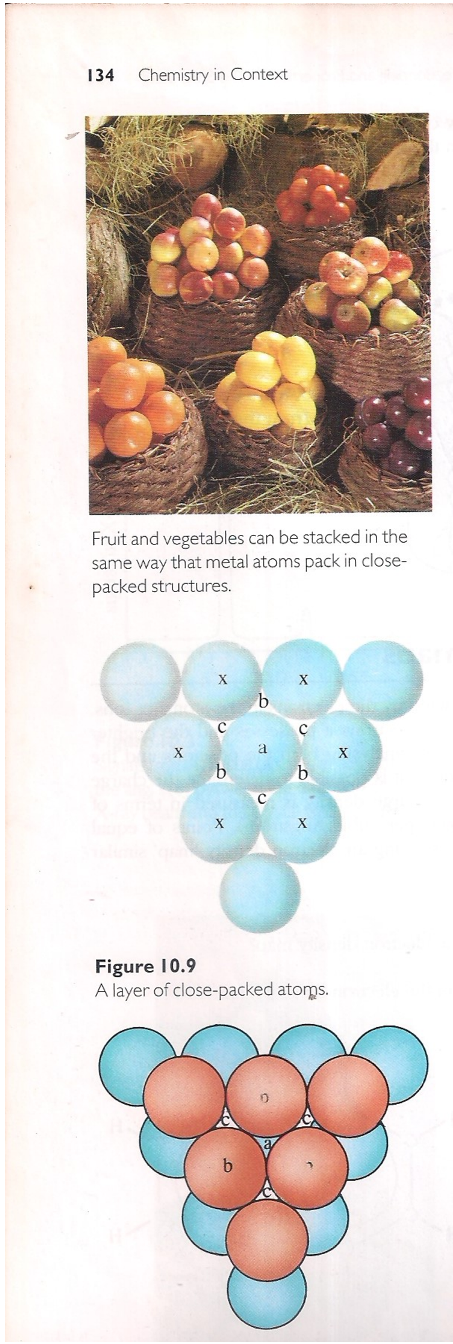
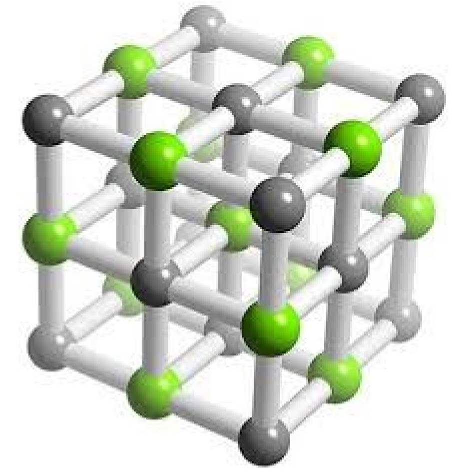
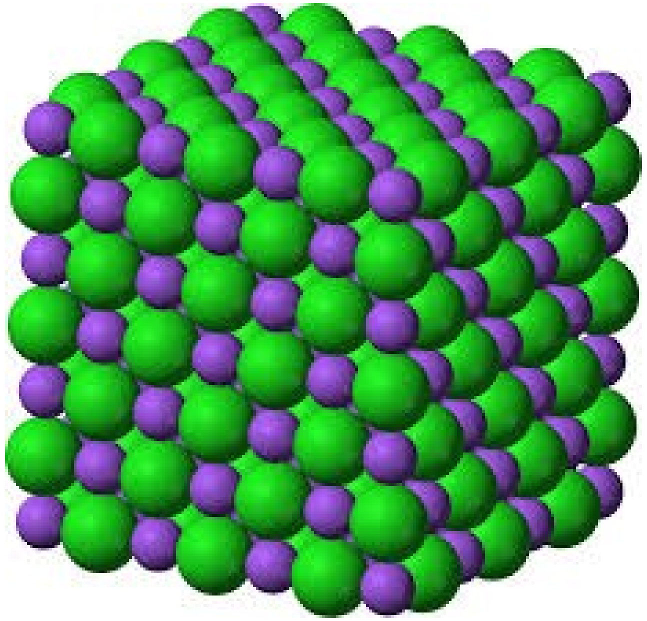


134 Chemistry in Context

Fruit and vegetables can be stacked in the same way that metal atoms pack in close-packed structures.

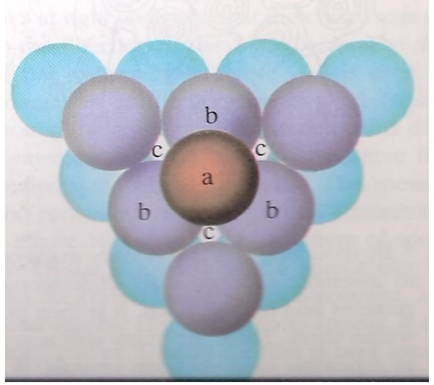
Figure 10.9
A layer of close-packed atoms.

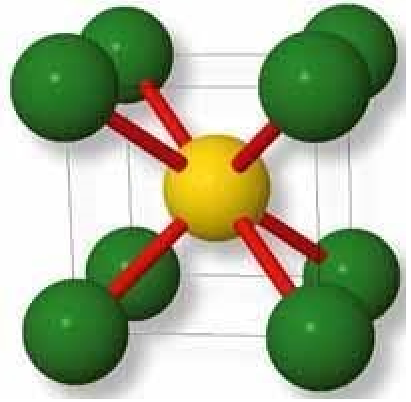


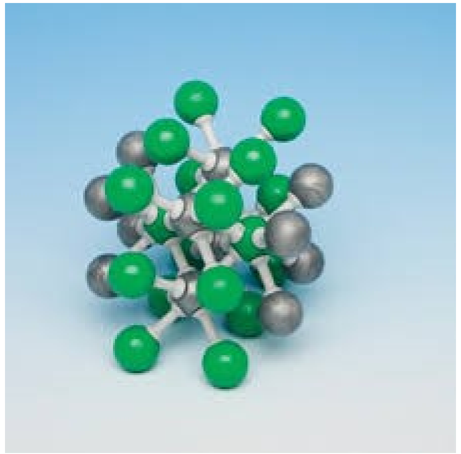


SOLIDS

Dr. Sangeeta Kumar, Dept of Chemistry

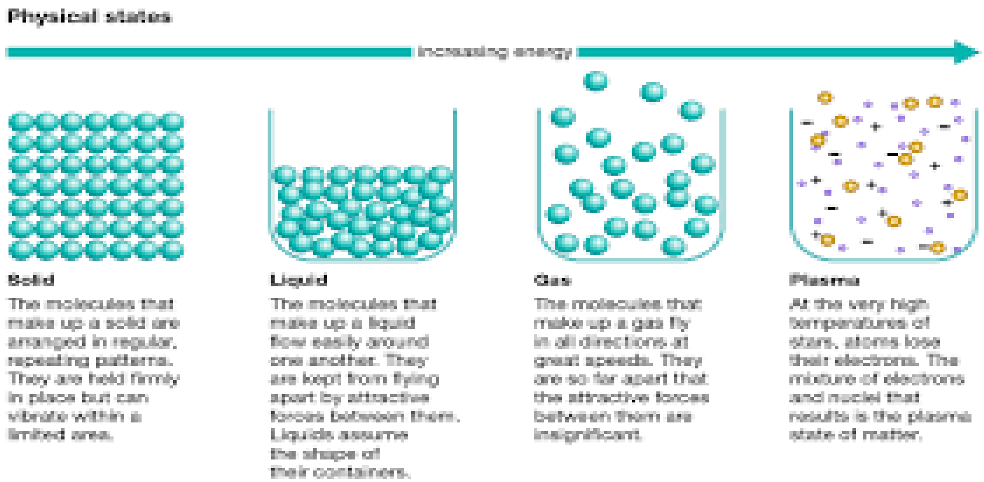






DIFFERENCE BETWEEN SOLIDS, LIQUIDS AND GASES

SOLIDS	LIQUIDS	GASES
Have definite shape and definite volume	Have no definite shape but have definite volume	Have no definite shape and no definite volume
Cannot be easily compressed	Slightly compressible	Highly compressible
Have a long range order	Have a short range order	No order at all
Distance between particles is very less, almost non existent.	Distance between particles is larger as compared to solids, hence slightly compressible.	Distance between particles is very large, hence highly compressible.



The molecules that make up a solid are arranged in regular, repeating patterns. They are held firmly in place but can vibrate within a limited area.

The molecules that make up a liquid flow easily around one another. They are kept from flying apart by attractive forces between them. Liquids assume the shape of their containers.

The molecules that make up a gas fly in all directions at great speeds. They are so far apart that the attractive forces between them are insignificant.

At the very high temperatures of stars, atoms lose their electrons. The mixture of electrons and nuclei that results is the plasma state of matter.

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TYPES OF SOLIDS

CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS
A Crystalline solid exists as small crystals.	An Amorphous solid has atoms, molecules or ions arranged randomly.
Each crystal has a characteristic geometrical shape	There is no definite shape.
In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the crystal lattice.	It lacks the ordered Crystalline lattice. In their disordered structure, Amorphous solids resemble liquids.
Sugar and salt are Crystalline solids.	Examples are rubber, plastic and glass. Glasses are to be considered as super cooled or highly viscous liquids.
Crystalline solids exhibit Anisotropy They have long range order. They have sharp melting points.	Amorphous solids show Isotropy. They have short range order They do not have sharp melting points

CRYSTALLINE SOLIDS AND AMORPHOUS SOLIDS

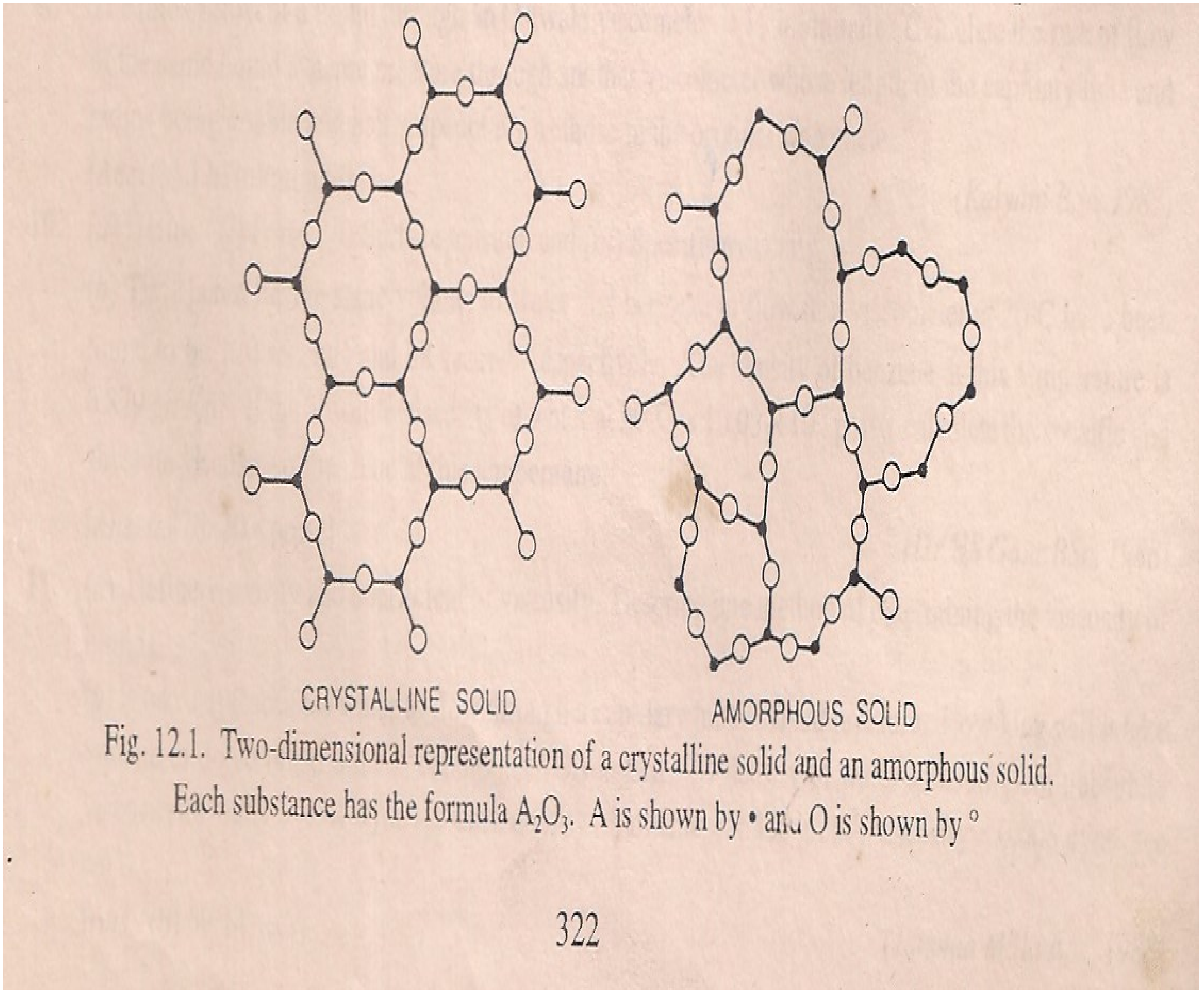
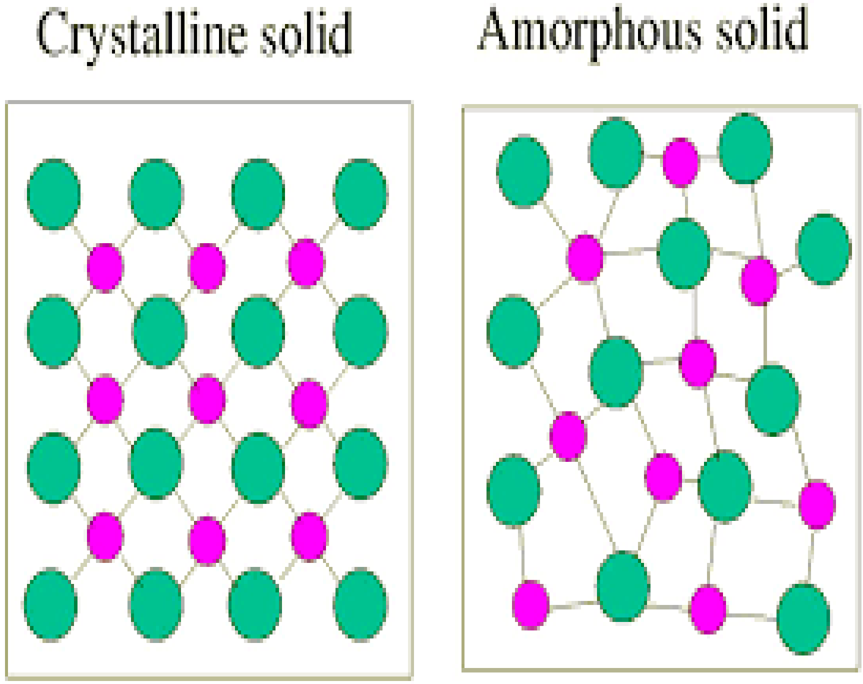


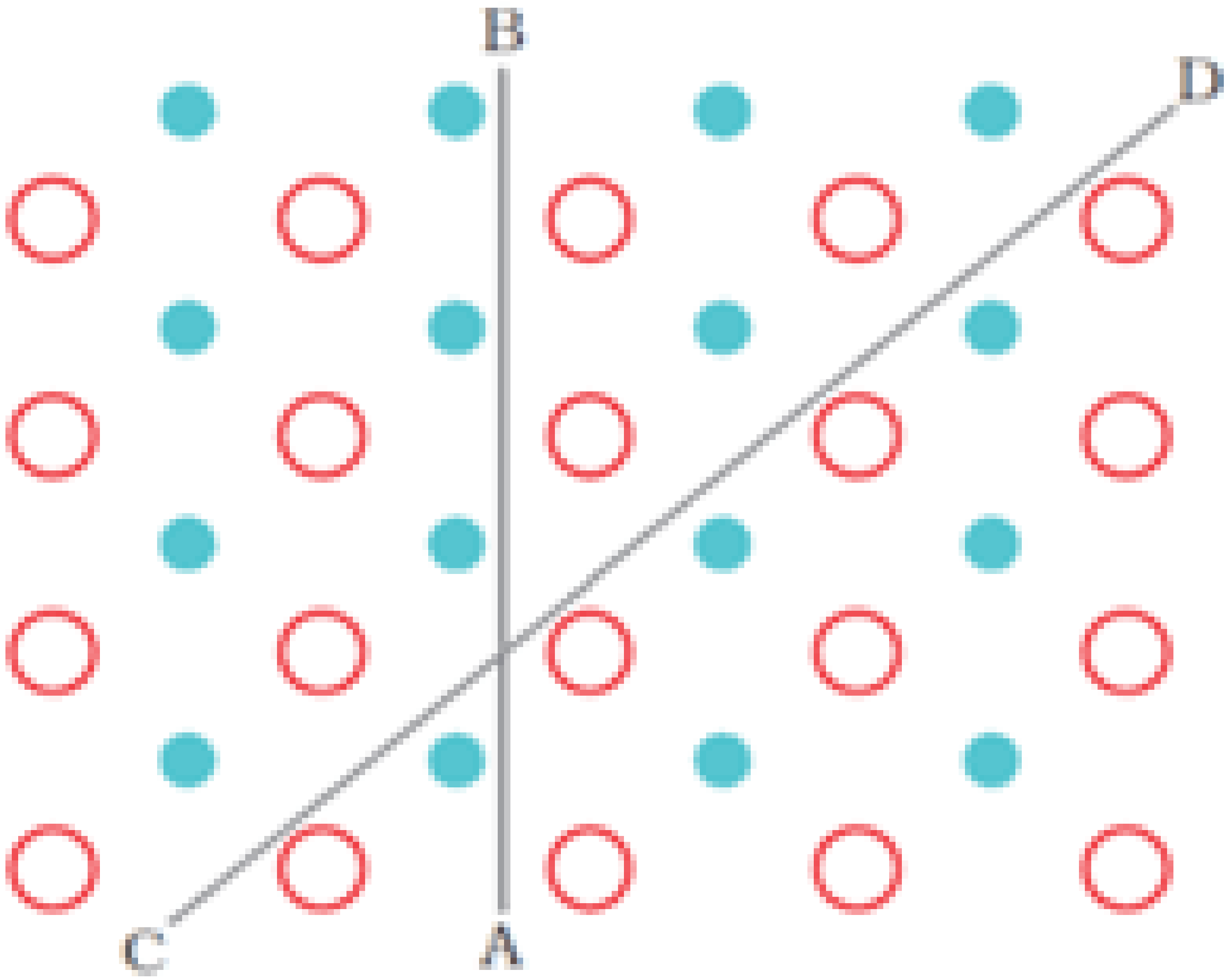
Fig. 12.1. Two-dimensional representation of a crystalline solid and an amorphous solid. Each substance has the formula A_2O_3. A is shown by • and O is shown by °



ISOTROPY AND ANISOTROPY

- Properties like Refractive index , thermal and electrical conductivity, and coefficient of thermal expansion depend upon the arrangement of particles in any solid.
- In a crystalline solid, the arrangement of particles is different in different directions. However, in an amorphous solid, because of the short range order, the structure averages out and the above mentioned properties show same value along every direction. This is called Isotropy.
- Crystalline solids have long range order. They show different values of these properties in different directions. This is called Anisotropy.
- The next slide will show the effect of long and short range order.

ANISOTROPY

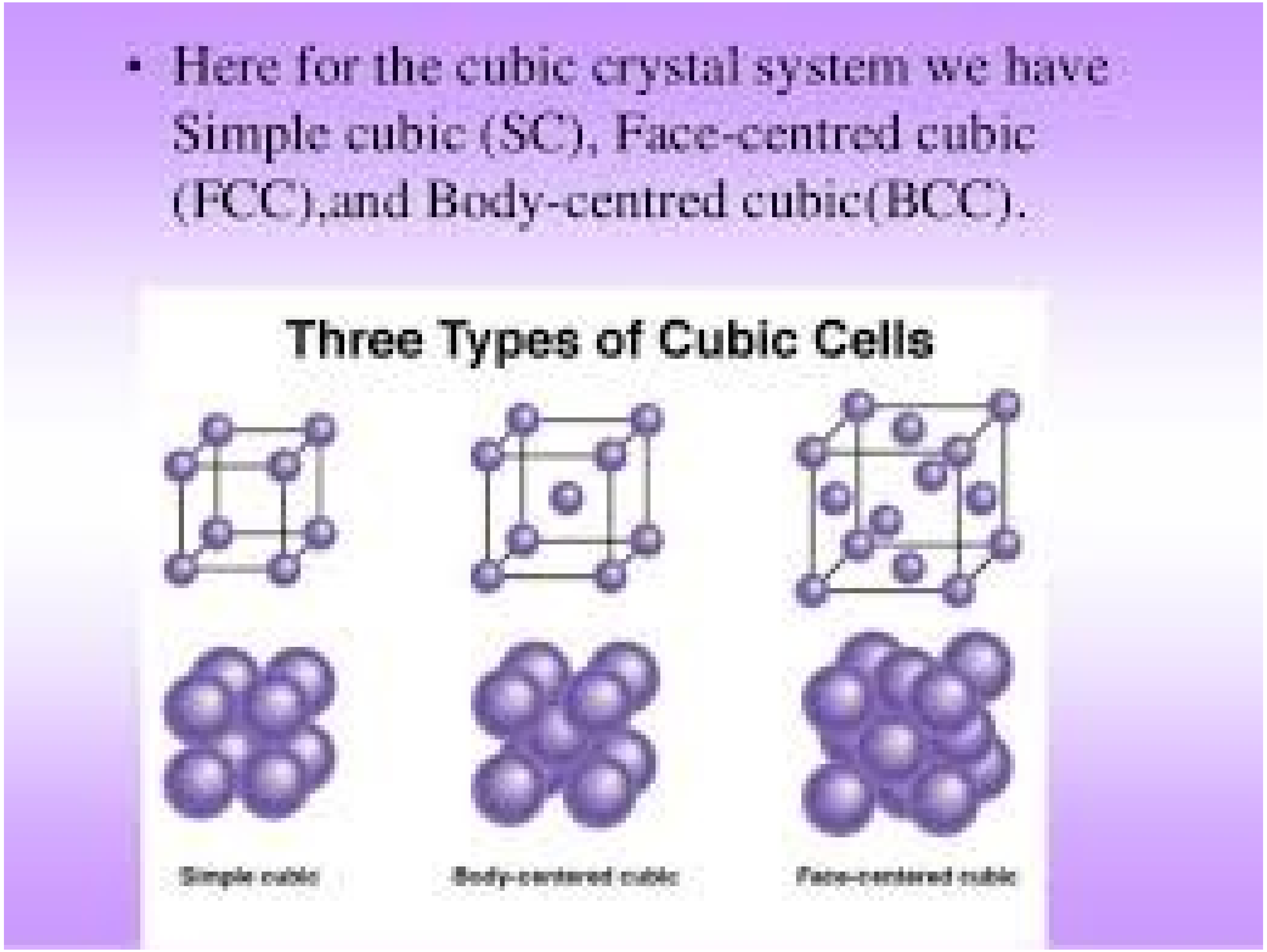


CRYSTAL LATTICE AND UNIT CELLS

- A crystal lattice is an array of points which show how the particles are arranged at different sites in 3-d space.
- The crystal lattice is a repetition of small units. Each repeating unit is called a UNIT CELL.
- There are three types of crystal lattices:

1. Simple cubic cell in which lattice points are arranged at the corners of the cell.(sc)
2. Body centred cubic in which lattice points are arranged at the corners as well as the centre of the cell. (bcc)
3. Face centred cubic in which there are lattice points at each corner as well as centre of each face. (fcc)

TYPES OF CRYSTAL LATTICES



- Here for the cubic crystal system we have Simple cubic (SC), Face-centred cubic (FCC),and Body-centred cubic(BCC).

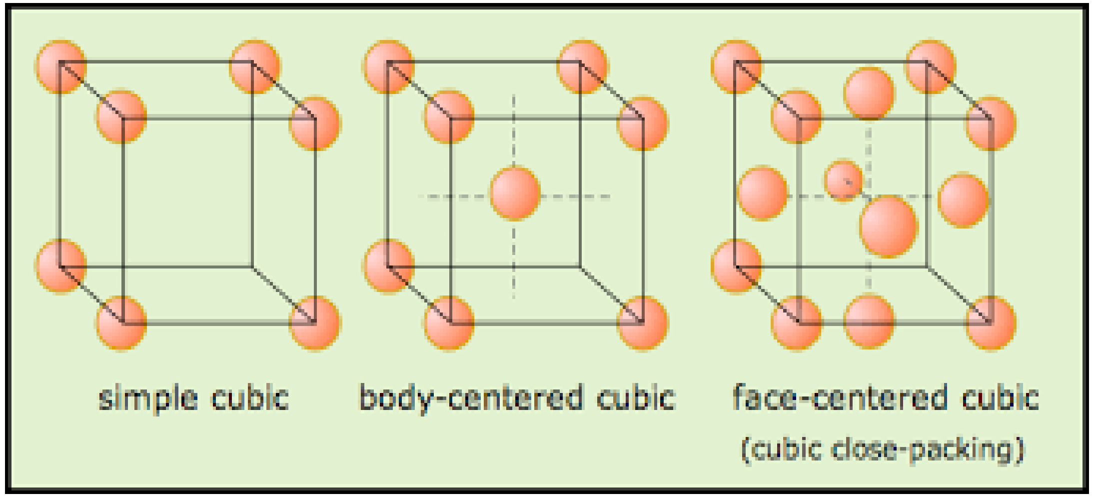
Three Types of Cubic Cells

EFFECTIVE ATOMIC NUMBERS OF CELLS

In a Simple Cubic Cell, 8 unit cells share each corner. Therefore, at each corner we have 1/8 atom. At 8 corners there will be 1/8X8=1 atom per unit cell in Simple Cubic Cell.

In Face centred Cubic, each corner contributes 1/8 atom. In addition, there is one atom on every face which is shared between 2 cells. There are 6 such faces. So, the effective atomic number will be 1/8X8+1/2X6=4 atoms in Face Centred Cubic.

In Body Centred Cubic, apart from the corner atoms, there is one atom in the centre of the cell which is not shared at all. Thus, Effective Atomic number in a Body Centred Cubic Cell is 1/8X8+1=2 atoms.



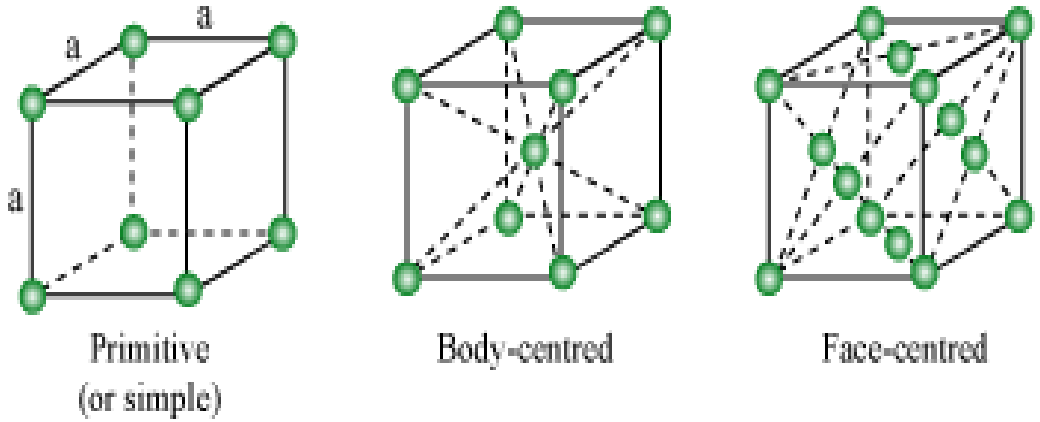
COORDINATION NUMBER IN CELLS

The Coordination number of a crystal structure is the number of particles immediately adjacent to each particle in the lattice.

In a **Simple Cubic Lattice**, each particle is surrounded by 6 other particles so its Coordination Number is 6.

In **Face Centred Cubic**, the closest number of particles in one plane are 4. So in three planes they are 12. So coordination number of fcc is 12.

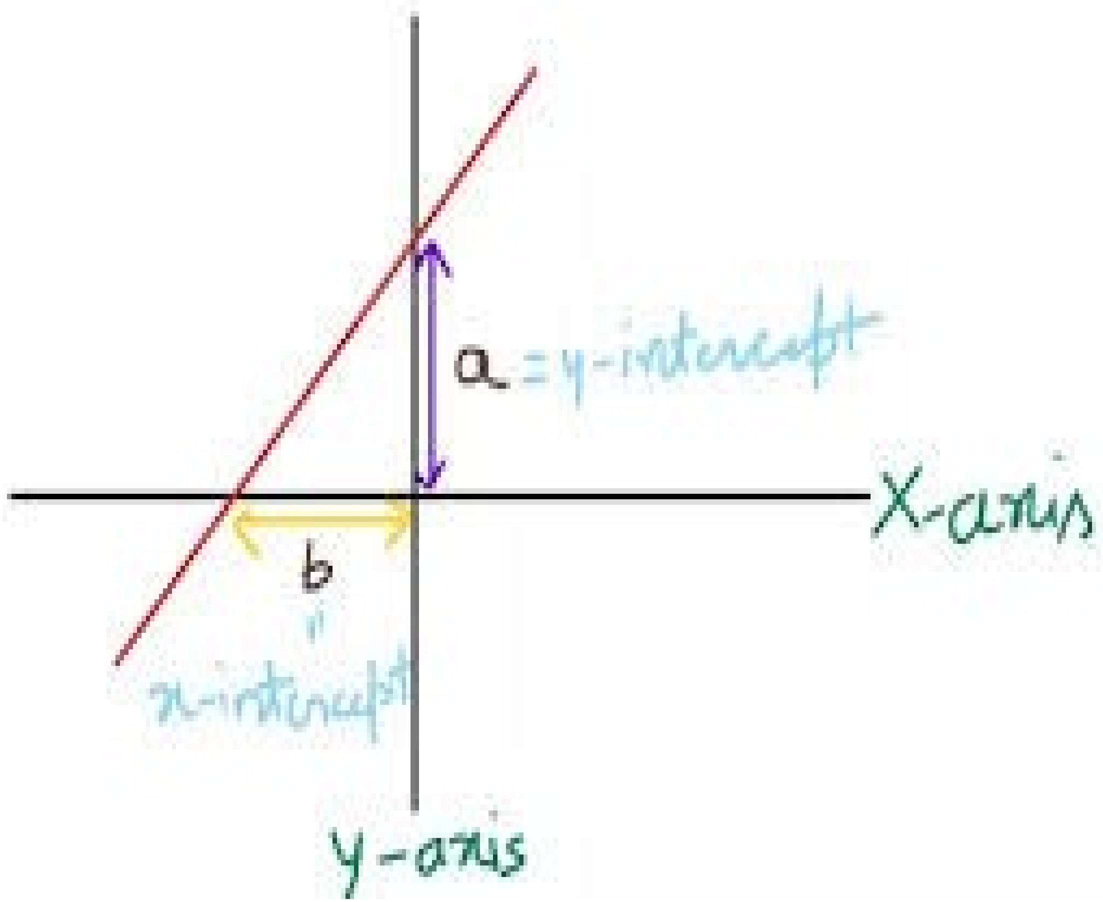
In **Body Centred Cubic**, number of atoms that are closest to a given atom is 8, one in the centre of each 8 adjoining cells. So coordination number of bcc is 8.



Cubic

CRYSTALLOGRAPHIC DESIGNATIONS

- In order to understand the crystallographic designations, it is important to know ‘intercepts’.
- When a line or a plane cuts an axis at some point, the distance of that point from the origin is called the ‘intercept’.
- So you can have an x-intercept, y-intercept or a z-intercept.



MILLER INDICES

- In this figure, ABC is the face of a crystal which intersects the crystal axes a, b and c at the distance OA, OB and OC respectively from the origin O.

- If we need to find the Miller indices of another plane ADE, we first express the intercepts of plane ADE in terms of intercepts of plane ABC.

- We can see that OD=2OB, OE=1/2 OC

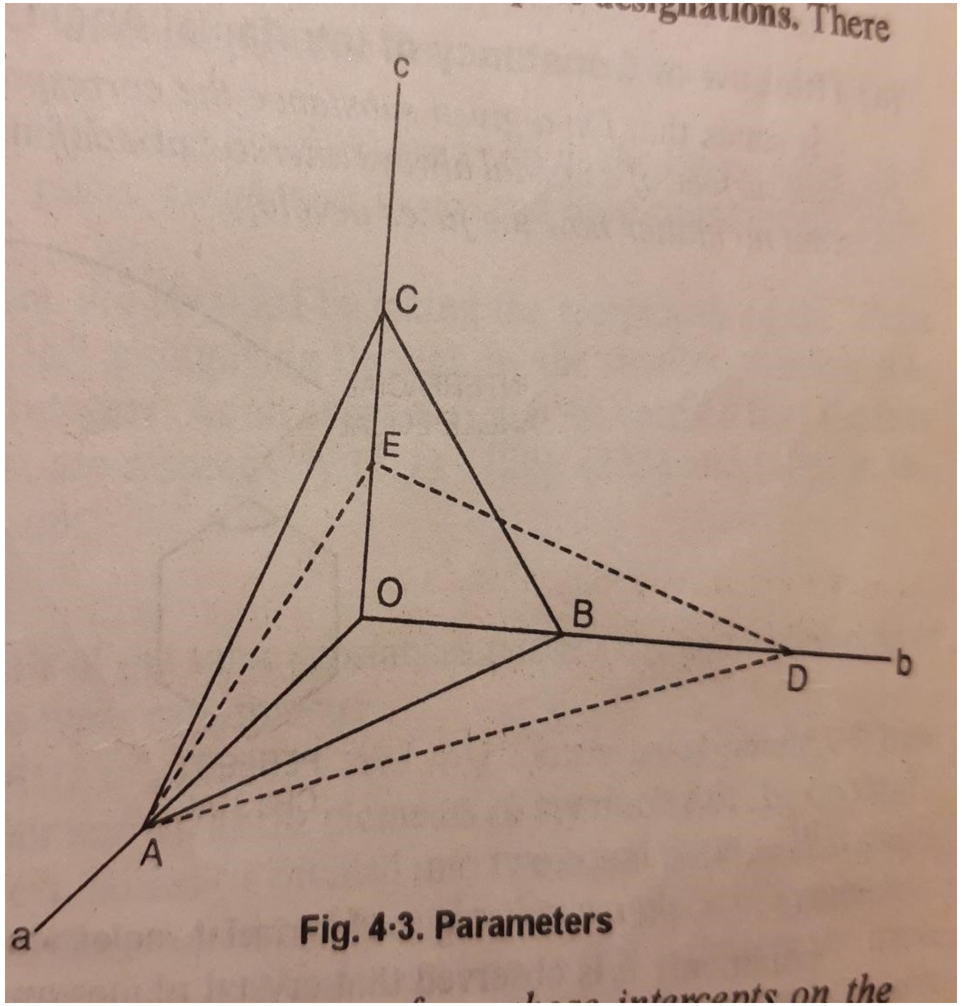


Fig. 4·3. Parameters

HOW TO FIND MILLER INDICES

1. Write the intercepts as multiples of a, b, c, say *la, mb, nc.*
2. Take reciprocal of *l, m, n.*
3. Clear fractions by multiplying with LCM to get whole numbers h,k, l
4. Miller indices of the plane are (hkl).

In the given example, writing the steps, we have,

1. Intercepts are 1a, 2b, 1/2c

2.Reciprocals are1/1, 1/2, 1/1/2=1, ½, 2

3.Multiplying by LCM of denominators, we get 2,1,4.

4. Miller indices of the plane ADE are (214).

WEISS INDICES

For the same example, the Weiss indices are written as follows:

1. Write the intercepts as multiples of a, b, c.
2. If there are fractions, clear the fractions .
3. You get the Weiss indices.

So in the previous example, the Weiss indices of the plane ABE are written as 1a, 2b, 1/2c

Clearing the fractions, we get 2,4,1.

Weiss indices of the plane ABE are (241).

RELATION BETWEEN MILLER INDICES AND INTERPLANAR SPACING

If 'a' is the side of the cubic cell and h,k,l are the miller indices of a given plane, the distance 'd' between the parallel planes will be given by the following relation:

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

Q. Find the interplanar distance between the planes having miller indices (100),(110) and (111).

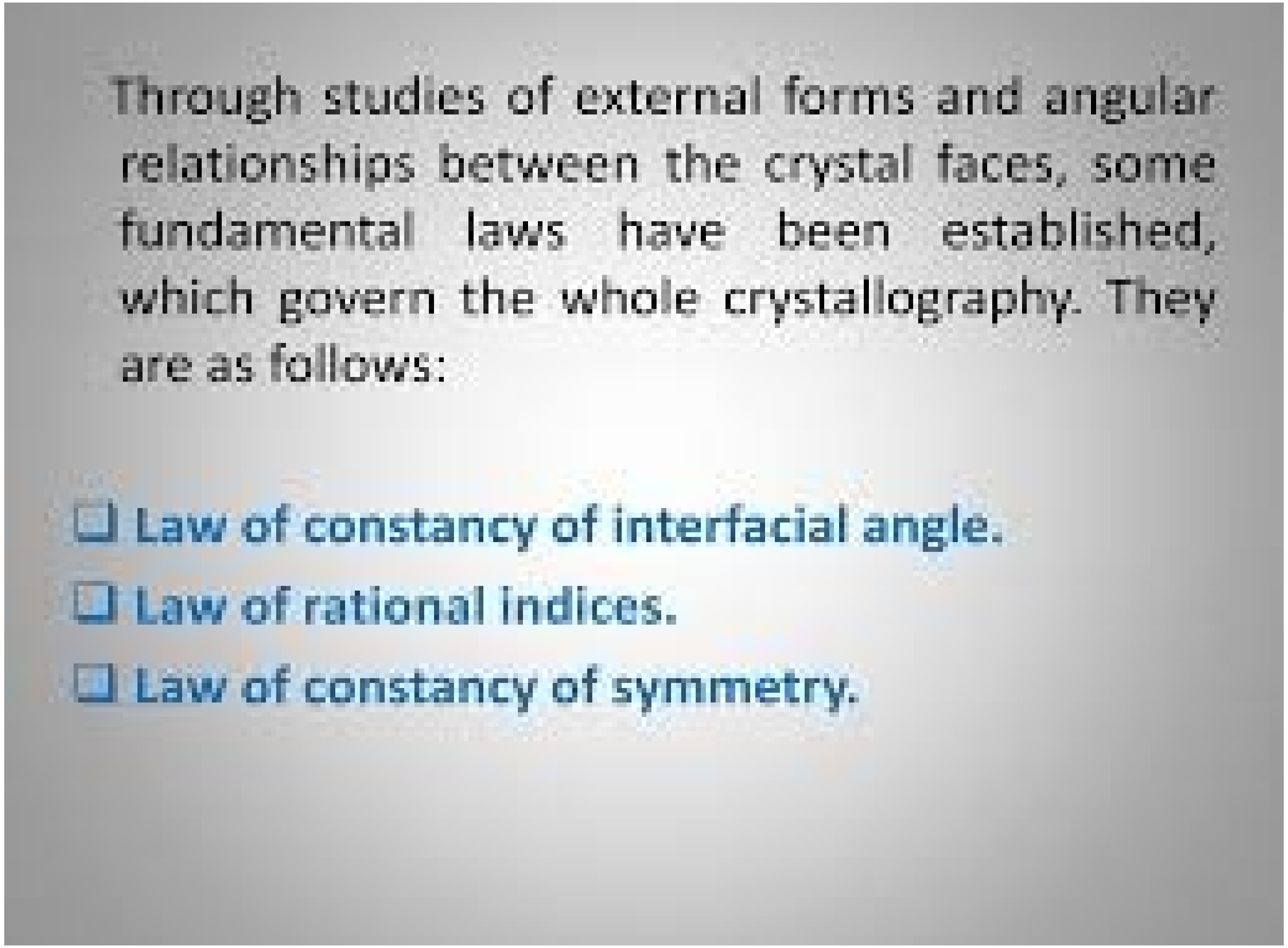
Ans. In the plane (100), the values of h,k,l are 1,0,0. Thus $\sqrt{1^2+0^2+0^2} = 1$

Therefore, $d_{100}=a$.

Similarly, $d_{110}=a/\sqrt{2}$

And, $d_{111}=a/\sqrt{3}$

LAWS OF CRYSTALLOGRAPHY



Through studies of external forms and angular relationships between the crystal faces, some fundamental laws have been established, which govern the whole crystallography. They are as follows:

- Law of constancy of interfacial angle.
- Law of rational indices.
- Law of constancy of symmetry.

LAW OF CONSTANCY OF INTERFACIAL ANGLES

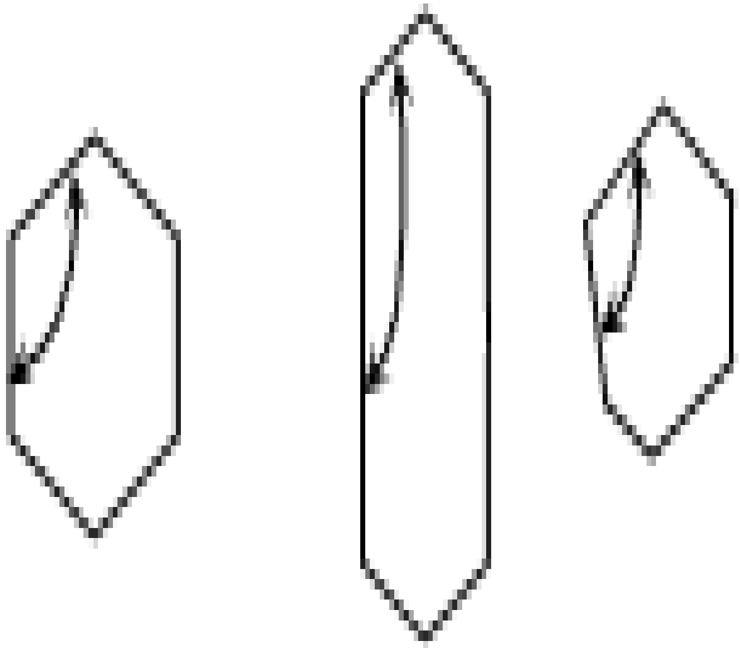


Fig 5.4 Constancy of interfacial angles

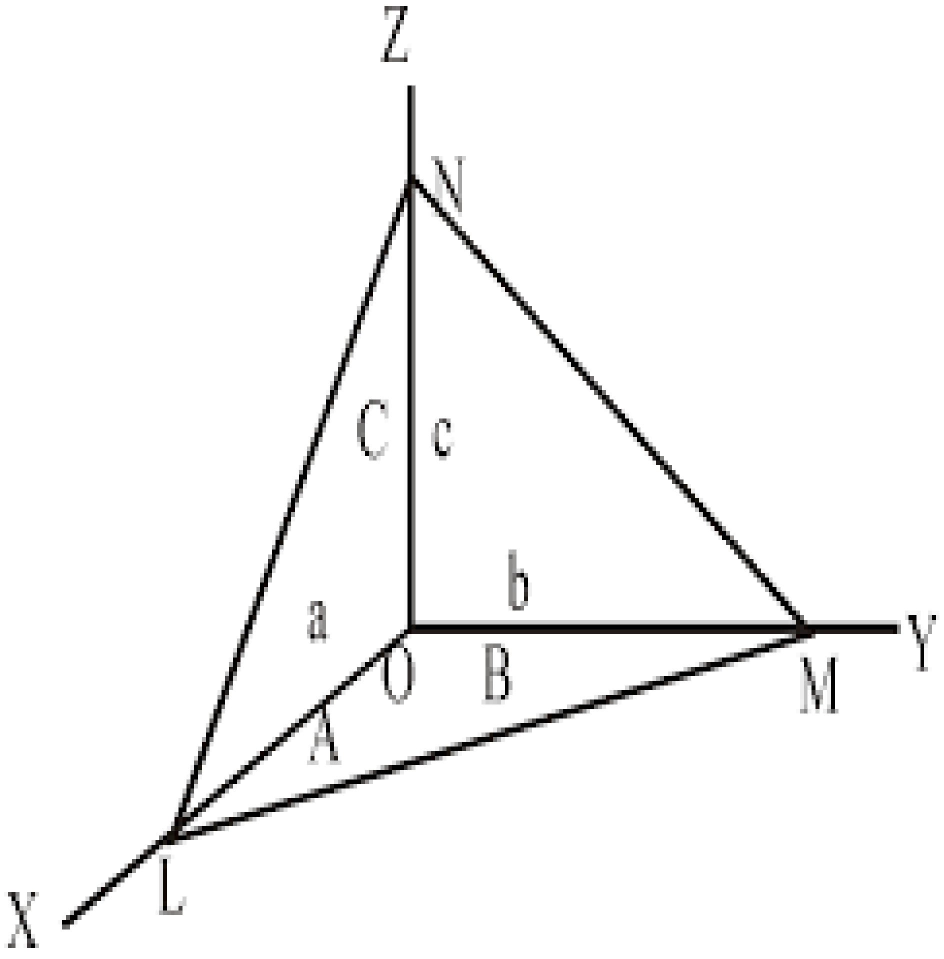
For a given substance, the corresponding faces or planes which form the external surface of a crystal always intersect at a definite angle and this angle remains constant, no matter how the faces develop.

It has been observed that crystal planes are often unequally developed, producing crystals of variable size and shape, but the angle of intersection of any two planes is found to be the same for a given substance.

LAW OF RATIONAL INDICES

The intercepts that any face of the crystal makes with the crystallographic axes are either equal or small rational multiples of the intercepts made by the unit face.

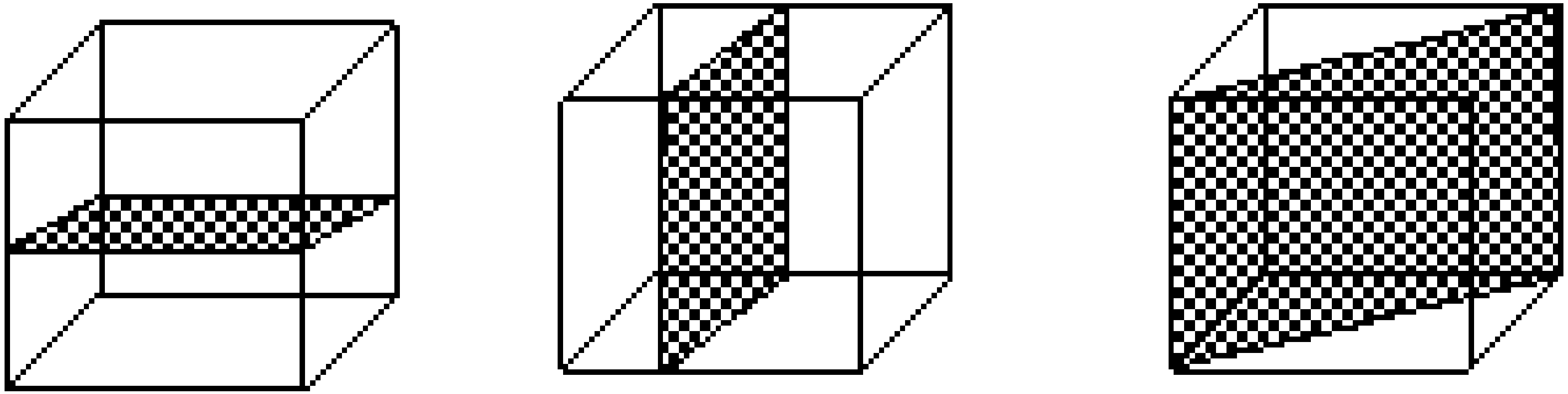
We have already dealt with the Miller indices and Weiss indices in the earlier section.



THE LAWS OF SYMMETRY

- This law states that all crystals of the same substance possess the same elements of symmetry. There are three elements of symmetry:

1.PLANE OF SYMMETRY. If a crystal can be divided into two equal parts, so that one part is the exact mirror image of the other, then the crystal is said to have a Plane of Symmetry.



Plane of symmetry

Rectangular plane of symmetry

Diagonal plane of symmetry

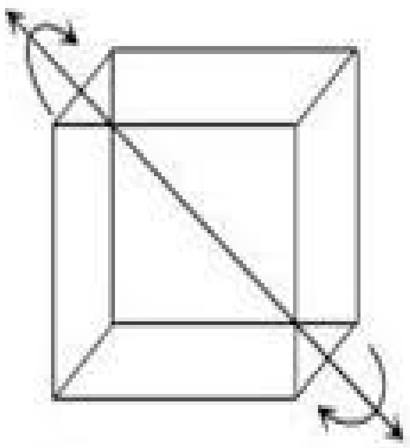
Fig. 5.1

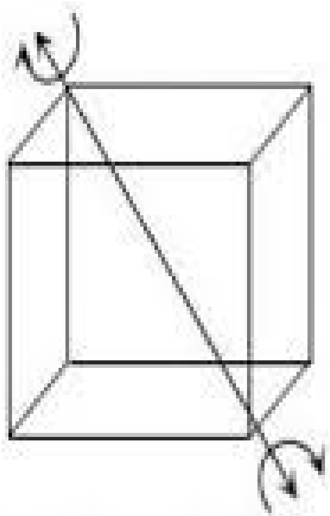
THE LAWS OF SYMMETRY

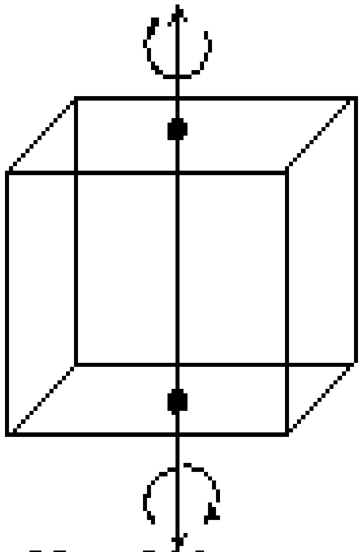
2. AXIS OF SYMMETRY

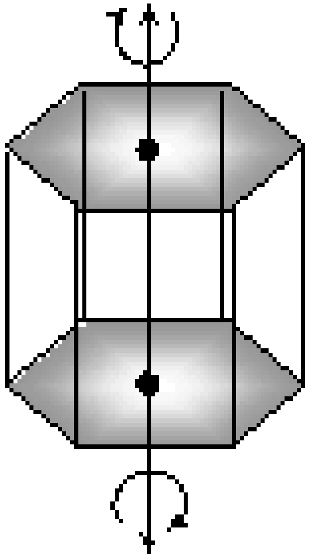
If a crystal can be rotated about a line so that it presents an appearance more than once during the complete rotation, then the crystal is said to have an Axis of Symmetry.

If a particular face appears again after a rotation of 180, the axis is Two fold axis of Symmetry(Diad axis). If a particular face appears after every 120 rotation, then the crystal is said to have a Three fold axis of Symmetry.


Axis of two fold symmetry


Axis of three f old symmetry


Axis of four fold symmetry


Axis of six fold symmetry

THE LAWS OF SYMMETRY

3. CENTRE OF SYMMETRY

A crystal is supposed to have a Centre of Symmetry if every face has an identical face on the opposite side at an equal distance from its centre. There are many crystals that do not possess any Centre of Symmetry at all.

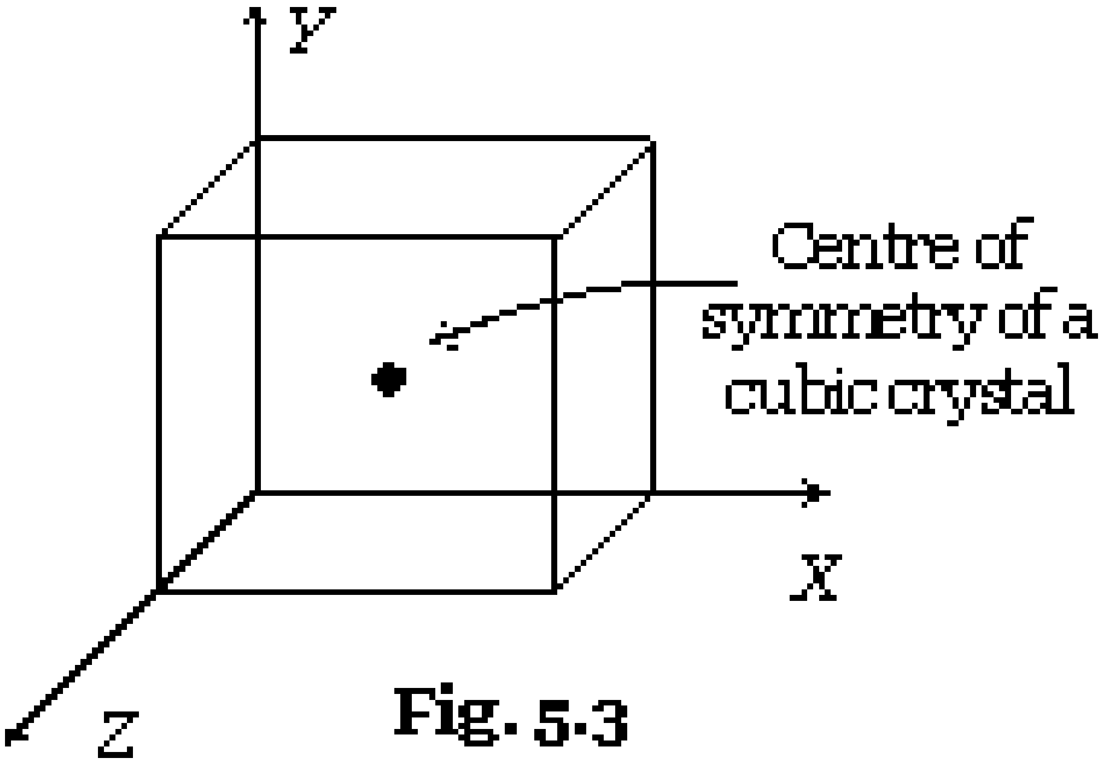


Fig. 5.3

X- RAY CRYSTALLOGRAPHY AND BRAGG EQUATION

A crystal lattice consists of layers or planes of atoms equal distance apart.

As the wavelength of X-Rays is comparable to the interatomic distance, Laue in 1912 proposed that a crystal can function as grating to the X-Rays.

The rays falling on the crystal undergo interference and diffraction. On the basis of the overall diffraction patterns produced by the crystal, we can obtain the detailed position of particles in a crystal.

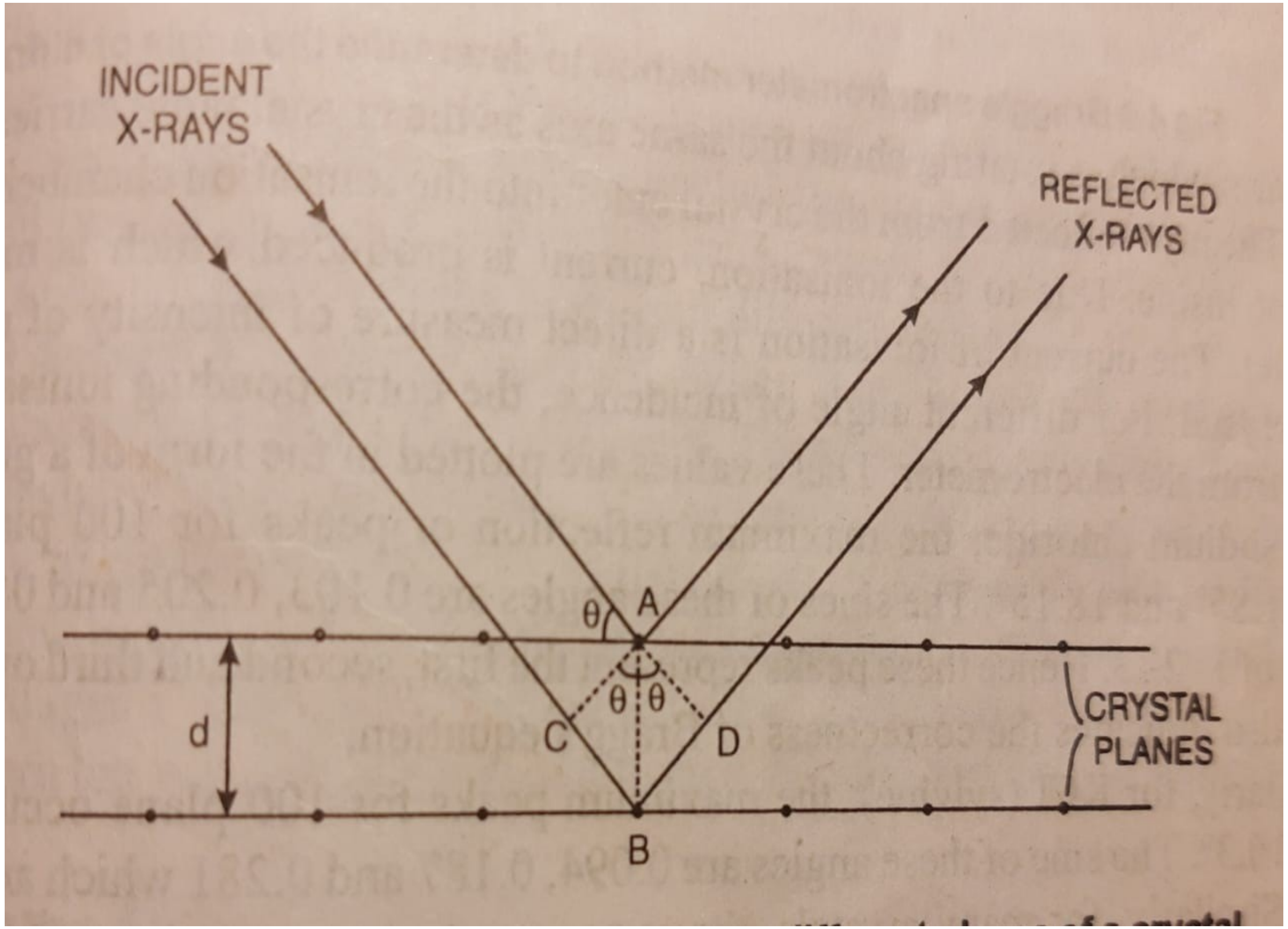
The study of crystal structure by means of X-Rays is called X-Ray Crystallography

In 1913, W.L Bragg and W.H. Bragg formulated a mathematical equation to work out interatomic distances from X-Ray diffraction patterns. This relation is known as the Bragg Equation.

DERIVATION OF BRAGG EQUATION

Bragg and Bragg proved that:

1. The X-Rays diffracted from atoms in crystal planes follow the Laws of reflection.
2. The two rays reflected by successive planes will be in phase provided the extra distance covered by the second ray is an integral number of wavelengths.



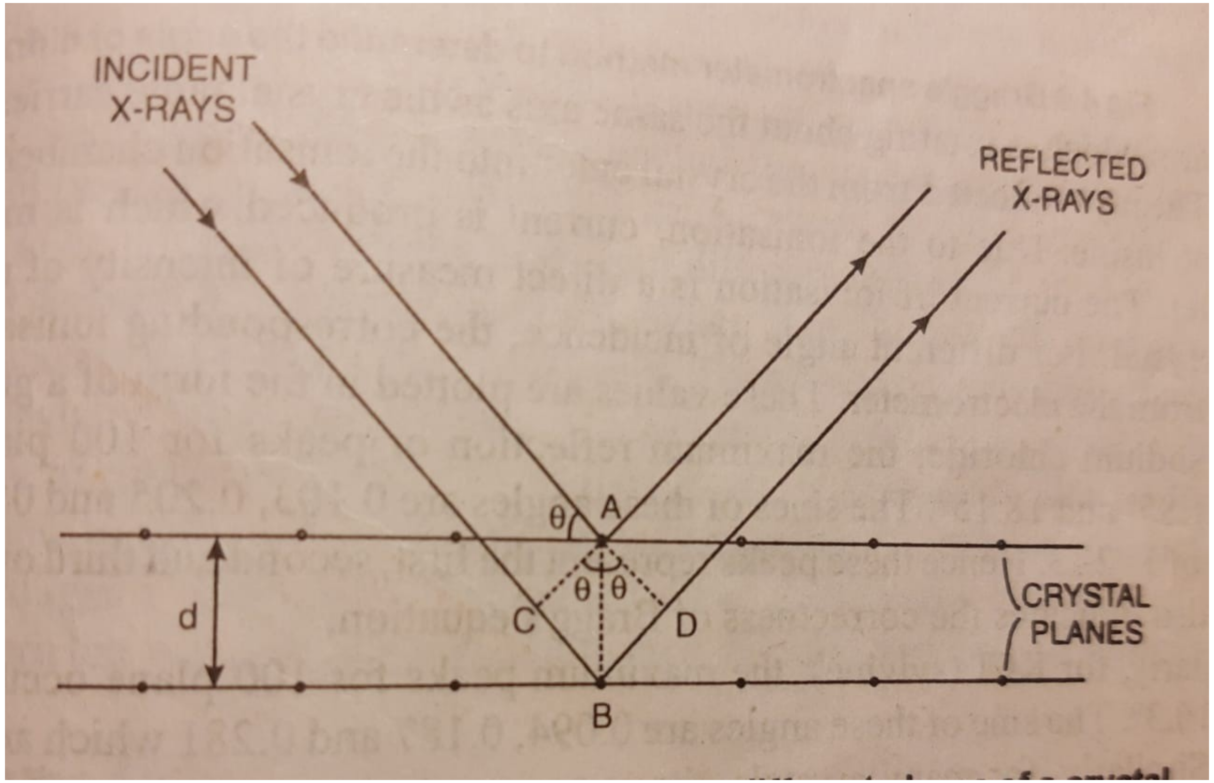
BRAGG EQUATION

This figure shows a beam of X-Ray falling on the Crystal Surface. Rays 1 and 2 are parallel and fall on parallel planes .

The angles that the rays make with the planes are equal(corresponding angles).

Triangle ACB is right angled at C. The distance BC is ABsinϴ or dsinϴ.

The extra distance travelled by ray 2 is CB+BD. Also CB=BD as triangles ACB=ADB



BRAGG EQUATION

The extra distance travelled by the second ray is equal to integral number of wavelengths.

Thus, $CB+BD=n\lambda$

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

This is called the Bragg Equation

The reflection corresponding to n=1 is known as a first order reflection, corresponding to n=2 is called the second order reflection.

SIGNIFICANCE OF BRAGG EQUATION

1. If we use X-Rays of known wavelength(ƛ), then the interatomic distance (d) in an unknown crystal can be calculated. If we use a crystal whose interatomic distance is known,, then the wavelength of X-Rays can be known.

2. The Bragg's equation gives the gives the essential condition for diffraction to occur.

3. When the experiment is done, there will be a maximum reflection at a particular angle, ϴ. This angle is noted. It corresponds to first order reflection(n=1). If we increase the angle ϴ, again maximum reflection occurs at some higher angle. It corresponds to second order reflection(n=2) and so on.

RELATION BETWEEN MILLER INDICES AND INTERPLANAR SPACING

If ‘a’ is the side of the cubic cell and h,k,l are the miller indices of a given plane, the distance ‘d’ between the parallel planes will be given by the following relation:

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

Q. Find the interplanar distance between the planes having miller indices (100),(110) and (111).

Ans. In the plane (100), the values of h,k,l are 1,0,0. Thus $\sqrt{1^2+0^2+0^2} = 1$

Therefore, $d_{100} = a$.

Similarly, $d_{110} = a/\sqrt{2}$

And, $d_{111} = a/\sqrt{3}$

NUMERICALS

Q 1. Find the interplanar distance in a crystal in which a series of planes produce a first order reflection from a Copper X-ray tube(λ=1.539A^0) at an angle of 22.5^o. (sin 22.5^o=0.383)

Ans. From Bragg equation, $2d\sin\Theta = n\lambda$

$$d = \lambda/2\sin\Theta$$

$$= 1.539A^0/2\sin 22.5$$

$$= 1.539A^0/2X0.383$$

$$=2.01A^0$$

Q 2. The interplanar spacing of a crystal was found to be $1.85 A^o$. If the First order reflection takes place at an angle of 30^o, find out the wavelength of X-rays.

Ans. $n=1$, $\Theta = 30^o$

$\sin 30^o = 0.5$

$\lambda = 2d \sin \Theta / n$

$= 2 X 1.85 X 0.5/1$

$= 1.85 A^o$.

The wavelength of X-rays is $1.85 A^o$.

HOMEWORK

Q 3. When X-rays of 0.98A^o are used, the first order Bragg's reflection For (111) plane of a crystal was obtained at an angle of 10^o. Find out the interatomic distance. (sin 10^o=0.1736)

Ans.

INTERPLANAR SPACINGS IN DIFFERENT CELLS

The ratios d100: d110: d111 for the three cubic systems is as follows:

Simple cubic

$d100:d110:d111=a: a/\sqrt{2}: a/\sqrt{3}$

$=1:0.707:0.577$

Face Centred Cubic

$d100:d110:d111=a/2: a/2\sqrt{2}: a/\sqrt{3}$

$=1:0.707:1.154$

Body Centred Cubic

$d100:d110:d111=a/2: a/\sqrt{2}: a/2\sqrt{3}$

$=1: 1.414: 0.577$

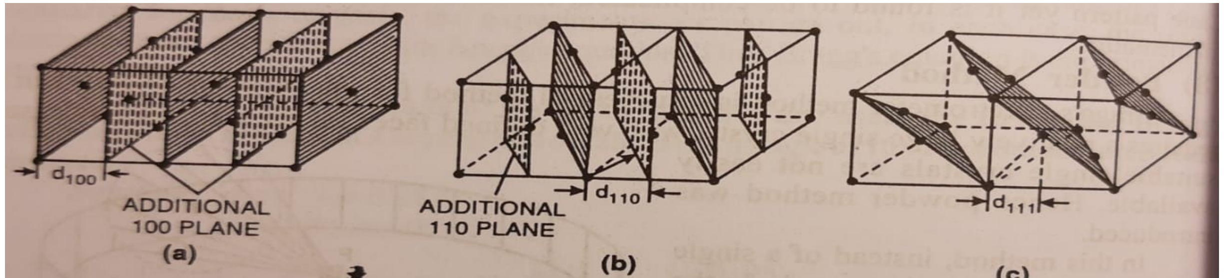


Fig 7.7. Successive separation in simple cubic lattice

For simple cubic distance between two

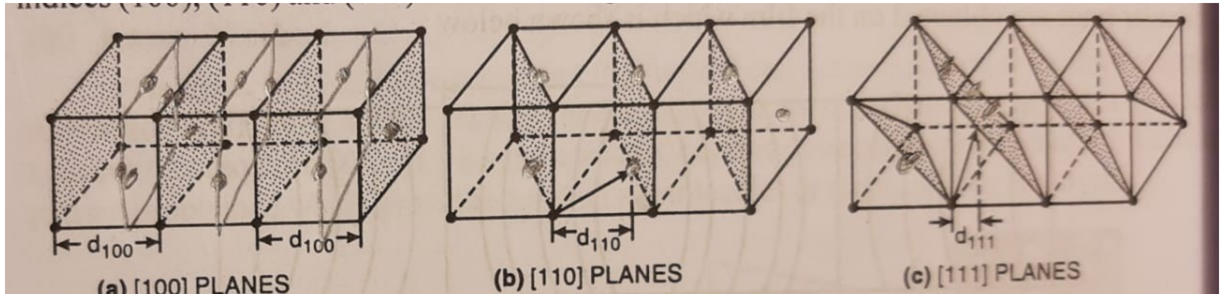


Fig 7.8. Successive separation in face centred cubic lattice

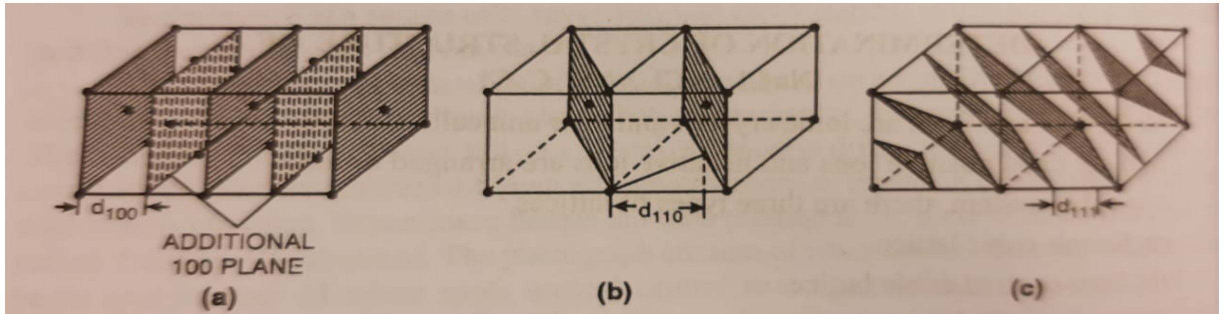


Fig 7.9. Successive separation in body centred cubic lattice

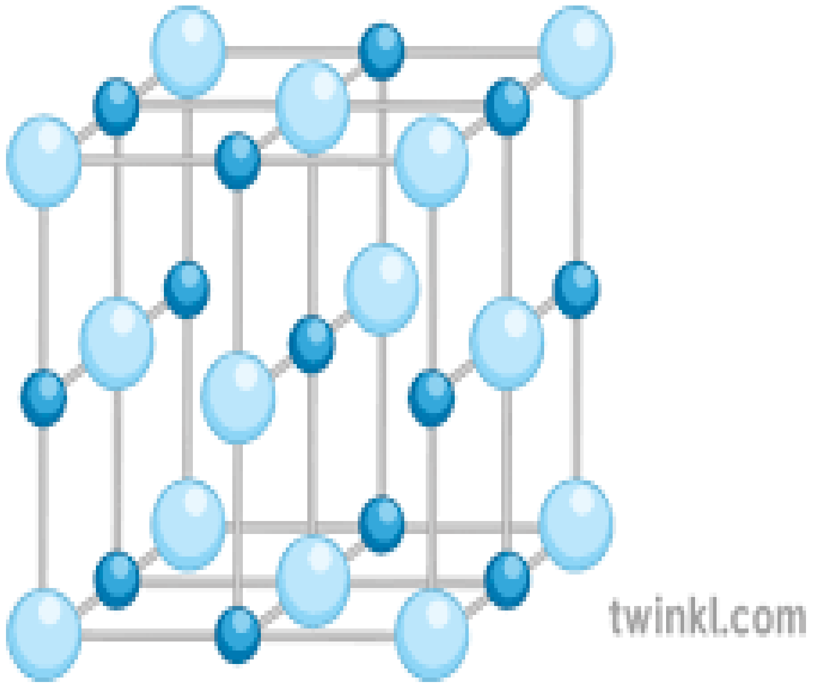
CRYSTAL STRUCTURE OF SODIUM CHLORIDE

In the unit cell of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The coordination number is six, as required by simple cubic.

The first order reflections from (100), (110) and (111) faces using K line from Palladium anticathode are 5.9^0, $8.4^0$and 5.2^0 respectively. From Bragg's Equation $n\lambda=2d\sin\Theta$, the ratio d100:d110:d111 is

1/sin5.9: 1/sin8.4: 1/sin5.2

=1:0.707:1.136 This ratio is almost identical with face centred cubic lattice.



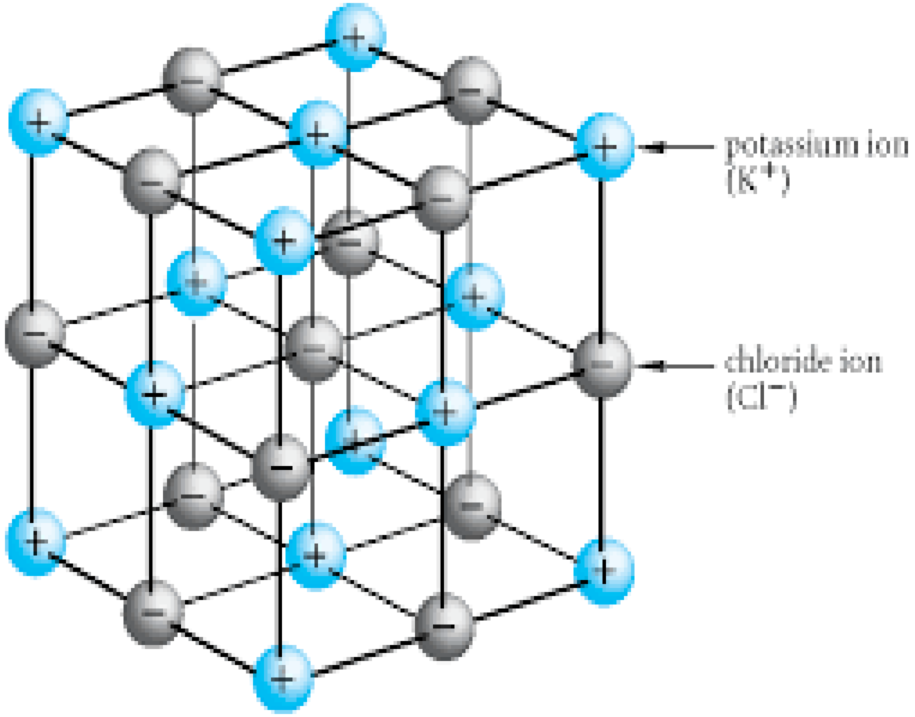
Crystal structure of NaCl

Face centred cubic

d=2.814 A°

CRYSTAL STRUCTURE OF POTASSIUM CHLORIDE

The first order reflection (100), (110) and (111) planes of Potassium Chloride show that the d100:d110:d111 ratio is 1: 0.707: 0.577. This corresponds to the Simple Cubic cell.

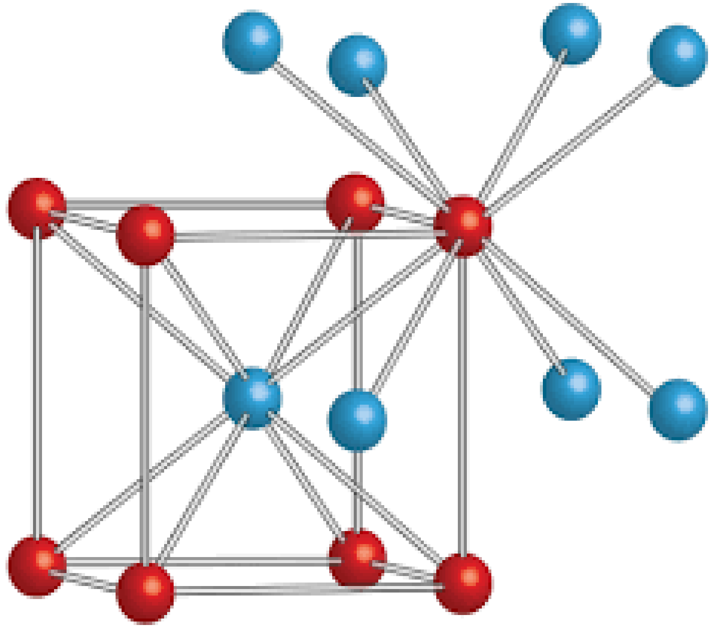


Potassium Chloride
Simple Cubic
d=3.1465 A°

CRYSTAL STRUCTURE OF CAESIUM CHLORIDE

Caesium Chloride has a Body Centred Cubic Structure. Each chloride ion is surrounded 8 Caesium ions and each Caesium ion is surrounded by 8 Chloride ions.

The X-Ray diffraction pattern of CsCl shows the ratio of d100:d110:d111=1:1.414:0.577 This confirms that Caesium Chloride has a Body Centred Cubic Structure.



Caesium Chloride
Body Centred Cubic
d=3.510 Aº

THANK YOU