1. BONDING IN SOLIDS

INTRODUCTION

In the gaseous state of matter, individual atoms or molecules can move freely in space with a velocity determined by the temperature. But in solid state, the constituent atoms or molecules that build the solid are confined to a localized region. The principle region between the two states is bonding. In gases, the atoms or molecules are free whereas in solids they are bound in a particular form because of which, they possess certain physical properties such elasticity, electrical and optical properties.

BONDING

Bonding is the physical state of existence of two or more atoms together in a bound form. The supply of external energy is required to get back the bonded atoms to the Free State as energy is needed to break the bonds. This energy is called dissociation (binding) or cohesive energy.

Bonding occurs between similar or dissimilar atoms, when an electrostatic interaction between them produces a resultant state whose energy is lesser than the sum of the energies possessed by individual atoms when they are free.

TYPES OF BONDING IN SOLIDS

Bonds in solids are classified basically into two groups namely primary and secondary bonds. Primary bonds are inter atomic bonds i.e. bonding between the atoms and secondary bonds are intermolecular bonds i.e. between the molecules.

Primary bonds

The primary bonds are interatomic bonds. In this bonding interaction occurs only through the electrons in the outermost orbit, i.e. the valence electrons. These are further classified into three types

Ionic bonding
Covalent bonding
Metallic bonding

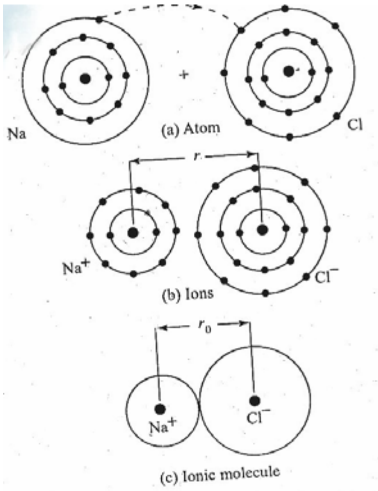
1. *Ionic Bonding* :

Ionic bonding results due to transfer of one or more electrons from an electropositive element to an electronegative element. The two types of atoms involved in the bonding are of dissimilar type.

Example:

In NaCl crystal, Na atom has only one electron in outer most shell and a Cl atom needs one more electron to attain inert gas configuration. During the formation of NaCl molecule, one electron from the Na atom is transferred to the Cl atom resulting which, both Na and Cl ions attain filled- shell configuration.

$$Na + Cl \rightarrow Na^{+} + Cl^{-} \rightarrow NaCl$$



Schematic representation of the formation of an ionic molecule of sodium chloride.

A strong electrostatic attraction is set up that bond the Na^{+} cation and the Cl^{-} anion into a very stable molecule NaCl at the equilibrium spacing.
Since Cl exist as molecules, the chemical reaction must be written as

$$2Na + Cl_2 \rightarrow 2Na^{+} + 2Cl^{-} \rightarrow 2NaCl$$

Other examples of ionic crystals are

$$2Mg + O_2 \rightarrow 2Mg^{++} + 2O^{--} \rightarrow 2MgO$$

$$Mg + Cl_2 \rightarrow Mg^{++} + 2Cl^{-} \rightarrow MgCl_2$$

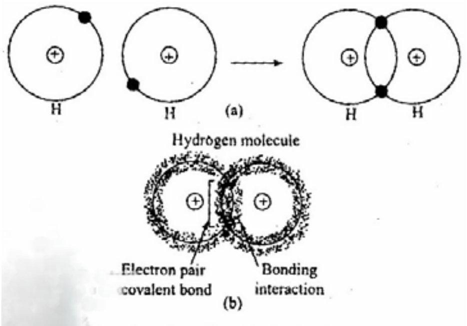
Properties:

1. As the ionic bonds are strong, the materials are hard and possess high melting and boiling points.
2. They are good ionic conductors, but poor conductors of both heat and electricity
3. They are transparent over wide range of electromagnetic spectrum
4. They are brittle. They possess neither ductility (ability to be made into sheets) nor malleability (ability to be made into wires).
5. They are soluble in polar liquids such as water but not in non-polar liquids such as ether.

2. Covalent Bonding

Covalent bond is formed by sharing of electrons between two atoms to form molecule.

Example: Covalent bonding is found in the H_2 molecule. Here the outer shell of each atom possesses 1 electron. Each H atom would like to gain an electron, and thus form a stable configuration. This can be done by sharing 2 electrons between pairs of H atoms, there by producing stable diatomic molecules.



Covalent bonding in the hydrogen molecule

Thus covalent bonding is also known as shared electron pair bonding.

Properties:

1. Covalent crystals are very hard since the bond is strong. The best example is diamond which is the hardest naturally occurring material and possess high melting and boiling points, but generally lower than that for ionic crystals.
2. Their conductivity falls in the range between insulators and semiconductors. For example, Si and Ge are semiconductors, where as diamond as an insulator.
3. They are transparent to electromagnetic waves in infrared region, but opaque at shorter wavelengths.

They are brittle and hard.

They are not soluble in polar liquids, but they dissolve in non-polar liquids such as ether, acetone, benzene etc.

The bonding is highly directional.

3. Metallic Bonding:

The valance electrons from all the atoms belonging to the crystal are free to move throughout the crystal. The crystal may be considered as an array of positive metal ions embedded in a cloud of free electrons. This type of bonding is called metallic bonding.

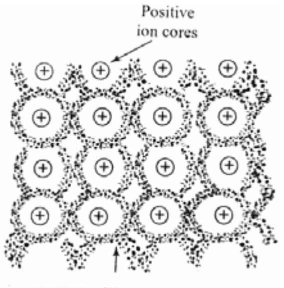


Fig. [redacted] Atomic arrangement in metal crystal.

In a solid even a tiny portion of it comprises of billions of atoms. Thus in a metallic body, the no. of electrons that move freely will be so large that it is considered as though there is an electron gas contained with in the metal. The atoms lay embedded in this gas but having lost the valence electrons, they become positive ions. The electrostatic interaction between these positive ions and the electron gas as a whole, is responsible for the metallic bonding.

Properties:

1. Compared to ionic and covalent bonds, the metallic bonds are weaker. Their melting and boiling points are also lower.
2. Because of the easy movement possible to them, the electrons can transport energy efficiently. Hence all metals are excellent conductors of heat and electricity.
3. They are good reflectors and are opaque to E.M radiation.
4. They are ductile and malleable.

Secondary Bonds

There are two types of secondary bonds. They are Vander Waal's bonds and Hydrogen bonds.

1. **Vander Waal's bonding:** Vander Waal's bonding is due to Vander Waal's forces. These forces exist over a very short range. The force decreases as the 4th power of the distance of separation between the constituent atoms or molecules when the ambient temperature is low enough. These forces lead to condensation of gaseous to liquid state and even from liquid to solid state though no other bonding mechanism exists.(except He)

Properties:

1. The bonding is weak because of which they have low melting points.
2. They are insulators and transparent for visible and UV light.
3. They are brittle.
4. They are non-directional

2. **Hydrogen bonding:** Covalently bonded atoms often produce an electric dipole configuration. With hydrogen atom as the positive end of the dipole if bonds arise as a result of electrostatic attraction between atoms, it is known as hydrogen bonding.

Properties:

1. The bonding is weak because of which they have low melting points.
2. They are insulators and transparent for visible and UV light.
3. They are brittle.
4. The hydrogen bonds are directional.

Forces between atoms:

In solid materials, the forces between the atoms are of two kinds. 1) Attractive force 2) Repulsive force

To keep the atoms together in solids, these forces play an important role. When the atoms are infinitely far apart they do not interact with each other to form a solid and the potential energy will be zero. From this, it can be understood that the potential energy between two atoms is inversely proportional to some power of the distance of separation. In all atoms, moving electric charges will be present, hence either attractive interaction or repulsive interaction takes place as they approach each other.

The attractive forces between the atoms bring them close together until a strong repulsive force arises due to overlap of electron shell. The atoms attract each other when they come close to each other due to inter-atomic attractive force which is responsible for bond formation. Suppose two atoms A and B experiences attractive and repulsive forces on each other, then the interatomic or bonding force ‘f(r)’ between them may be represented as

$$F(r)=A / r^M - B / r^N \qquad (N > M) \text{--------------}(1)$$

Where ‘r ‘ is the interatomic distance

A, B, M, N are constants.

In eqn-1, the first term represents attractive force and the second the repulsive force.

At larger separation, the attractive force predominates. The two atoms approach until they reach equilibrium spacing. If they continue to approach further, the repulsive force pre dominates, tending to push them back to their equilibrium spacing.

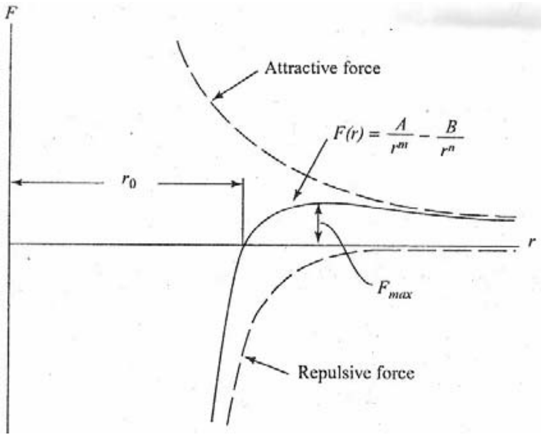


Fig. Variaration of interatomic force with interatomic spacing

To calculate equilibrium spacing r_0 :

The general expression for bonding force between two atoms is

$$F(r) = A / r^M - B / r^N$$

At equilibrium spacing $r = r_0$, $F = 0$

$$\text{Hence} \qquad \mathbf{A / r_0^M = B / r_0^N}$$

$$\text{i.e.} \quad (r_0)^{N-M} = B / A$$

$$\text{or} \quad r_0 = (B / A)^{1/(N-M)}$$

Cohesive energy:

The energy corresponding to to the equilibrium position $r = r_0$ is called the bonding energy or the energy of cohesion of the molecule. Since this is the energy required to dissociate the atoms, this is also called the energy of dissociation.

The potential energy or stored internal energy of a material is the sum of the individual energies of the atoms plus their interaction energies. Consider the atoms are in the ground state and are infinitely far apart. Hence they do not interact with each other to form a solid. The potential energy, which is inversely proportional to some power of the distance of separation, is nearly zero. The potential energy varies greatly with inter-atomic separation. It is obtained by integrating the eqn –(1)

$$U(r) = \int F(r)dr$$

$$= \int [\, A/r^M - B/r^N \,]\, dr$$

$$= [\, (A/1-M) x\, r^{1-M} - (B/1-N) x\, r^{1-N} \,] + c$$

$$= [-(A/M-1)\, r^{-(M-1)} + (B/N-1)\, r^{-(N-1)} + c$$

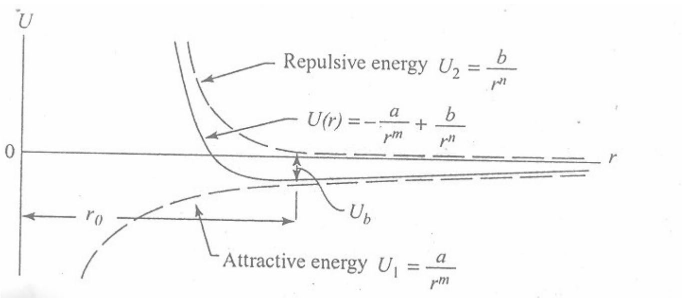
$= -a / r^m + b / r^n + c$ where $a = A/M-1$, $b = B/N-1$, $m = M-1$, $n = N-1$

At $r = \alpha$, $U(r) = 0$, then $c = 0$

Therefore $U(r) = -a / r^m + b / r^n$

The condition under which the particles form a stable lattice is that the function U(r) exhibits min. for a finite value of r i.e. $r = r_0$ this spacing r_0 is known as equilibrium spacing of the system. This min. energy Umin at $r = r_0$ is negative and hence the energy needed to dissociate the molecule then equals the positive quantity of (- Umin). Umin occurs only if m and n satisfy the condition $n>m$

When the system in equilibrium then $r = r_0$ and $U(r) = U_{min}$



Variation of potential energy U with interatomic spacing r.

$[dU / dr]_{r = ro} = 0$

$= d / dr [-a / r_o^m + b / r_o^n] = 0$

or $0 = [a\, m\, ro^{-m-1}] – [b\, n\, ro^{-n-1}]$

or $0 = [a\, m / r_o^{m+1}] – [b\, n / r_o^{n+1}]$ -------→ (2)

Solving for r_o

$r_o=[(b / a) (n / m)]^{1/n-m}$

or $r_o^n = r_o^m[(b /a) (n / m)]$

at the same time , n>m to prove this,

$[d^2U / dr^2]_{r = ro} = - [a\, m(m+1) / r_o^{m+2}] + [b\, n(n+1) / r_o^{n+2}] > 0$

$[r_o^{m+2}\, b\, n(n+1)] - [r_o^{n+2} a\, m(m+1)] > 0$

$r_o^m\, b\, n (n+1) > r_o^n\, a\, m (m+1)$

$b\, n (n+1) > a\, m (m+1) r_o^{n-m}$

$b\, n (n+1) > a\, m (m+1) (b / a) (n / m)$

i.e. $n > m$

Calculation of cohesive energy:

The energy corresponding to the equilibrium position $r = r_0$ **,** denoted by $U(r_0)$ is called boning energy or cohesive energy of the molecule.

Substituting 'r_o^n' in expression for U_{min},

We get

$U_{(min)} = - a / r_o^m + b / r_o^n$

$= - a / r_o^m + b (a / b) (m/ n)1 / r_o^m$

$= - a / r_o^m + (m/ n) (a / r_o^m)$

$= - a / r_o^m[1-m / n]$

$U_{min} = - a / r_o^m [1-m / n]$

Thus the min. value of energy of U_{min} is negative. The positive quantity $|U_{min}|$ is the dissociation energy of the molecule, i.e. the energy required to separate the two atoms.

Calculation of cohesive energy of NaCl Crystal

Let Na and Cl atoms be free at infinite distance of seoarartion. The energy required to remove the outer electron from Na atom (ionization energy of Na atom), leaving it a Na+ ion is 5.1eV.

i.e. $Na + 5.1eV \rightarrow Na^+ + e^-$

The electron affinity of Cl is 3.6eV. Thus when the removed electron from Na atom is added to Cl atom, 3.6eV of energy is released and the Cl atom becomes negatively charged.

Hence $Cl + e^- \rightarrow Cl^- + 3.6eV$

Net energy = 5.1 – 3.6 = 1.5 eV is spent in creating Na^+ and Cl^- ions at infinity.

Thus $Na + Cl + 1.5 eV \rightarrow Na^+ + Cl^-$

At equilibrium spacing r0= 0.24nm, the potential energy will be min. and the energy released in the formation of NaCl molecule is called bond energy of the molecule and is obtained as follows:

$V = e^2 / 4\Pi\varepsilon_0 r_0$

$= - [(1.602x10^{-19})^2 / 4\Pi(8.85x10^{-12})(2.4x10^{-10})]$ joules

$= - [(1.602\text{x}10^{-19})^2 / 4\Pi(8.85\text{x}10^{-22}\text{x}2.4)(1.602\text{x}10^{-19})]$ eV

$= -6$ eV

Thus the energy released in the formation of NaCl molecule is (5.1 - 3.6 – 6) = - 4.5 eV

To dissociate NaCl molecule into Na^+ and Cl^- ions, it requires energy of 4.5 eV.

Madelung Constant

Let r be the distance of separation between the two ions, z1 and z2 be the atomic numbers of the respective nuclei.

The coulomb's force of attraction F between the positive and negative ions is,
$F = (z_1z_2)e^2 /4\Pi\varepsilon_0r^2$

The work done while they move under the attractive force towards each other through a distance dr,

$W = Fdr = [(z_1z_2)e^2 / 4\Pi\varepsilon_0r^2]\, dr$

Therefore the work done while they move from infinite distance of separation to a distance r,

$= {}_{\infty}\int^{r} fdr = [(z_1z_2)e^2 / 4\Pi\varepsilon_0]\, {}_{\infty}\int^{r} dr/ r^2$

$= - (z_1z_2)e^2 / 4\Pi\varepsilon_0 r$

Work done by them becomes the attractive potential energy U_a
Therefore $U = - (z_1z_2)e^2 / 4\Pi\varepsilon_0 r$

$= - \alpha [e^2 / 4\Pi\varepsilon_0 r]$

Where α is constant called Madelung constant which has different values for different crystals.

2. CRYSTALLOGRAPHY AND CRYSTAL STRUCTURES

CRYSTALLOGRAPHY

The branch of science which deals with the study of geometric form and other physical properties of the crystalline solids by using X-rays, electron beam, and neutron beams etc is called crystallography or crystal physics.

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 my 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.

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.

Space lattice or Crystal lattice: The totality of all the lattice point in space is called space lattice, the environment about any two points is same or An array of points in space such that the environment about each point is the same.

Consider the case of a 2-dimensional array of points.

Let O be any arbitrary point as origin, r1, r2 are position vectors of any two lattice points joining to O.

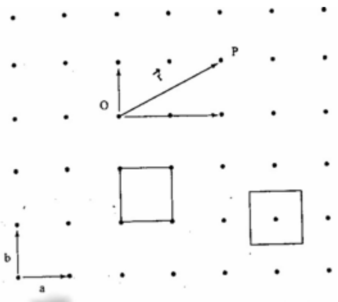


Fig. A two-dimensional square array of points.

If T (translational vector) is the difference of two vectors r1, r2 and if it satisfies the condition

$$T = n_1 a + n_2 b \quad \text{where } n_1, n_2 \text{ are integers}$$

Then T represent 2-dimensional lattice.

For 3- dimensional lattice,

$$T = n_1 a + n_2 b + n_3 c$$

Note: crystal lattice is the geometry of set of points in space where as the structure of the crystal is the actual ordering of the constituent ions, atoms, molecules in space

Basis and Crystal structure:

Basis or pattern is a group of atoms, molecule or ions identical in composition, arrangement and orientation. When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure.

Crystal structure = Lattice + Basis

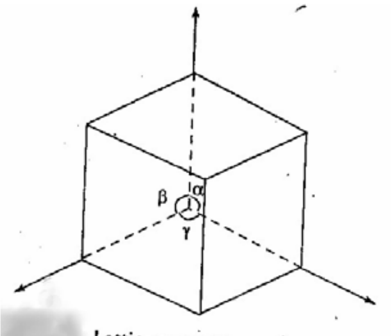
FIG………………………..

The crystal structure is real while the lattice is imaginary.

In crystalline solids like Cu and Na, the basis is a single atom
In NaCl and CsCl- basis is diatomic
In CaF_2 – basis is triatomic

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 varies directions. In describing the crystal structure, it is convenient to subdivided 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.



Lattice parameters of an unit cell.

A unit cell can be described by 3 vectors or intercepts **a, b, 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:

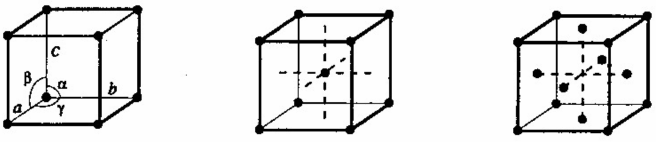
There are 7 basic crystal systems which are distinguished based on three vectors or the intercepts and the 3 interfacial angles between the 3 axes of the crystal. They are

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

$a = b = c, \alpha = \beta = \gamma = 90^0$



Simple

Body-centered (bcc)

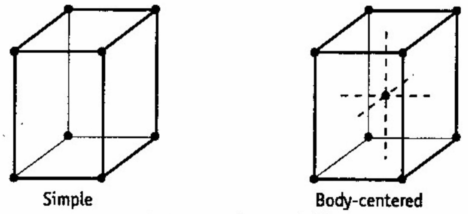
Face-centered (fcc)

$a=b=c,\ \alpha=\beta=\gamma=90°$

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

$a = b \neq c,\ \alpha = \beta = \gamma = 90^0$



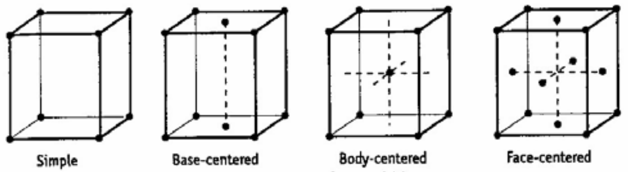
$a = b \neq c,\quad \alpha = \beta = \gamma = 90°$

TETRAGONAL SYSTEM

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.

$a \neq b \neq c,\ \alpha = \beta = \gamma = 90^0$



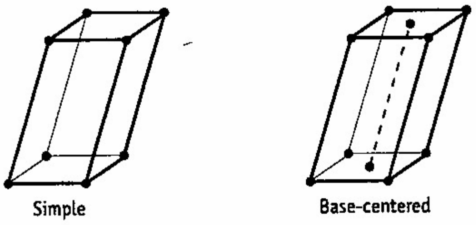
$a \neq b \neq c$; and $\alpha = \beta = \gamma = 90°$

ORTHORHOMBIC SYSTEM

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

$a \neq b \neq c,\ \alpha = \beta = 90^0 \neq \gamma$



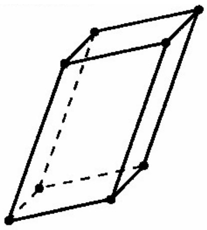
$a \neq b \neq c,\quad \alpha = \gamma = 90° \neq \beta$

MONOCLINIC SYSTEM

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

$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^0$

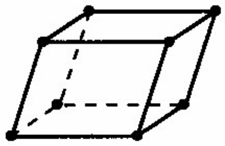


$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$
TRICLINIC SYSTEM

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

$a = b = c, \alpha = \beta = \gamma \neq 90^0$

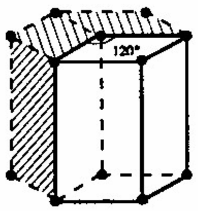


$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
IOMBOHEDRAL (TRIGONAL) SYSTEM

The three axes are equal in length and are equally inclined to each other at an angle other than 90^0

7. Hexagonal crystal system.

$a = b \neq c, \alpha = \beta = \gamma = 90^0, \gamma = 120^0$



$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$
HEXAGONAL SYSTEM

Two of the crystal axes are 60^0 apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60^0 apart, but the interval along the third axis is different.

Basic Crystal Structures:

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

1. **Nearest neighbouring distance** (2r) : the distance between the centres of two nearest neighbouring atoms is called nearest neighbouring distance. If r is the radius of the atom, nearest neighbouring distance= 2r.
2. **Atomic radius** (r) : It is defined as of the distance between the nearest neighbouring atoms in a crystals.
3. **Coordination number** (N): It is defined as the number of equidistant nearest neighbours that an atom as in a given structure. More closely packed structure as greater coordination number.
4. **Atomic packing factor or fraction**: It is the ratio of the volume occupied by the atoms in unit cell(v) to the total volume of the unit cell (V).

P.F. = v/ V

Simple cubic (SC) structure:

In the simple cubic lattice, there is one lattice point at each of the 8 corners of the unit cell. The atoms touch along cubic edges.

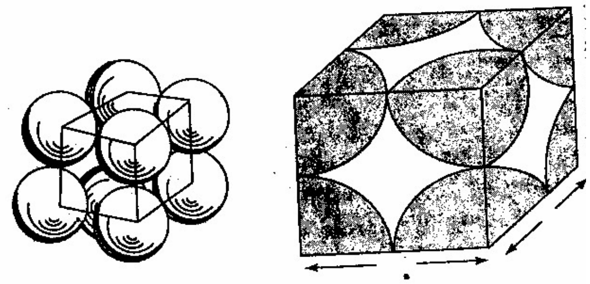


Fig. Simple Cubic Structure

Nearest neighbouring distance = 2r = a

Atomic radius = r = a / 2

Lattice constant = a = 2r

Coordination number = 6 (since each corner atom is surrounded by 6 equidistant nearest neighbours)

Effective number of atoms belonging to the unit cell or no. of atoms per unit cell = $(1/8)$x8 = 1 atom per unit cell.

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

$$= 1 \times (4 / 3) \prod r^3 / a^3 = 4\prod r^3 / 3(2r)^3$$

$$= \prod / 6 = 0.52 = 52\%$$

This structure is loosely packed. Polonium is the only element which exhibits the simple cubic structure.

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.

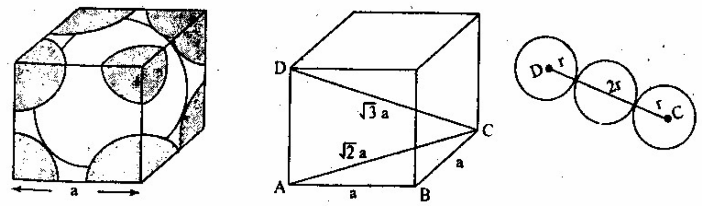


Fig. Body Centered Cubic Structure

Diagonal length = 4r

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

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

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

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

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 1/8th to the unit cell. In addition to it, there is a centre atom.

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

$$= 2 \times (4 / 3) \prod r^3 / a^3 = 8\prod r^3 / 3(4r / \surd 3)^3$$

$$= \surd 3 \prod / 8 = 0.68 = 68\%$$

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

Face centered cubic (FCC) structure:

In FCC structure, ther 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.

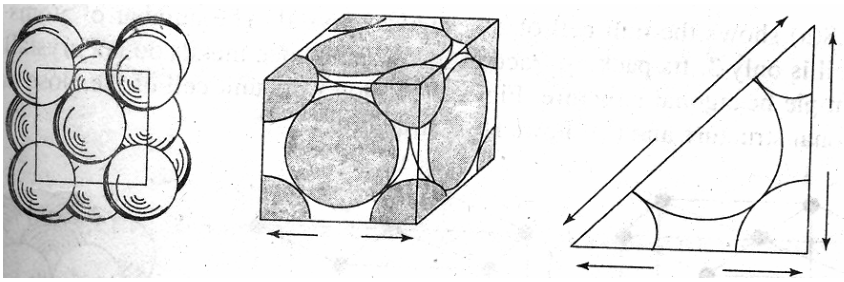


Fig. Face Centered Cubic Structure

Face diagonal length = $4r = (\surd 2)\, a$

Nearest neighbouring distance = $2r = (\surd 2)a / 2 = a / \surd 2$

Atomic radius = $r = a / 2\surd 2$

Lattice constant = $a = 2\surd 2\, r$

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.

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

$$= 4 * (4 / 3) \prod r^3 / a^3 = 16\prod r^3 / 3(2\surd 2\, r)^3$$

$$= \prod / 3\surd 2 = 0.74 = 74\%$$

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

3. X-RAY DIFFRACTION

Directions & Planes in Crystals:

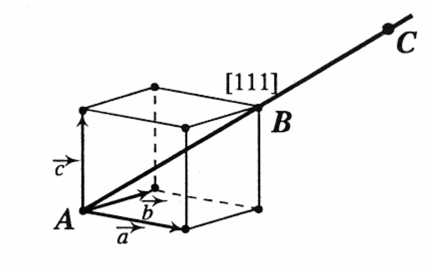
While dealing with the crystals, it is necessary to refer to crystal planes, and directions of straight lines joining the lattice points in a space lattice. For this purpose, an indexing system deviced by Miller known as Miller indices is widely used.

Directions in A Crystal:

Consider a cubic lattice in which a straight line is passing through the lattice points A, B, C etc and 1 lattice point on the line such as point A is chosen as the origin.

Then the vector R which joins A to any other point on the line such as B (position vector) can be represented by the vector eqn.

R = n1 a + n2 b + n3 c------ (1) where a, b, c are basic vectors



DIRECTION OF LINE IN A LATTICE

The direction of the vector R depends on the integers n1, n2, n3 since a, b, c are constants. The common multiple is removed and n1, n2, n are re-expressed as the smallest integers bearing the same relative ratio. The direction is then specified as [n1 n2 n3].

R =a+b+c, which provides the value of 1 for each of n1, n2, n3

Thus the direction is denoted as [1 1 1].

All lines in the space lattice which are parallel to the line AB possess either same set of values for n1, n2, n3 as that of AB, or its common multiples.

Ex: 1. The direction that connects the origin and (1/3, 1/3, 2/3) point is [1 1 2].

i.e, (1/3, 1/3, 2/3)

L.C.M = 3.

(1/3x3 1/3x3 2/3x3)= [1 1 2].

2. [2 1 1] is the direction that connects the origin (0, 0, 0) and point (1, 1/2, 1/2)

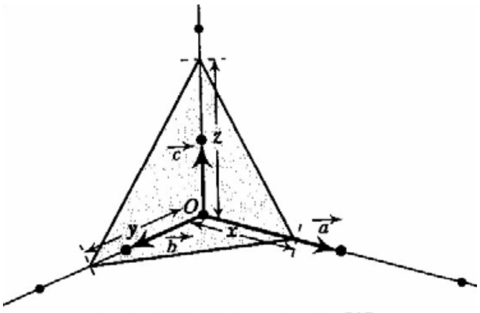
Largest Number = 2

(2/2, 1/2, 1/2) = (1, 1/2, 1/2)

Planes in Crystals (*Miller Indices*):

It is possible for defining a system of parallel and equidistant planes which can be imagined to pass through the atoms in a space lattice, such that they include all the atoms in the crystal. Such a system of planes is called crystal planes. Many different systems of planes could be identified for a given space lattice.

The position of a crystal plane can be specified in terms of three integers called Miller indices.



PLANE ORIENTATION IN A LATTICE

Consider a crystal plane intersecting the crystal axes.
Procedure for finding Miller indices

1. Find the intercepts of the desired plane on the three coordinate axes.
   Let these be (pa, qb, rc).

2. Express the intercepts as multiples of unit cell dimensions or lattice parameters i.e. (p, q, r)

3. Take the reciprocals of these numbers i.e. 1/p: 1/q: 1/r

4. Convert these reciprocals into whole numbers by multiplying each with their LCM to get the smallest whole number.

This gives the Miller indices (h k l) of the plane.

Ex: (3a, 4b, αc)

(3, 4, α)

$1/3 \quad 1/4 \quad 1/\alpha$

$(4\ 3\ 0) = (h, k, l)$

Def: Miller indices is a set of 3 lowest possible integers whose ratio taken in order is the same as that of the reciprocals of the intercepts of the planes on the corresponding axes in the same order.

Important features of Miller indices:

1. When a plane is parallel to any axis, the intercept of the plane on that axis is infinity. Hence its Miller index for that axis is zero.
2. When the intercept of a plane on any axis is negative, a bar is put on the corresponding Miller index.
3. All equally spaced parallel planes have the same index number (h k l)

Ex : The planes (1 1 2) and (2 2 4) are parallel to each other.

Separation Between successive (h k l) Planes:

Let (h k l) be the Miller indices of the plane ABC.

Let $OP = d_{hkl}$ be the normal to the plane ABC passing through the origin O.

Let OP make angles α, β, γ with X, Y & Z axes respectively.

Then $\cos\alpha = d / OA = d / x = d / (a / h)$

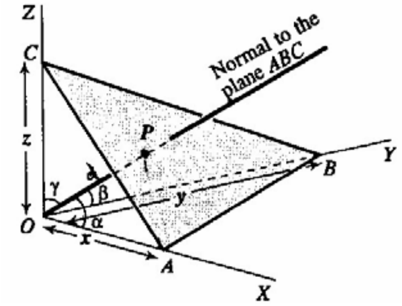


Fig. Interplanar Spacing.

$\cos\beta = d / OB = d / y = d / (b / k)$

$\cos\gamma = d / OC = d/z = d/(c/l)$

(Since convention in designing Miller indices $x=a/h$, $y=b/k$, $z=c/l$)

Now $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

Hence $d^2 / (a / h)^2 + d^2 / (b/k)^2 + d^2 / (c/l)^2 = 1$

➔ $(d h / a)^2 + (d k / b)^2 + (d l / c)^2 = 1$

➔ $d_{(h k l)} = OP = 1 / \sqrt{(h^2/a^2 + k^2/b^2 + l^2/c^2)}$.

Therefore for cubic structure, a=b=c,

$$d_{(h k l)} = a / \sqrt{(h^2 + k^2 + l^2)}$$

Let the next plane be parallel to ABC be at a distance OQ from the origin. Then its intercepts are 2a / h, 2a / k, 2a / l.

Therefore $OQ = 2d = 2a / \sqrt{(h^2 + k^2 + l^2)}$

Hence the spacing between adjacent planes = OQ - OP = PQ.

i.e. $d = a / \sqrt{(h^2 + k^2 + l^2)}$

Expression for Space Lattice Constant 'a' For a Cubic Lattice:

Density p = (total mass of molecules belonging to unit cell) / (volume of unit cell)

Total mass of molecule belonging to unit cell = nM / N_A

Where n-number of molecules belonging to unit cell
M-Molecular weight
N_A -Avagadro Number

Volume of cube = a^3

Therefore $p = nM / a^3 N_A$

Or $a^3 = nM / p N_A$

Lattice Constant for Cubic Lattice $a = (nM / p N_A)^{1/3}$.

Diffraction of X- Rays by Crystal Planes:

X-Rays are electromagnetic waves like ordinary light, therefore, they should exhibit interference and diffraction .Diffraction occurs when waves pass across an object whose dimensions are of the order of their own wavelengths. The wavelength of X-rays is of the order of 0.1nm or 10 -8 cm so that ordinary devices such as ruled diffraction gratings do not produce observable effects with X-rays. Laue suggested that a crystal which consisted of a 3-dimensional array of regularly spaced atoms could serve the purpose of a grating. The crystal differs from ordinary grating in the sence that the diffracting centers in the crystal are not in one plane. Hence the crystal acts as a space grating rather than a plane grating. There are 3 main X-ray diffraction methods by which the crystal structure can be analysed.

(1) Laue Method – for single crystal

(2) Powder Method- for finely divided crystalline or polycrystalline powder

(3) Rotating crystal Method - for single crystal

Bragg's Law:

It states that the X-rays reflected from different parallel planes of a crystal interfere constructively when the path difference is integral multiple of wavelength of X-rays.

Consider a crystal made up of equidistant parallel planes of atoms with the interplanar spacing d.

Let wave front of a monochromatic X-ray beam of wavelength ʎ fall at an angle θ on these atomic planes. Each atom scatters the X-rays in all directions.

In certain directions these scattered radiations are in phase ie they interfere constructively while in all other directions, there is destructive interference.

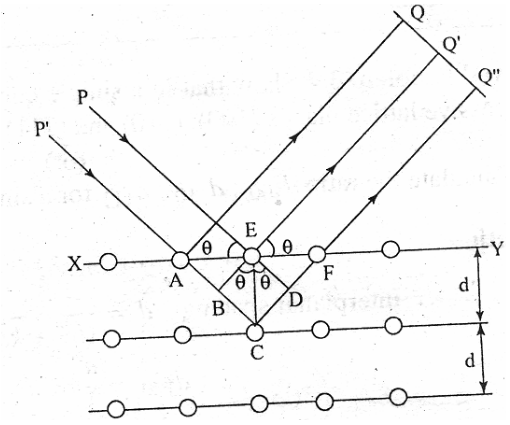


Figure 1 X-Ray Scattering by Crystal.

Consider the X-rays PE and P'A are inclined at an angle θ with the top of the crystal plane XY. They are scattered along AQ and EQ' at an angle θ w.r.t plane XY. Consider another incoming beam P'C is scattered along CQ"

Let normal EB & ED be drawn to AC &CF . if EB & ED are parallel incident and reflected wave fronts then the path difference between the incident and reflected waves is given by

Δ = BC + CD ---------------(1)

In Δ ABC , $\sin\theta$ = BC / EC = BC / d

i e BC = $d \sin\theta$

Similarly, in Δ DEC , CD = $d \sin\theta$

Hence path difference Δ = $2d \sin\theta$

If the 2 consecutive planes scatter waves in phase with each other , then the path difference must be an integral multiple of wavelength.

i e $\Delta = n\lambda$ where $n = 0, 1, 2, 3, \ldots$ is the order of reflection

Thus the condition for in phase scattering by the planes in a crystal is given by

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

This condition is known as Bragg's Law .

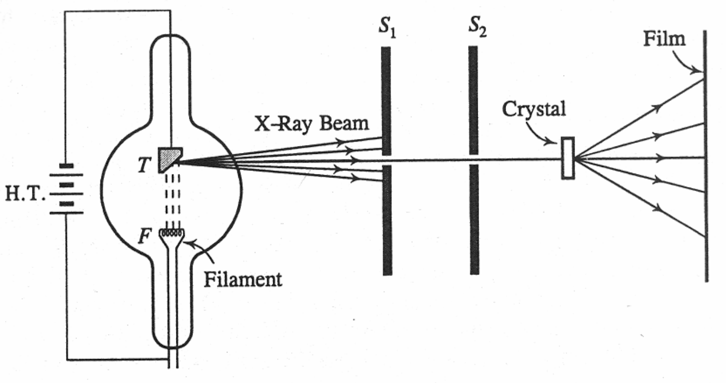
The maximum possible value for θ is 1 .

$$n\, d / 2\, d \leq 1$$

the wavelength λ should not exceed twice the inter planar spacing for diffraction to occur.

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.

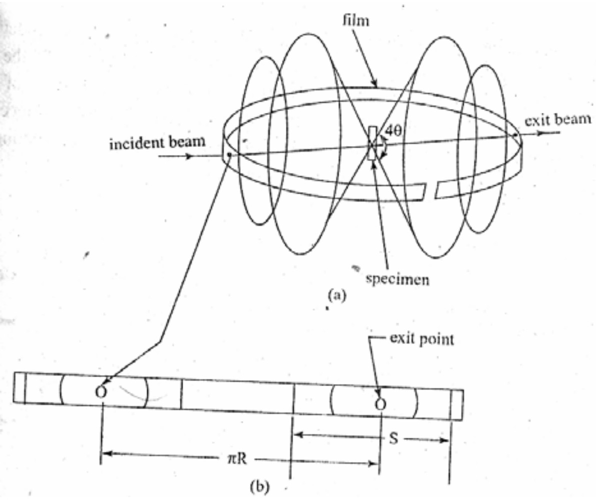


X–RAY DIFFRACTION (LAUE's METHOD)

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

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

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

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.

Questions

1. Explain the various types of bonding in crystals. Illustrate with examples.
2. Distinguish between ionic and covalent bonding in solids.
3. Obtain a relation between potential energy and inter atomic spacing of a molecule.
4. Derive an expression for cohesive energy of a solid.
5. Obtain an equation for total binding energy of sodium chloride crystal.
6. Differentiate between crystalline and amorphous solids.
7. Explain the terms i) Basis ii) Space lattice iii) Unit cell
8. Explain with neat diagram the following crystal structures.

i) simple cubic structure(SC)
ii) body centered cubic structure(BCC)
iii) face centered cubic structure (FCC)

9. What do you understand by packing density? Show that packing density for simple lattice, body centered lattice and face centered lattice is ∏/6 , √3∏/8 , √2∏/6 respectively
10. Show that FCC is the most closely packed of the three cubic structures.
11. a) For a crystal having $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^0$, what is the crystal system?
    b) For a crystal having $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^0$, what is the crystal system?
    c) Can you specify the Bravais lattices for parts (a) and (b) explain.
12. Explain the special features of the three types of lattices of cubic crystals?
13. What are ionic crystals? Explain the formation of an ionic crystal and obtain an expression for its cohesive energy?
14. What is a Bravais lattice? What are the different space lattices in the cubic system?
15. What are the miller indices? How they obtained?
16. Derive the expression for the interplannar spacing between two adjacent planes of miller indices (h k l) in a cubic lattice of edge length 'a '.
17. Derive bragg's law
18. Describe Laue's method of determination of crystal structure.
19. Explain the power method of crystal structure analysis.