Unit - IV

Solid State

Solids are classified as crystalline and amorphous solids.

Crystalline Solids

Crystalline Solids are solids which possess characteristic geometrical shapes and melting points. They are anisotropic. They have a long range order, i.e., the atoms or molecules constituting the crystals are in a perfect order over extended regions within each individual crystal. Throughout the bulk of the crystalline solid, each particle has an identical environment. Examples of crystalline solids are NaCl, KCl, diamond, graphite, metals etc.

Amorphous Solids

Amorphous solids are solids which do not possess characteristic geometrical shapes and melting points. They gradually soften on heating. They are isotropic. They have only short range order. Examples of amorphous solids are glass, rubber plastic atc.

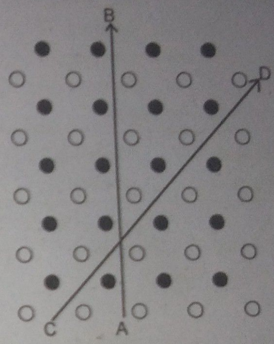
Isotropic and Anisotropic Solids :

Isotropic Substances :

Some substances have equal values of properties in all directions. Some of the properties are ; refractive index, thermal expansion, electrical and thermal conductivity, solubility, tensile strength. These substances are called isotropic substances. Amorphous substances behave in this manner. So they are called isotropic. Liquids and gases also behave in a similar manner, and hence they are also called isotropic.

Anisotropic Crystals :

Some substances have different values for these properties in two or more directions. They are called anisotropic substances. Most crystalline substances are anisotropic. For example, the velocity of light passing through a crystal varies with the direction in which it is measured. Thus a ray of light entering such a crystal may split up into two components. Each component may follow a different path and travel with different velocity. This phenomenon is known as double refraction. The anisotropy in itself is a strong evidence for the existence of ordered molecular arrangements in crystals.



In figure a simple two dimensional arrangement of different atoms are shown. If the properties are measured along the line CD, they will be different from those measured along the line AB. The reason is that, along CD each row is made up of alternate types of atoms and along AB each row is made up of one type of atoms only.

E.g: i. The coefficient of thermal expansion of AgI is positive in one direction while it is negative in another direction.

ii. The indices of refraction for sodium D line for $K_2Cr_2O_7$ crystals are different along different axis.

Nature of the Solid State :

In solid state, the atoms, ions or molecules i.e., the particles constituting the state are confined to a given position surrounded by others. In this state the particles are closely packed and are held strongly by forces of attraction between them. Because of this, the state is characterised by (i) definite shape (ii) rigidity (iii) non-compressibility (iv) definite volume (v) anisotropy.

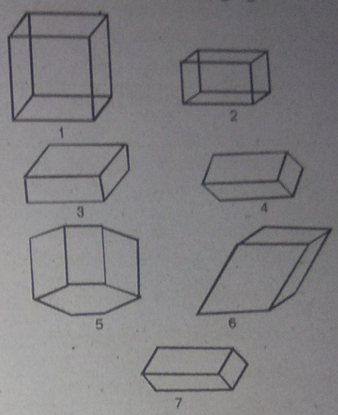
Seven Crystal Systems :

Origin of crystal system and their classifications :

It can be shown from geometrial consideration that there can be thirty two different combinations of elements of symmetry of a crystal. These are called point groups. These thirty two point groups are grouped, according to certain minimum symmetries, into seven crystal system. This is the basis on which the crystals are classified. The seven crystal systems are, cubic tetragonal, orthorhombic, monoclinic, hexagonal, rhombohedral and triclinic. Description i.e., the characteristics of the seven crystal systems are given in the following table.

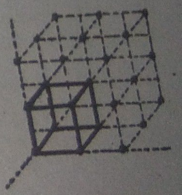
Crystal System	Axes and angles	Minimum symmetry	Examples
1. Cubic	$a = b = c$ $\alpha=\beta=\gamma=90^0$	4 three fold axes (along the diagonals of the cube)	NaCl, KCl, Ag, diamond
2. Tetragonal	$a = b \neq c$ $\alpha=\beta=\gamma=90^0$	1 four fold axes	White tin, MgF_2, $NiSO_4$
3. Ortho rhombic	$a \neq b \neq c$ $\alpha=\beta=\gamma=90^0$	3 two fold axes	$HgCl_2$, KNO_3 Rhombic S.
4. Mono clinic	$a = b \neq c$ $\alpha =\gamma=90^0$ $\beta=90^0$	1 two fold axis	$KClO_3$ mono clinic S.
5. Hexagonal	$a = b \neq c$ $\alpha=\beta=90^0$ $\gamma=120^0$	1 six fold axis	Mg, graphite, ZnO, HgS.
6. Rhomo hedral	$a \neq b \neq c$ $\alpha=\beta=90^0$ $\gamma=120^0$ (or) $\alpha=\beta=\gamma$	1 three fold axis	Al_2O_3, calcite
7. Triclinic	$a \neq b \neq c$ $\alpha\neq\beta\neq\gamma\neq90^0$	None	$CuSO_4$, $5H_2O$

Here a, b and c are the axis. The angle between 'a' and 'b' is 'α'; that between 'b' and 'c' is 'β' and that between 'c' and -a' is 'γ'. These seven systems are shown in the following figure.



In the study of crystals two geometrical concepts are used, They are space lattice and unit cell.

Space lattice or Crystal lattice :



A space lattice is an array of points showing how molecules, atoms or ions arranged at different sites in three dimensional space.

Such points indicate the positions of molecules, atoms or ions in a crystal relative to one another in space.

An example of the arary of points in a three dimenssonal space lattice is shown in figure. Each point represents an identical atom, molecule or ion. The lines are imaginary.

The, lattice points can be broken up into a number of unit cells.

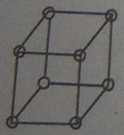
Bravais Lattice :

Bravais showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged in a three dimensional space. Thus the total number of space lattices belonging to all the seven crystal systems put together is only 14 As shown in the table given below.

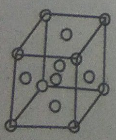
	Crystal system	Bravais Lattices	Total Lattices
1.	Cubic	(i) Primitive (ii) face centered (iii) body centered.	3
2.	Orthorhombic	(i) Primitive (ii) face centerd (iii)body centered, (iv) end centered.	4
3.	Tetragonal	(i) Primitive (ii) body centered	2
4.	Monoclinic	(i) Primitive (ii) end centered	2
5.	Tricilnic	Primitive	1
6.	Hexogonal	Primitive	1
7.	Rhombohedral	Primitive	1
		Total	**14**

The crystals belonging to cubic system have three kinds of Bravais lattices depending upon the shapes of unit cells.

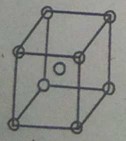
a) The Simple or primitive cubic lattice (P) in which there are point only at the corners of each unit cell. In this arrangement the co-ordination number is 6. Total number of spheres (atoms) in an unit cell is 1.



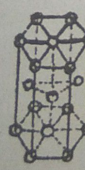
sc



fcc



bcc



hcp

b) The face centered cubic lattice (F) in which there are points at the corners as well as at the centre of each of the six faces of the cube. (Fig 8 c). Total number of spheres is 4. The co-ordination number is twelve.

c) The body centered cubic lattice (I) In which there are points at the corners as well as the centre of each cube. The total number of spheres is 2. The co-ordination number is 8.

The crystals belonging to hexagonal system have only one kind of Bravais lattice - It is hexagonal close packed hcp systerm -The over all co-ordination number is twelve. The number of atoms present per unit cell in the bcp system is 2. The hcp arrangement has three unit cells in it. (Fig 8 b). The efficiency of packing decreases in the order of fcc = hcp > bec > sc.

The other five systems are not discussed in this book.

Summary

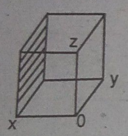
Lattice	*Co-ordination number*	*Number of atoms/unit cell*	*Examples*
Cubic			
Simple/ primitive (sc)	6	1	Mn, KCI
Body centered (bcc)	8	2	Ba, Cs, K, Li diamond, ZnS
Face centered (fcc)	12	4	Noble gases Ag, Al, Au, Cu, Ni, Pd, H_2, NaCl
Hexogonal close packed (acp)	22	2	Noble gases Cd, Zn, Mg, ice

Unit Cell :

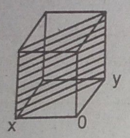
An unit cell is the smallest repeating space lattice which when repeated over and over results in a crystal of the given substance. The points joined by the thick lines in figure is one unit cell. Thus the space lattice contains a lot number of unit cells.

Lattice planes :

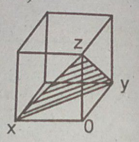
The point in a space lattice may be arranged in a large number of ways in a series of parallel and equidistant planes known as the lattice planes. In terms of these planes, it is convenient to describe a crystal lattice. Simplest types of crystals belong to the cubic system. The simple cubic crystal has the important planes (100) (110) and (III). The face centred,cubic crystal has the planes (200), (220) and (I I I). The body centred cubic crystal has planes (200), (110) and (222).



(100)



(110)



(111)

Born - Lande equation

This equation is used to calculate the latice energy of ionic compounds. The equation i s

$$U_o = \frac{N_o A Z^2 e^2}{r_o}\left(\frac{1}{n} - 1\right)$$

U_o - Unit of lattice energy per mole

N_o - Avogadro number

A - Madelung constant

r_o - Inter ionic distance

e - Electronic charge

n - Born exponent

z - Charge of ions ($Z_1 = Z_2 = Z$)

Charges of the cation and anion

The equation may be further improved by considering the following correction factors.

i. Vander Walls forces between the ions.

ii. Zero point energy of the crystals. This type of energy is due to vibration of the ion in the crystal.

iii. **Resonance energy :** This type of energy is due to covalent nature of the ionic bond.

Law of Rational Indices :

There are three fundamental laws in crystallography. The law of rational indices is one among them.

Law :

The intercepts of any face of a crystal along the crystallographic axis are either equal to the unit intercepts (a, b c) or some simple multipies of them".

Explanation :

Let OX, OY and OZ be the crystallographic axis. Let ABC be a unit plane.

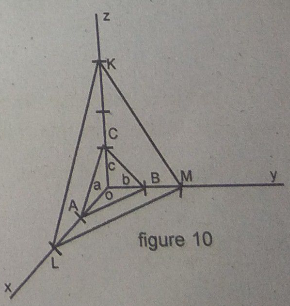


figure 10

The unit intercepts are a, b, and c. According to the law of rationallity of indices or intercepts, the intercepts of any face such as KLM on the same three axis will be simple multiples of a, b and c. From the figure 10 the intercepts of the plane KLM on the three axis are 2a : 2b : 3c.

The coefficient of a, b and c are known as 'Weiss indices' Weiss indices are not always whole numbers as in the given example. They may have fractional values as well as infinity. Therefore instead of Weiss indices, Miller indices have been introduced.

Miller Indices :

They are a set of integers'(h, k, l) which is used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axis.

To get the miller indices, the reciprocals of the Wesis indices are taken. They are converted into whole numbers by multilying them throughout by the least common denominator.

In figure for the plane KLM the Weiss indices of the planes are 2, 2 and 3. The reciprocals are ½, ½ and Multiplyiug them by least common denominator i.e., 6, we get 3 3, and 2. Thus the Miller indices for the plane KLM are 3 : 3 : 2. The plane is designated as (332) place. In general the planes are termed as (hkl) planes. Here for the K LM plane in figure 10, h = 3, k = 3 and I = 2.

For the plane ABC in the figure 10, the Weiss indices are 1, 1 and 1 and the Miller indices are also 1, 1 and 1 . Therefore the plane ABC is called (111) plane.

Use :

Miller indices are used to calculate the distance between two parallel planes in a crystal, if the length of the side of the cube is known.

The distance between the parallel planes in a crystal are designated as d_{hkl}. For a cubic lattice.

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + K^2 + l^2)}}$$

where a' is the length of the side of the cube and h, k and l are the Miller indices of the plane.

From d, the ratio $d'_{100} : d_{110} : d_{111}$ are calculated. From these values we can determine the crystal system and the crystal class to which the crystal belongs. Some important crystal planes for a simple cupic crystal are shown in figure. 9

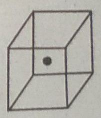
Symmetry Elements in Crystals

a) Centre of symmetry :

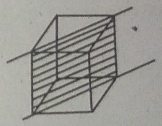
It is a point in a crystal through which if an imaginary straight line is drawn, it meets equivalant points at equal distances on either side. For any crystal only one centre of symmetry is possible.

b) Plane of symmetry :

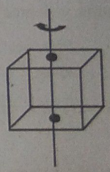
It is an imaginary plane which divides the crystal into two halves so that one half is the mirror image of the other.



Centre of Symmetry



Plane of Symmetry



axis of symmetry
(4 - fold axis)

For a cubic crystal, there are two types of planes of symmetry (i) three rectangular plans of symmetry, since there are six faces (ii) six diagonal planes of symmetry, since there are twelve edges.

c) Axis of symmetry :

It is an imaginary axis around which if the crystal is rotated through 360°, the crystal presents, exactly the same apperance more than one time. There are two types of axis of symmetry.

i) n-fold axis of symmetry :

n-fold axis of symmetry is an imaginary line (axis) around which if the crystal is rotated through 360^{0}C the crystal presents exactly the same appearance 'n' times. If n = 2,3,4 or 6 it is called 2,3,4 or 6 fold axis of symmetry respectively]

ii) n-fold axis of rotation-inversion :

n-fold axis of rotation inversion is an imaginary line (axis) through which if the crystal is rotated through 360^{0}C and then inverted through the centre the crystal presents the same appearance. if n = 2 or 4 it is called 2 or 4 fold axis of rotation-inversion respectively.

Every crystal does not have all these elements of symmetry. There are 32 possible combinations of these elements of symmetry. Thus crystals are divided into 32 crystal classes. according to the elements of symmetry possessed by the crystals.

Symmetry elements of a cube :

There are 23 elements of symmetry in a simple cubic crystal. They are as follows

Centre of symmetry	I	
	—	1
Planes of symmetry		
Rectangular planes of symmetry	3	
Diagonal planes of symmetry	6	9
Axis of symmetry	—	
Two fold axis of symmetry	6	
Three fold axis of symmetry	4	
Four fold axis of symmetry	3	13
		23

X-RAY DIFFRACTION BY CRYSTALS

Principle :

X-rays are electromagnetic radiations with wave lengths of about 0 - I nm or A°. X rays can be prepared by producing cathode rays in highly evacuated discharge tube and allowing them to fall on a metal target called an anticathode.

Laue suggested that the distance between the lattice planes in the crystals are in the order of a few angstroms. Therefore be suggested that the crystal should act as a diffraction grating for the X-rays since the wave length of X-rays are also in the order of 1 A° Bragg suggested that crystal's can act as reflection grating also. He developed a simple equation to determine the structure of a crystal using the X-rays. This equation is known as the Bragg's equation or Bragg's law.

Derivation of Bragg's Equation :

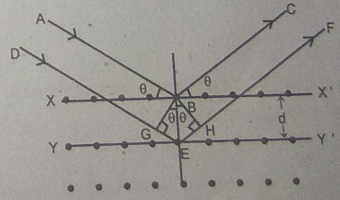
Equation : $n\lambda = 2d \sin \theta$

Explanation of the terms :

n = order of refletion : λ = wavelength of the X-ray used ; d = Inter planar distance; θ = glancing angle of the incident X-ray.

Derivation :

The figure show, the reflection of monochromatic X-rays with wavelength l by the planes of atoms or ions with inter planar distance 'd' (BE). Let all the incident rays be in phase. Let the glancing angle be θ. If the reflected rays are in phase they reinforce. If they are out of phase they



will cancel out each other. Let us consider two waves, 1 and 2 failing on planes XX' and YY' respectively at anangle q. Let the two waves be in phase with each other. The wave 2 travels, a longer distance before and after it is reflected by the plane YY' than wave I is reflected by the plane XX'. The path difference d of the two waves is got by drawing BG ⊥ DE and BH ⊥ EF.

Then $\delta = GE + EH \qquad (1)$

If the reflected waves are to be in phase the condition is

$GE + EH = \lambda$ or $n\lambda$

where 'n' is an integer

i e., $n\lambda = GE + EH$

From figure

$\angle GBE = \angle ABX = \theta (= 90 - \angle XBG) \qquad (2)$

Similarly $\angle HBE = \angle CBX' = \theta$

∴ Triangles BGE and BHE are congruent

$\therefore GE = EH \qquad (3)$

$\therefore n\lambda = 2GE \qquad (4)$

$\boxed{\therefore n\lambda = 2d\sin\theta} \qquad (5)$

$$\left\{\therefore \frac{GE}{BE} = \frac{GE}{d} = \sin\theta\right\}$$

When n=1, 2, 3...

'n' is known as the order of reflection. The equation (5) is known as the Bragg's equation or the Bragg's Law.

Uses :

i) We know from Bragg's equation $n\lambda = 2d\sin\theta$. By knowing λ and θ we can find the ratio dλ. From this we can calculate d if λ is known and vice versa

ii) From Bragg's law we can determine the crystal structure [Refer the heading "crystal structures of NaCl, KCl and CsCl in subsequent pages.]

iii) We can determine the Avogadro's number using Bragg's law.

1. LAUE'S METHOD :

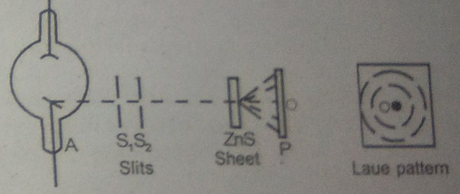
Principle : We know from Bragg's equation

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

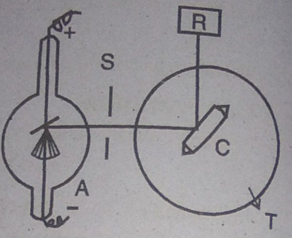
In this method, the angle of incidence (θ) is fixed and X-rays with the whole range of wave lengths are used. A certain set of planes which fulfil the condition given by Bragg's Law gives a spot. The various sets of planes present in the crystal give several such spots. We get the Laue pattern of spots.

Procedure :

The apparatus is shown in figure 16. X-ray from the X-ray tube, 'A' are passed through slits S_1, S_2 and converted into a beam. It is allowed to fall on ZnS sheet and then fall on a crystal 'C'. The various atoms in various planes of the crystal satifying the Bragg's Law scatter or deflect some of the X-rays from the original path. Tnese X-rays are photographed and developed. We get the Laue pattern 'D'. From a study of the Laue patterns crystal structure is determined.



2. Bragg's Mothod:



Principle :

In the Bragg's method 'l' the wevelenght of the X-ray is fixed, and θ is varied by rotating the crystal about it's axis. The angles for which reflections are maximum give the'θ' values which are substituted in the equation.

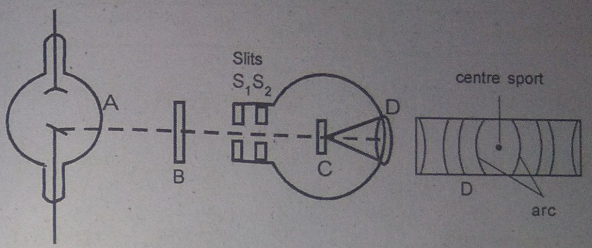
$$n\lambda = 2d \sin\theta$$

The lowest angle at which the maximum reflection occurs corresponds to $n = 1$. This is called the first order reflection. The next higher angle at which the maximum reflection occurs corresponds to $n = 2$. Similarly, we can explain other orders of reflections also. This is called the second order reflection and so on. The process in carried out for each plane of the crystal.

Procedure : X-rays are generated in the X-rays tube 'A'. They are passed through a focussing slit 'S'. A narrow beam is got. It is allowed to strike a single crystal 'C' mounted on a turn table, T' A particular face is exposed to the X-ray. The crystal is rotated gradually and the glancing angle θ at which the reflections are maximum is determined using a recording device 'R'. The experiment is repeated for $n = 1,2.....$ Similarly different faces are exposed to the X-rays and the θ values are determined from which d values for various planes are calculated. From these values we can determine the crystal system and the crystal class to which the crystal belongs.

Powder Method : (Debye - Scherre)

Principle : In Laue's method and the Bragg's method we require well-formed single crystals which are difficult to get. In Debye-Ścherrer method we use very fine powder. In the powder the crystal planes are oriented at all possible angles to the beam of X-rays i.e., some particales will have their (100) planes properly oriented to the X-rays : some will have (110) planes and some others will have (iii) planes correctly oriented for reflection.



Procedure:

X-rays are generated in the X-ray tube 'A'. (figure I8). They are passed through a focussing slit S_1 and S_2 and 'B'. A narrow beam is got. It is allowed to strike the powdered crystals in a glass capillary 'C'. The diffractad X - rays strike a photographic film strip D' which is placed in the form of a circular arc. We get a bright spot at the centre and arcs appear on either side of the bright spot. Each pair of arc is equi-distant from the centre. They correspond to a particular order of diffraction for a set of planes. q can be calculated from

$$2\theta = \frac{s}{r}$$

Where S = the distance of an are from the central spot and
r = distance from the powder to the film.

θ will be in radians. To convert into degree the q' is multiplied by 180/p . From θ we can calculate 'd'. From'd' the ratios of $d_{100} ; d_{110} : d_{111}$ are calculated. From these values we can determine the crystal system and the crystal class to which the, crystal belongs.

Crystal Structure of Sodium Chloride :

For sodium chloride (rock salt) the θ for first order reflection for the three planes viz, (100), (110) and (I 11) planes, were found to be 5.9^0, 8.4^0 and 5.2^0 respectively. The ratio $d_{100} : d_{110} : d_{111}$ is calculated. It is found to be I : 0.704 : 1.136. This ratio is compared with the following table.

Type of Lattice	(d_{100}) :	(d_{110}) :	(d_{111})	
Simple cube	1 :	$\frac{1}{\sqrt{2}}$:	$\frac{1}{\sqrt{3}}$	i.e., 1: 0.707 : 0.577
Face centered cube	1 :	$\frac{1}{\sqrt{2}}$:	$\frac{2}{\sqrt{3}}$	i.e., 1: 0.707 : 0.154
body centered cube	1 :	$\frac{2}{\sqrt{2}}$:	$\frac{1}{\sqrt{3}}$	i.e., 1: 1.414 : 0.577

The ratio for sodium chloride is very close to the spacing among the three planes of a face centred cube, It is concluded that sodium chloride crystal has a face centred cubic structure.

The first order reflection Patterns of its (111) planes of these alternate weak and strong peaks. The alternation of these atoms intensities are due to alternate layers or planes of chlorine atoms and sodium atoms. This alternation of intensities also show that the particles that are present in lattice sites are ions.

The raidus ratio of NaCl i.e., $r_{Na^+} r_{Cl^-} = 0.59/1.81 = 0524$. This value lies between 0.414 and 0.732. So we predict that the co-ordination number should be 4 or 6. Its shape should be square palanar or octahedral.

X-ray studies of NaCl crystals have shown that it has octahedral structure i.e., each Na^+ ion is surrounded by six equidistant Cl^- ions placed at the corners of a regular octahedron and similarly each Cl^- ion is surrounded by six equidisatant Na^+ ions. In other words, stoichiometry of $Na^+ : Cl^- = 1 : 1$ and co-ordination number is 6 : 6.

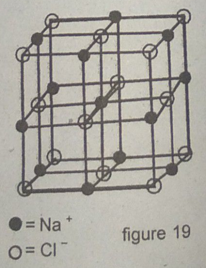


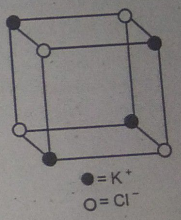
figure 19

Thus the crystal structure of sodium chloride is as follows:

1. It contains two interpenetrating face centered cubic lattices one containing chloride ions and the other containing sodium ions (Figure).
2. Each unit cell of sodium chloride consists of 14 sodium ions and 13 chloride ions.
3. Each sodium ion is surrounded by six chloride ions.
4. Each chloride ion is surrounded by six sodium ions.

Crystal Structure of Potassium Chloride :

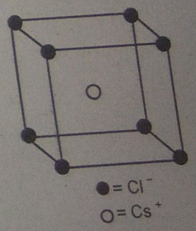
For KCI (sylvine) the q for first order reflection for (100) (110) and (111) planes were found to be 5.38°, 7.61° and 9. 38° respectively. The ratio $d_{100} : d_{110} - d_{111}$ is 1:0.704 ; 0.575 This ratio corresponds to that for a simple cubic lattice. KCI is isomorphous with NaCl. So KCI also should have a crystal structure similar to that of NaCl. But it is not so. This observed discrepancy in the results of X-ray analysis can be easily explained.



The X-ray scattering power of atoms and ions depends on the number of extra nuclear electrons. K^+ and Cl^- ions possess equal number of extra nuclear electrons. So their scattering powers will also be the same. The first order reflections from (111) planes are extinguished due to destructive interference. So the result of X-ray analysis indicate a simple cubic structure to KCl (Figure 20)

Crystal Structure of Cecium Chloride :

X-ray analysis shows that it has a body centered cubic structure. The radius ratio of CsCl i.e., $r_{Cs}^{+} / r_{C}^{-} = 1.69 / 1.84 = 0.93$. The value lies between 0 .7 32 and I . So we predict that the co-ordination number should be 8. Its shape should be a body centered cubic structure.



i.e., each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ion is surrounded by 8 Cs^+ ions. Thus stoichiometry of Cs^+ Cl^- is 1 : 1 and the co-ordination number is 8:8.

Radius / Ratio rule :

It is defind as the ratio of radii of cations to those of anions Mathematically it can be written as $R_r = r_c^+ / r_a^-$

Where R_r is the radius ratio, r_c+ is the ionic radius of the cation and r_a- is the ionic radius of the anion. The co-ordination number and geometry of ah ionic crystal can be determined from radius ratio. From known ionic radio the radius ratio has been calculated for each co-ordication number and geometry. This calculated radius ratio is known as limiting radius ratio.

Its limitations :

The radius ratio values are not accurate. They are applicable to some cases only. There are exceptions to the predictions made from radius ratios.

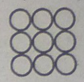
PACKING IN CRYSTALS

If the radius ratio of a particular ionic crystal falls below the limiting radius ratio the corresponding structure will be unstable - Some common co-ordination numbers are 2, 4, 6 and 8. We can work out the limiting radius ratio for these and their corresponding shapes may be predicted. The following table illustrates these facts.

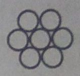
Co-Ordination number	*shape with examples*	*Limiting radius ratio*
2	Linear	0 to 0.155
3	Plne triangle (Boron oxide)	0.155 o 0.225
4	Tetrahedral (Zns)	0.225 to 0.414
4	Square planar	0.414 to 0.732
6	Octahedral (NaCl)	0.414 to 0.732
8	Body centered cubic (CsCl)	0.732 to 1.000
12	Close packing ccp and hap (metals)	1

X-ray studies on the structure of metallic crystals have revealed the fact that each atom in a metal crystal has eight or twelve neighbours and that these atoms have closest packed arrangements. We can imagine that such crystals have closely packed atoms in a number of layers. These layers are arranged one above the other. The packing of atoms in metals is in One of the three following geometrical arrangements : 1) cubic close packed (ccp) or face centered cubic (fcc) : 2) hexegonal close packed (hcp) : or 3) body-centered cubic (bcc).

The metal ions are assumed to be spherical. These spheres can be arranged in layers in two ways.



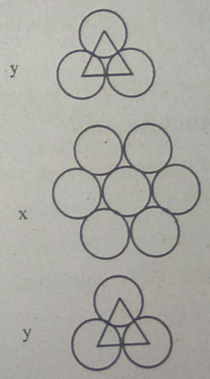
Type I



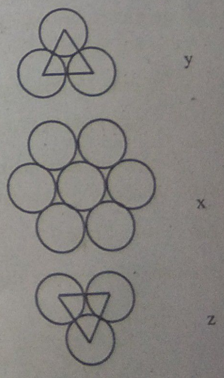
Type II

bcc - arrangement :

To build up a crystal in bcc type of arrangement, the first layer of atoms is arranged as shown in Type I. Let this by x type layer. The second layer is arranged by putting the atoms in the shaded space shown in the figure.



A



B

Let this be y type layer. The third layer can be arranged as the first layer. Now the crystal will have only two types of .layer denoted by x and y, and the pattern of layers is xy, xy, xy........ we get a bcc arrangement. The over all co-ordination number is eight. E.g., Cr, Fe, W, Na, fluorite.

hcp - arrangement :

To build up a crystal in hcp type of arrangement the first layer of atoms is arranged as shown in type II. Let this be x type layer. The secound layer is arranged by putting the atoms in the shaded space shown in the figure. Let this be y type layer. The third layer can be arranged as the first layer. Now the crystal will have only two type of layers denoted by x and y and the pattern of layers is xy, xy, xy.... We get a hcp arrangement. The over a)i co-ordination number is twelve. (Fig. 23 A) E.g,, Co, Mg, Ti, Zn, Zinc sulphide (wurtzite).

ccp or fcc - arrangement :

To build up a crystal in ccp or fcc type of arrangement, the first layer of atoms is arrangement as shown in figure (x). The second layer is arranged by putting the atoms as in the figure (y). The third layer can be arranged by putting the atoms as in the figure (z). Now the crystal will have three types of layers, denoted by x, y and z and the pattern of layers is xyz, xyz, xyz.... We get a ccp or fcc arrangement. In this arrangement also the over all co-ordination number is twelve. E.g., Al, Cu, Au, Pb, Ag, Ni, Pd, Pt., zinc sulphide (zinc blende) and spinel.

The different arrangements given above are illustrated in figure 8.

DETERMINATION OF AVOGADRO NUMBER

Besides the determination of crystal structure, we can determine Avogadro number by X-ray diffraction studies.

We know, $n\lambda = 2d \sin\theta$

when n , λ and θ are known, d can be calculated. For a cubic lattice

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + K^2 + l^2)}}$$

where d_{hkl} = distance between parallel planes whose Miller indices are h, k and l.

Knowing h, k, I and d we can calculate 'a' which is length of the side of the cube : From 'a' we can calculate the volume of the unit cell.

$$\text{Volume of the unit cell} = a^3$$

From the volume of the unit cell we can calculate its molar volume.

Molar volume = Volume of unit cell x Number of unit cells in one mole.

$$\rho = \frac{M \times Z}{a^3 \times N} \qquad (6)$$

$$N = \frac{M \times Z}{a^3 \times \rho}$$

We know, density of a crystal r = (7)

Substituting the value of V from (6) in (7) we have

$$V = a^3 \times \frac{N}{Z} \qquad (8)$$

and $\frac{M}{V}$ (9)

Where, ρ = density of the crystal, which could be experimentally determined

M = Molecular weight of the sustance analysed

N = Avogadro number

Z = Lattice site

[The number of atoms present in one unit cell is called the lattice site. The number of atoms present in an unit cell is as follows :

Simple cubic (sc) system = *1 atom*

Face centred cubic (fcc) system = *4 atom*

Body centred cubic (bcc) system = 2 atoms

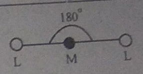
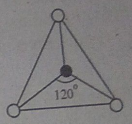
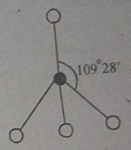
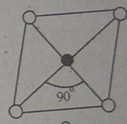
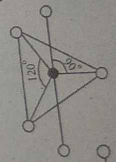
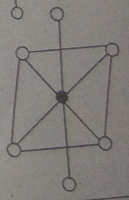
Thus Avogadro number "N" can be determined knowing the values of d and r.

BOND THEORY AND DEFECTS

Valance bond theory (or) Pauling's Theory

1. The central metal atom or ion provides a number of empty s,p and d atomic orbitals equal to its C.N. These orbitals can accommodate electrons donated by the ligands.
2. The vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These are vacant, equivalent in energy and have definite geometry.
3. The metal orbitals and ligand orbitals overlap to form strong bonds (co-ordinate bonds).
4. The d-orbitals involved in the hybridisation may be inner (n–1) d orbitals (d^2sp^3) or outer (n) d orbitals (sp^3d^2). The complexes formed using these orbitals are referred to as low spin or inner orbital complexes and high spin or outer orbital complexes respectively.
5. Each ligand donates a pair of electrons to the central metal ions.
6. The non-bonding metal electrons present in the inner orbitals do not take part in chemical bonding.
7. If the complex contains unpaired electrons, the complex is paramagnetic in nature, whereas, if it does not contain unpaired electrons it is diamagnetic.
8. Under the influence of a strong ligand, the electrons can be forced to pair up against Hund's rule of maximum multiplicity.

Geometry of complex compound :

C.N.	*Hybrid-sation*	*Arrangement*	*Geometrical Shapes*	*Examples*
2	sp	Linear		$Ag(NH_3)^{2+}$ $[Ag(CN)_2]^-$
3	sp^2	Trigonal Planar		$[HgI_3]^-$
4	sp^3	Tetrahedral		$[Co(NH_3)_4]^{2+}$ [Ni(N[illegible] [Ni[illegible] $[Cu(CN)_4]^-$ $[Cd(CN)_4]^{2-}$ $[FeCl_4]^{2-}$
	dsp^2	Square planar		$[NiCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{2+}$ $[Cu(NH_3)_4]^{3+}$
5	$dsp^3(sp^3d)$	Trigonal bipyramidal		$[Fe(CO)_5]^0$ $[Cu(Cl)_5]^{2-}$
6	$d^2sp^3(sp^3d^2)$	Octahedral		$[Co(NH_3)_6]^{3+}$ $[Cr(NH_3)_6]^{3+}$ $[Fe(CN)_6]^{3-}$ $[CoF_6]^{3-}$ $[Ni(NH_3)_6]^{3+}$ $[FeF_6]^{3-}$

Explanation by Valence Bond Theory :

According to Pauling strong bonds are not formed by pure s, p or d orbitals. Strong bonds are generally formed by hybridised orbitals. Thus they postulated that hybridisation takes place in the central atom. There are several types of hybridizations. Each hybridisation leads to a definite geometry various hybridisations and the related geometries are given as before.

1. Magnetic properties of complex compounds :

The complexes having paired electrons do not exhibit magnetic moment and they are said to be diamagnetic. The complexes having one or more unpaired electrons show definite value of magnetic moment and are called paramagnetic complexes. The greater the number of unpaired electrons in a substance the greater is the magnetic moment of the substance. The magnetic moment of a substance can be calculated using the formula.

$\eta = \sqrt{n(n+2)}$ B.M. ; μ = Magnetic movement

η = Number of unpaired electrons ; B.M = Bohr Magneton.

When, $\eta = 1$, $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ B.M.

Using this formula the number of unpaired electrons in an ion can be calculated. The values of n calculated for different magnetic moments are as follows :

Magnetic moment Bohr Magneton	*Number of unpaired electrons*
0	0
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

The magnetic studies (measurement of m) will reveal whether a co - ordination compound has unpaired electrons in it or not. Now any theory on co - ordination compounds should account for the magnetic properties of the co - ordination compounds.

Explanation by Valence Bond Theory :

The magnetic properties of co - ordination compounds can be interpreted successfully by Pauling's Valence Bond Theory.

I. *Octahedral complexes :*

Octahedral complexes result from either d^2sp^3 or sp^3d^2 hybridisation.

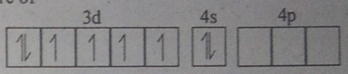
E.g.1 : $K_4[Fe(CN)_6]$

Fe^{2+} is the central metal ion and $[Fe(CN)_6]^{4-}$ is the complex ion

Electronic structure of

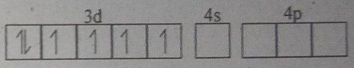
Fe (At. No. 26)

$3d^6\ 4s^2$



Fe^{2+} ion

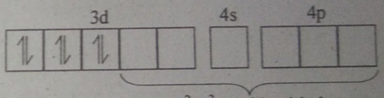
$3d^6\ 4s^0$



In the presence of CN^- ligands the electrons in the 3d orbitals are forced to pair up against Hund's Rule of maximun multiplicity to make room for the electrons donated by the ligands.

Fe^{2+} in $[Fe(CN)_6]^{4-}$

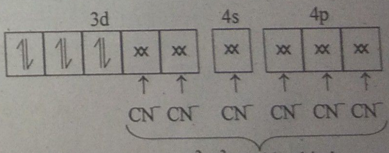
after rearrangement



d^2sp^3hybrid orbitals

In order to give the same properties and strength to all the metal ligand bonds, all the six orbitals (two 3d, one 4s and three 4p orbitals) hybridise to give six equivalent d^2sp^3 hybrid orbitals. These six hybrid orbitals which are vacant accept six electron pairs donated by six CN^- ligands and thus form $[Fe(CN)_6]^{4-}$ ion.

$[Fe(CN)_6]^{4-}$



d^2sp^3hybrid orbitals

Since the complex results from d^2sp^3 hybridisation, it has octahedral shape. Since there is no unpaired electrons in the complex the complex is diamagnetic. In the above complex the d orbitals used are from a lower shell (3d) than the s and p-orbitals (4s and 4P). Complexes using the inner d - orbitals (3d orbitals) are called inner complexes. They are also known as covalent complexes or spin paired or low spin complexes.

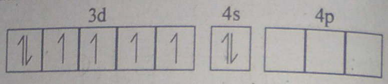
Other examples : i) $[Co(NH_3)_6]^{3+}$ ii) $[Co(CN)_6]^{3-}$

E.g. 2 : $K_3[Fe(CN)_6]$

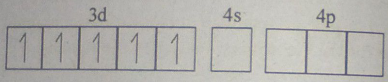
Fe^{3+} is the central metal ion and $[Fe(CN)_6]^{3-}$ is the complex ion.

on the basis of d^2sp^3 hybridisation the nature of bonding in the complex can be explained as follows :

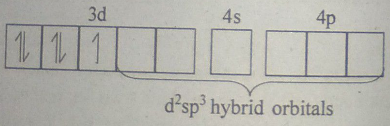
Fe (atom)
$3d^6 4s^2$



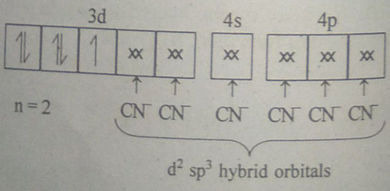
Fe^{3+} ion
$3d^5 4s^0$



Fe^{3+} in $[Fe(CN)_6]^{3-}$
after rearrangement



$[Fe(CN)_6]^{3-}$

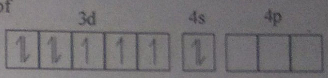


The complex has octahedral shape corresponding to d^2sp^3 hybridisation. The number of unpaired electron is one. So the complex is paramagnetic. $K_3[Fe(CN)_6]$ is an inner orbital octahedral complex.

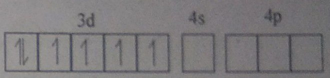
E.g. 3. : $[CoF_6]^{3-}$ ion

Co^{3+} is the central metal ion and $[CoF_6]^{3-}$ is the complex ion.

Electronic structure of
Co(At. No. 27)
$3d^7 4s^2$

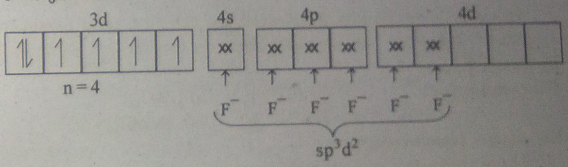


Co^{3+} ion
$3d^6 4s^0$



In a weak ligand field such as in $[CoF_6]^{3-}$ electrons do not have sufficient energy needed for pairing. Hence there are no vacant orbitals in the 3d shell. The six ligands donate one lone pair of electrons each to the first six vacant orbitals. Thus in this case, one 4s, three 4p and two 4d orbitals hybridise to give six equivalent sp^3d^2 hybrid orbitals. These accept an electron pair from each of the six fluoride ions (ligands).

$[Co(F_6)]^{3-}$ ion



Complexes such as $[CoF_6]^{3-}$ are called outer orbital complexes since the d orbitals involved in the hybridisation are from the same shell as the s and p orbitals. The outer orbital complexes are also known as ionic complexes or spin free or high spin complexes.

The four 3d orbital electrons which remain unpaired explains the paramagnetic character of $[CoF_6]^{3-}$ ion.

Other examples :

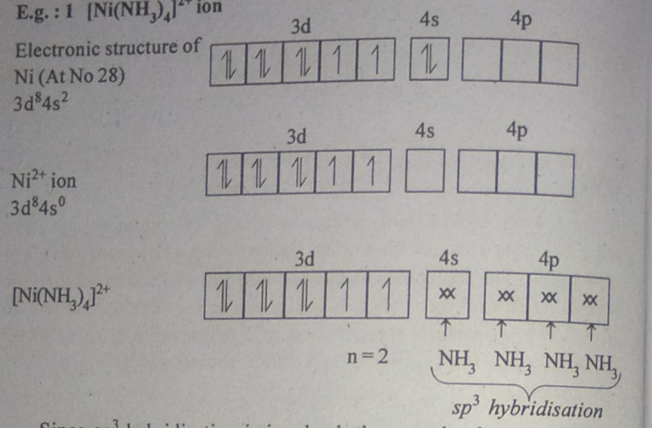
i. $[Ni(NH_3)_4]^{2+}$;

ii. $[PtCl_4]^{2-}$

iii. $[Fe(H_2O)_6]^{2+}$ $[FeF_6]^{3-}$

II. Tetrahedral Complexes : These are formed by sp^3 hybridisation.

E.g. : 1 $[Ni(NH_3)_4]^{2+}$ ion



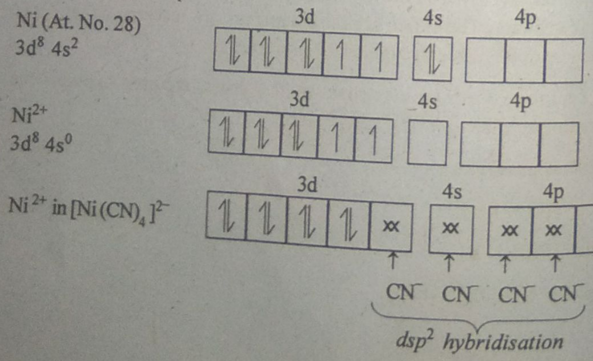
Since sp^3 hybridisation is involved, the complex has a tetrahedral structure. There are two unpaired electrons and the ion is therefore paramagnetic.

Other examples : i) $[Ni(CO)_4]^0$ iii) $[ZnCl_4)^{2-}$ ii) $[Zn(NH_3)_4]^{2+}$ iv) $[MnCl_4]^{2-}$

III. Square planar complexes :

These are formed by dsp^2 hybridisation

Example : $[Ni(CN)_4]^{2-}$



$Ni(CN)_4]^{2-}$ is diamagnetic. Hence it must involve dsp^2 hybridisation resulting in square planar structure. The two unpaired 3d electrons are coupled making one d - orbital empty and avilable for hybridisation so that dsp^2 hybrid orbitals can be formed. These vacant orbitals accept four electron pairs donated by four CN^- ligands, to form a square planer ion.

Other examples :

i) $[Pt(NH_3)_4]^{2+}$; ii) $[Pt(Cl_4)]^{2-}$

2. Colour of complex compound :

Most of the complexes are coloured. For example copper sulphate crystals are blue while anhydrous copper sulphate is white. On adding NH_4OH to $CuSO_4$ solution first is blue precipitate is formed which dissolves in excess NH_4OH giving a deep blue coloured solution.

$CuSO_4.5H_2O$ exists as $[Cu(H_2O)_6]SO_4.5H_2O$ which is blue in colour. On adding NH_4OH first $[Cu(H_2O)_6]OH_2$ is formed which is insoluble in water. So it is precipitated, On adding excess $NH_4OH[Cu(NH_3)(OH)_2$ is formed which is soluble in water and which is coloured deep blue. thus when there is an exchange of ligands the colour deepens.

In general when complexes are formed from colourless compounds, they are invariably coloured. When complexes are formed from coloured compounds the colour of complex deepens.

Explanation by Valence bond Theory :

Valence bond theory is NOT in a position to explain the colour of the complexes or depending of colour during complex formation.

Comparison between Werner's theory and Valance bond Theory :

Similarities :

i. Both account for the formation of complexes.
ii. Both recognize the geometry of the complex compounds.
iii. Both the unable to explain colour of complexes.

Distinctions :

i. Werner's theory does not rationalise the geometries of complexes through the concept of hybridisation.

ii. Wener's theory is not in position to explain the magnetic properties of complexes. Valance bond theory offers a satisfactory explanation for the magnetic properties of complexes.

Since Valance bond theory rationalises the geometry of complexes through hybridisation and since it is in a position to offer satisfactory explanation for the magnetic properties it is considered to be superior to the Werner's theory.

Merits of Valence Bond Theory :

1. It provides a satisfactory pictorial representation of the complex.
2. It is a good model for qualitative prediction of the magnetic behaviour and reactivity of complexes. Thus Valance bond theory is an improvement on Werner's theory.

Limitations of Valence Bond Theory (Pauling Theory) :

1. It is limited to qualitative explanation ; quantitative interpretation of the stability of the complexes is not possible.
2. It does not offer any explanation to the absorption spectra of complexes or reactivities.
3. The colour and magnetic moments of transition metal complexes are due to their possessing d - orbital electrons. So, there should be a quantitative connection between spectra and magnetic moment. But this connection is not revealed by Pauling's theory.
4. VBT does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
5. Sometimes the same metal assumes different geometries when formation of complex takes place. This theory does not explain as to why at one time the electrons must be rearranged against Hund's rule while at other times the electronic configuration is not disturbed.

Univeristy Questions :

1. What are isotropic solids? Give examples.
2. What are anisotropic solids? Give examples.
3. What are the difference between isotropic and anisotropic solids?
4. What are the properties of isotropic solids?
5. What are the properties of anistopic solids?
6. What are the seven types of crystal systems?
7. Define unitcell and space lattice?
8. Write short notes on Bravals lattics
9. What are Miller indices? How are they obtained ? Give example?
10. What are the uses of Miller indices?
11. Explain any three elements of symmetry with neat sketch.
12. Derive Bragg's equation of X-ray diffraction.
13. What are the uses of Bragg's equation?
14. Discuss the powder method used to determine the structure of a crystal system.
15. Describe the rotating crystal method used to determine the structure of a crystal system.
16. How is the crystal system determine using Laue's method?
17. Describe the crystal structure of sodium chloride.
18. Describe the crystal structure of potasium chloride.
19. Explain the structure of Cecium chloride.
20. Define radius ratio, and limiting radius ratio.
21. Expalin the applicaton of radius ratio in determining the structure of crystals.