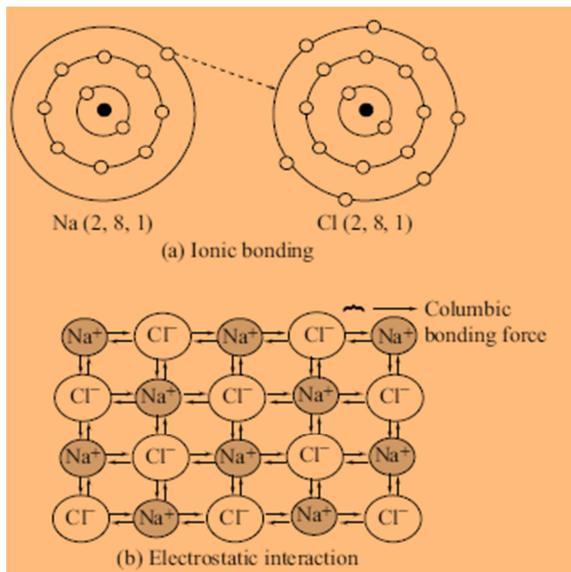
Primary Bonds

The primary bonds are further classified into three types namely, ionic, covalent and metallic. The ionic bonds are formed between a metal and a nonmetal (e.g., NaCl). The bond which is formed between nonmetals, i.e., molecules (e.g., CO₂) is known as covalent

bond. Similarly, the metallic bonds are formed between the atoms of metallic elements (e.g., bronzes). In addition, there are also bonds which are not pure ionic, covalent, etc., but have some partial character of different bonds and are known as mixed bonds. The primary bonds are stronger in nature with higher energy in the range from 1 to 5 eV.

i. Ionic Bonding

An ionic bond or electrovalent bond is a type of chemical bond which is formed between atoms of any two different types of ions i.e., very often between the metal and nonmetal ions through electrostatic interactions. In short, it is a bond formed by the attraction between the electro-positive metal and electronegative metal. The transfer of electrons from one atom to the other atom results in stable outer shells. The attractive bonding forces are columbic, i.e., positive and negative ions by virtue of their net electrical charge. The number of positive and negative charges is equal in ionic bonded materials. This type of bond is mainly formed in inorganic compounds like NaCl, KOH, MgO, MgCl₂, etc.



Ionic bonding - Sodium Chloride (NaCl)

In case of NaCl, there are more electrons around Cl forming Cl⁻ and fewer electrons around Na forming Na⁺. The transfer of one valence electron from its outermost shell of sodium atom to the chlorine atom which has seven electrons in the outermost shell results in the formation of stable electronic configuration (Fig. (a)). After the exchange of valence electrons, all sodium atoms exist as positive ions and chlorine atoms exist as negative ions. The ionic bond formation in NaCl is illustrated schematically in above Figure. The energy required to remove an electron from a metal atom like sodium is known as energy of

ionisation. The energy required for sodium is 5.1 eV per atom. Similarly, the electron affinity of chlorine is 3.8 eV per atom.

ii. Covalent Bonding

Covalent chemical bonding is formed between the two atoms by sharing a pair of valence electrons between like atoms rather than electron transfer. Therefore, it is known as homopolar or homonuclear bonding. Generally, covalent bonds are existing in all organic compounds and semiconductors. Let us consider some examples of molecules with the existence of covalent bonding. Hydrogen gas forms the simplest covalent bond in the diatomic hydrogen molecule.

In H_2 molecule, hydrogen atomic number is 1 and it has its one electron in 1s shell. The hydrogen atom is more stable if there are two electrons in 1s shell. When two hydrogen atoms come very close to each other, their 1s shells overlap, to form a molecule by sharing their valence electron as shown in below Fig.

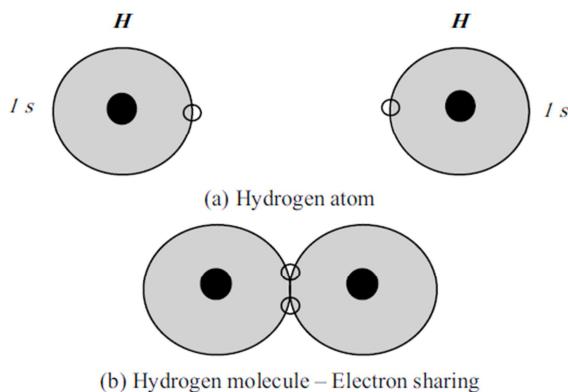


Fig. Covalent bond - Hydrogen molecule

iii. Metallic Bonding

Metallic bond is existing both in metals and their alloys. In metals, the metal atoms lose their outer electrons to form metal cations. The electrons from all the metal atoms form an electron sea or cloud which can flow throughout the space occupied by the atoms. These electrons are often described as delocalised electrons. Metallic bonding is different from both ionic and covalent bonding. The metal cations and electrons are oppositely charged, and hence, they are attracted by each other. The electrostatic forces are called metallic bonds. When the variable number of electrons is shared by variable number of atoms, the formation of metallic bond takes place. The nucleus of the crystals constitutes the ion core, while the electrons produce a space charge around the ion as shown in below Figure.

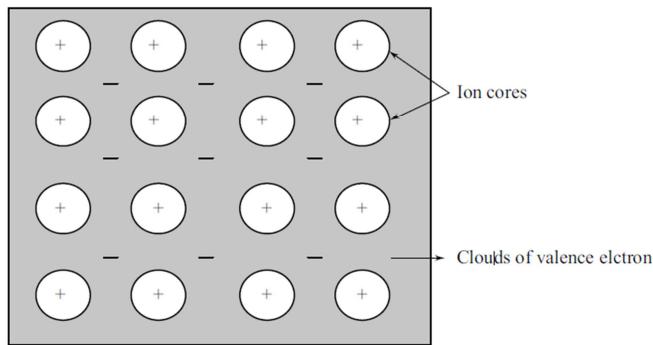


Fig. Metallic bonding - illustration

Secondary Bonds

Secondary bonds are much weaker than primary bonds. Secondary bonds exist virtually between all atoms or molecules, but its presence may be reduced if any of the three primary bonding types are present. They often provide a weak link for deformation or fracture. The interatomic distance is larger i.e., $2 - 5 \text{ \AA}$ and hence, the strength of secondary bonds is in the range of $0.02 - 0.5 \text{ eV}$. Examples of secondary bonds are Hydrogen and Van der Waals bond.

i. Hydrogen Bonding

Hydrogen bond is formed when a charged part of a molecule having polar covalent bonds forms an electrostatic interaction with a substance of opposite charge. Molecules which are having non – polar covalent bonds do not form hydrogen bonds. Hydrogen bonds are common in covalently bonded molecules which contain hydrogen, such as water (H_2O). It is primarily a covalent bond, the electrons are shared between the hydrogen and oxygen atoms. However, the electrons tend to spend more time around the oxygen atom. This leads to a small positive charge around the hydrogen atoms, and a negative charge around the oxygen atom. Below Figure shows the schematic illustration of hydrogen bonding.

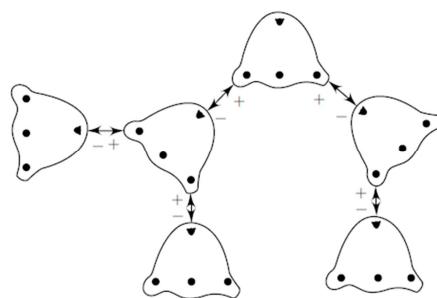


Fig. Hydrogen bonding - Water

ii. Van der Waals Bond

The dipole bond is known as secondary bond. The energy of the dipole bonds is very less than any other bonds. Consider two atoms of an inert gas having completed electronic shells. When the atoms are at neutral, the positive and negative charge centers are exactly at the same location as shown in below Fig. (a). When the two atoms are brought closer together, a displacement of positive and negative charge centers takes place relatively. Then, the positive and negative charges are separated as shown in below Fig. (b). As a result, it creates an electric dipole and hence, results in fluctuating dipole mode. The fluctuating dipole bonds are known as Van der Waals bonds.

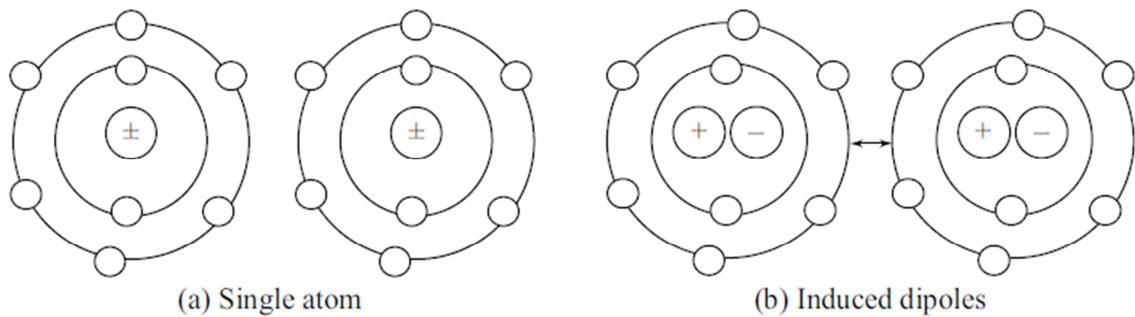


Fig. Bonds – induced dipole

The applied electric field causes an induced dipole moment between the neighbouring atoms. The fluctuating dipole moment and induced dipole moment interacts to form a weak bond.

Comparison of Various Types of Bonds

<i>Sr. No.</i>	<i>Properties</i>	<i>Ionic Bonds</i>	<i>Covalent Bonds</i>	<i>Metallic Bonds</i>	<i>Van der Waals Bond</i>
1.	Bonding force	Electrostatic force between positive and negative ions	Mutual sharing of valence electrons between atoms	Electrostatic force between negative electron cloud and positive ions	Electrostatic force due to oscillating dipoles
2.	Character of bond	Nondirectional	Directional	Nondirectional	Directional for dipole and hydrogen bonds. Nondirectional for dispersion bonds
3.	Bond formation condition	One of the atoms has small number of valence electrons	Atomic orbitals of two atoms overlap	For elements having small number of valence electrons	Molecules forming dipoles
4.	Bond energy	150 – 370 kcal/mol	125 – 300 kcal/mol	25 – 200 kcal/mol	<10 kcal/mol
5.	Conductivity	Low	Low	Good	Low
6.	Hardness	High	Less	High	Poor
7.	Density	Intermediate	Intermediate	High	Low
8.	Melting point	Intermediate	High (if any)	High	Low
9.	Examples	NaCl, MgO, etc.	Si, C, etc.	Al, Fe, Na, etc.	H ₂ O, Cl ₂ , etc.

Classification of solids

The solids are classified into two types crystalline and amorphous. A substance is said to be crystalline, when the arrangement of atoms, molecules or ions inside it is regular and periodic. Ex. NaCl, Quartz crystal. Though two crystals of same substance may look different in external appearance, the angles between the corresponding faces are always the same. In amorphous solids, there is no particular order in the arrangement of their constituent particles. Ex. Glass.

CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS
1. Crystalline solids have regular periodic Arrangement of particles (atoms, ions, Or molecules).	1. Amorphous solids have no regularity in the arrangement of particles.
2. They are un-isotropic i.e., they differ in Properties with direction.	2. They are usually isotropic i.e., They possess same properties in different directions
3. They have well defined melting and Freezing points. Melting and freezing points occurs at different temperatures at different locations in the solids.	3. They do not posses well defined melting and freezing points.
4. Crystalline solids may be made up of materials are metallic crystals or non-metallic crystals. Some of the metallic crystals are Copper, silver, aluminum, tungsten, and manganese. Non-metallic crystals are crystalline carbon, crystallized polymers or plastics.	4. Most important amorphous glasses, plastics and rubber.
5. Metallic crystals have wide use in engineering because of their favorable Properties of strength, ductility, conductivity and reflection.	5. An amorphous structure does not generally posses elasticity but only plasticity.

FUNDAMENTAL TERMS OF CRYSTALLOGRAPHY

Lattice points: They are the imaginary points in space about which the atoms are located.

Lattice: The regular repetition of atomic, ionic or molecular units in 2-dimensional, 3-dimensional space is called lattice.

The term lattice can be defined in another way. In an arrangement of points, if the surrounding environment looks the same when the arrangement is viewed from different lattice points, then that arrangement is said to be a lattice.

Basis

To construct a crystal structure, some basic arrangement is to be fixed at each and every lattice point. This basic arrangement is said to be a **basis**. Consider below Fig. (a) and (b). To obtain the structure shown in below Fig. (c), the arrangement shown in Fig. (b) is to be fixed in each and every lattice point. So, the arrangement shown in blow Fig. (b) is said to be a basis.

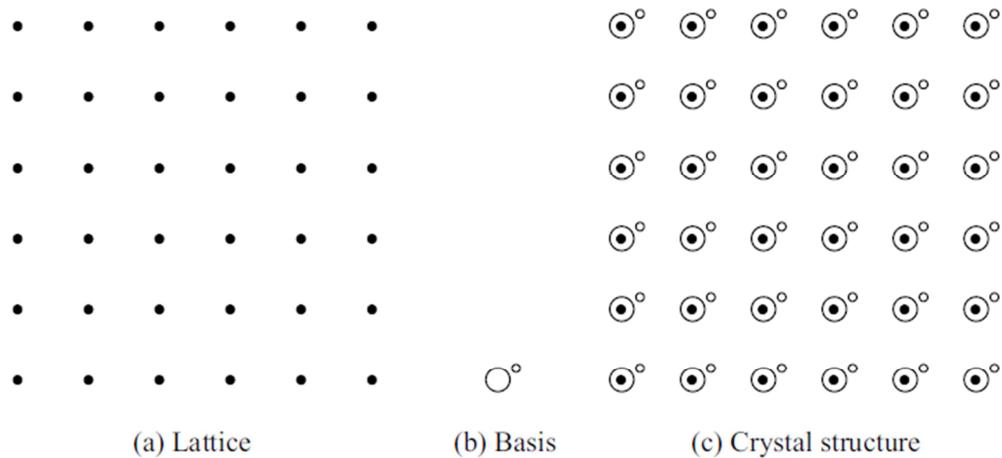


Fig. Arrangement of basis and lattice point

Crystal Structure

A crystal structure is obtained by arranging the basis in each and every lattice point. It can be written as,

Crystal structure = lattice + basis

A crystal structure is formed by arranging the basis in each and every lattice point.

Unit cell and Lattice parameters:

Unit cell is the smallest portion of the space lattice which can generate the complete crystal by repeating its own dimensions in various directions. In describing the crystal structure, it is convenient to subdivide the structure into small repetitive entities called unit cells. Unit cell is the parallelepiped or cubes having 3 sets of parallel faces. It is the basic structural unit or the building block of the crystal.

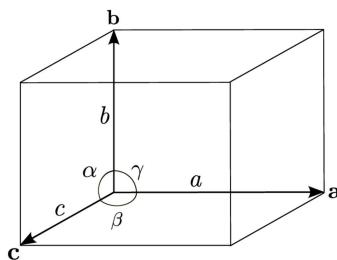


Fig. A A unit cell with lattice parameters a , b and c . a , b and c are the unit cell vector magnitudes. α is the angle between b and c , β is the angle between c and a and γ is the angle between a and b .

A unit cell can be described by 3 vectors or intercepts \mathbf{a} , \mathbf{b} , \mathbf{c} , the lengths of the vectors and the interfacial angles α , β , γ between them. If the values of these intercepts and interfacial angles are known, then the form and actual size of the unit cell can be determined. They may or may not be equal. Based on these conditions, there are 7 different crystal systems.

Primitive Cell: A unit cell having only one lattice point at the corners is called the primitive cell. The unit cell differs from the primitive cell in that it is not restricted to being the equivalent of one lattice point. In some cases, the two coincide. Thus, unit cells may be primitive cells, but all the primitive cells need not be unit cells.

CRYSTAL SYSTEMS AND BRAVAIS LATTICES:

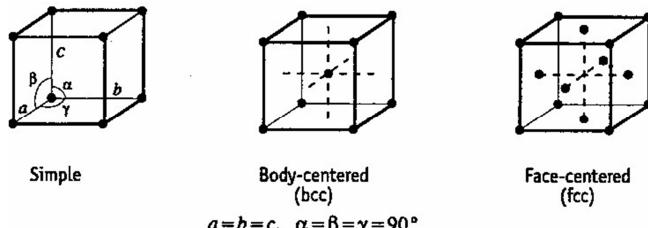
There are 7 basic crystal systems which are distinguished based on three vectors or the intercepts and the 3 interfacial angles between the 3 axes of the crystal. They are

1. Cubic
2. Tetragonal
3. Orthorhombic
4. Monoclinic
5. Triclinic
6. Trigonal (Rhombohedral)
7. Hexagonal

More space lattices can be constructed by atoms at the body centres of unit cells or at the centres of the faces. Based on this property, bravais classified the space lattices into 14.

1. Cubic crystal system

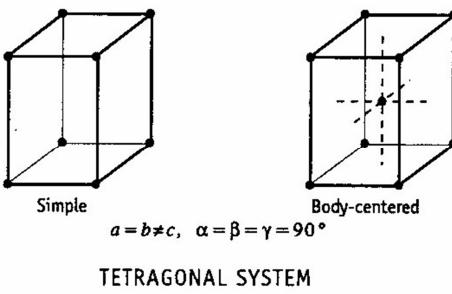
$$a = b = c, \alpha = \beta = \gamma = 90^\circ$$



The crystal axes are perpendicular to one another, and the repetitive interval in the same along all the three axes. Cubic lattices may be simple, body centered or face-centered.

2. Tetragonal crystal system

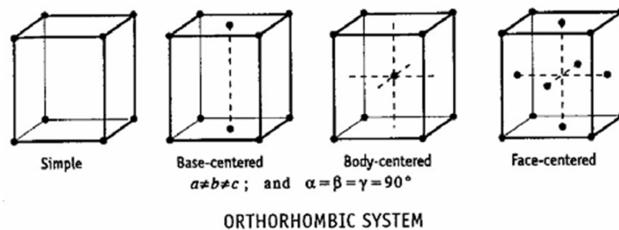
$$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$$



The crystal axes are perpendicular to one another. The repetitive intervals along the two axes are the same, but the interval along the third axes is different. Tetragonal lattices may be simple or body-centered.

3. Orthorhombic crystal system.

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

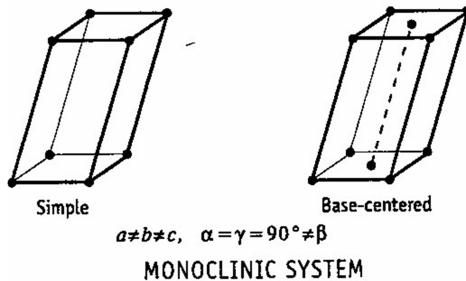


The crystal axes are perpendicular to one another but the repetitive intervals are different

along the three axes. Orthorhombic lattices may be simple, base centered, body centered or face centered.

4. Monoclinic crystal system

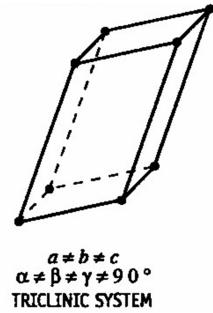
$$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$$



Two of the crystal axes are perpendicular to each other, but the third is obliquely inclined. The repetitive intervals are different along all the three axes. Monoclinic lattices may be simple or base centered.

5. Triclinic crystal system

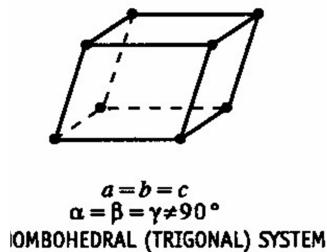
$$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$$



None of the crystal axes is perpendicular to any of the others, and the repetitive intervals are different along the three axes.

6. Trigonal(rhombohedral) crystal system

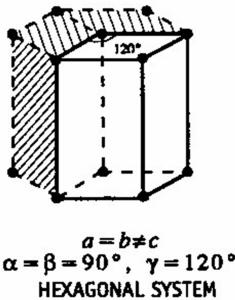
$$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$$



The three axes are equal in length and are equally inclined to each other at an angle other than 90° .

7. Hexagonal crystal system.

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



Two of the crystal axes are 60° apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60° apart, but the interval along the third axis is different.

Table. The Seven Crystal Systems (Primitive (P), Body centred (I), Face centred (F) and base centred (C))

Sr. No.	Name of the system	Relation between primitives and angles	Lattice symbols	No. of possible lattices	Examples
1.	Cubic	$a = b = c,$ $\alpha = \beta = \gamma = 90^\circ$	P I F	3	Po Na, W, α - Fe Ag, Au, Pb
2.	Tetragonal	$a = b \neq c,$ $\alpha = \beta = \gamma = 90^\circ$	P I	2	TiO ₂ , SnO ₂ KH ₂ PO ₄
3.	Orthorhombic	$a \neq b \neq c,$ $\alpha = \beta = \gamma = 90^\circ$	P I F C	4	— PbCO ₃ , BaSO ₄ KNO ₃ , K ₂ SO ₄ α - S
4.	Monoclinic	$a \neq b \neq c,$ $\alpha = \beta = 90^\circ \neq \gamma$	P C	2	CaSO ₄ .2H ₂ O K ₂ MgSO ₄ .6H ₂ O
5.	Triclinic	$a \neq b \neq c,$ $\alpha \neq \beta \neq 90^\circ \neq \gamma$	P	1	K ₂ Cr ₂ O ₇
6.	Trigonal	$a = b = c,$ $\alpha = \beta = \gamma \neq 90^\circ$ (but less than 120°)	P	1	Calcite, As, Sb, Bi
7.	Hexagonal	$a = b \neq c,$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	P	1	SiO ₂ , AgI

Miller Indices

Miller devised a method to represent a crystal plane or direction. In this method, to represent a crystal plane, a set of three numbers are written within the parentheses. Similarly, crystal direction is represented as a set of three numbers written within the square brackets. Miller index is one in which the crystal plane is represented within the parenthesis.

Rules to Find the Miller Indices of a Plane

To find the Miller indices for a given plane, the following steps are to be followed:

- a. The intercepts made by the plane along X, Y and Z axes are noted.
- b. The coefficients of the intercepts are noted separately.
- c. Inverse is to be taken.
- d. The fractions are multiplied by a suitable number so that all the fractions become integers.
- e. Write the integers within the parentheses.

For example, Miller indices of the plane shown in below Fig. can be found by the following method:

- (i) The given plane ABC makes intercepts $2a$, $3b$ and $2c$ along the X, Y and Z axes, respectively. Hence, the intercepts are $2a$, $3b$ and $2c$.
- (ii) The coefficients of the intercepts are 2, 3 and 2. The inverse are $1/2$, $1/3$, $1/2$.
- (iv) The LCM is 6. Multiply the fractions by 6, so that they become integers as 3, 2, 3.
- (v) The integers are written within the parenthesis as (323). (323) represents the Miller indices of the given plane ABC

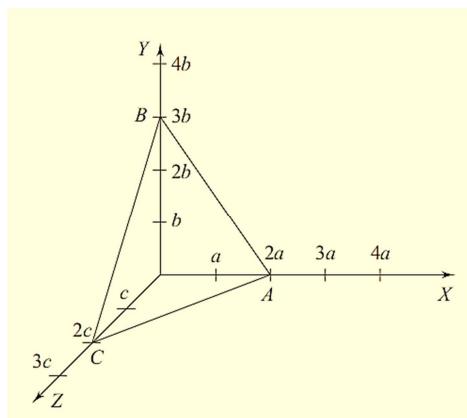


Fig. Miller indices of a plane

The relation between the interplanar distance and the interatomic distance is given by

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

Basic Crystal Structures:

The important fundamental quantities which are used to study the different arrangements of atoms to form different structure are

- (1) **Atomic Radius (r)** It is half the distance between any two successive atoms. For a simple cubic unit cell, the atomic radius

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

where a is the interatomic distance.

- (2) **Coordination Number** It is the number of nearest neighbouring atoms to a particular atom. For a simple cubic unit cell, the coordination number is 6.

- (3) **Packing Density** It is the ratio between the total volume occupied by the atoms or molecules in a unit cell and the volume of unit cell.

i.e.,

$$\begin{aligned} \text{Density of packing} &= \frac{\text{Total volume occupied by atoms in a unit cell}}{\text{Volume of the unit cell}} \\ &= \frac{\text{Number of atoms present in a unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}} \end{aligned}$$

Simple cubic (SC) cell

A unit cell is said to be primitive when the cell has lattice points only at its corners. The primitive cubic unit cell is also called a simple cubic (SC) unit cell. Below Fig. shows a SC cell.

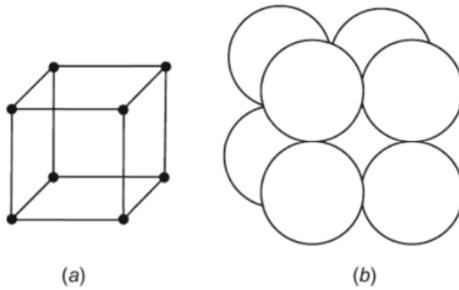


Fig. Simple cubic cell (a) atomic site model (b) hard sphere model

- (i) **Unit cell volume, V :** In case of cubic cell all the edges of the cube are of equal length, ' a '. Therefore, the volume is given by

$$V = a^3$$

(ii) Effective number of atoms per unit cell, Z: A unit cell is a part of an infinite scheme, and is not an isolated entity. Therefore, several adjacent cells share each lattice point. As a result, the basis attached to a lattice site contributes only a fraction of its mass and volume to one unit cell. Let only one atom, having a radius R , be attached to one lattice point. The effective number of atoms per unit cell is given by

$$Z = Z_B + \frac{Z_F}{2} + \frac{Z_C}{8}$$

where Z_B = Number of body centered atoms, Z_F = Number of face centered atoms and Z_C = Number of corner atoms.

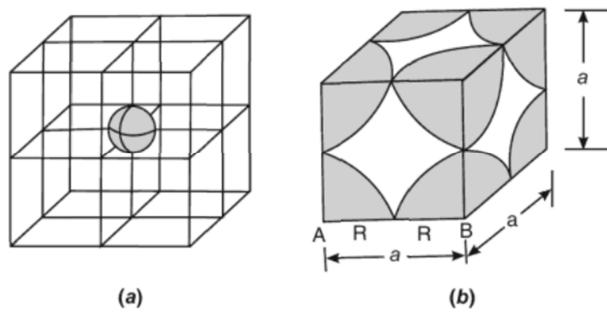


Fig. (a) An atom contributes one eighth to a unit cell when it is located at the corner of the cell. (b) Isolated SC cell

In the three-dimensional array, each corner atom is linked to eight surrounding cells, as shown in above Fig. (a). Hence, in effect, the atom contributes 1/8th of its content to a unit cell, as shown in above Fig. (b). SC cell being a primitive cell does not contain lattice points within the body volume or in the centre of faces. Therefore, the total contribution to Z comes from the corner atoms of the unit cell and it is given by

$$Z = Z_B + \frac{Z_F}{2} + \frac{Z_C}{8} = 0 + 0 + \frac{8}{8} = 0 + 0 + 1 \text{ atom / cell}$$

$$Z = 1 \text{ atom / cell}$$

(iii) Coordination Number, CN: The coordination number of an atom in a crystal is the number of nearest neighbour atoms. It signifies the tightness of packing of atoms in the crystal. Around an atom in a SC cell, there would be six equally spaced nearest neighbour atoms each at a distance 'a' from that atom, as shown in below Fig. Four atoms lie in the plane of the atom while one is vertically above it and one vertically below. Therefore, the coordination number $CN = 6$.

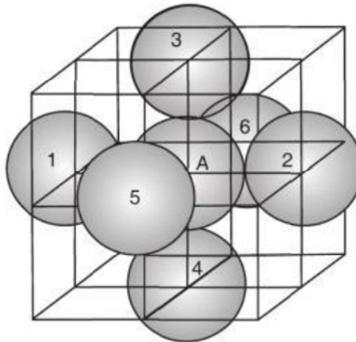


Fig. Determination of nearest neighbours. There are six close neighbours for any selected atom in a SC cell.

(iv) Atomic radius, R: The relationship between the apparent size of the atom and the edge of the unit cell can be determined where one atom is attached to a lattice site. The specific direction along which atoms are in contact is identified and by applying simple geometry, the relation between the atomic size and the unit cell edge can be computed. In a SC cell the atoms would be in contact along the edges of the cube. If 'a' is the edge of the cubic cell and R is the radius of the atom.

$$a = 2R \text{ or } R = a/2$$

(v) Packing Fraction, APF: The fraction of space occupied by atoms in a unit cell is known as atomic packing fraction. It is defined as the ratio of volume of effective number of atoms in the unit cell to the total volume of the unit cell. Thus,

$$\text{APF} = \frac{\text{Number of atoms/unit cell}}{\text{Volume of each atom}} \times \frac{\text{Volume of the unit cell}}{\text{Volume of the unit cell}}$$

$$\text{APF} = Z v / V$$

In case of SC cell, $Z = 1$

$$\text{Volume of unit cell, } V = a^3 = (2R)^3 = 8R^3.$$

$$\text{Packing density} = \frac{1 \times (4/3) \times \pi r^3}{a^3}$$

Substituting the value $r = a/2$

$$\therefore \text{Packing density} = \frac{1 \times (4/3) \times \pi (a/2)^3}{a^3}$$

$$\text{Therefore, packing density} = \frac{\pi}{6} = 0.52.$$

(vi) Percentage void space: The void space in the unit cell is the vacant space left unutilised in the cell. It is often expressed as percentage.

$$\% \text{ void space} = (1 - \text{APF}) \times 100 = (1 - 0.52) \times 100 = 48\%$$

Body centered cube structure (BCC):

BCC structure has one atom at the centre of the cube and one atom at each corner. The centre atom touches all the 8 corner atoms.

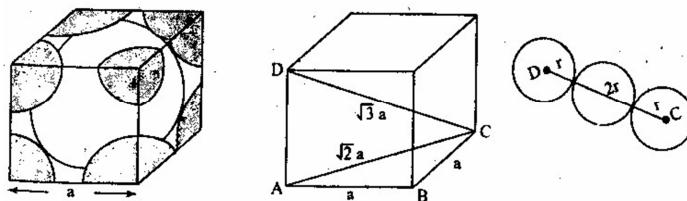


Fig. Body Centered Cubic Structure

$$\text{Diagonal length} = 4r$$

$$\text{Body diagonal} = (\sqrt{3})a$$

$$\text{i.e. } 4r = (\sqrt{3})a$$

$$\text{Nearest neighbouring distance} = 2r = (\sqrt{3})a / 2$$

$$\text{Atomic radius} = r = (\sqrt{3})a / 4$$

$$\text{Lattice constant} = a = 4r / \sqrt{3}$$

Coordination number = 8 (since the central atom touches all the corner 8 atoms)

Effective number of atoms belonging to the unit cell or no. of atoms per unit cell = $(1/8) \times 8 + 1 = 2$ atom per unit cell.

i.e. each corner atom contributes $1/8$ th to the unit cell. In addition to it, there is a centre atom.

$$\text{Atomic packing factor} = v/V = \frac{\text{volume of the all atoms in the unit cell}}{\text{volume of the unit cell.}}$$

$$\begin{aligned} &= 2 \times (4/3) \prod r^3 / a^3 = 8 \prod r^3 / 3(4r/\sqrt{3})^3 \\ &= \sqrt{3} / 8 = 0.68 = 68\% \end{aligned}$$

Tungsten, Na, Fe and Cr exhibits this type of structure.

Face centered cubic (FCC) structure:

In FCC structure, there is one lattice point at each of the 8 corners of the unit cell and 1 centre atom on each of the 6 faces of the cube.

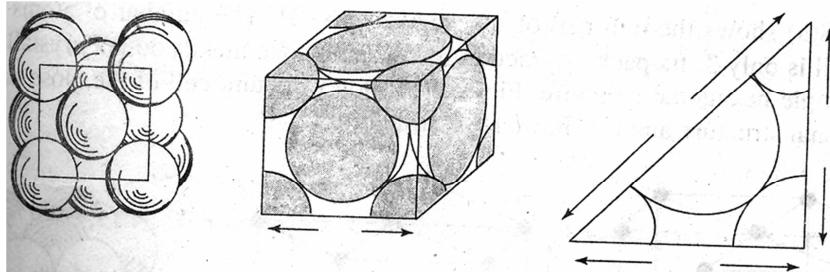


Fig. Face Centered Cubic Structure

$$\text{Face diagonal length} = 4r = (\sqrt{2})a$$

$$\text{Nearest neighbouring distance} = 2r = (\sqrt{2})a / 2 = a / \sqrt{2}$$

$$\text{Atomic radius} = r = a / 2\sqrt{2}$$

$$\text{Lattice constant} = a = 2\sqrt{2}r$$

Coordination number = 12 (the centre of each face has one atom. This centre atom touches 4 corner atoms in its plane, 4 face centered atoms in each of the 2 planes on either side of its plane)

Effective number of atoms belonging to the unit cell or no. of atoms per unit cell = $(1/8) \times 8 + (1/2) \times 6 = 1 + 3 = 4$ atom per unit cell.

i.e. each corner atom contributes $1/8$ th to the unit cell. In addition to it, there is a centre atom on each face of the cube.

$$\text{Atomic packing factor} = v/V = \frac{\text{volume of the all atoms in the unit cell}}{\text{Volume of the unit cell.}}$$

$$= 4 * (4/3) \pi r^3 / a^3 = 16 \pi r^3 / 3(2\sqrt{2}r)^3$$

$$= \pi / 3\sqrt{2} = 0.74 = 74\%$$

Cu, Al, Pb and Ag have this structure. FCC has highest packing factor.

Hexagonal closed packed structure

The hexagonal closed packed (hcp) structure is shown in below Fig. (a). The hcp structure consists of three layers of atoms as shown in below Fig. (b). The bottom layer has six corner atoms and one face centred atom. The middle layer has three full atoms. The upper layer has six corner atoms and one face centred atom.

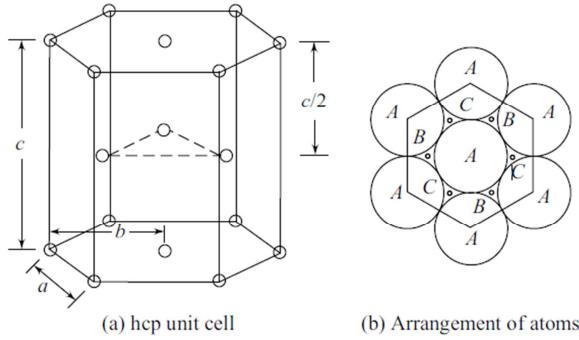


Fig. hcp structure

The arrangement of atoms in a hexagonally closed packed structure as shown in above Fig. is explained as follows. In the bottom layer, the central atom is surrounded by six other atoms having equal radius. The bottom layer of atoms is denoted by the letter A. Three places are marked as B and the remaining three places are marked as C over the bottom layer. The second layer of atom is placed either over the point marked as B or the point marked as C. Consider that the second layer is placed in the places marked as B. The third layer can be arranged in two ways, (i) the third layer of atoms placed directly over the first layer, and (ii) the third layer placed over the points marked as C. The stacking sequence goes on as ABABAB ... for case (i) representing the hcp structure, and as ABCABCABC for case (ii) representing the Fcc structure.

The total number of atoms present in a unit cell is

$$3/2 \text{ (Bottom)} + 3/2 \text{ (Upper)} + 3 \text{ (Middle)} = 6.$$

Atomic radius $a = 2r$

i.e., $r = a/2$

The atomic radius $r = a/2$

Coordination Number 12

$$\text{Packing density} = \frac{6(4/3)\pi r^3}{6(\sqrt{3}/4)a^2c}$$

Substituting the value of $r = a/2$

$$\therefore \text{Packing density} = \frac{6(4/3)\pi(a/2)^3}{6(\sqrt{3}/4)a^2c} = \frac{2\pi a}{3\sqrt{3}c}$$

Substituting the value of $c/a = \sqrt{(8/3)}$

$$\therefore \text{Packing density} = \frac{2\pi}{3\sqrt{3}} \sqrt{\frac{3}{8}} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Therefore, the packing density of hep unit cell = 0.74.

74 percent of the volume of hcp crystal structure is occupied by atoms and the remaining 26 percent volume is vacant.

The characteristics of the three types of cubic unit cells and the HCP cell

Sr.No.	Characteristics	Unit Cell			
		SC	BCC	FCC	HCP
1.	Unit cell volume, V	a^3	a^3	a^3	$3\sqrt{2}a^3$
2.	Atoms per unit cell, Z	1	2	4	6
3.	Atomic radius, r	$a/2$	$a\sqrt{3}/4$	$a/2\sqrt{2}$	$a/2$
4.	Coordination number, CN	6	8	12	12
5.	Atomic packing fraction, APF	$\pi/6$ = 0.52	$\pi\sqrt{3}/8$ = 0.68	$\pi/3\sqrt{2}$ = 0.74	$\pi/3\sqrt{2}$ = 0.74
6.	Void space	48%	32%	26%	26%
7.	Density, ρ	$\frac{M}{N_A a^3}$	$\frac{2M}{N_A a^3}$	$\frac{4M}{N_A a^3}$	$\frac{\sqrt{2}M}{N_A a^3}$

X-Rays

X-rays are electromagnetic waves of short wavelengths, ranging from 0.5 to 10 Å. The longer wavelength of the X-ray spectrum is known as soft X-rays and X-rays of shorter wavelength are known as hard X-rays.

Generation of X-rays

X-rays are produced when a beam of fast moving cathode rays (electrons) strike a heavy target material such as tungsten or molybdenum. The experimental set up for the production of X-rays uses the Coolidge tube.

Coolidge Tube

It is a specially designed and partially evacuated hard glass tube enclosed in a lead box, as shown in below Fig. The electrons are emitted thermionically by the filament F using a Low Tension (LT) supply. These emitted electrons are focussed on the target material using a hollow metallic cylinder C by giving a small negative potential. This electron beam is then accelerated by a high positive potential applied between the anode and the filament. The anode is made up of a thick copper rod and the front face of the anode is inclined at an angle of 45°. The target material, tungsten or molybdenum, is embedded in the cut face of the copper rod. The accelerated electrons are focussed by the cylinder C on the target T. When the accelerated electrons strike the target, about 99.8% of the electrons are wasted in heating the target material. Due to heavy bombardment of electrons on the target material, while the remaining 0.2% of electrons penetrate through the target material, a large quantity of material gets melted. Hence, the target material should have high atomic number, high melting point and high thermal conductivity, such as molybdenum and tungsten. The heat produced by the electrons is easily conducted by the copper anode. To conduct the heat produced in the anode, a cooling arrangement is used in the copper anode. The penetrating electrons are converted into X-rays.

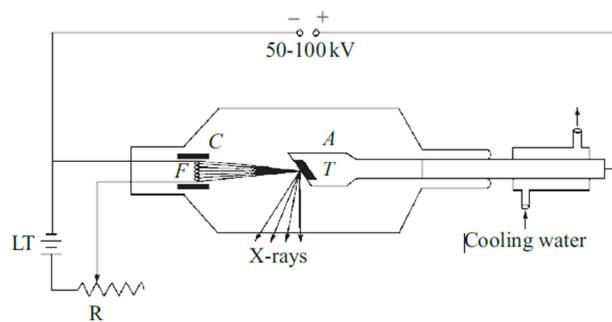


Fig. X-rays Coolidge tube

Intensity and Quality

The intensity of X-rays depends on the number of electrons striking the target material. The number of electrons striking the target material depends upon the concentrations of the electrons produced by the filament. Thus, the number of electrons emitted by the filament is determined by the current flowing through the filament. Hence, by controlling the filament current with the help of a rheostat, the intensity of the X-rays can be controlled. Based on the penetrating power of electrons, the quality of X-rays is termed as soft and hard X-rays. X-rays having low penetrating power are known as soft X-rays, while those having high penetrating power are known as hard X-rays. The penetrating power of X-rays depend upon the potential difference applied between the filament and the anode. Therefore, by varying this potential difference, one can control the quality of X-rays.

Bragg's Law

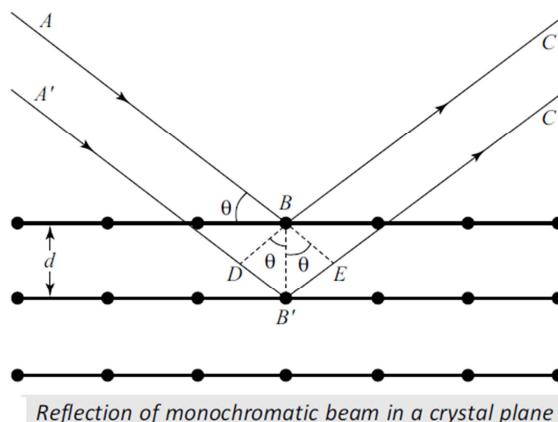
The fundamental equation which gives a simple relation between the wavelength (λ) of X-rays, the interplanar distance (d), and the glancing angle (θ), is known as Bragg's law. It is given as,

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

where $n = 1, 2, 3, \text{ etc.}$, represents the order of the spectrum.

Derivation of Bragg's Law

Let us consider a set of parallel planes in a crystal spaced by interplanar distance d . Consider a narrow, monochromatic X-ray beam of wavelength λ , incident on the first plane, at a glancing angle θ , as shown in below Fig. The incident beam undergoes multiple reflections between the parallel planes of the crystal.



Consider a ray AB, incident on the first plane and is reflected in the direction BC from that plane by the atom B. Let the incident beam AB make a glancing angle θ to the first plane. Similarly, consider a parallel ray A' B' is reflected in the direction B' C' by another atom B' in the second plane.

To determine the path difference between the two rays ABC and A' B'C', draw normals from the point B to the lines A'B' and B'C'. Let the normals be BD and BE. Therefore, the path difference between these two rays is equal to B'D' + B'E'.

In the triangle BDB', $\sin \theta = DB'/BB'$

Therefore, $DB' = BB' \sin \theta = d \sin \theta$

Similarly, $B'E = d \sin \theta$

Therefore, the path difference is given as,

$$d \sin \theta + d \sin \theta = 2d \sin \theta$$

Therefore, the two rays BC and B'C' will reinforce with each other and produce a maximum intensity when

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

where n (= 1, 2, 3, etc.) is the order of the spectrum, and λ the wavelength of the X-rays used. Above equation is known as Bragg's law.

Bragg's X-ray Spectrometer

The construction of Bragg's spectrometer is similar to an optical spectrometer. The essential parts of a Bragg's spectrometer are shown in below Fig.

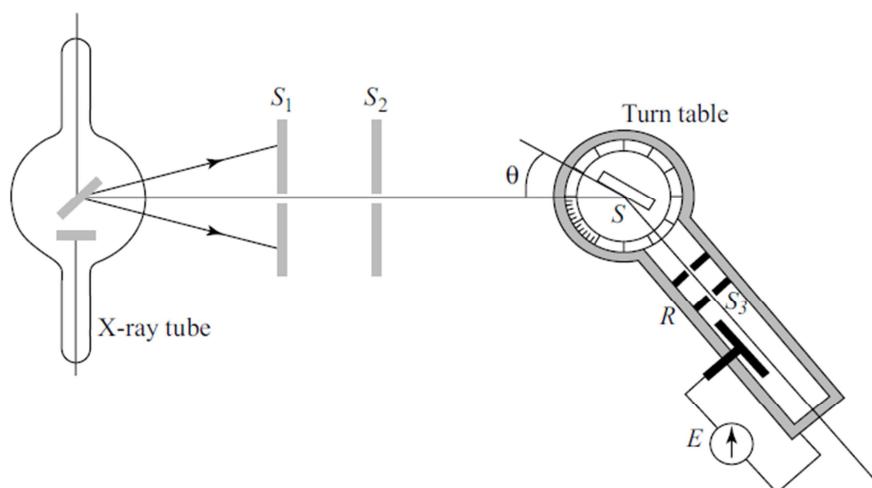


Fig. Bragg's spectrometer

The spectrometer consists of the following two parts, namely

- (1) A circular table, and
- (2) An ionisation chamber

Description

Bragg's X-ray spectrometer consists of a circular table on which a crystal is mounted. It is capable of rotating through any desired position by a vertical axis. The position of this circular table can be found out by using a circular scale S, attached to the table. A radial arm R, is linked with this turn table. The radial arm carries an ionisation chamber. The radial arm R is geared such that, when the turn table rotates through an angle of θ , the radial arm turns through an angle of 2θ . The reflected beam is collimated by a slit S3 and is collected by an ionisation chamber. Using the electrometer E, the ionisation current in the chamber is measured.

Working

The collimated beam is allowed to fall on the crystal. The glancing angle (θ) for the incident beam is kept very small while starting the experiment. The ionisation chamber is adjusted so as to receive the maximum intensity of the reflected beam. The glancing angle θ and the intensity of the X-rays are measured. The glancing angle θ is varied in steps and the corresponding values of the intensity of the reflected X-rays are noted. A graph is drawn between the glancing angle and intensity, as shown in below Fig.

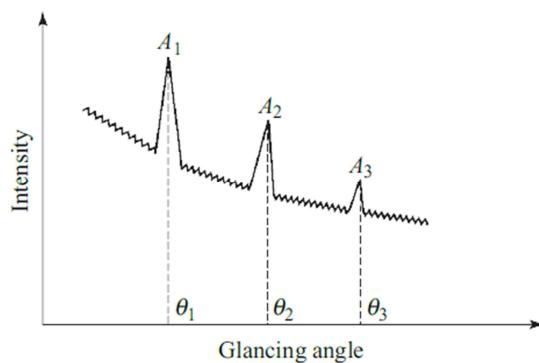


Fig. Glancing angle versus intensity

The above graph is known as the X-ray spectrum. The angles corresponding to the prominent peaks A1, A2 and A3 are taken as θ_1 , θ_2 , and θ_3 , respectively. It is found that

$$\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$$

This shows that the peaks A1, A2 and A3 refer to first, second and third order reflection respectively, of the same wavelength. By substituting the values of θ , n, d, and λ , the Bragg's law is verified using the relation.

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

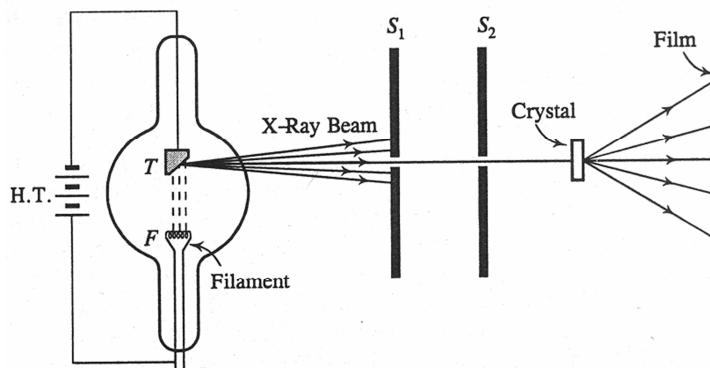
DETERMINATION OF CRYSTAL STRUCTURE

The crystal structure of a given specimen is determined with X-rays using the following methods:

- (1) Laue's
- (2) Powder crystal, and
- (3) Rotating crystal

Laue Method: S_1 & S_2 are 2 lead screens in which 2 pin holes act as slits. X-ray beam from an X – ray tube is allowed to pass through these 2 slits S_1 & S_2 . The beam transmitted through S_2 will be a narrow pencil of X – rays. The beam proceeds further to fall on a single crystal such that Zinc blended (ZnS) which is mounted suitably on a support. The single crystal acts as a 3 – dimensional diffraction grating to the incident beam. Thus, the beam undergoes diffraction in the crystal and then falls on the photographic film. The diffracted waves undergo constructive interference in certain directions, and fall on the photographic film with reinforced intensity. In all other directions, the interference will be destructive and the photographic film remains unaffected.

The resultant interference pattern due to diffraction through the crystal as a whole will be recorded on the photographic film (which requires many hours of exposure to the incident beam). When the film is developed, it reveals a pattern of fine spots, known as Laue spots.

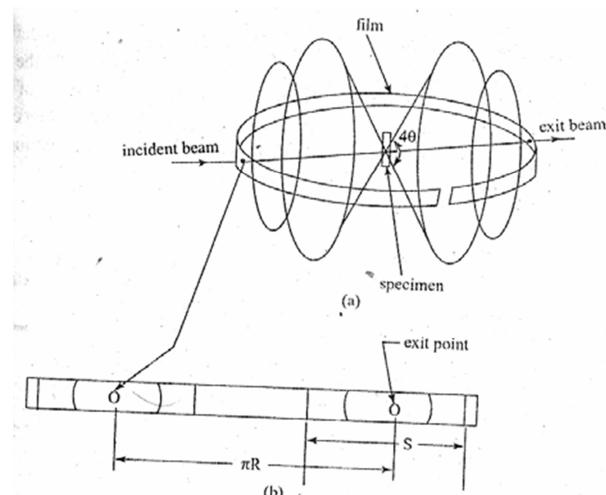


X-RAY DIFFRACTION (LAUE's METHOD)

The distribution spots follow a particular way of arrangement that is the characteristic of the specimen used in the form of crystal to diffract the beam. The Laue spot photograph obtained by diffracting the beam at several orientations of the crystal to the incident beam are used for determining the symmetry and orientations of the internal arrangement of atoms, molecules in the crystal lattice. It is also used to study the imperfections in the crystal.

POWDER METHOD (Debye – Scherrer Method):

This method is widely used for experimental determination of crystal structures. A monochromatic X-ray beam is incident on randomly oriented crystals in powder form. In this we used a camera called Debye – Scherrer camera. It consists of a cylindrical cassette, with a strip of photographic film positioned around the circular periphery of cassette. The powder specimen is placed at the centre, either pasted on a thin fibre of glass or filled in a capillary glass tube. The X-ray beam enters through a small hole in the camera and falls on



the powder specimen. Some part of the beam is diffracted by the powder while the remaining passes out through the exit port.

Since large no. of crystals is randomly oriented in the powder, set of planes which make an angle θ with the incident beam can have a no. of possible orientations. Hence reflected radiation lies on the surface of a cone whose apex is at the point of contact of the radiation with the specimen. If all the crystal planes of interplanar spacing d reflect at the same bragg angle θ , all reflections from a family lie on the same cone.

After taking $n=1$ in the Bragg's law

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

There are still a no of combinations of d and θ , which satisfies Bragg's law. Hence many cones of reflection are emitted by the powder specimen. In the powder camera a part of each cone is recorded by the film strip.

The full opening angle of the diffracted cone 4θ is determined by measuring the distance S between two corresponding arcs on the photographic film about the exit point direction beam. The distance S on the film between two diffraction lines corresponding to a particular plane is related to bragg's angle by the equation

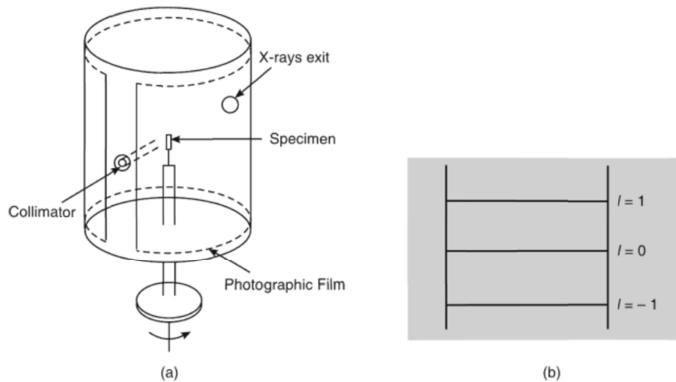
$$4\theta = (S / R) \text{ radians} \quad (\text{or})$$

$$4\theta = (S / R) \times (180 / \pi) \text{ degrees} \quad \text{where } R - \text{radius of the camera}$$

A list of θ values can be thus be obtained from measured values of S . Since the wavelength ' λ ' is known, substitution of λ gives a list of spacing 'd'. Each spacing is the distance between neighbouring plane ($h k l$). From the ratio of interplanar spacing, the type of lattice can be identified.

ROTATING CRYSTAL METHOD

The rotating crystal method is used when single crystals of moderate size are available. The experimental set up of the method is shown in below Fig. The crystal is mounted on a rotating spindle which is rotated by a rotator. The crystal is mounted in such a way that one of the crystal axes is along the axis of the spindle. A photographic film is mounted inside the drum which is concentric with the rotating spindle.



A monochromatic beam of x-rays is allowed through the aperture in the drum to impinge on the crystal at right angles. As the crystal rotates, various planes come successively into positions for which Braggs condition is satisfied. The diffracted beams produce spots on the

photographic film. The planes parallel to the axis of rotation diffract the incident rays in a horizontal plane. The planes inclined to the rotation axis produce reflections above or below the horizontal plane depending on the angle of inclination. The horizontal lines produced by diffraction spots on the film are called layer lines. If the crystal is placed such that its c-axis coincides with the axis of rotation, all the planes with Miller indices $(h, k, 0)$ will produce the central layer line (Fig. b). The planes having Miller indices (h, k, l) and $(h k \bar{l})$ will produce layer lines above and below the central line respectively, and so on. The vertical spacing between the layer lines depends on the distance between the lattice points along the c-axis. Similarly, we can determine the translational vectors a and b on mounting the crystal along a and b axes, respectively. Thus, the dimensions of the unit cell of the crystal are determined.

CRYSTAL IMPERFECTIONS

In crystals, atoms or ions are arranged in a regular and periodic manner in three dimensions. Generally, natural crystals are always not perfect and there are some deviations from their regular arrangements. Any deviation in the crystal from the perfect periodic lattice or structure is known as **crystal imperfections** or **crystal defects**.

Classification of imperfections

The crystal imperfections can be classified on the basis of their geometry as given below.

- (1) Point imperfections (0D)
- (2) Line imperfections (1D)
- (3) Surface imperfections or planar defects (2D)
- (4) Volume imperfections or bulk defects (3D)

POINT DEFECT OR IMPERFECTION

Point defects are localised disruption of the lattice involving one or several atoms. In a crystal, if there are imperfect point-like regions, then it is said to be a point imperfection. The point defects are introduced by any one of the methods namely, the movement of atoms when they gain energy by heating or during processing of materials or introduction of impurities or intentionally alloying. The size of the point imperfection is nearly one or two atomic distance. These imperfections are called as zero dimensional imperfections. The point defects are further classified as,

- (1) Vacancy defect
- (2) Substitutional defect

- (3) Interstitial defect
- (4) Frenkel defect, and
- (5) Schottky defect

Vacancy Defect:

The missing of an atom from the atomic site of a crystal is known as vacancy. Vacancies are introduced into the crystal during solidification at high temperature or as a consequence of radiation damage. The lattice vacancy is represented by a square \square . It is produced at the surface of crystal diffuses into the bulk crystal.

Substitutional defect:

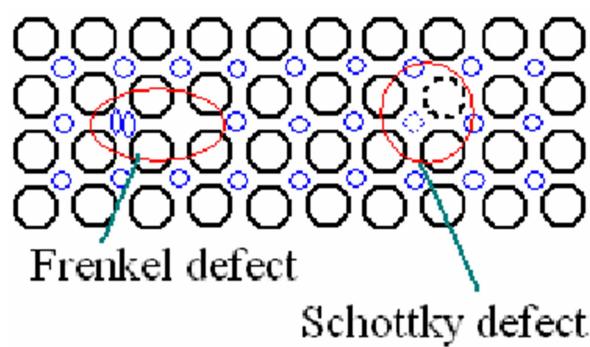
A substitutional defect is produced when an atom is replaced by different types of atom. An impurity that occupies a normal lattice site is known as a substitutional impurity atom. The defect in which an impurity atom occupies a normal lattice site is known as a substitutional defect. The addition of impurity having larger or smaller size compared to that of the host atom produces or disturbs lattice

Interstitial defect

An **interstitial** is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity atom. In the case of vacancies and interstitials, there is a change in the coordination of atoms around the defect. This means that the forces are not balanced in the same way as for other atoms in the solid, which results in lattice distortion around the defect. A high temperature is needed to have a high *thermal* concentration of vacancies.

Frenkel-defect is a vacancy-interstitial pair of cations

Schottky-defect is a pair of nearby cation and anion vacancies



Dislocations—Linear Defects

Dislocations are abrupt changes in the regular ordering of atoms, along a line (dislocation line) in the solid. They occur in high density and are very important in mechanical properties of material. They are characterized by the Burgers vector, found by doing a loop around the dislocation line and noticing the extra inter atomic spacing needed to close the loop. The Burgers vector in metals points in a close packed direction.

Line Defects

- Line defects or Dislocations are abrupt change in atomic order along a line.
- They occur if an incomplete plane inserted between perfect planes of atoms or when vacancies are aligned in a line.
- A dislocation is the defect responsible for the phenomenon of slip, by which most metals deform plastically.
- Dislocations occur in high densities ($10^8\text{-}10^{10}\text{ m}^{-2}$), and are intimately connected to almost all mechanical properties which are in fact structure-sensitive.
- Dislocation form during plastic deformation, solidification or due to thermal stresses arising from rapid cooling.

Line Defects – Burger's Vector

- A dislocation is characterized by Burger's vector, b .
- It is unique to a dislocation, and usually has the direction of close packed lattice direction. It is also the slip direction of a dislocation.
- It represents the magnitude and direction of distortion associated with that particular dislocation.
- Two limiting cases of dislocations, edge and screw, are characterized by Burger's vector perpendicular to the dislocation line (t) and Burger's vector parallel to the dislocation line respectively. Ordinary dislocation is of mixed character of edge and screw type.

Edge dislocations occur when an extra plane is inserted. The dislocation line is at the end of the plane. In an edge dislocation, the Burgers vector is perpendicular to

the dislocation line.

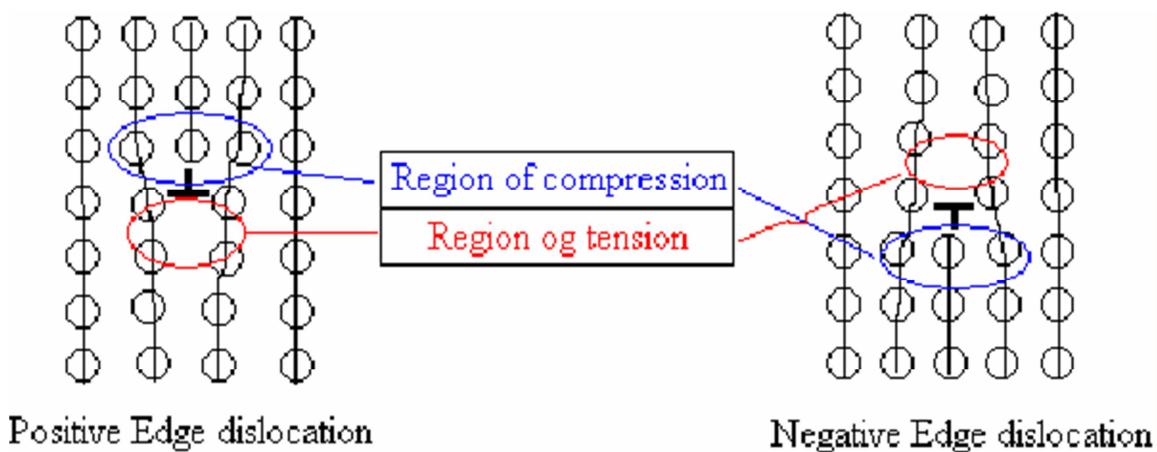
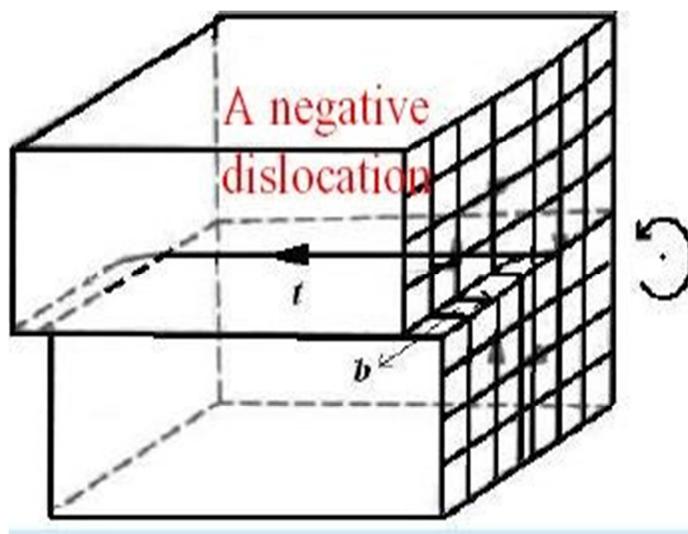
Line Defects – Edge Dislocation

- It is also called as Taylor-Orowan dislocation.
- It will have regions of compressive and tensile stresses on either side of the plane containing dislocation.

Screw dislocations result when displacing planes relative to each other through shear. In this case, the Burgers vector is parallel to the dislocation line.

Line Defects – Screw Dislocation

- It is also called as Burger's dislocation.
- It will have regions of shear stress around the dislocation line
- For positive screw dislocation, dislocation line direction is parallel to Burger's vector, and vice versa.

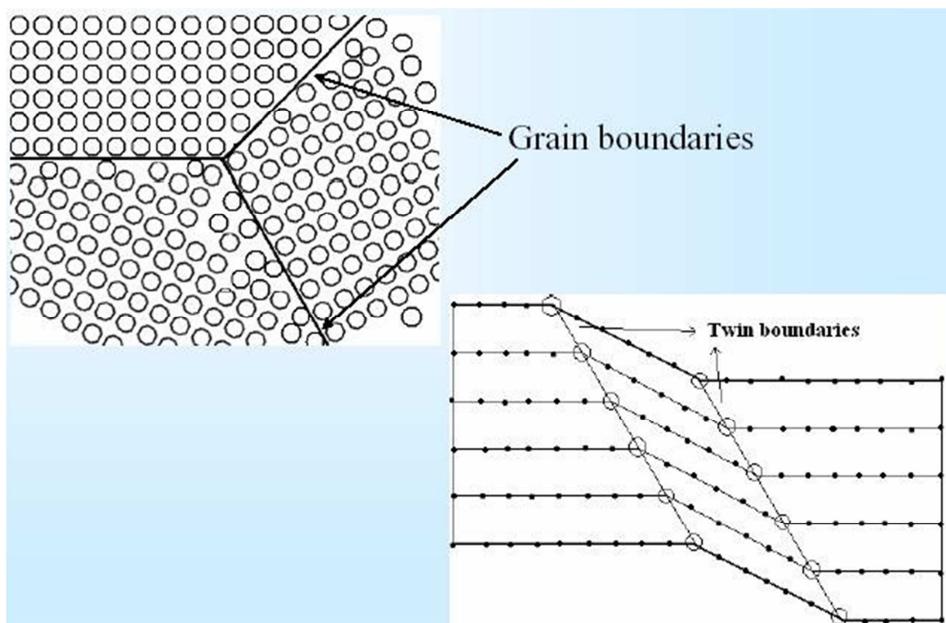


Surface imperfections or planar defects or Interfacial Defects:

The environment of an atom at a surface differs from that of an atom in the bulk, in that the number of neighbors (coordination) decreases. This introduces unbalanced forces which result in *relaxation* (the lattice spacing is decreased) or *reconstruction* (the crystal structure changes). The density of atoms in the region including the grain boundary is smaller than the bulk value, since void space occurs in the interface. Surfaces and interfaces are very reactive and it is usual that impurities segregate there. Since energy is required to form a surface, grains tend to grow in size at the expense of smaller grains to minimize energy. This occurs by diffusion, which is accelerated at high temperatures.

Interfacial Defects

- An interfacial defect is a 2-D imperfection in crystalline solids, and have different crystallographic orientations on either side of it.
- Region of distortion is about few atomic distances.
- They usually arise from clustering of line defects into a plane.
- These imperfections are not thermodynamically stable, but meta-stable in nature.
- E.g.: External surface, Grain boundaries, Stacking faults, Twin boundaries, Phase boundaries.



Volume defects:

Volume defects such as cracks may arise in crystal either while being grown or while being used. While growing any possible small electrostatic dissimilarity between stacking layers may result in a crack.

When the crystal is used for some device applications, and is subjected to sudden thermal waves, cracks generate.

Pores - can greatly affect optical, thermal, mechanical properties

Cracks - can greatly affect mechanical properties

Foreign inclusions - can greatly affect electrical, mechanical, optical properties

Voids: Voids in nanocrystallites may be situated at either triple junctions or as large porosities due to insufficient compaction and sintering of nanocrystallites synthesized from the powder route.

Although both types of voids influence the behavior of the nanocrystallites, the former is structurally more important. It is suggested that triple junction voids arise as a result of relaxation of nanocrystalline grain boundaries.