

Solid State Chemistry

Introduction

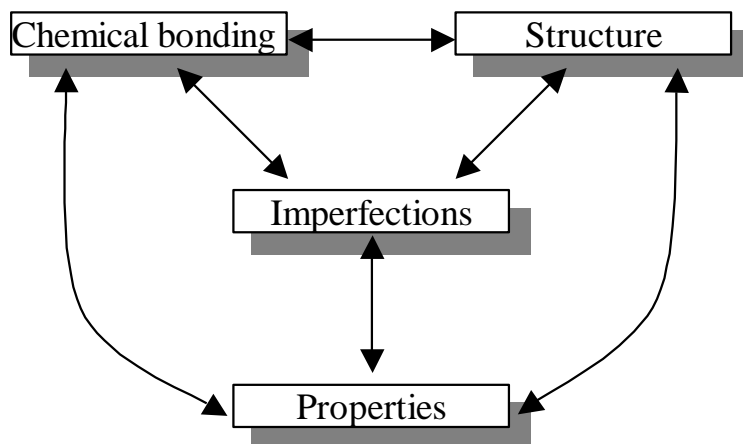
Solid state chemistry deals with the synthesis, structure, properties and applications of solid materials. There is great diversity in range of properties and applications of solids. With the advent of structure-property relations, it is becoming possible to design new materials, which have specific structure and properties.

Properties of Solid

- They are incompressible, inflexible and Mechanical strength.
- They have specific mass, volume and shape.
- Intermolecular force is physically powerful.
- Intermolecular distance is minute.

These properties indicate that the molecules, atoms or ions make up a solid are closely packed i.e., they are held together by strong forces and cannot move at random.

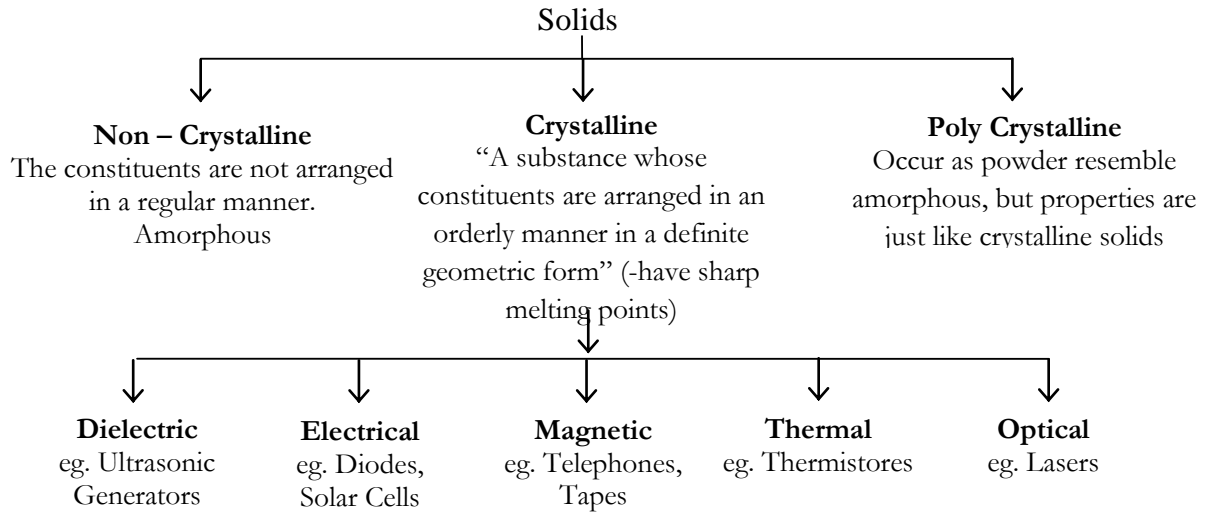
Interrelations of chemical bonding, structure, imperfections and properties due to electronic arrangements presents a birds eye-view of the applications of solids in various spheres.



Classification of Solids

Solids can be classified into three categories based on their structural features:

1. Crystalline solids
2. Amorphous solids (non-crystalline)
3. Poly Crystalline solids



Crystalline Solids

The solids that have their atoms, ions, or molecules which are arranged in a definite three dimensional pattern are called as crystalline solids.

They have the following characteristics

- Crystalline Solids have a characteristic geometrical shape.
- Crystalline solids have sharp melting points, indicating the presence of a long range order arrangement in them
- Crystalline solids are anisotropic by nature i.e., their mechanical, electrical and optical properties depend upon the direction along which they are measured.
- When cut or hammered gently they show a clean fracture along a smooth surface.

Some of the examples of crystalline solids are

Sodium chloride, Cesium Chloride and etc.

Amorphous Solids

Substances whose constituent's atoms, ions, or molecules do not possess a regular orderly arrangement are called amorphous solids. They are different from crystalline solids in many respects.

They have the following characteristics

- These Solids do not have a definite geometrical shape.
- Amorphous solids do not have a fixed melting point. They melt over a wide range of temperature.
- Amorphous solids are isotropic in nature.
- Amorphous solids do not break at a fixed cleavage planes.

The common examples of amorphous solids are

Glass, Rubber, Cotton candy, Fused silica, Ceramic, Plastics, Glue.

The above properties suggest that the properties of the solids not only depend upon the nature of the constituents, but also on their arrangements.

Difference between amorphous and crystalline solids

Crystalline Solids	Amorphous Solids
They have long range order	They lack in long range order
They have sharp Melting points	They don't have sharp melting point
They are anisotropic	They are isotropic
Cleavage of crystal occurs along certain planes	They give a rough surface on cutting along any direction

Types of Crystalline Solid

Crystalline solids may be classified into four types depending upon the nature of bonds present in them. Crystalline solids can be further classified depending on the nature of the bonding as:

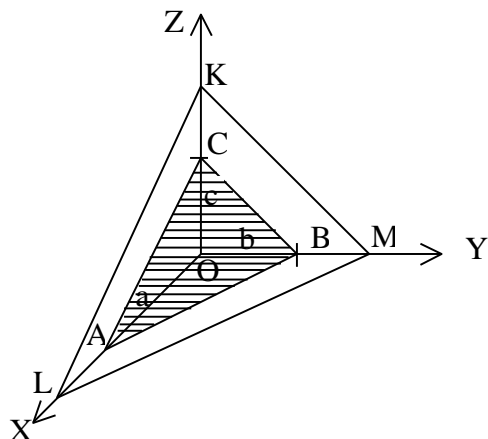
1. **Ionic** (*Nature of force*: Strong electrostatic forces of attraction) Eg: NaCl, LiF, MgO and etc.
2. **Molecular**, contain discrete molecular units held by relatively weak intermolecular forces (VanderWaal's forces, Dipole interaction, Hydrogen bonding). Eg: Solid Ar, Kr and etc.
3. **Covalent** (Covalent bonds). Lattice points are atoms. Eg: Diamond, graphite, Si, Ge and etc.
4. **Metallic** (Metallic bonds). Eg: Al, Cu and etc

Miller indices

Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal. The procedure for determining the Miller indices for a plane is as follows.

Importance

- i) Used to characterise the crystal pattern.
- ii) Used to calculate the edge length of the unit cell.



- i) Let OX, OY and OZ represent the 3 crystallographic axes.
- ii) Let ABC a unit plane
- iii) Let a, b, c be unit intercepts.
- iv) Let KLM are the multiples of abc.

The procedure for determining the Miller indices for a plane is as follows.

- Prepare a three column table with the unit cell axes at the top of the column.
- Enter in each column the intercepts (expressed as a multiples of a, b or c)
- Invert all the numbers.
- Clear the fraction to obtain the whole number h, k and l.

(Note: The negative sign in the Miller indices are indicated by placing a bar on the integer. The Miller indices are enclosed within parentheses).

Weiss indices: The coefficients of a, b, c are known as Weiss indices.

Problems:

- Calculate the Miller indices of Crystal planes which cut through the crystal axes at (2a,3b,c)?

Solution:

Unit cell axes	a	b	c
intercepts	2	3	1
reciprocals	1/2	1/3	1
Clear fractions	3	2	6

Hence, the Miller indices are (326)

- Calculate the Miller indices of Crystal planes which cut through the crystal axes at (2a,-3b,-3c)?

Unit cell axes	a	b	c
intercepts	2	-3	-3
reciprocals	1/2	-1/3	-1/3
Clear fractions	3	-2	-2

Hence, the Miller indices are $(3\bar{2}\bar{6})$

Exercise Problems:

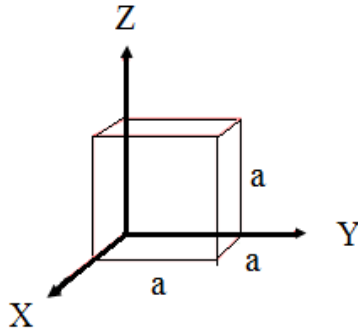
- If a plane cuts the axes at distance in the ratio (4:3:α), calculate the Miller indices?

[Ans: (340)]

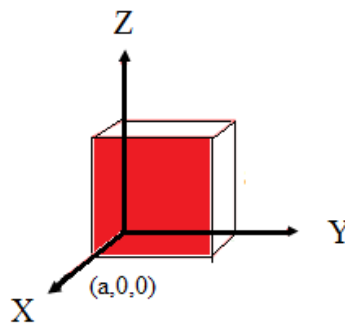
Miller Indices (hkl): Indexing of Crystal Planes

The orientation of a surface or a crystal plane may be defined by considering how the plane (or any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices, (hkl); a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

The following treatment of the procedure used to assign the Miller Indices is a simplified one (it may be best if you simply regard it as a "recipe") and only a **cubic** crystal system (one having a cubic unit cell with dimensions $a \times a \times a$) will be considered.



The procedure is most easily illustrated using an example so we will first consider the following surface/plane:



Step 1: Identify the intercepts on the x , y and z axes.

In this case the intercept on the x-axis is at $x = a$ but the surface is parallel to the y and z axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the x- , y- and z-axes are thus

Intercepts: a , ∞ , ∞

Step 2: Specify the intercepts in fractional co-ordinates

Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (x,y,z) in a unit cell of dimensions $a \times b \times c$ has fractional co-ordinates of $(x/a , y/b , z/c)$. In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant , a . This gives

Fractional Intercepts: $a/a , \infty/a , \infty/a$ i.e. $1 , \infty , \infty$

Step 3: Take the reciprocals of the fractional intercepts

This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are

also enclosed within standard brackets (...) when one is specifying a unique surface such as that being considered here.

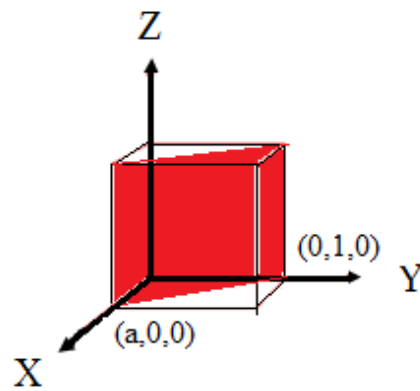
The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding

Miller Indices: **(100)**

So the surface/plane illustrated is the (100) plane of the cubic crystal.

Other Examples

1. The (110) surface

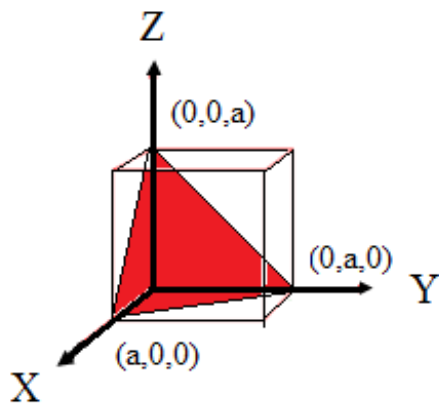


Intercepts : a, a, ∞

Fractional intercepts : $1, 1, 0$

Miller Indices: **(110)**

2. The (111) surface

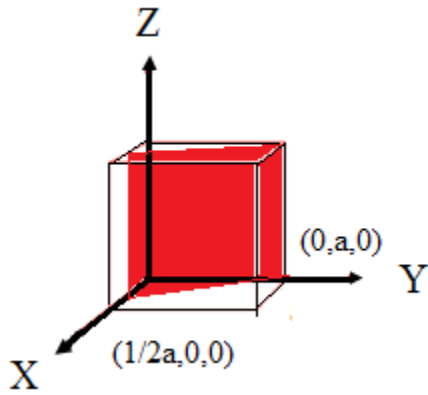


Intercepts : a, a, a

Fractional intercepts : $1, 1, 1$

Miller Indices : **(111)**

3. The (210) surface

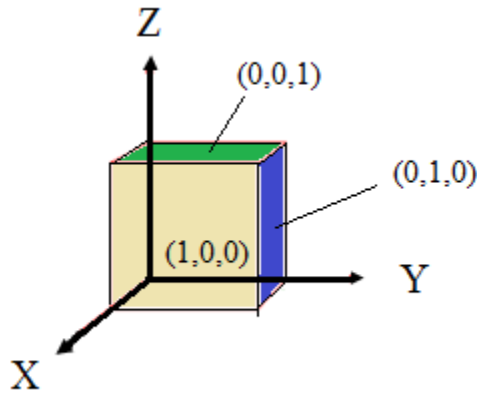


Intercepts : $\frac{1}{2}a, a, \infty$

Fractional intercepts : $\frac{1}{2}, 1, \infty$

Miller Indices : **(210)**

4. The (1,0,0), (0,1,0) and (0,0,1) planes



Interplanar Spacing in a crystal system:

It can be shown that in a crystal, the interplanar distance is the distance between two identical planes.

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \quad \text{————— (1)}$$

Where h, k, l are Miller indices of the plane and a, b, c are the dimensions of the unit cell.

For Cubic system, $a = b = c$, Hence, the equation (1) becomes

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

For Tetragonal system, $a = b \neq c$, Hence, the equation (1) becomes

$$\frac{1}{(d_{hkl})^2} = \frac{h^2 + k^2}{a^2} + \left(\frac{l}{c}\right)^2$$

For Orthorhombic system, $a \neq b \neq c$, Hence, the equation (1) becomes as such

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

Problem: 1) the parameters of an orthorhombic unit cell are $a = 50$ pm, $b = 100$ pm and $c = 150$ pm. Calculate the spacing between the (123) plane?

Solution:

For Orthorhombic system, $a \neq b \neq c$, Hence, d_{hkl} is given by

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

$$\begin{aligned} \frac{1}{(d_{hkl})^2} &= \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \\ &= \left(\frac{1}{50}\right)^2 + \left(\frac{2}{100}\right)^2 + \left(\frac{3}{150}\right)^2 = 3 \left(\frac{1}{50}\right)^2 \\ \frac{1}{(d_{123})} &= \frac{\sqrt{3}}{50} \end{aligned}$$

$$\text{Therefore } d_{123} = \frac{50}{\sqrt{3}} = 29 \text{ pm}$$

Symmetry elements and Symmetry operations

Symmetry operations

It is an action that leaves an object looking like the same after it has been carried out. It includes rotation, reflection and inversion.

Symmetry elements

For each symmetry operation, there is a corresponding symmetry element which is the point, line or plane with respect to which the symmetry operation is performed. Symmetry based on simple rotation is often called symmetry of first kind and symmetry based on reflection (or) rotation/reflection is known as symmetry of second kind.

Symmetry Elements	Symmetry Operation
1. Plane (σ)	Reflection in the plane
2. Proper axis (C_n)	One or more rotations about the axis
3. Improper axis (S_n)	One or more repetition of the sequence: rotation followed by reflection in a plane perpendicular to the rotation axis.
4. Center of symmetry (or) Center of Inversion	Inversion of all atoms through the center.

Symmetry elements present in Cubic Crystal

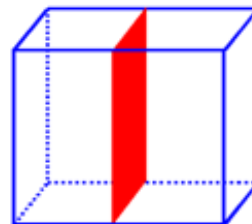
The elements of symmetry present in a cube are represented below.

Plane of symmetry

Two types of plane of symmetry are possessed by cubic system.

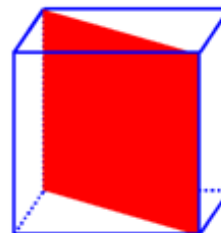
1. Rectangular plane of symmetry

This is shown in the fig- There will be two more such planes hence there are three rectangular plane of symmetry in all.



2. Diagonal plane of symmetry

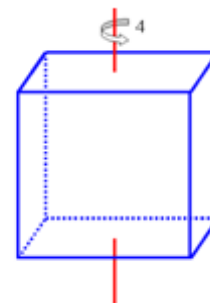
There are the planes passing diagonally through the cube as shown in the fig There are total of 6 such planes passing diagonally through the cube.



Axis of symmetry

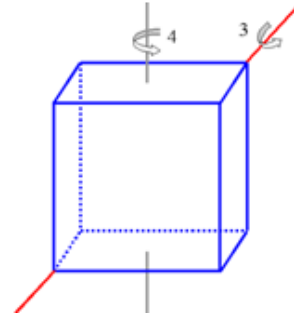
1. Four- fold axis of symmetry

One of the four-fold axes is shown in the fig. evidently there can be a total of 3 such four-fold axes are possible passing through pairs of opposite face centres, parallel to cell axes.



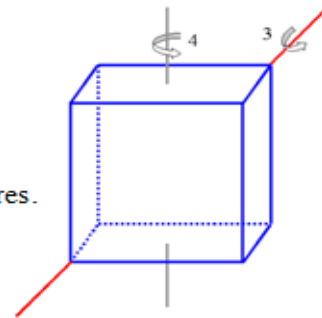
2. Three-fold axis of symmetry

One of the three-fold axes is shown in the fig.
Evidently there can be a total of 4 such three-fold axes are possible passing through cube body diagonals.



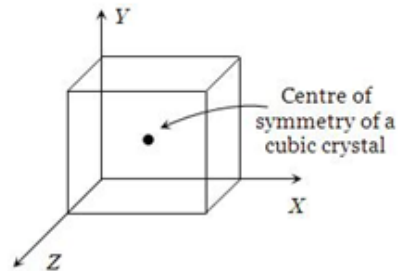
3. Two-fold axis of symmetry.

One of the two-fold axes is shown in the fig.
Evidently there can be a total of 6 such two-fold axes are possible, passing through diagonal edge centres.



Centre of symmetry

Only simple cubic system has one centre of symmetry. Other system do not have centre of symmetry. it is shown in the figure

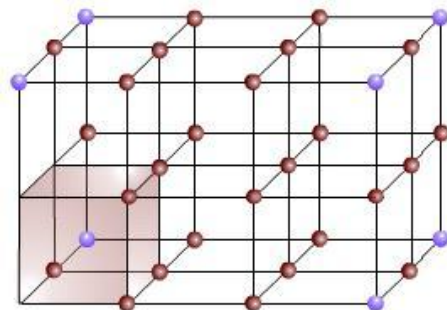


Hence, a cubic crystal possesses total 23 elements of symmetry.

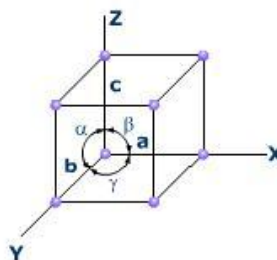
$$\begin{aligned}
 \text{Plane of symmetry (3 + 6)} &= 9 \\
 \text{Axes of symmetry (3 + 4 + 6)} &= 13 \\
 \text{Centre of symmetry (1)} &= 1 \\
 \text{Total symmetry} &= 23
 \end{aligned}$$

Space lattice or crystal lattice

A space lattice is an array of points showing how atom, molecules or ions are arranged at different sites in a 3D space. The points are known as lattice points.



Representation of space lattice and unit cell



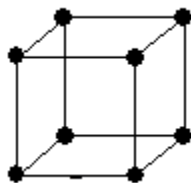
Representation of dimensions of a unit cell

Unit Cell

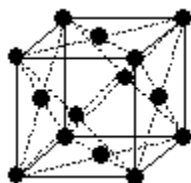
- The unit cell is a smallest repeating unit in the space lattice when repeated again and again, it results in the crystal of the substance.
- The crystal may be considered to consist of infinite number of unit cells.
- Thus, the unit cell may be considered as the brick of wall (where wall represents the crystal).
- Just as the shape of the wall depends on the shape of the brick, the shape of the crystal also depends on the shape of the unit cell.
- The size and shape of a unit cell is determined by the lengths of the edges of the unit cell (a, b and c) and by the angles α , β and γ .
- Therefore, a unit cell is the fundamental pattern of a crystalline solid and it is characterized by the distance a, b and c and the interfacial angles α, β and γ .

Types of unit cell: *There are four different types of unit cells.*

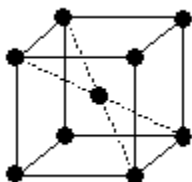
Simple or primitive or basic unit cell (P): The unit cell having lattice points only at the corners is called Simple or primitive or basic unit cell.



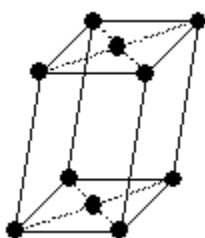
Face centred unit cell (FC): The unit cell having lattice points at the center of each face in addition to the lattice points at the corners is called Face centred unit cell. Fig1b



Body centered unit cell (BC) . The unit cell having lattice point at the center of the body in addition to the lattice points at the corners is called Face centered unit cell.



End face centered unit cell or Base centred unit cell (I). The unit cell having lattice points at the two opposite faces in addition to the lattice points at the corners is called Face centred unit cell.

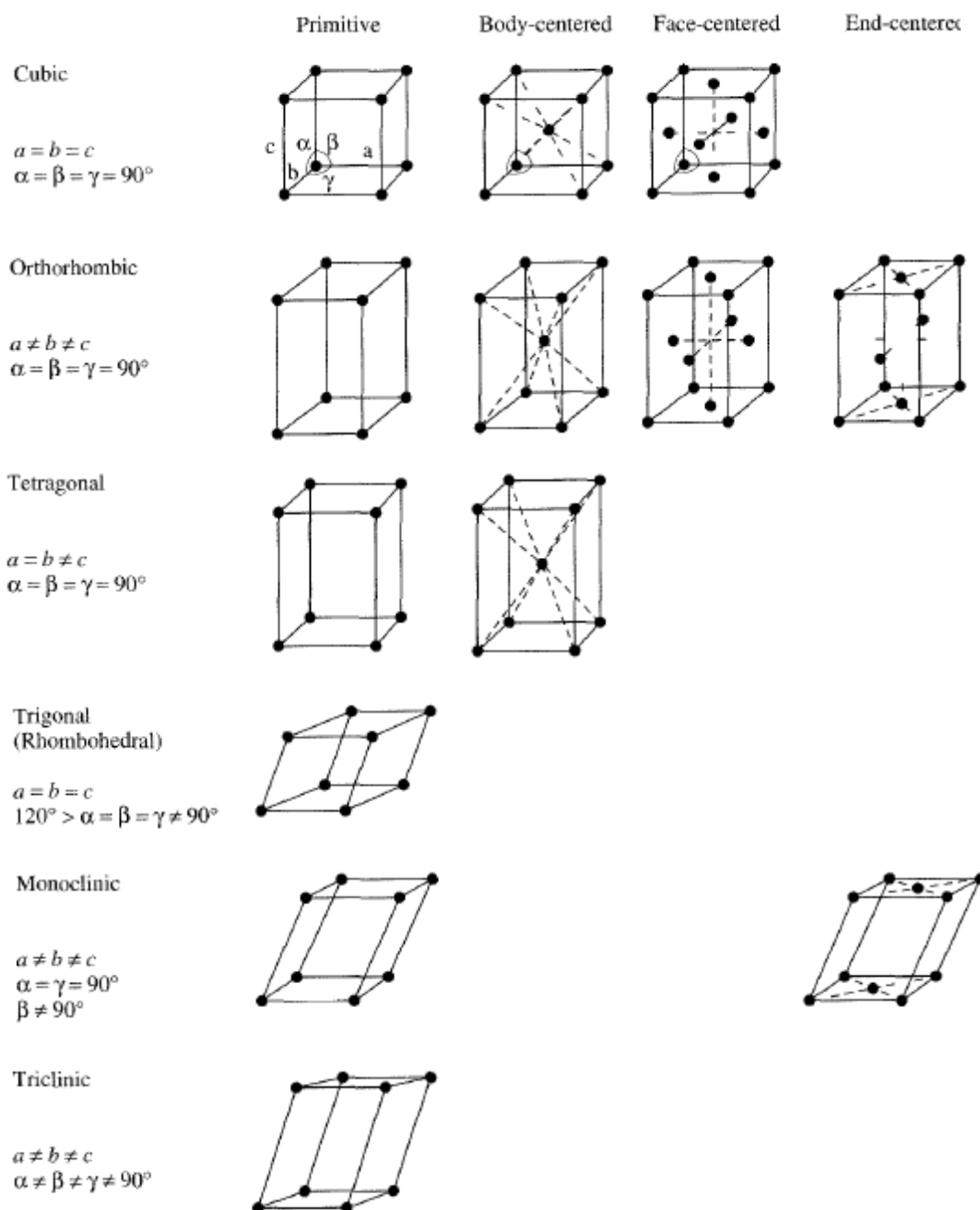


Seven Crystal System

Crystal system	Intercepts & Crystal angle	Bravais lattice	Examples
1. Cubic	$a = b = c; \alpha = \beta = \gamma = 90$	P, BC , FC \rightarrow (3)	NaCl, Diamond, ZnS, CaF ₂
2.Ortho Rhombic	$a \neq b \neq c; \alpha = \beta = \gamma = 90$	P, BC, FC, I \rightarrow (4)	PbCO ₃ , BaSO ₄ , K ₂ SO ₄
3. Tetragonal	$a = b \neq c; \alpha = \beta = \gamma = 90$	P, BC \rightarrow (2)	TiO ₂ , PO ₄ , SnO ₂
4.Rhombohedral	$a = b = c; \alpha = \beta = \gamma \neq 90$	P \rightarrow (1)	Calcite, Magnacite, Quartz.
5. Monoclinic	$a \neq b \neq c; \alpha = \gamma = 90 \neq \beta$	P, I \rightarrow (2)	CaSO ₄ .2H ₂ O, K ₂ MgSO ₄ .6H ₂ O
6. Triclinic	$a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90$	P \rightarrow (1)	CuSO ₄ .5H ₂ O, K ₂ Cr ₂ O ₇
7. Hexagonal	$a = b \neq c; \alpha = \beta = 90;$ $\gamma = 120$	P \rightarrow (1)	Graphite, Zn, Cd, MgS.
Total = (14)			

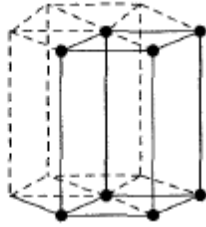
There are 14 Bravais Lattices

Bravais in 1848 showed that there are only 14 different ways by which atoms, ions and molecules can be arranged in three dimensions. Of these 7 are primitive systems and others may be body centered, face centered or end centered. These 14 different types of arrangement are called Bravais lattices.



Hexagonal

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



Cubic crystal system

The cubic crystal system is the simplest system analysed mathematically (although other systems can also be analysed accordingly).

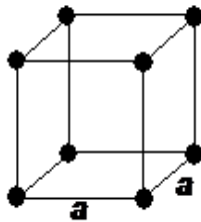
The analysis reflects the following characteristics

1. Atomic radius
2. Number of atoms per unit cell
3. Coordination number
4. Density of lattice crystal
5. Packing fraction (efficiency of packing or % efficiency or density of packing)

Atomic radius

It is defined as 'Half the distance between nearest neighboring atoms' in a crystal. The atomic radius is represented in terms of length of edge 'a' in the unit cell.

Simple cubic structure (SC)

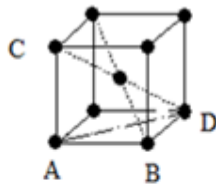


The distance between the nearest neighbour (d) = a

$$\text{Radius is } r = d/2$$

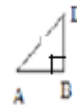
$$r = a/2$$

Body centered cubic structure (BCC)



The distance between the nearest neighbour (d) = 1/2 CD

In the right angled triangle ABD,



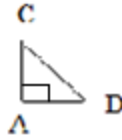
$$AD = \sqrt{AB^2 + BD^2}$$

$$= \sqrt{a^2 + a^2}$$

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

$$AD^2 = 2a^2$$

Now, triangle, ACD

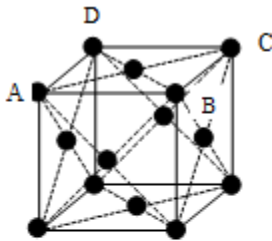


$$\begin{aligned}
 CD &= \sqrt{AC^2 + AD^2} \\
 &= \sqrt{a^2 + 2a^2} \\
 &= \sqrt{3a^2} \\
 &= \sqrt{3} \ a
 \end{aligned}$$

Therefore

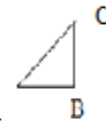
$$\begin{aligned}
 d &= \frac{1}{2} CD = \frac{\sqrt{3} \ a}{2} \\
 r &= \frac{d}{2} = \frac{\sqrt{3} \ a}{4}
 \end{aligned}$$

Face centered cubic structure (FCC).



The distance between nearest neighbours (d) = $1/2$ AC

In the right angled triangle ABD,



$$\begin{aligned}
 AC &= \sqrt{AB^2 + BC^2} \\
 &= \sqrt{a^2 + a^2} \\
 &= \sqrt{2} \ a
 \end{aligned}$$

Therefore

$$\begin{aligned}
 d &= \frac{1}{2} AC = \frac{\sqrt{2} \ a}{2} \\
 r &= \frac{d}{2} = \frac{\sqrt{2} \ a}{4} \\
 r &= \frac{a}{2\sqrt{2}}
 \end{aligned}$$

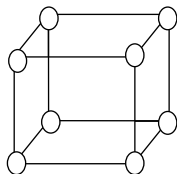
Number of atoms per unit cell

Keeping the following points in mind, we can calculate the number of atoms in a unit cell.

- An atom at the corner is shared by eight unit cells.
Hence an atom at the corner contributes $1/8$ to the unit cell
- An atom at the face is shared by two unit cells, hence, Contribution of each atom on the face is $1/2$ to the unit cell.
- An atom within the body of the unit cell is shared by no other unit cell, hence, Contribution of each atom within the body is 1 to the unit cell.
- An atom present on the edge is shared by four unit cells, hence, Contribution of each atom on the edge is $1/4$ to the unit cell.
- By applying these rules, we can calculate the number of atoms in the different cubic unit cells of monatomic substances.

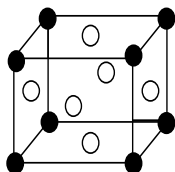
Simple cubic

Simple Cubic Lattice (Primitive-P): In which there are points only at the corners of each unit.



$$\text{Total number of atoms per unit cell of P} = (1/8) \times 8 = 1$$

Face Centered Cubic Lattice (FC): In which there are points at the corners as well as at the center of each of the six faces of the cube.



$$\text{Total number of atoms per unit cell} = 8 \times (1/8) = 1$$

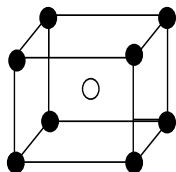
(since 8 corners occupied $1/8$ atoms)

6 faces shared by $1/2$ atoms each

$$\therefore 6 \times 1/2 = 3$$

$$\text{Total} = 1 + 3 = 4$$

Body Centered Cubic Lattice (BC): In which there are points at the corners as well as in the center of each cube.

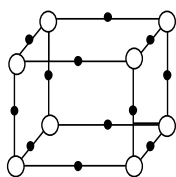


$$\text{Total number of atoms} = 8 \times (1/8) = 1$$

At the center 1 atom

$$\therefore \text{Total} = 1 + 1 = 2$$

Base Centered Cubic Lattice (C): In which there are points at the corners as well as in the edges of each cube



At the corners $8 \times (1/8) = 1$

At the edges $12 \times (1/4) = 3$

\therefore Total = $1 + 3 = 4$

Number of atoms per unit cell in cubic lattice

Types of Lattice	Location of atoms	Portion in the unit cell	Number of atoms in the unit cell
Primitive (P)	Corner	1/8	1
FC	Face + Corner	1/2	$3+1 = 4$
BC	Body + Corner	1+1	2
Edge or base centered	Edge + Corner	1/4	$3+1 = 4$

Coordination number

It is defined as the number of nearest neighbors that an atom has in a unit cell. In an ionic crystal, the number of oppositely charged ions surrounding each ion is called its coordination number. Thus, the coordination number of a crystal depends upon the structure. *For any system, the number of atoms touching the particular atom is called coordination number.*

Simple cubic structure has coordination number = 6

Body centered cubic structure has coordination number = 8

Face centered cubic structure has coordination number = 12

Density of lattice crystal

Calculation of Density of a Cubic Crystal from its Edge Length 'a' (The edge length should be in cm)

The edge length of a cubic crystal can be obtained from X-ray studies and knowing the crystal structure possessed by it so that the number of particles per unit cell are known, the density of the crystal can be calculated.

$$\text{Density} = \frac{\text{Mass per unit cell}}{\text{Volume of unit cell}}$$

$$m = \text{mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

Therefore,

$$\text{Density} = \frac{n \times \text{atomic mass}}{\text{Avogadro number} \times \text{vol. of unit cell}}$$

Where, n is the number of atoms per unit cell. The volume of unit cell is to be calculated for the given crystal system

For cubic crystal, volume of unit cell is a^3 .

For simple cubic, the density is given by

$$\rho = \frac{1 \times M}{N_A \times a^3}$$

For body centered cubic the density is given by

$$\rho = \frac{2 \times M}{N_A \times a^3}$$

For face centered cubic the density is given by

$$\rho = \frac{4 \times M}{N_A \times a^3}$$

Density of the substance is same as the density of the unit cell.

For the density equation it is also possible to calculate the edge length (a) of the unit cell.

Packing fraction (efficiency of packing or % efficiency or density of packing) and Void (or) Empty Space in Cubic Lattices

It is defined as ratio of volumes occupied by atom in unit cell (u) to the total volume of the unit cell (V).

$$\text{Packing Fraction} = \frac{\text{Vol. occupied by atom in unit cell}}{\text{Total vol. of unit cell}} = \frac{u}{V}$$

It suggests that how closely the atoms are packed (stacked) together in the unit cell. For three cubic cells, these are illustrated.

Efficiency of packing in simple cubic structure

Let 'a' be the edge length of unit cell and 'r' be the atomic radius. In Simple Cubic system, the total number of atoms per unit cell is ONE. Thus the volume of atoms in the unit cell is given by

$$\begin{aligned}
 u &= 1 \times \frac{4}{3} \pi r^3 \\
 &= \frac{4}{3} \times \pi \times (a/2)^3 \quad \text{Since, } r = a/2 \text{ for Simple cubic system} \\
 &= \frac{\pi \times a^3}{6}
 \end{aligned}$$

Since the total volume of the unit cell is $V = a^3$

$$\begin{aligned}
 \text{Therefore, Packing fraction of simple cubic system} \\
 \text{is given by} &= \frac{u}{V} = \frac{\pi \times a^3}{6 \times a^3} \\
 &= \frac{\pi}{6} \\
 &= \frac{22.6}{6 \times 2} \\
 &= 0.52
 \end{aligned}$$

This reveals that 52% of the unit cell is occupied by atoms and remaining 48% is empty.

Efficiency of packing in Body centered cubic structure

We know, for a bcc structure

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

In bcc structure, the total number of atoms per unit cell is 2.

$$\text{Volume of two spheres} = 2 \times \frac{4}{3} \pi r^3$$

Volume of the cube = a^3

$$= \left(\frac{4}{\sqrt{3}} r \right)^3$$

Therefore, Percentage efficiency

$$\begin{aligned}
 &= \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell}} \\
 &= \frac{2 \times (4/3) \pi r^3 \times 100\%}{\left(\frac{4}{\sqrt{3}} r \right)^3} \\
 &= \frac{(8/3) \pi r^3 \times 100}{\left(\frac{64}{3\sqrt{3}} \right) r^3} \\
 &= 68\%
 \end{aligned}$$

This reveals that 68% of the unit cell is occupied by atoms and 32% is empty.

Efficiency of packing in Face centered cubic structure

We have found that for a ccp arrangement

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

We also know that, per unit cell in ccp arrangement has effectively 4 spheres.

$$\text{Volume of four spheres} = 4 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of the cube is} = a^3 = (2\sqrt{2}r)^3$$

Therefore, Percentage efficiency

$$= \frac{\text{volume occupied by four spheres} \times 100}{\text{Total volume of the unit cell}}$$

$$= \frac{4 \times (4/3) \pi r^3 \times 100}{(2\sqrt{2}r)^3}$$

$$= \frac{(16/3) \pi r^3 \times 100}{16\sqrt{2}r^3} = 74\%$$

This reveals that 74% of the unit cell is occupied by atoms and 26% is empty.

Thus, the % efficiency of packing in SC, BCC and FCC are 52%, 68% and 74% respectively.

The packing density data; FCC > BCC > SC

That is, FCC is more closely packed and more stable.

Packing efficiency of hcp and ccp structures

Show that the volume occupied by the spheres in the CCP or FCC structure is 74%

If the repetition sequence is ABC, ABC, ABC, ... then the resulting structure is hexagonal closest packing or fcc closest packing.

In this case

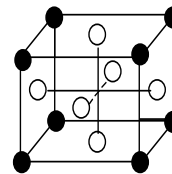
(i) each corner atoms are shared by (8) surrounding cubes and each face centered atoms are shared by 2 surrounding cubes.

$$\therefore \text{Total number of atoms in fcc cube is} = 1/8 \times 8 = 1$$

$$6 \times 1/2 = 3 \quad \left. \vphantom{6 \times 1/2 = 3} \right\} 4 \text{ atoms / mol}$$

(ii) atomic radius

$$\therefore r = \frac{\sqrt{2} a}{4}$$



(iii) Packing factor (v/V):

$$\text{volume of 4 atoms (v) i.e., } 4 \times \frac{4}{3} \pi r^3$$

$$\begin{aligned}
 \therefore v &= 4 \times \frac{4}{3} \pi \times \left[\frac{\sqrt{2}}{4} a \right]^3 \\
 &= \frac{4 \times 4 \pi \times \sqrt{2} \times \sqrt{2} \times \sqrt{2} \times a^3}{3 \times 4 \times 4 \times 4} \\
 &= \frac{\pi \times 2 \sqrt{2} \times a^3}{3 \times 4} \\
 &= \frac{\pi \times \sqrt{2} \times a^3}{6}
 \end{aligned}$$

Volume of unit cell = $V = a^3$

$$\therefore \text{Packing Factor } v/V = \frac{3.141 \times 1.414 \times a^3}{6 a^3} = 0.74 = 74\%$$

Hence, we notice that in the cubic closest packed structure only 74% of the space is actually occupied by spheres.

Summary:

Characters of the unit cell	SC	BCC	FCC
Atomic radius	$r = a/2$	$r = \frac{\sqrt{3} a}{4}$	$r = \frac{a}{2\sqrt{2}}$
Number of atoms per unit cell	1	2	4
Coordination number	6	8	12
Density of lattice crystal.	$\rho = \frac{1 \times M}{N_A \times a^3}$	$\rho = \frac{2 \times M}{N_A \times a^3}$	$\rho = \frac{4 \times M}{N_A \times a^3}$
Packing fraction	52%	68%	74%

Problems:

- Chromium has mono atomic body-centred cubic structure. Its cell edge is 300 pm, what is its density? (Molar mass of Cr = 52 g mol⁻¹, Avogadro number N = 6.023 x 10²³ mol).

Suggested solution:

Given data:

$n = 2$ since structure is body-centered cubic

$$M = 52 \text{ g mol}^{-1}$$

$$a = 300 \text{ pm} = 300 \times 10^{-10} \text{ cm}$$

$$N = 6.023 \times 10^{23} \text{ mol}^{-1}$$

Formula to be used is

$$2 \times M$$

$$\rho = \frac{\quad}{N_A \times a^3}$$

$$\rho = \frac{2 \times 52 \text{ g mol}^{-1}}{(300 \times 10^{-10})^3 \text{ cm}^3 \times 6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$= \frac{2 \times 52}{2.7 \times 10^{-23} \times 6.023 \times 10^{23}} \text{ g cm}^{-3}$$

$$= \frac{2 \times 52}{2.7 \times 6.023} \text{ g cm}^{-3} = 6.40 \text{ g cm}^{-3}$$

2. An element of atomic mass 98.0 g mol^{-1} occurs in FCC structure. If the unit cell edge length is 500 pm and its density is 5.22 g cm^{-3} . What is the value of the Avogadro's constant?

Suggested solution:

Given data:

$n = 4$, Since the structure is FCC:

$$M = 98.0 \text{ g mol}^{-1}$$

$$a = 500 \text{ pm} = 500 \times 10^{-10} \text{ cm} = 5 \times 10^{-8} \text{ cm}$$

$$\rho = 5.22 \text{ g cm}^{-3}$$

Formula to be used is

$$4 \times M$$

$$\rho = \frac{\quad}{N_A \times a^3}$$

$$\therefore N_A = \frac{4 \times 98.0 \text{ g mol}^{-1}}{(5 \times 10^{-8})^3 \text{ cm}^3 \times 5.22 \text{ g cm}^{-3}}$$
$$= 6.0 \times 10^{23} \text{ mol}^{-1}$$

3. Sodium chloride crystal has FCC structure. Its density is $2.163 \times 10^3 \text{ kg m}^{-3}$. Calculate the edge of the unit cell cube.

Suggested solution:

Given data:

$$\text{Density} = 2.163 \times 10^3 \text{ kg m}^{-3}$$

$$(M_{\text{NaCl}} = 58.45 \times 10^{-3} \text{ kg mol}^{-1}$$

$$N_A = 6.023 \times 10^{23})$$

Formula to be used is

$$4 \times M$$

$$\rho = \frac{\quad}{N_A \times a^3}$$

$$a^3 = \frac{4 \times 58.45 \times 10^{-3} \text{ kg mol}^{-1}}{2.163 \times 10^3 \text{ kg m}^{-3} \times 6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$a^3 = 179.5 \times 10^{-30} \text{ m}^3$$

(or) $a = 5.64 \times 10^{-10} \text{ m} = 564 \text{ pm}$.

4. Assuming aluminium (At mass = 27) has a density of 2.7 g cm^{-3} and its unit cell has an edge of 400 pm, what is the nature of the crystal lattice for the metal?

Suggested solution:

Given data:

$$\text{Density} = 2.7 \text{ g cm}^{-3}$$

$$\text{The edge length} = 400 \text{ pm} = 400 \times 10^{-8} \text{ cm}$$

Formula to be used is

$$n \times M$$

$$\rho = \frac{\quad}{N_A \times a^3}$$

$$= \frac{2.7 \times 6.023 \times 10^{23} \times (4 \times 10^{-8})^3}{27}$$

$$n = 3.85$$

$$n = 4$$

Hence Al crystallises in face-centered cubic lattice.

5. Lithiumborohydride crystallizes in orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are $a = 6.8 \text{ \AA}$, $b = 4.4 \text{ \AA}$ and $c = 7.2 \text{ \AA}$. if the molar mass is 21.76, calculate the density of the crystal?
6. The length of the unit cell edge of a body centered cubic metal crystal is 352 pm. Calculate the radius of an atom of the metal.

Suggested solution:

In body-centered cubic unit cell, the radius r of the atom is related to the edge of the unit cell by the relation.

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

$$= \frac{\sqrt{3} \times 354}{4} = 153.3 \text{ pm}$$

6. Calculate the density of Mo which forms body centered cubic crystal in which the distance between the centers of closest atoms is 274 pm. Atomic mass of Mo is 95.94.

Suggested solution:

In a body centered cubic crystal, the closest distance between touching atom is

$$d_B = 2r = \frac{\sqrt{3}}{2} a = 274 \text{ pm}$$

$$\therefore a = \frac{274 \times 2}{\sqrt{3}} = 316.4 \text{ pm} = 3.164 \times 10^{-8} \text{ cm}$$

and here $n = 2$

$$\rho = \frac{n \times M}{N_A \times a^3}$$

$$= \frac{2 \times 95.94}{6.023 \times 10^{23} \times (3.164 \times 10^{-8})^3}$$

$$\rho = 10.06 \text{ g cm}^{-3}.$$

Packing of Constituent Particles in Crystals

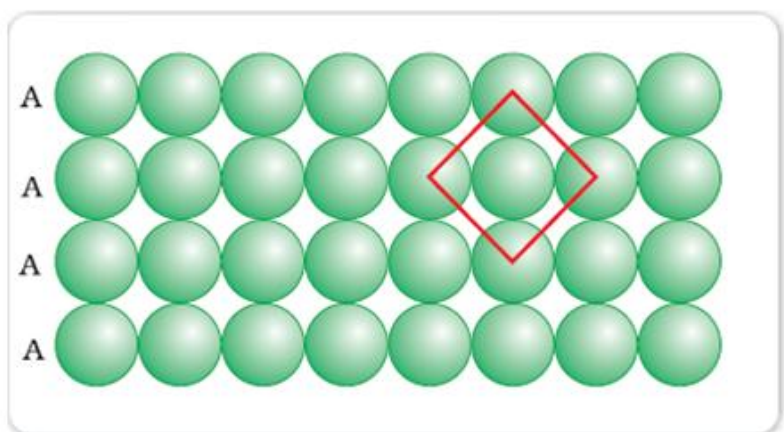
It is assumed that the atoms are hard spheres of identical size. Packing is done in such a way that they occupy maximum available space and leave minimum space empty. . This type of packing is called close packing.

Close packing of spheres in one dimension. It is shown in the figure this forms an edge of the crystal.



Close packing of spheres in two dimensions. It is two types.

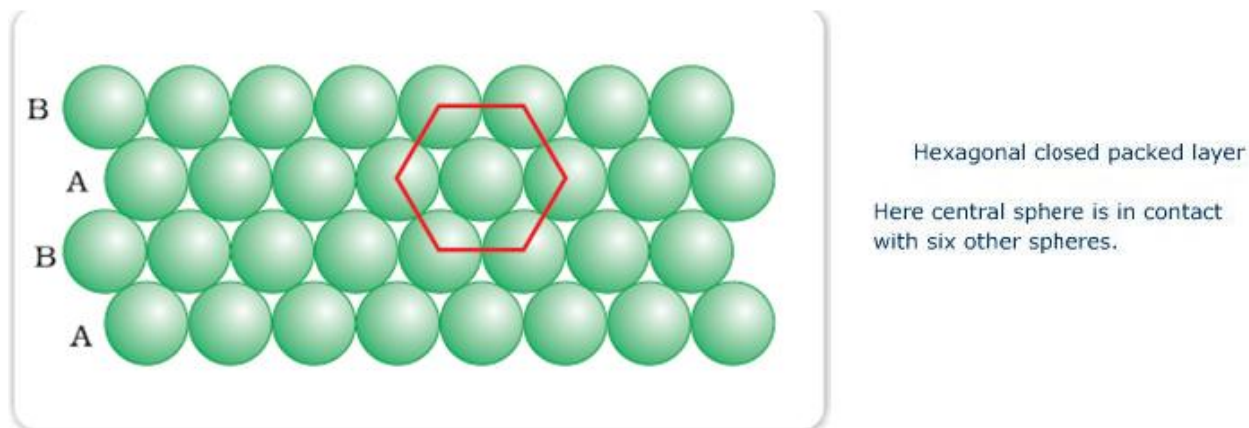
i) Square close packing - Particles when placed in the adjacent rows show a horizontal as well as vertical alignment and form squares.



Square closed packed layer

Here central sphere is in contact with four other spheres.

ii) **Hexagonal close packing** - Packing in every next row are placed in the depression between the particles of the first row. Hexagonal close packing with triangular voids is more efficient. Hence, Hexagonal close packing is the most efficient two dimensional closes packing.



Close Packing in Three Dimensions

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. We discussed close packing in two dimensions which can be of two types; square close-packed and hexagonal close-packed. Let us take hexagonal close packing since it is more efficient and see what types of three dimensional close packing can be obtained from this.

Three dimensional close packing from two dimensional hexagonal close packed layers:

Three dimensional close packed structure can be generated by placing layers one over the other.

(A) Placing second layer over the first layer

Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed from Fig.1 that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called **tetrahedral voids** because a **tetrahedron** is formed when the centres of these four spheres are joined. They have been marked as 'T' in Fig. 1. One such void has been shown separately in Fig. 2.

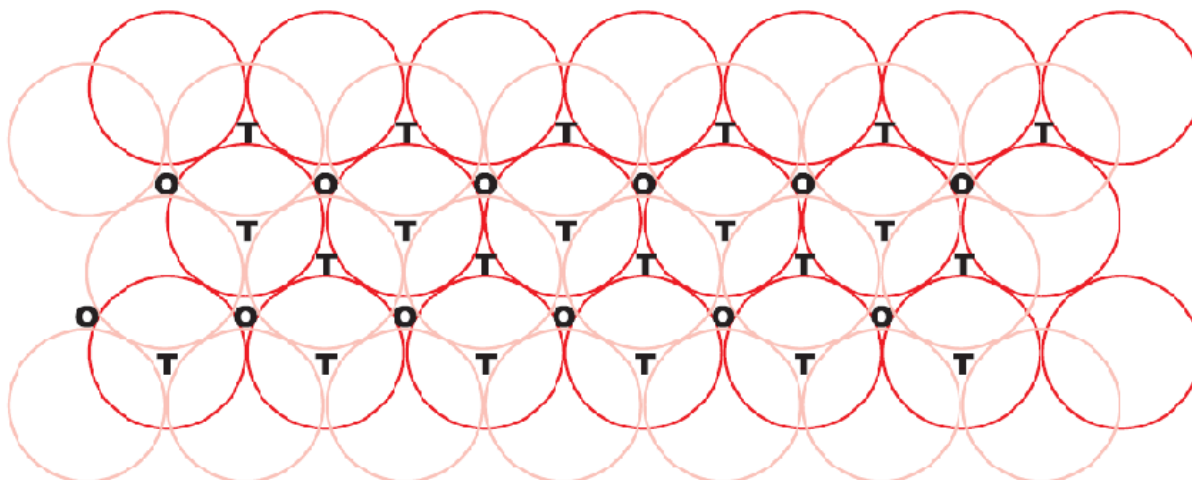


Fig.1 A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

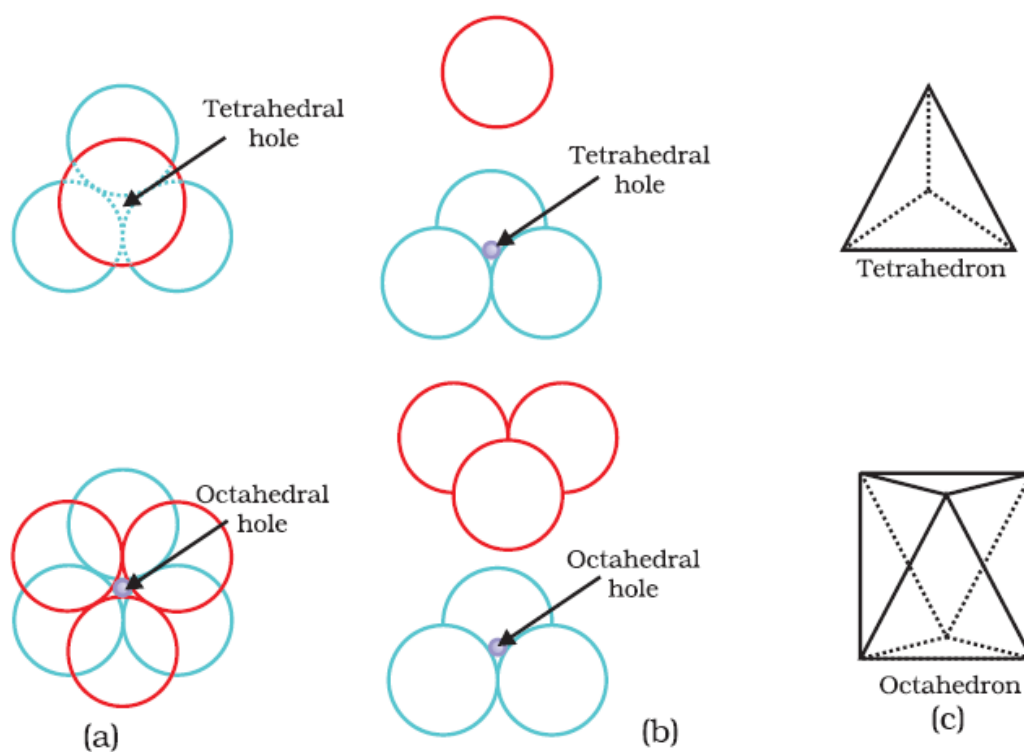


Fig.2. Tetrahedral and Octahedral Voids a) Top View b) Exploded Side view c) Geometrical Shape of the Void

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in Fig. 1. Such voids are surrounded by six spheres and are called **octahedral voids**. One such void

has been shown separately in Fig. 2. The number of these two types of voids depends upon the number of close packed spheres.

Let the number of close packed spheres be N , then:

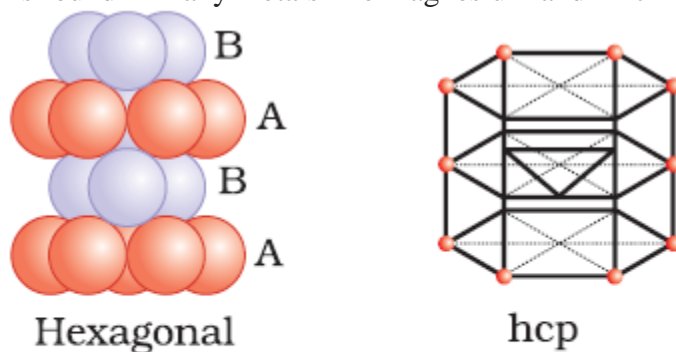
The number of octahedral voids generated = N

The number of tetrahedral voids generated = $2N$

(B) Placing third layer over the second layer: When third layer is placed over the second, there are two possibilities.

i) **Covering tetrahedral voids [Hexagonal close packing (*hcp*)]**

Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB pattern. This structure is called hexagonal close packed (*hcp*) structure (Fig.3a). This sort of arrangement of atoms is found in many metals like magnesium and zinc



**Fig.3 (a) Hexagonal cubic close-packing
ABABAB... arrangement**

ii) **Covering octahedral voids [Cubic close packing (*ccp*)]**

The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called ‘C’ type. Only when fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 1.18 and 1.19. This pattern of layers is often written as ABCABC This structure is called cubic close packed (*ccp*) or face-centred cubic (*fcc*) structure. Metals such as copper and silver crystallise in this structure. Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

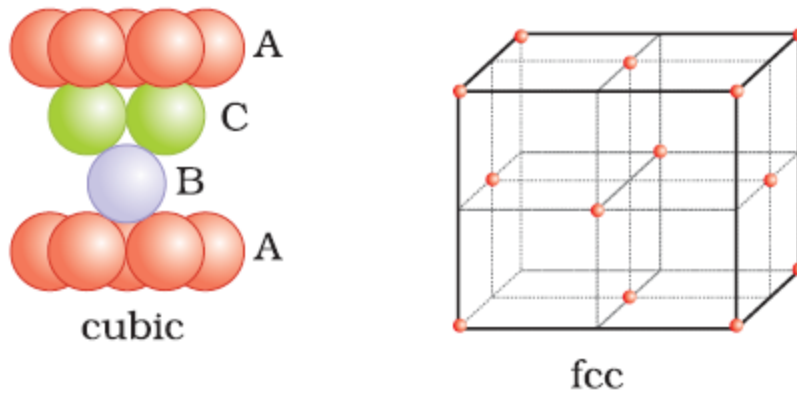
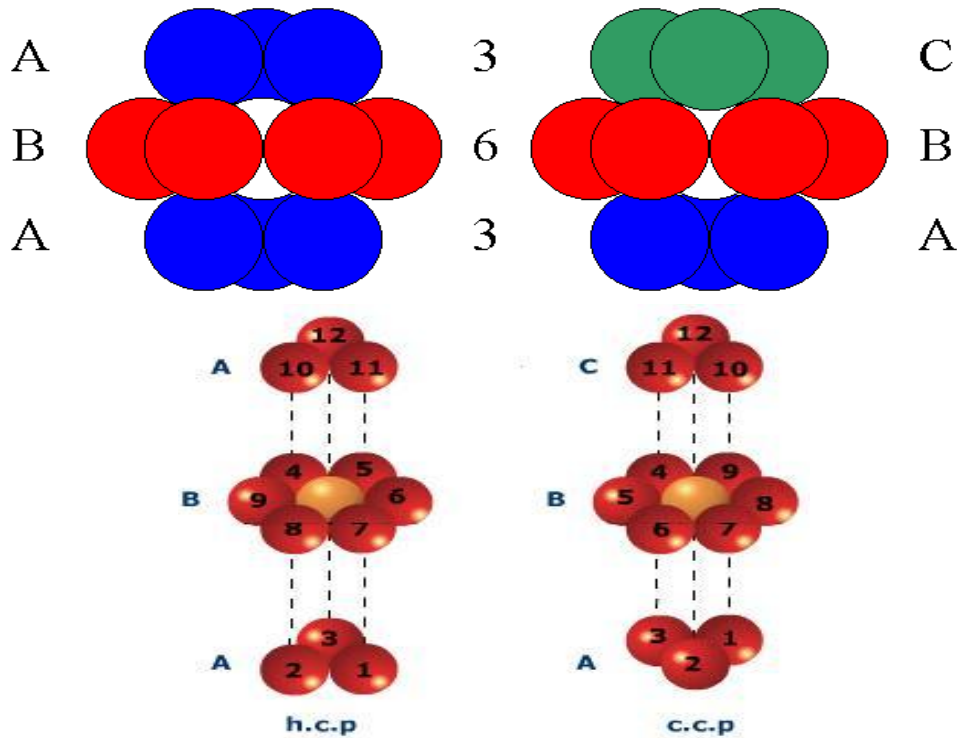


Fig.3 b) ABCABC... arrangement of layers when octahedral void is covered

In both the above patterns of arrangements, the maximum occupied volume is 76% of the available volume.

In both HCP and CCP the coordination number is 12 because a sphere is in contact with 6 spheres in its own layer. It touches three spheres in the layer above and three in the layer below



What is Radius Ratio Rule?

Radius ratio rule states:

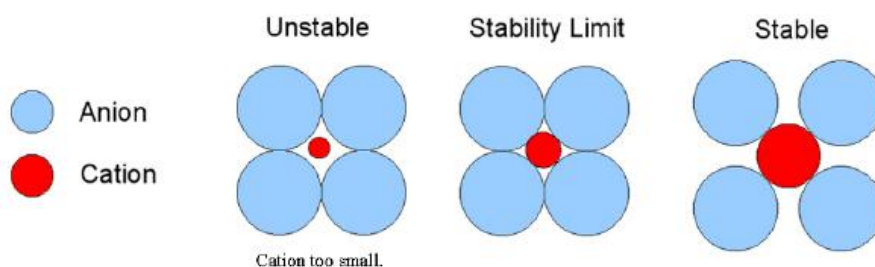
- The difference in the crystal structure depends on the size of the ions

- As the size (ionic radius r) of a cation increases, more anions of a particular size can be packed around it.
- Knowing the size of the ions, we should be able to predict which type of crystal packing will be observed.
- Thus, the geometrical requirement for a given structure in terms of the size of the two ions is expressed by radius ratio which is defined as

$$R = \frac{r^+}{r^-}$$

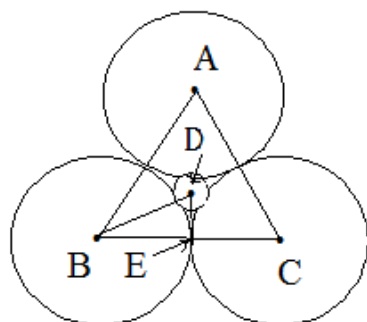
What is Limiting Radius Ratio?

For a specific structure, we can calculate the limiting radius ratio, which is the minimum allowable value for the ratio of ionic radii (r^+/r^-) for the structure to be stable.



Calculation of Radius Ratio for coordination number 3

Figure shows that the smaller positive ion of radius r^+ is in contact with three larger negative ions of radius r^- . In this figure, $AB = BC = AC = 2r^-$ and $BE =$ radius r^- , $BD = r^+ + r^-$. Further, the angle A-B-C is 60° and the angle D-B-E is 30° . By trigonometry,

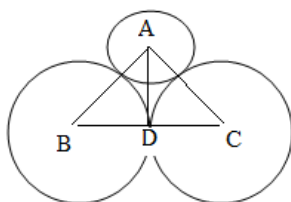


$$\begin{aligned} \cos 30^\circ &= BE/BD \\ BD &= BE / \cos 30^\circ \\ r^+ + r^- &= r^- / \cos 30^\circ \\ &= r^- / 0.866 \\ &= r^- \times 1.155 \\ r^+ &= (1.155 r^-) - r^- \\ &= 0.155 r^- \\ r^+ / r^- &= 0.155 \end{aligned}$$

This will be the limiting ratio for coordination number 3 since a cation will be stable in a hole only if it is at least large enough to keep the anion from touching $r^+ / r^- < 0.155$.

Calculation of Radius Ratio for coordination number 4.

Part of the tetrahedral arrangement is shown in the figure. It can be seen that the angle ABC is the tetrahedral angle of $109^{\circ} 28'$ and hence the angle ABD is half of this, that is $54^{\circ} 44'$.



In this triangle ABD,

$$\sin \text{ABD, i.e. } \sin 54^{\circ} 44' = 0.8164 = \frac{AD}{AB} = \frac{r^-}{r^+ + r^-}$$

taking reciprocals

$$\frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} = 1.225$$

rearranging

$$\frac{r^+}{r^-} + 1 = 1.225$$

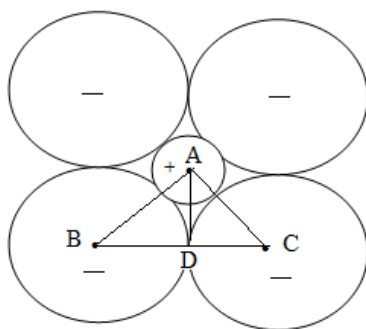
hence

$$\frac{r^+}{r^-} = 0.225$$

This will be the limiting ratio for coordination number 4 since a cation will be stable in tetrahedral hole only if it is at least large enough to keep the anion from touching $r_+/r_- > 0.225$. Smaller cations will fit into trigonal holes in the lattice.

Calculation of Radius Ratio for coordination number 6.

An octahedral site is shown in the figure and the smaller positive ion of radius r^+ touches six negative ions of radius r^- . Note that only four negative ions are shown in this figure and one is above and another is below the paper.



It is obvious that $AB = r^+ + r^-$ and $BD = r^-$.

The angle ABC is 45° . In the triangle ABD,

$$\cos \text{ABD i.e. } \cos 45^{\circ} = 0.7071 = \frac{BD}{AB} = \frac{r^-}{r^+ + r^-}$$

taking reciprocals

$$\frac{r^+ + r^-}{r^-} = \frac{1}{0.7071} = 1.414$$

rearranging

$$\frac{r^+}{r^-} + 1 = 1.414$$

hence

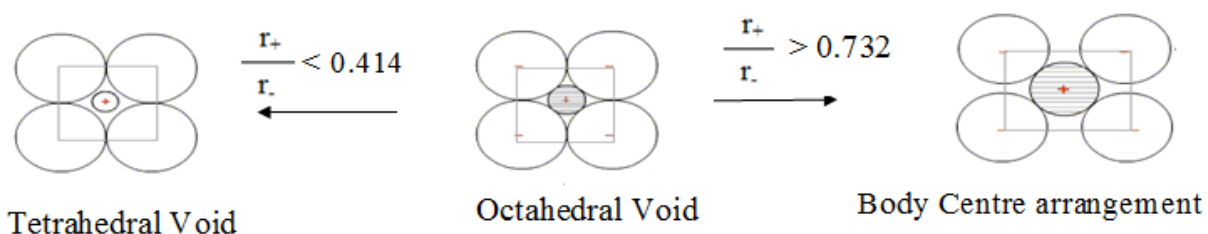
$$\frac{r^+}{r^-} = 0.414$$

This will be the limiting ratio since a cation will be stable in an octahedral hole only if it is at least large enough to keep the anion from touching $r_+/r_- > 0.414$. Smaller cations will fit into tetrahedral holes in the lattice.

By similar geometric calculation it is possible to find the ratio when one cation can accommodate eight anions (0.732) or twelve anions (1.00).

The limiting radius ratio value is given in the table

Radius ratio	C. N	Structure
Less than 0.225	3	Trigonal planar
0.225 - 0.414	4	Tetrahedral
0.414 – 0.73	6	Octahedral(FCC Patern)
More than 0.73	8	BCC



Application of radius ratio:

1. It is used to rationalize the structures and to predict the coordination numbers of 1:1 or 2:2 types of salts.

Examples

- Consider beryllium sulfide

$$\frac{r_{\text{Be}^{2+}}}{r_{\text{S}^{2-}}} = \frac{59 \text{ pm}}{170 \text{ pm}} = 0.35$$

Thus it is expected that coordination number is 4 as the Be^{2+} ion fits most readily into the tetrahedral holes of the closest packed lattice and indeed it is found experimentally. Hence BeS adopts a wurtzite structure.

- Consider the sodium Chloride

$$\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = \frac{116 \text{ pm}}{167 \text{ pm}} = 0.69$$

Thus it is expected that coordination number is 6 as the Na^+ ion fits most readily into the octahedral holes of the closest packed lattice and indeed it is found experimentally.

Consider the Cesium Chloride

$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = \frac{181 \text{ pm}}{167 \text{ pm}} = 1.08$$

The coordination number of cation is 8

2. It is used to rationalize the structures and to predict the coordination numbers of salts with different numbers of cations and anions. In such cases it is usually best to perform two calculations.

Examples:

Consider the structure of SrF₂

$$\frac{r_{\text{Sr}^{2+}}}{r_{\text{F}^-}} = \frac{132}{119} = 1.11 \quad \text{Maximum C.N. of Sr}^{2+} = 8$$

$$\frac{r_{\text{F}^-}}{r_{\text{Sr}^{2+}}} = \frac{119}{132} = 0.90 \quad \text{Maximum C.N. of F}^- = 8$$

There must be twice as many fluoride ions as strontium ions, so the coordination number of the strontium ions must be twice as large as that of fluoride. Coordination number of 8 (Sr²⁺) and 4(F⁻) are compatible with the maximum allowable coordination numbers and with the stoichiometry of the crystal. Hence, Strontium fluoride crystallizes in the fluorite lattice.

Consider the structure of SnO₂

$$\frac{r_{\text{Sn}^{4+}}}{r_{\text{O}^{2-}}} = \frac{83}{126} = 0.66 \quad \text{Maximum C.N. of Sn}^{4+} = 6$$

$$\frac{r_{\text{O}^{2-}}}{r_{\text{Sn}^{4+}}} = \frac{126}{83} = 1.52 \quad \text{Maximum C.N. of O}^{2-} = 6$$

Considering the stoichiometry of the salt, the only feasible arrangement is with C.N. of O²⁻ is 3 and C.N. of Sn⁴⁺ is 6. Hence tin dioxide assumes the TiO₂ or rutile structure.

Consider the structure of K₂O

$$\frac{r_{\text{K}^+}}{r_{\text{O}^{2-}}} = \frac{152}{126} = 1.21 \quad \text{Maximum C.N. of K}^+ = 8$$

$$\frac{r_{\text{O}^{2-}}}{r_{\text{K}^+}} = \frac{126}{152} = 0.83 \quad \text{Maximum C.N. of O}^{2-} = 8$$

Considering the stoichiometry of the salt, the only feasible arrangement is with C.N. of O²⁻ is 8 and C.N. of K⁺ is 4. Hence tin dioxide assumes the antifluorite structure.

Problem:

Predict the crystal structure of TiCl. The ionic radii are $r_{\text{Ti}^+} = 159$ pm and $r_{\text{Cl}^-} = 181$ pm,

Solution:

The radius ratio is 0.88. We can therefore predict that TiCl is likely to adopt a cesium-chloride structure with (8, 8) coordination. That is the structure found in practice.

Diffraction of X-rays by Crystals

It is known that when light falls on an object, which is of the same size as the wavelength of light, it is diffracted. This fact is usually investigated by means of a diffraction grating, which consists of a large number of fine, equidistant and parallel lines drawn on the metal or some other materials.

W.H Bragg and W.L.Bragg discovered that a *crystal could behave as a three-dimensional diffraction grating to x-rays*. Thus they used x-ray for the purpose of studying the internal structure of crystals.

The Bragg's Equation

The following equation is the mathematical statement of Bragg's law of x-ray diffraction

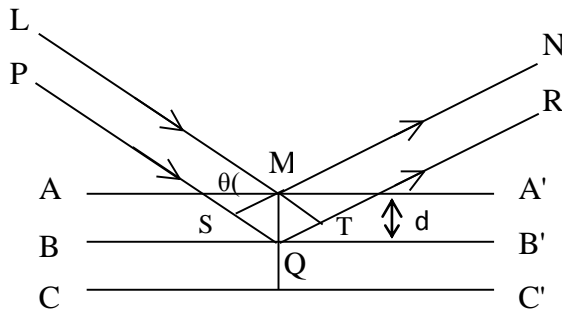
$$n\lambda = 2d \sin\theta$$

Where λ = the wavelength of the x-rays used; d = the interplanar distance;

n = the order of reflection; and θ = the angle of incidence.

Derivation

A beam of x-rays incident on the atoms, which constitute a plane, is diffracted in such a way as to cause either interference or reinforcement of the beam diffracted from the first or the outer plane. The whole beam behaved as if it had been reflected from the surface of the crystal. The crystal behaves as transmission grating because it contains a series of equally spaced atomic planes.



When x-rays are incident on a crystal face they penetrate into the crystal and scattered by the atoms or ions.

Consider a set of parallel and equidistant planes AA', BB', etc. in the crystal as shown in Fig.

These planes characterize the arrangement of the atoms or ions in the crystal. A parallel beam of monochromatic x-ray of wavelength λ strikes these planes at an angle of incident θ .

Some of the rays will be reflected by atoms from the upper layer AA', with angle of reflection being equal to the angle of incident.

When the rays reflected from the successive layers are in phase, constructive interference will occur and a bright diffraction spot would be obtained from these planes.

The condition for the constructive interference is that the path difference between the reflected rays from successive planes must be an integral multiple of wavelength.

The condition for reinforcement can be obtained as follows.

The path difference for **LMN** and **PQR** is equal to **SQ + QT**, where **MS** and **MT** are perpendiculars drawn from **M** to **PQ** & **QR** respectively.

If **d** is the interplanar spacing between the successive planes, then both **SQ** and **QT** are equal to **d Sinθ**, since the angles **SMQ** and **QMT** are equal to **θ**.

$$(SQ = MQ \sin \theta) (MQ = d)$$

$$(QT = MQ \sin \theta) (SQ = QT)$$

The total path difference is thus $2d \sin \theta$.

For a reflection of maximum intensity this quantity must be an integral number (**n**) of wavelength **λ**, as stated above.

Hence the condition for maximum reflection is $n\lambda = 2d \sin \theta$, where $n = 1, 2, 3, \dots$ and is known as the order of reflection.

If $n = 1$, the order of reflection is one. If $n = 2$, the order of reflection is two and so on.

The equation $n\lambda = 2d \sin \theta$, is known as Bragg equation and gives the relationship between the interplanar spacing 'd' and the angle at which the reflected radiation has maximum reflection for a given wavelength **λ**.

Experimental Methods of Crystal Analysis: Single Crystal Method: (Bragg – x-ray spectrometer)

It is evident from Bragg equation that if the angles of incidence **θ** are measured for the various orders of maximum reflection, the interplanar spacing **d** between the successive planes of a given type of crystal can be calculated, provided the wavelength **λ** of the x-ray is known.

The reflection angle **θ** and the intensities of the reflected beams corresponding to these angles can be determined with a Bragg x-ray spectrometer.

The x-rays generated in x-ray tube are passed through a series of slits to give a sharp and monochromatic beam.

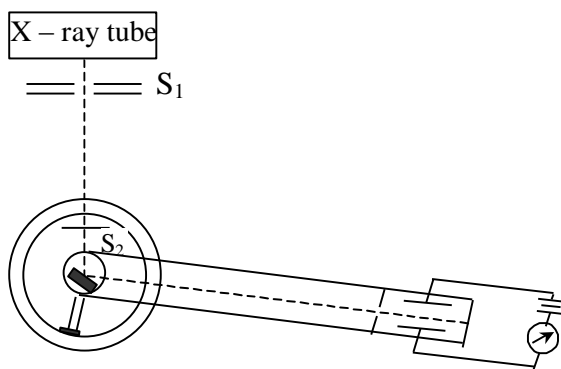
The beam is then directed to strike the face of a crystal, which is mounted on a graduated rotating table.

The rays reflected from the crystal are allowed to pass through a detector known as an ionizing chamber filled with vapour of methyl bromide.

The chamber is rotated coaxially with the crystal table.

The crystal table and the chamber are so adjusted that when the crystal rotates through any angle, the chamber rotates at twice that angle so that the reflected rays always enter the chamber.

The extent of ionization produced by the reflected beam is measured by the electrometer.



Bragg x-ray spectrometer

The value of incident angle θ is gradually increased by rotating the table.

The intensities of the reflected x-rays for various angles are determined.

Strong reflections are obtained from those planes which contain larger number of atoms and for those values of θ which satisfy the Bragg equation.

The process is repeated for each plane of the crystal. The intensities of the reflected rays are plotted against twice the angle of incidence of the beam to the crystal and the lines are indexed.

Thus, when the crystal is rotated, the angles are obtained to satisfy Bragg's equation, signals are produced. The intensity of these signal flashes is measured. From this and the angle of rotation, the values of 'n' and the angle of incidence θ are determined.

Experimental Methods of Crystal Analysis: The powder Method: (Bragg – x-ray spectrometer)

Powder specimen can also be used instead of single crystals. In this method, the crystal under study is ground into fine powder. The fine powder contains small granules of crystals with random orientations. If we have enough powder randomly oriented on the surface, we expect some of the different atomic planes to lie parallel to the surface. Therefore, if we scatter an incident X-ray beam from 0 to 90 degrees, we should find all the angles where diffraction occurred. Each of these angles will correspond to a different atomic spacing. The instrument used to make these measurements is the X-ray powder diffractometer.

The data recorded in the detector is the X-ray intensity in counts/second. By plotting the intensity against the angle of the incident X-ray, we can produce a series of peaks. These diffraction peaks correspond to d-spacing and can be converted using the Bragg equation.

Structures of some typical lattices

1) AB type Structures of ionic crystals

Example: NaCl, CsCl and ZnS (Sphalerite)

2) AB₂ type Structures of ionic crystals

Example: CaF₂ (Fluorite structure)

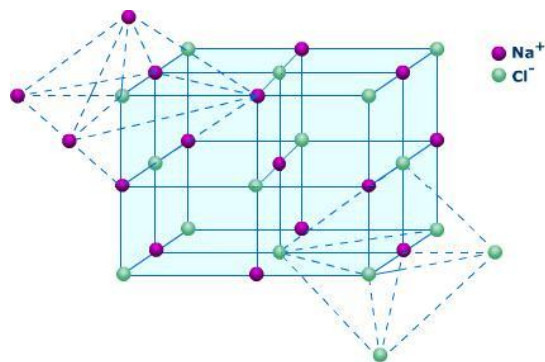
3) A₂B type Structures of ionic crystals

Example: Na₂F (Anti-fluorite structure)

4) ABX₃ type Structures of ionic crystals

Example: Perovskite structure (CaTiO₃)

Structure of NaCl Crystal



Main features

It has a face centred arrangement (or CCP). Cl^- ions occupy the corners and face centers, Na^+ occupy body centre and edge centers.

Each Na^+ is surrounded by six Cl^- and each Cl^- is surrounded by 6 Na^+ . Therefore it has 6:6 coordination.

Number of NaCl Units per unit cell.

i) Number of Cl^- ions

8 at the corners contribute $1/8$ per unit cell $8 \times \frac{1}{8} = 1$

6 at the face center contribute $\frac{1}{2}$ per unit cell $6 \times \frac{1}{2} = 3$

Total number of Cl^- ions = 4

ii) Number of Na^+ ions

12 at the edge centers contribute $\frac{1}{4}$ per unit cell $12 \times \frac{1}{4} = 3$

One at the body center contributes fully = $1 \times 1 = 1$

Total Number of $\text{Na}^+ = 3+1=4$

Therefore, there are 4 NaCl molecules in one Unit cell.

There are four 4 Chloride ions and 4 Na ions in one unit cell. These are totally 8 ions in one unit cell.

Problem

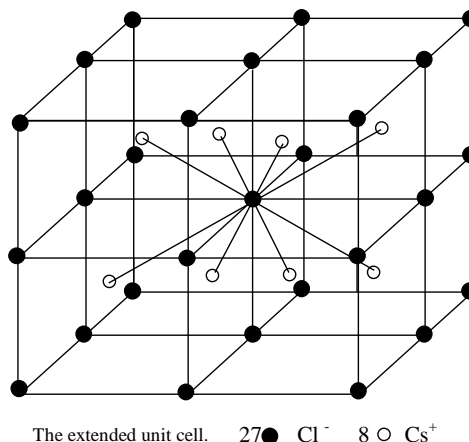
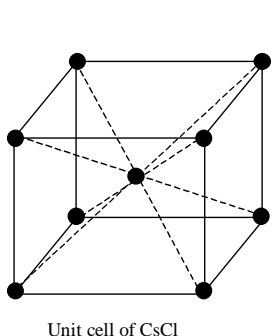
1. How many unit cells are there in one mole of NaCl crystal?
2. How many unit cells are there in 10 gram of NaCl?

Other examples of NaCl structure

- Halides of alkali metals (except caesium) and that of ammonium
- Oxides and sulphides of alkaline earth metals (except BeS)
- Halides of silver (except silver iodide).

Structure of CsCl Crystal

In this structure, Cs ions are represented by hallow circles whereas Cl ions are represented by solid circles. The crystal structure of CsCl can be discussed as follows.



a) Arrangement of Cs⁺ and Cl⁻ ions

The unit cell of the crystal CsCl contains 27 Cl⁻ ions and 8Cs⁺ ions. 8 Cl⁻ ions are present at the eight corners of the unit cell, 6 Cl⁻ ions are present at the center of each of the six faces, 12Cl⁻ ions are present at the center of 12 edges and one Cl⁻ ion is located at the center of the cubic unit cell. All the 8 Cs⁺ ions are present with in the unit cell.

b) Formula of CsCl crystal and occupation of cubic interstitial sites

If the entire cubic unit cell of CsCl is divided into 8 small cubic unit cell, then we may see that each of these small cubic unit cells has 8 Cl⁻ ions and one Cs⁺ ion. 8 Cl⁻ ions are present at the eight corners of the cube and Cs⁺ion is located at the center of the cube.

Since each of the 8 corner Cl⁻ ion is shared by 8 adjacent cubes, 8 corner Cl⁻ ions contributes only $8 \times \frac{1}{8} = 1$ Cl⁻ ion to the cube. Thus each of the 8 small cubes into which the whole cell is divided contains one Cs⁺ ion and one Cl⁻ ion and hence the formula of Cesium chloride is CsCl. i.e., the stoichiometry of the compound is 1:1.

Each small cube contains eight ions (Cl⁻) at its eight corners and one ion (Cs⁺) at its body center, and this arrangement of ions (8Cl⁻ and 1Cs) is called body-centered arrangement, but actual definition of body-centered cubic is that the arrangement should contain the same ions at the corners as well as at the body center. Consequently to call the arrangement of Cs and Cl⁻ ions a body-centered cubic arrangement is misnomer.

Main features of CsCl structure:

- The radius ratio (r_+/r_-) value for **CsCl crystal is 0.884**. Since the value lies in the range 0.732 – 1.000, which suggests that it has a bcc type lattice
- Cl^- ions are at the corners, centers of the faces, centre of the edges and center of the body and Cs ions are present at the centre of the body of individual unit cell.
- Each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ions is surrounded by 8 Cs^+ ions. Therefore the crystal has 8:8 co-ordination.

Number of Cl^- ions

Atoms at the corner contribute = $1/8 \times 8 = 1$

Atoms at the centre of the face contributes = $1/2 \times 6 = 3$

Atoms at the centre of the edge contributes = $12 \times 1/4 = 3$

Atoms at the centre of the body contributes = $1 \times 1 = 1$

Hence the total number of Cl ions is 8.

Number of Cs^+ ions

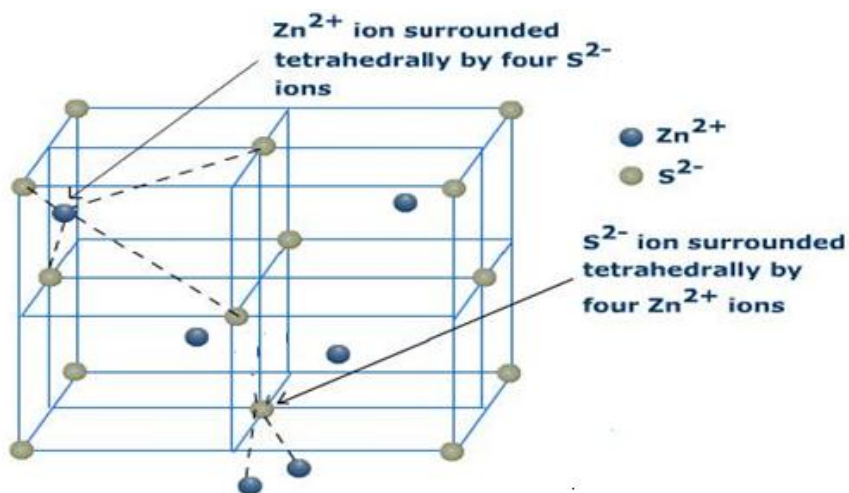
For smaller unit it is 1

For bigger unit it is 8

- Hence the total number of Cl^- and Cs^+ ions is $(8+8)16$.
- Therefore, there are 8 CsCl molecules in one unit cell of CsCl.
- Other examples : CsBr, CsI, CsCN, TiCl, TiBr, TiCN etc.

Zinc blende, ZnS (Sphalerite)

ZnS has two common crystalline forms, both with coordination number 4. Zinc blende is the most common zinc ore and has essentially the same geometry as diamond, with alternating layers of Zn and S. It can also be described as having zinc ions and sulfide ions, each in face-centered lattices, so that each ion is in a tetrahedral hole of the other lattice. The stoichiometry requires half of these tetrahedral holes to be occupied, with alternating occupied and vacant sites.



Main features

- Arrangement is F.C.C. (or C.C.P). The S^{2-} ions are present at the corners and face centers.

- Zn^{2+} ions are present in alternate tetrahedral voids.(ie, Zn^{2+} ions at the body centre of small cube in alternative cubes)
- Each Zn^{2+} ion is surrounded tetrahedrally by S^{2-} ions each and S^{2-} ion is surrounded tetrahedrally by Zn^{2+} ions. Therefore this structure has 4:4 coordination.

Number of S^{2-} ions per unit cell.

At corners contributed

$$\frac{1}{8} \text{ per unit cell} = 8 \times \frac{1}{8} = 1.$$

6 at the face centre contribute

$$\frac{1}{2} \text{ per unit cell} = 6 \times \frac{1}{2} = 3$$

$$\text{Total number of } \text{S}^{2-} \text{ per unit cell} = 4.$$

Number of Zn^{2+} ions per unit cell.

At the centre of the body in each small cube $1 \times 4 = 4$

- Hence, there are 4 Zn^{2+} ions and four S^{2-} ions, totally there are 8 ZnS ions, and 4 ZnS molecule in one unit cell.
- Since Zn^{2+} ions occupy half the tetrahedral sites, the number of Zn^{2+} ions per unit cell will be 4.
- Total number of ZnS per unit cell = 4.

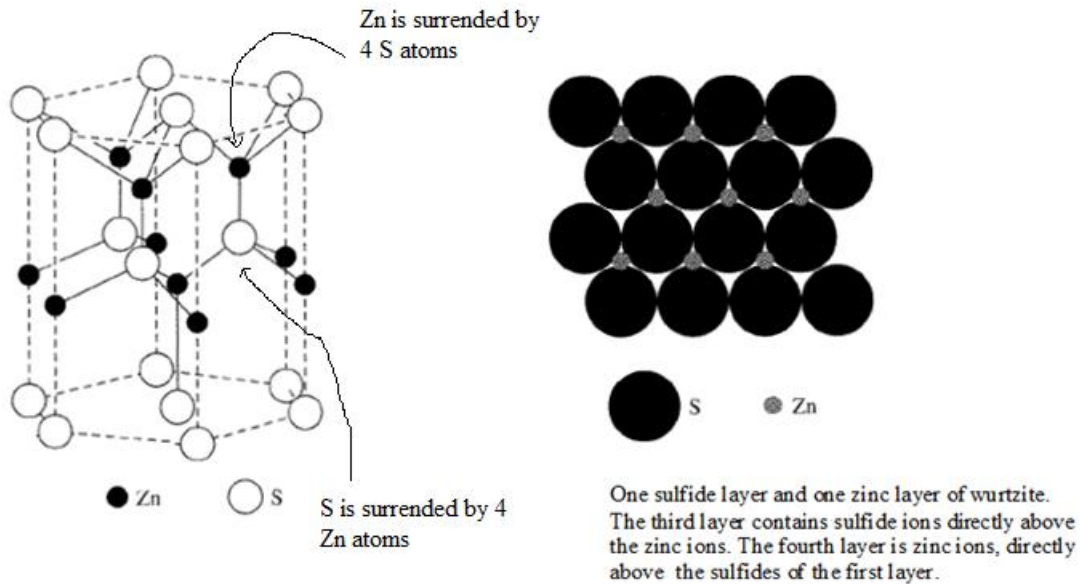
Other examples : CuCl, CuBr, CuI, AgI, BeS.

Wurtzite (ZnS)

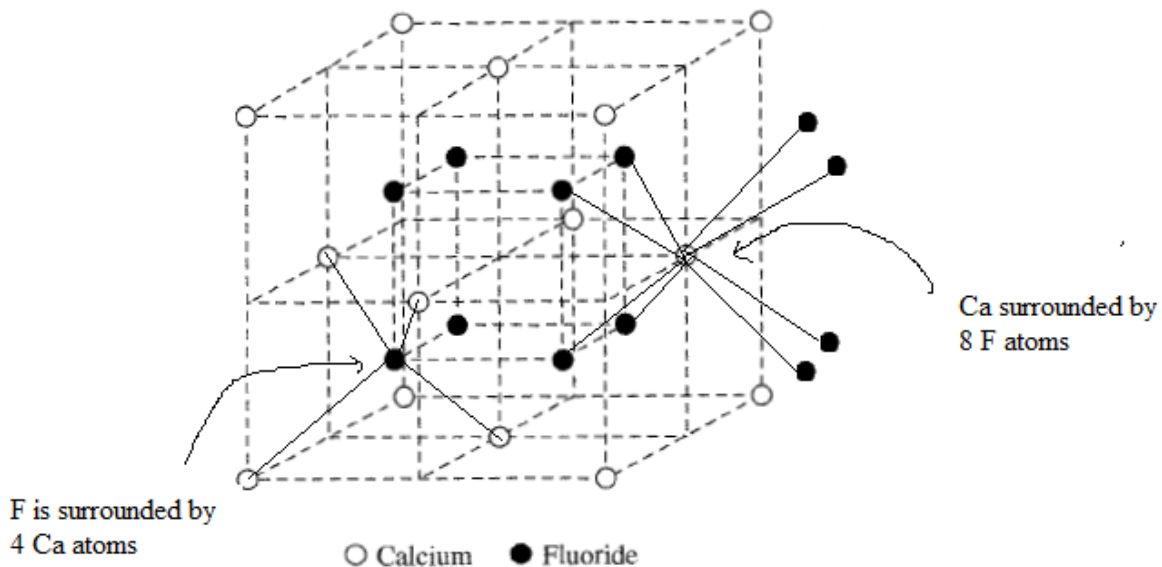
The wurtzite form of ZnS, Figure is much rarer than zinc blende, and is formed at higher temperatures than zinc blende. It also has zinc and sulfide each in a tetrahedral hole of the other lattice, but each type of ion forms a hexagonal close-packed lattice. As in zinc blende, half of the tetrahedral holes in each lattice are occupied.

Main features

- Sulphide ions are arrangement in Hexagonal Close Packing.
- Zn^{2+} ions occupy half of the tetrahedral site
- Each Zn^{2+} ion is surrounded tetrahedrally by S^{2-} ions each and S^{2-} ion is surrounded tetrahedrally by Zn^{2+} ions. Therefore this structure has 4 : 4 coordination.
- The radius ratio (r_+/r_-) value for **Wurtzite crystal is 0.40**, which suggests that it has a coordination number 4
- The basic difference between Zinc blende and Wurtzite is that in Wurtzite, the S^{2-} ions are arranged in HCP (ie, ABABB type) and in Zinc blend it is CCp (ie, ABCABC tye).



Fluorite Structure (CaF_2) - AB_2 type



The fluorite crystal belongs to AX_2 type. This is also called calcium fluoride crystal (CaF_2).

The Salient features of CaF_2 Crystal

- Arrangement of Ca^{2+} and F^- ions and occupation of tetrahedral sites
 - Since Calcium ion is larger than fluoride ion, Ca^{2+} ions have ccp arrangement (FCC)
 - Ca^{2+} ions are at all the eight corners and at all centers of the six faces of the cube.
 - F^- ions are present in the body of each small cube (i.e. in all the available tetrahedral voids).
- Formula of calcium fluoride crystal and coordination number:

Number of calcium ions

- At the corners $1/8 \times 8 = 1$
- At the face centre $6 \times 1/2 = 3$
- Hence total number of calcium ions is 4
- Number of Fluoride ions = 8
- i.e. Each Ca^{2+} is surrounded by 8F^- where as each F^- is surrounded by 4Ca^{2+} so it has 8:4 co-ordination.
- It is supported by its radius ratio value of CaF_2 crystal is 0.73. Since the value lies in the range 0.732 – 1.000, coordination number of Ca^{2+} ion in CaF_2 is equal to 8.
- Similarly the coordination number of F^- ion in CaF_2 is 4 since tetrahedral arrangement of 4Ca^{2+} ions around F^- ions.
- Therefore, CaF_2 is 8:4 ionic crystal.
- Number of Ca^{2+} per unit cell is 4. Number of F^- is 8 (because all the tetrahedral voids are occupied by F^- ions). Therefore 4CaF_2 units per unit cell.
- Other examples of fluorite structure: BaF_2 , BaCl_2 , SrF_2 , SrCl_2 .

Antifluorite crystal structure

Main features

- It is the reverse of fluorite structure. The anions are in the ccp type of lattice and the cations are at the body centre.
- Generally the alkaline metal oxides and sulfides prefer this structure.
- O^{2-} ions (i.e.anions) are present at the corners and centres of faces (i.e. constitute F.C.C. or C.C.P.).
- Na^+ ions (i.e.) are present at the body of the each cube(i.e. occupy all the tetrahedral sites.

Number of anions

At the corners $1/8 \times 8 = 1$

At the centre of face $6 \times 1/2 = 3$

Hence total number of oxide ions per unit cell is 4

Number of cations = 8

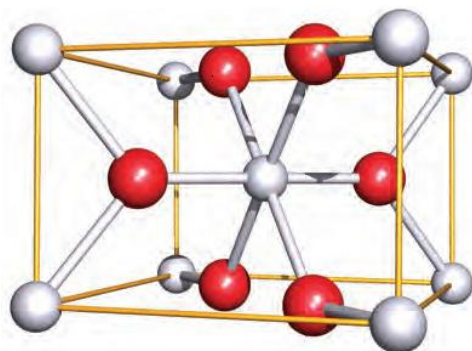
Each O^{2-} is surrounded by 8 Na^+ ions.

Each Na^+ by four O^{2-} ions.

Na_2O has 4:8 co-ordination.

Number of Na_2O molecule per unit cell is 4.

Rutile Structure (TiO₂)



The unit cell of rutile

Main features

- The cube is not perfect cube. Along of the axes, the length is shorter than the other two by about 30%. Thus it is called distorted cube i.e. elongated cube.
- Titanium ion is at the corners and body centre of the cube.
- Oxygen ion is at the position shown above (red).

Number of titanium ion

- At the corners $1/8 \times 8 = 1$
- At the body $1 \times 1 = 1$
- Hence total number of titanium ions per unit cell is $= 2$

Number of oxide ion.

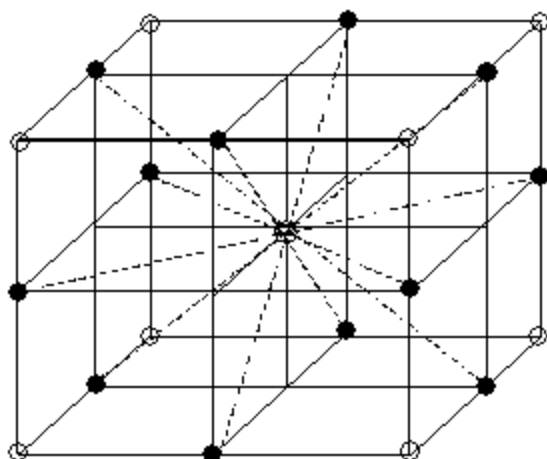
- At the face $4 \times 1/2 = 2$
- The other two oxygen atoms are inside
- Hence total number of oxygen ions per unit cell is $= 4$
i.e. Number of TiO₂ molecule per unit cell is 2

- Each Ti⁺ is surrounded by 6 oxide ions.
- Each oxide is surrounded by 3 titanium ions.
- TiO₂ has 6:3 co-ordinations.

Since oxygen is smaller, the cavity generated by six oxygen is enough to hold the Ti. Hence, CN is 6. Since titanium is large. The cavity generated by 3 titanium is enough to hold the oxygen. Hence CN is 3.

Perovskite structure (CaTiO₃)

It has a structure of CCP array of ABX₃ type. In an ABX₃ crystal, A is Ca, B is Ti and X₃ is O₃. In this structure, Ca atom surrounded by 12 oxygen atoms and the Ti surrounded by 6 oxygen atoms. The Oxygen atom is surrounded by 4 titanium atoms. Therefore, the coordination number of Calcium is 12, Ti atom is 6 and Oxygen atom is 4. Other examples: SrTiO₃ and BaTiO₃.

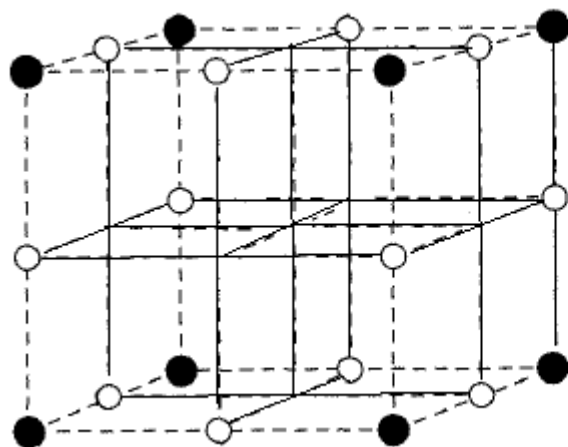


- Ca Body center
- Ti (corners)
- O (Center of all the edges)

The Pervoskite Structure

The sum of the charge on the A and B ions must be 6, but that can be achieved in several ways ($A^{2+}B^{4+}$ and $A^{3+}B^{3+}$ among them), including the possibility of mixed oxides i.e., $A(B_{0.5}B^{1.5})O_3$ for e.g. $La(Ni_{0.5}Ir_{0.5})O_3$.

Rhenium trioxide structure (ReO_3)



- Re atom
- Oxygen atom

Main features

- Oxygen ions are at the center of the all 12 edges.
- Re atoms are at all 8 corners.

Number of oxygen atoms

- At the corners $12 \times \frac{1}{4} = 3$
- Hence total number of oxide ions per unit cell is 3

Number of Re atoms

- At the edges $8 \times \frac{1}{8} = 1$
- Hence, there are totally 4 atoms in one molecule of ReO_3 per unit cell.
- Each Re is surrounded by 6 oxide ions.
- Each oxide is surrounded by 2 Rhenium ions.
- Hence, Coordination number is 6:2.

The structure of Diamond and Graphite

- Until 1985, carbon was encountered primarily in two allotropes, *diamond and graphite*. The diamond structure is very rigid, with each atom surrounded tetrahedrally by four other carbon atoms and each carbon atom in this structure may be viewed as being sp^3 hybridized. As a result, diamond is extremely hard, the hardest of all naturally occurring substances. Graphite, on the other hand, consists of layers of fused six-membered rings of carbon atoms.
- The carbon atoms in these layers may be viewed as being sp^2 hybridized. The remaining, one unhybridized p orbitals are perpendicular to the layers and participate in extensive π bonding, with π electron density delocalized over the layers. Because of the relatively weak interactions between the layers, the layers are free to slip with respect to each other, and π electrons are free to move within each layer, making graphite a good lubricant and electrical conductor.
- The structures of diamond and graphite are shown in Figure 1 and 2, and their important physical properties are given in Table.1.

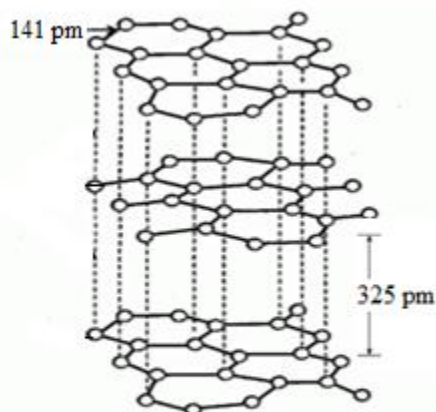


Fig.1 The layered structure of graphite



Fig.2 The structure of diamond showing four covalent bonds to each carbon atom.

Table-1: Physical Properties of Diamond and Graphite

<i>Property</i>	<i>Diamond</i>	<i>Graphite</i>
Density	3.513	2.260
Electrical resistivity (ohm)	10^{11}	1.570×10^{-5}
Standard molar entropy ($J \text{ mol}^{-1} \text{ K}^{-1}$)	2.365	5.740
C-C distance (pm)	1.54	141(within layer) 325 (between layer)

- At room temperature, graphite is thermodynamically the more stable form. However, the density of diamond is much greater than that of graphite, and graphite can be converted to diamond at very high pressure. Since the first successful synthesis of diamonds from graphite in the mid-1950s, the manufacture of industrial diamonds has developed rapidly, and nearly half of all industrial diamonds are now produced synthetically.

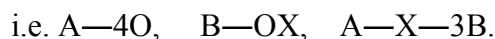
Normal spinel and inverse spinel

The spinel structure

Spinel has the formula AB_2O_4 after the name of the mineral $MgAl_2O_4$, where A can be a group IIA (2) metal or a transition metal in +2 oxidation state and B is a group IIIA (3) metal or a transition metal in the +3 oxidation state. The oxide ions form a close-packed cubic lattice with eight tetrahedral holes and four octahedral holes per AB_2O_4 unit.

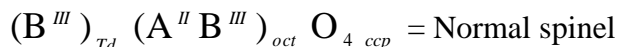
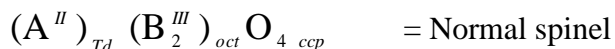
In a so-called normal spinel such as $MgAl_2O_4$, the Mg^{2+} ions occupy one-eighth of the tetrahedral holes and Al^{3+} ions occupy one half of the available octahedral holes. This is the arrangement that would be predicted to be the most stable as it yields a coordination number of 4 for the divalent ion and 6 for the trivalent ion.

The structure is the one in which each A ion is tetrahedrally coordinated by 4 O ions and each B ion is octahedrally coordinated by 6 O ions and each O ion is bonded to 1A and 3B ions in CCP arrangement.



The structure described above is said to be *normal spinel structure or simply spinel structure* and the arrangements are found in many AB_2O_4 oxides. Some oxides of this composition have the alternate structure called *inverse spinel structure or anti spinel structure*.

i.e.



If N ions are arranged in CCP, there will be N number of octahedral holes and 2N number of tetrahedral holes

Therefore, There is 4 oxide ions in CCP and hence there will be 4 octahedral holes and 8 tetrahedral holes.

So, in spinel,

- 4 oxide ions are in CCP
- Only 1/8 of tetrahedral holes are occupied by A
- Half (1/2) of the octahedral holes are occupied by B

But in the case of inverse spinel,

- 4 oxide ions are in CCP
- All A metals are in octahedral holes (i.e. 1/4 of octahedral holes are occupied by metal ion A)
- 1/4 of metal B are in octahedral holes.
- 1/4 of metal B are in tetrahedral holes.

Some examples for normal spinel

- $M^{2+} [Al_2^{3+}] O_4$ where $M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}$
[Note: $Ni^{2+} Al_2^{3+} O_4$ is inverse spinel]
- $Mn_3O_4, Co_3O_4,$
- $Mg^{2+} Cr_2^{3+} O_4, Ni^{2+} Cr_2^{3+} O_4$
- The spinel structures include many ternary oxides with the stoichiometry AB_2O_4 that contain a 3d-series metal, such as $NiCr_2O_4$ and $ZnFe_2O_4$, and some simple binary d-block oxides, such as Co_3O_4 , and Mn_3O_4 ; note that in these structures A and B are the same element but in different oxidation states, as in $Co^{2+}[Co^{3+}]_2O_4$.

Some examples for inverse spinel

- There are also a number of compositions termed **inverse spinels**, in which the cation distribution is $B[AB]O_4$ and in which the more abundant cation is distributed over both tetrahedral and octahedral sites.
- Fe_3O_4 (Magnetite)
- $Ni^{2+} Al_2^{3+}$ etc.

Predicting the structures of spinel and inverse spinel by crystal field factor

1. The **occupation factor**, λ , of a spinel is the fraction of B atoms in the tetrahedral sites: $\lambda=0$ for a normal spinel and $\lambda=0.5$ for an inverse spinel, $B[AB]O_4$; intermediate λ values indicate a level of disorder in the distribution.

The distribution of cations in (A^{2+}, B^{3+}) spinels (Table 1) illustrates that for d^0 A and B ions the normal structure is preferred as predicted by electrostatic considerations.

Table 1 shows that, *when A^{2+} is a $d^6, d^7, d^8,$ or d^9 ion and B^{3+} is Fe^{3+} , the inverse structure is generally favored.* This preference can be traced to the lack of ligand-field stabilization of the high-spin $d^5 Fe^{3+}$ ion in either the octahedral or the tetrahedral site and the ligand-field stabilization of the other d^n ions in the octahedral site.

For other combinations of d-metal ions on the A and B sites the relative ligand-field stabilization energies of the different arrangements of the two ions on the octahedral and tetrahedral sites need to be calculated. It is also important to note that simple ligand-field stabilization appears to work over this limited range of cations. More detailed analysis is necessary when cations of different radii are present or any ions that are present do not adopt the high-spin configuration typical of most metals in spinels (for instance, Co^{3+} in Co_3O_4 , which is low-spin d^6). Moreover, because λ is often found to depend on the temperature, care has to be taken in the synthesis of a spinel with a specific distribution of cations because slow cooling or quenching of a sample from a high reaction temperature can produce quite different cation distributions

The compound $CoAl_2O_4$ is among the normal spinels in Table 1 with $\lambda=0$ and thus has the Co^{2+} ions at the tetrahedral sites. The colour of $CoAl_2O_4$ (an intense blue) is that expected of tetrahedral Co^{2+} . Other mixed d-metal spinels that exhibit strong colours, for example $CoCr_2O_4$ (green), $CuCr_2O_4$ (black), and $(Zn,Fe)Fe_2O_4$ (orange/brown), are also

used as pigments, with applications that include colouring various construction materials, such as concrete.

Table 1: Values of λ

	A	Mg ²⁺	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
B		d^0	d^5	d^6	d^7	d^8	d^9	d^{10}
Al ³⁺	d^0	0	0	0		0.38	0	--
Cr ³⁺	d^3	0	0	0	0	0	0	0
Mn ³⁺	d^4	0	--	--	--	--	--	0
Fe ³⁺	d^5	0.45	0.1	0.5	0.5	0.5	0.5	0
Co ³⁺	d^6	--	--	--	--	0	--	0

$\lambda = 0$ corresponds to normal spinel $\lambda = 0.5$ corresponds to inverse spinel

2. Use of CFSE for predicting the structures of spinel

The role of LFSE's in determining site preferences is provided by the series of oxides Fe₃O₄, Mn₃O₄ and Co₃O₄, of which only the first is inverted. All energy connected with inversion should be similar in the three compounds except the differences in LFSE's, and these are just such as to favor inversion in Fe₃O₄ but not in the others. Thus, transfer of the d^5 Fe³⁺ ion involves no change in LFSE, but transfer of the high-spin d^6 Fe²⁺ ion from a tetrahedral to an octahedral hole produces a net gain in LFSE. For Mn₃O₄, transfer of the d^5 Mn²⁺ ion makes no change in LFSE, but transfer of the d^4 Mn³⁺ ion from an octahedral to a tetrahedral hole would decrease the LFSE, so that the process of inverting Mn₃O₄ is disfavored. For Co₃O₄ the transfer of the Co²⁺ ions to octahedral holes would be only slightly favored by the LFSE's, whereas the transfer of a low-spin d^6 Co³⁺ ion from an octahedral hole to a tetrahedral one where it would presumably become high-spin would cause a enormous net decrease in LFSE, so here, even more than in the case of Mn₃O₄, we do expect inversion.

Problems: Predicting the structures of spinel compounds

1. Is MnCr₂O₄ likely to have a normal or inverse spinel structure?

Answer We need to consider whether there is a ligand-field stabilization. Because Cr³⁺ (d^3) has a large ligand-field stabilization energy ($1.2\Delta_O$ from Table 20.2) in the octahedral site (but a much smaller one in a tetrahedral field) whereas the high spin d^5 Mn²⁺ ion does not have any LFSE, a normal spinel structure is expected. Table 1 shows that this prediction is verified experimentally.

Self-test : Table 1 indicates that FeCr₂O₄ is a normal spinel. Rationalize this observation.

Solid State Chemistry (Unit I)

1. Define the terms unit cell and Weiss indices.
2. What are miller indices?
3. Explain why it is not possible to distinguish K^+ ions from Cl^- ions by X-ray diffraction studies?
4. What is the relation between lattice constant and density?
5. Show that the volume occupied in CCP or FCC structure is 74%
6. Derive the Bragg's equation and show that $\lambda = d_{hkl} \sin\theta$. What is the physical significance of 'n' in the equation $n\lambda = 2d\sin\theta$?
7. Describe the powder method for the determination of crystal structure.
8. How many Zn^{2+} ions and how many S^{2-} ions are in the sphalerite unit cell? Draw its structure.
9. Compare the crystal structure of rutile and cesium chloride.
10. Define the terms i) Crystal Lattice ii). Unit cell.
11. Calculate the miller indices of a crystal plane which cut through crystal axes at
i). (2a, -3b, -3c) ii) (a/3, b, -c/2) and (4:3:∞)
12. Give the relationship between volume of a unit cell and density.
13. A substance with fcc lattice has density 6250kg/m^3 and molecular weight 60.2. Calculate the lattice constant 'a'. Given Avogadro number is 6.02×10^{25} kg/mol.
14. A beam of x-rays is incident on a sodium chloride crystal (lattice spacing is $2.82 \times 10^{-10}\text{m}$). The first order Bragg's reflection is observed at a glancing angle of $8^\circ 35'$. What is the wavelength of x-rays. At what angle the second and third order Bragg's reflection occur?
15. In the closest packed structure, 26% of the space is vacant. Explain with an example.
16. Draw and describe the crystal structure of Zinc blende and wurzite.
17. Describe the crystal structure of Zinc blende. What is the cation to anion ratio in this structure? What geometric arrangement of cations is there about each case?
18. Copper has fcc structure and its atomic radius is 1.278° . Calculate its density. The atomic weight of copper is 63.5.
19. Calculate the interplanar spacing (d_{hkl}) for cubic system between the following sets of planes (220) and (222). Assume that 'a' is the length of the cube.
20. Account for the fact that LiCl, KCl, RbCl have fcc structure while Cesium chloride has a bcc structure.
21. Solids are essentially incompressible where as gases are easily compressed. Explain.
22. How do you account for the abnormal behavior of (111) plane from (100) and (110) planes?
23. Draw the (200) and (220) planes of a face centered cubic lattice.
24. Explain why it is not possible to replace x-rays by UV of 10nm wavelength in the diffraction studies of crystals?
25. How do you account for fcc is more closely packed than bcc?
26. Prove that the interplanar spacing (d_{hkl}) in a cubic system is given by
$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$
 where a is edge length of the cube.
27. Describe the rotating crystal method for determination of crystal structure.
28. Prove that in the bcc structure only 68% of the space is actually occupied by spheres.

29. What is understood by the closest packing of identical spheres? What is meant by the stacking sequences ABAB and ABC ABC? How do these structures differ from each other?
30. What is the coordination number of a Ti atom in perovskite?
31. Calculate the number of atoms per unit cell of i). Face centered cube and ii). Simple orthorhombic.
32. Describe the crystal structure of Rutile.
33. Differentiate Fluorite and antiferite structures.
34. Write a note on Bravais lattice.
35. Polonium crystallizes in a simple cubic unit cell. The atomic mass and density of Polonium are 209 and 9.15 kg m^{-3} respectively. What is the edge length of its unit cell?
36. Metal X (at mass 55.8) crystallizes in bcc pattern. What is the number of nearest neighbours? What is the volume of the unit cell?

Choose the correct answer:

1. The crystal structure of CsCl is
(a) Simple cubic (b) face-centered cubic (c) Tetragonal (d) Body centered cubic
2. Rutile is
(a) TiO_2 (b) Cu_2O (c) MoS_2 (d) Ru
3. The total number of atoms per unit cell in fcc is
a) 1 b) 2 c) 3 d) 4

Problems:

1. A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution:

The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY.

2. Atoms of element B form *hcp* lattice and those of the element A occupy $\frac{2}{3}$ rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?

Solution :

The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only $\frac{2}{3}$ rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is $2 \times (\frac{2}{3}):1$ or 4:3 and the formula of the compound is A_4B_3 .