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RCEI Bilal

P-II

UNIT - 3

Solid state physics

Completed

UNIT-3

Solid state physics

All solids are composed of atoms and molecules. If the atoms and molecules in solids are arranged in some regular fashion then it is known as crystalline, when atoms or molecules in solids are arranged in an irregular fashion, then it is known as Amorphous solids.

Solids



<u>Crystalline Solids</u>	<u>Amorphous Solids</u>
1) The atoms or molecules are arranged in some regular fashion	1) Atoms or molecules are arranged in some irregular fashion. (i.e. random arrangement)
2) They have long range periodicity	2) They do not have long range periodicity.
3) They have different physical properties in different directions. They are anisotropic.	3) They have same physical prop. in all directions. Hence they are isotropic.
4) The melting point is sharp	4) They do not have sharp melting point.
5) Eg: Quartz, diamond.	5) Ex: glass, wood.

The atoms are closely packed in crystalline solids, hence crystalline solids are more dense than Amorphous solids.

Hence "A crystal is defined as an orderly or periodic array of atoms in space."

Crystalline solids are of two types —

(1) Single crystal :—

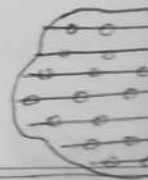
In this periodicity extends throughout the material.

(2) Polycrystalline Crystal :—

In polycrystalline solids periodicity does not extend throughout the materials, they consist of many tiny crystals, called grains separated by well defined boundaries and oriented in different directions.

Eg: metals.

Grains are smaller than the size of the pattern unit which forms the periodicity. When size of grains becomes comparable with

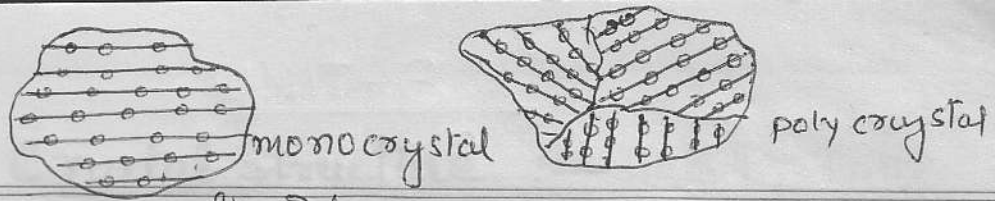


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the size of pattern unit, periodicity of structure is completely disturbed. Then it is no longer a crystal but becomes an amorphous substance.

Space lattice :-

A crystal is three dimensional array of atoms or molecules in space, called crystal structure. The crystal structure can be described in terms of idealized geometrical concept called space lattice.

The space lattice may be defined as an array of points in space such that the environment about each point is the same.

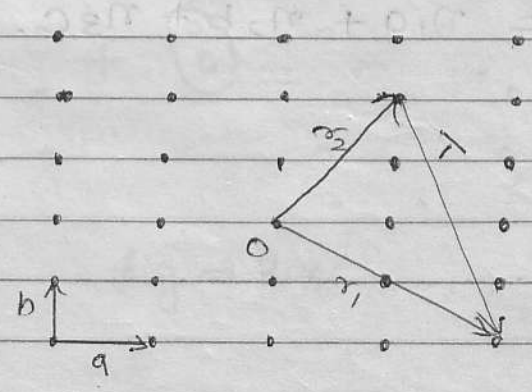


fig - 3.2

The space lattice may be defined in a more rigorous mathematical way as under ;
Choose any arbitrary point O as origin and let vectors r_1 and r_2 join any two lattice points to this origin. The difference T of the vectors should satisfy the following relation -

$$T = n_1 a + n_2 b.$$

where a and b are the fundamental translation vectors characteristic of the array and n_1 and n_2 are integers. When above relation is true for all values of r_1 and r_2 , the array of points is a two dimensional lattice. Similarly, in a 3-dimensional lattice,

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

Crystal Structure :-

Crystal structure is obtained when a basis is added at each point in the lattice. The basis must be identical in composition, arrangement and orientation such that crystal appears exactly the same at one point as it does at other equivalent points.

Figure shows the basis consisting of group of two atoms. When the basis is associated with each lattice site, the crystal structure is obtained.

Thus
space lattice + Basis \Rightarrow crystal structure.

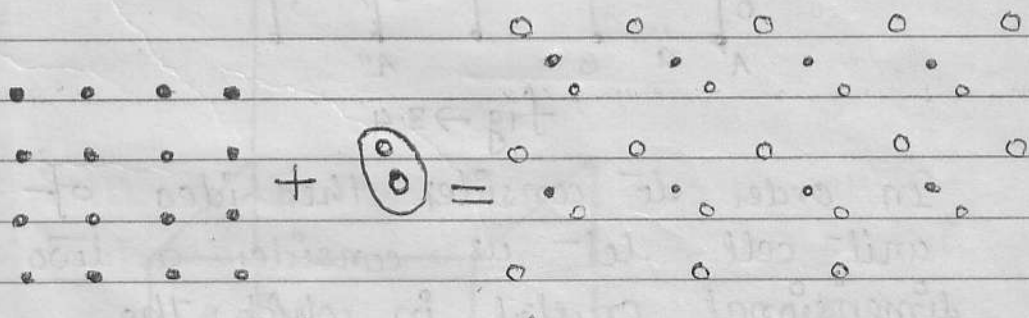


fig \rightarrow 3.3

UNIT-CELL :-

" A unit cell is the smallest geometric figure, the repetition of which gives the actual crystal structure. The unit cell may also be defined as the fundamental elementary pattern of minimum number of atoms, molecules or group of molecules which represents fully all characteristic of crystals."

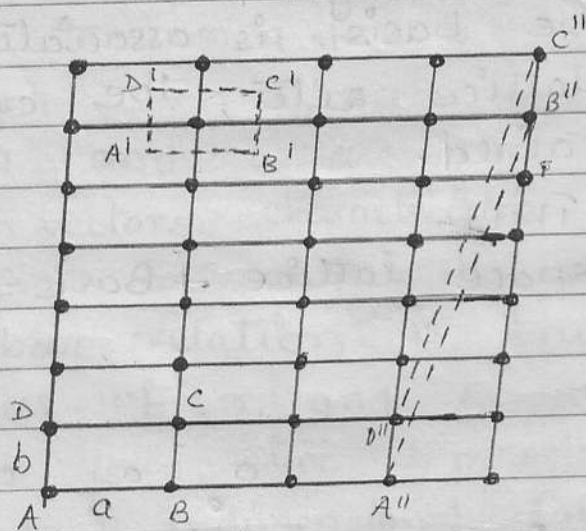


fig → 3.4

In order to consider the idea of unit cell let us consider a two dimensional crystal in which the atoms are arranged as shown.

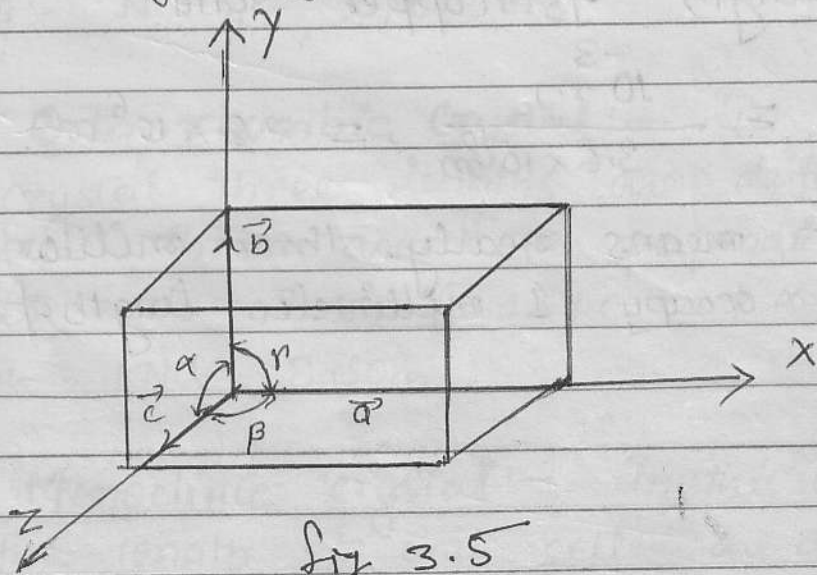
If we consider a parallelogram such as ABCD with sides $AB = a$

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and $AD = b$ then rotating this parallelogram by any integral multiple of \vec{a} and \vec{b} the whole crystal lattice may be obtained. In this way this fundamental unit is called unit cell.

The choice of unit cell is not unique but it can be constructed into number of ways as $A'B'C'D'$ and $A''B''C''D''$ shown in fig.

For the three dimensional case, the three dimensional unit cell is shown in figure. The unit cell is a parallelepiped formed by the basis vectors \vec{a} , \vec{b} , \vec{c} and including angles are α , β , γ .



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Each edge of unit cell is the distance between the atoms of same kind and is called lattice constant.

The axial lengths a, b, c and interaxial angles α, β, γ are known as lattice parameters.

The size of the unit cell can be chosen for particular crystal structure.

The size of unit cell is extremely small.

Eg: The size of cell has side of 3.6 \AA and in solid the cubic unit cell are lined up side by side. Let us estimate the no. of unit cell in 1 mm length of copper solid

$$= \frac{10^{-3} \text{ m}}{3.6 \times 10^{-10} \text{ m}} = 2.8 \times 10^6$$

It means nearly three million cell occupy 1 millimeter length of solid.

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The Seven crystal systems :-

On the basis of the lengths and directions of the axes of symmetry, all crystals may be classified into following seven systems:-

(1) Cubic crystal:- In this crystal all the three lengths of unit cell are equal and are at right angles to each other i.e. ($a=b=c$ and $\alpha=\beta=\gamma=90^\circ$)

Eg:- NaCl, CaF_2 , etc.

(2) Tetragonal crystal:- In this crystal the two lengths are equal while third one is longer or shorter. The three axes are perpendicular i.e. ($a=b \neq c$) and ($\alpha=\beta=\gamma=90^\circ$)

Eg:- NiSO_4 , SnO_2 etc.

(3) Orthorhombic crystal:- In this crystal three lengths are different but three axes are perpendicular to each other, ($a \neq b \neq c$ and $\alpha=\beta=\gamma=90^\circ$)

Eg:- KNO_3 , BaSO_4 .

(4) Monoclinic crystal:- In this crystal the lengths of unit cell are different

Two axes are right-angled and third is obliquely inclined
ie $(a \neq b \neq c)$ and $(\alpha = \beta = 90^\circ \neq \gamma)$
Eg:- Na_2SO_3 , FeSO_4

(5) Triclinic crystal:- In this crystal the lengths of unit cell are different and oblique to each other ie $(a \neq b \neq c)$ and $(\alpha \neq \beta \neq \gamma)$
Eg:- CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc.

(6) Rhombohedral crystal:- In this crystal all the three lengths of unit cell are equal in lengths moreover they are equally inclined to each other at angle other than 90°
ie $(a = b = c)$ and $(\alpha = \beta = \gamma \neq 90^\circ)$
Eg:- CaSO_4 etc.

(7) Hexagonal Crystal:- In this crystal the three axes of unit cell are equal in one plane at 120° with each other as fourth axis is perpendicular to this plane ie
 $(a = b \neq c)$ and $(\alpha = \beta = 90^\circ, \gamma = 120^\circ)$
Eg:- SiO_2

BRavais SPACE LATTICE

Bravais showed that there are only fourteen ways of arranging points in space so that the environment looks the same from each point. The lattices are called Bravais lattices.

In case of cubic system there are three Bravais lattices

(1) Simple (or primitive) Cubic lattice:-

There is one lattice point at each of the eight corners of the unit cell. There is no lattice point inside.

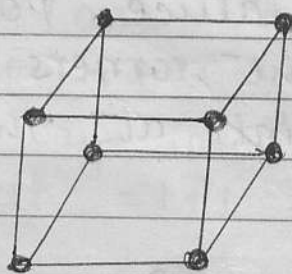


fig 3.6

(2) Face centered cubic (fcc) lattice

There is one lattice point at each of the eight corners of unit cell, and one lattice point at center of each six faces of the cubic cell.

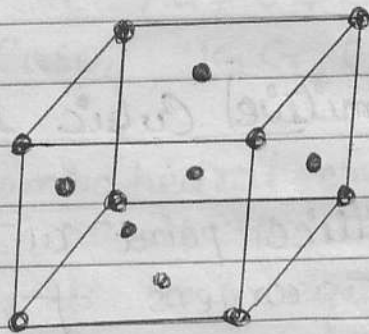


fig - 3.7

(3) Body centered cubic (bcc) lattice

There is one lattice point at each of eight corners and one lattice point at the center of the cell.

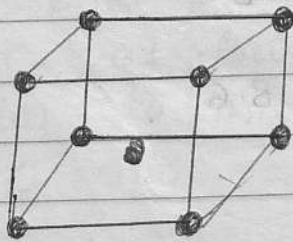


fig - 3.8

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Number of atoms per unit cell:

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(1) Simple cubic lattice:—

In case of simple cubic there are eight atoms at each corners and each corner atoms are shared by eight unit cells. Hence share of each unit cell is equal to $\frac{1}{8}$ of an atom. The total number of atoms per unit cell = $8 \times \frac{1}{8} = 1$ atom.

(2) Body centered cubic (BCC) lattice:—

In case of Body centered cubic lattice, there are eight atoms at the eight corners of unit cell and one atom at body center. As each corner atom is shared by eight unit cell, hence contribution to each cell is $8 \times \frac{1}{8}$ i.e. one. Moreover there is one atom per unit cell.

In this way total no. of atoms per unit cell = $1 + 1 = 2$

(3) Face centered cubic (fcc) lattice:

In case of face centered cubic lattice there are eight atoms at the eight corners of unit cell

and one atoms at each faces.

As each corner atoms is shared by eight unit cell hence contribution to each cell is $8 \times \frac{1}{8}$ i.e. one.

Moreover each face centered atom is shared by two unit cell, hence contribution of six face centered atoms of each unit cell is $6 \times \frac{1}{2}$ i.e. three. In this way the total number of atoms per unit cell is

$$1 + 3 = 4.$$

Coordination Number :-

The number of equidistant neighbours that an atom has in given structure is called coordination number.

When coordination number is large, the structure is more closely packed.

We shall calculate coordination number of simple cubic, bcc and fcc lattice.

(1) Simple Cubic lattice:

Around any atom in simple cubic cell, there would be six exactly, equally spaced nearest atoms each at distance ' a ' from that atom. Four atoms lie in one plane of that atom, while one is vertically above it and one vertically below.

Hence coordination number in this case $= 4 + 2 = 6$.

(2) Body centered Cubic (bcc) lattice:

In body centered cubic lattice, there is one atom at each corner of the cube and one atom at the center of cube. For any corner atom of unit cell the nearest atoms are the atoms which are at the centres of unit cells. As such corner atom is surrounded by eight unit cells having eight body centered atoms hence coordination number is 8. Similarly by considering the

center atom of each unit cell, we can say that coordination no. is eight,

(3) Face centered cubic (fcc) lattice:

In face centered cubic lattice there is one atom at each corner of the cube and one atom at the centre of each faces of the cube.

For any corner atom of unit cell the nearest one the face centered atoms, for any corner atom, there will be 4 face centered atoms of the surrounding unit cells in its own plane, 4 face centered atoms below this plane and 4 face centered atoms above this plane.

Hence coordination number in this case $= 4 + 4 + 4 = 12$

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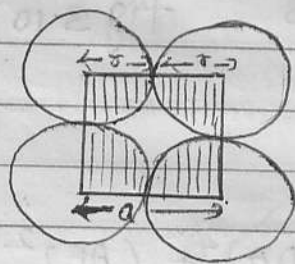
Atomic Radius :-

For the calculation of atomic radius, it is assumed that the atoms are sphere in contact in a crystal.

The atomic radius ' r ' is defined as half the distance between nearest neighbours in a crystal of pure element. The atomic radius is expressed in terms of cube edge ' a '.

Now we calculate atomic radius for following three cases -

(1) Simple cubic lattice (scc) :-



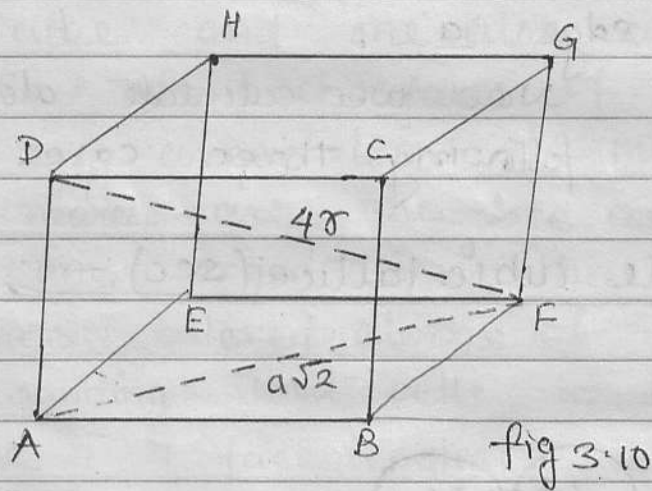
There are eight atoms per unit cell situated at eight corners. If ' a ' is the side of unit cell and ' r ' be the radius of atom, then from figure

$$2r = a \quad \text{or} \quad r = \frac{a}{2}$$

(2) Body centered cubic (bcc) lattice:

(3)

In a unit cell of bcc lattice there are eight atoms at corners each forming a member of eight cells and one atom per cell at the center



From figure

$$(DF)^2 = (DA)^2 + (AF)^2$$

$$(4r)^2 = a^2 + (a\sqrt{2})^2$$

$$(4r)^2 = 3a^2$$

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

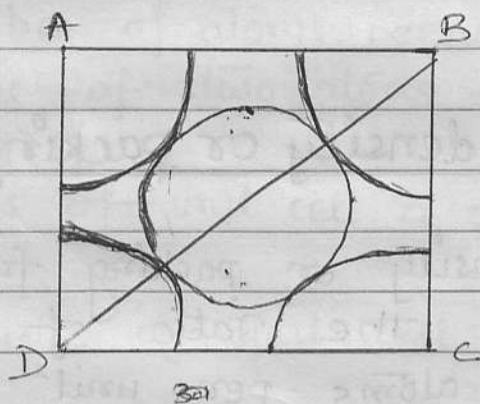
$$\text{or } a = \frac{4r}{\sqrt{3}}$$

c) lattice:

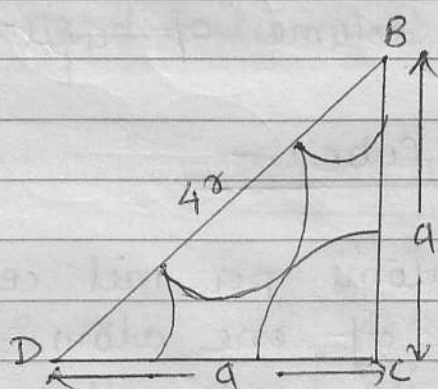
(3) face centered cubic (fcc) lattice:

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In face centered cubic lattice, there are eight corner atoms in the unit cell and one atom at the center of each face. figure shows front view and cut view of fcc lattice



(a)



(b)

fig 3.11

from 2nd figure we have

$$(DB)^2 = (DC)^2 + (CB)^2$$

$$(4r)^2 = a^2 + a^2 = 2a^2$$

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

$$\text{or } a = \frac{4r}{\sqrt{2}}$$

22

Packing density or packing factor:-

packing density or packing factor is defined as the ratio of the volume of atoms per unit cell to the total volume of unit cell.

(1) simple cube:-

$$\text{No. of atoms per unit cell} = 1$$

$$\text{Volume of one atom} = \frac{4}{3}\pi r^3$$

$$\text{sides of unit cell } a = 2r$$

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

$$\begin{aligned} \therefore \text{packing density} &= \frac{\left(\frac{4}{3}\right) \pi r^3}{a^3} \\ &= \frac{\left(\frac{4}{3}\right) \pi r^3}{(2r)^3} \\ &= \frac{\pi}{6} \end{aligned}$$

(2) Body centered cube ;

$$\begin{aligned} \text{Number of atoms per unit cell} &= 2 \\ \text{volume of two atoms} &= 2 \times \frac{4}{3} \pi r^3 \end{aligned}$$

$$\text{sides of unit cell } a = \frac{4r}{\sqrt{3}}$$

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

$$\begin{aligned} \therefore \text{Packing density} &= \frac{2 \times \left(\frac{4}{3}\right) \pi r^3}{a^3} \\ &= \frac{2 \times \left(\frac{4}{3}\right) \pi r^3}{a^3} \\ &= \frac{2 \times \left(\frac{4}{3}\right) \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3} \pi}{8} \end{aligned}$$

(3) Face centered cube (fcc)

Number of atoms per unit cell = 4

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

$$\text{Sides of unit cell } a = \frac{4r}{\sqrt{2}}$$

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

$$\begin{aligned} \therefore \text{Packing density} &= \frac{4 \times \left(\frac{4}{3}\right) \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} \\ &= \frac{\sqrt{2} \pi}{6} \end{aligned}$$

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Lattice planes and Miller indices;

A crystal may be regarded as made up of an aggregate of a set of parallel equidistant planes passing through lattice points which are known as lattice planes. For a given lattice, planes can be chosen in different number of ways.

Miller evolved a method to designate a plane in crystal by three numbers (h, k, l) known as Miller indices.

"The Miller indices are smallest possible integers which have same ratios as reciprocals of intercepts of the plane concerned on three axes"

The rules of finding Miller indices are as follows —

- (1) First of all determine the intercept of plane on three coordinate axes.
- (2) Secondly take the reciprocals of these intercepts.
- (3) Lastly reduce the reciprocals into whole numbers. This can be determined by multiplying each reciprocal by a number obtained after taking LCM of denominator.

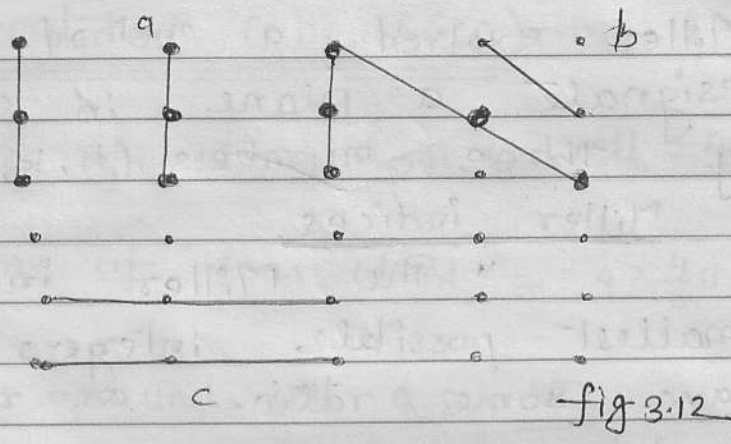


fig 3.12

Eg:- Let us consider Miller indices in particular case where Direct plane cuts the intercepts of 2, 3 and 4 unit along the three axes. (1)

Step 1:- Intercepts are 2, 3, 4

Step 2:- Reciprocal of these are $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$

Step 3:- LCM of denominators i.e 2, 3 and 4 is 12 hence multiply by 12, we have 6, 4, 3 Thus Miller indices of this plane is (6, 4, 3).

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General case:-

Let the intercepts of a crystal face on the three reference axes expressed in terms of axial units p, q, r and s . Obviously its numerical parameters are p, q, r . Then Miller indices of the face are given by three numbers (h, k, l) such that -

$$h:k:l = \frac{1}{p} : \frac{1}{q} : \frac{1}{r}$$

with the condition that h, k, l are smallest possible integers satisfying above condition.

Miller indices of cubic crystal planes:-

while finding Miller indices of a plane, the following points should be kept in mind:-

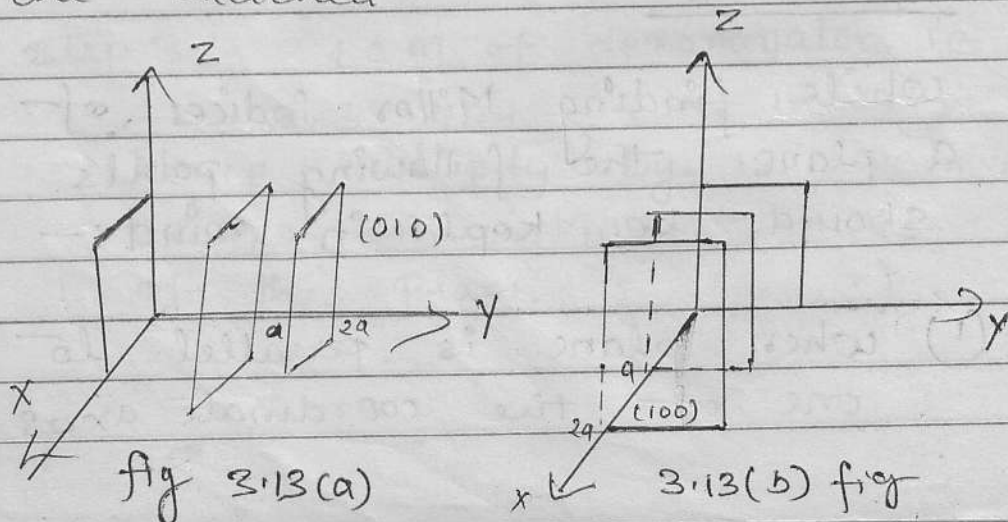
- (1) when plane is parallel to one of the coordinate axes

it is said to meet that axes at infinity, since $\frac{1}{\infty} = 0$, the Miller indices for that axis is zero.

(2) when the intercept is on the negative part of any axis, the Miller indices are distinguished by minus sign put directly over it.

Eg:— Consider the shaded plane.

The set of parallel planes perpendicular to y-axis are as shown in fig. has Miller indices $(0,1,0)$. Similarly planes normal to x-axis are designated (100) are sketched.



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indices

planes having equal intercepts
on x-axis and y-axis and parallel
to z-axis have Miller indices (110)

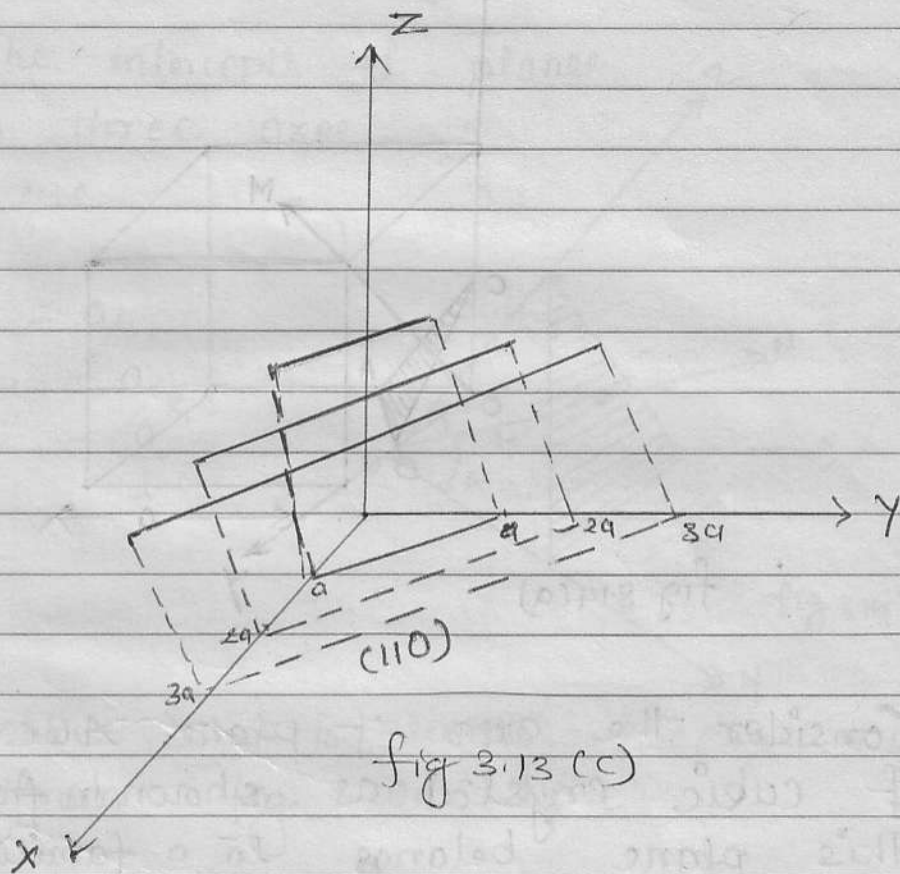


fig 3.13 (c)

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Separation between lattice planes

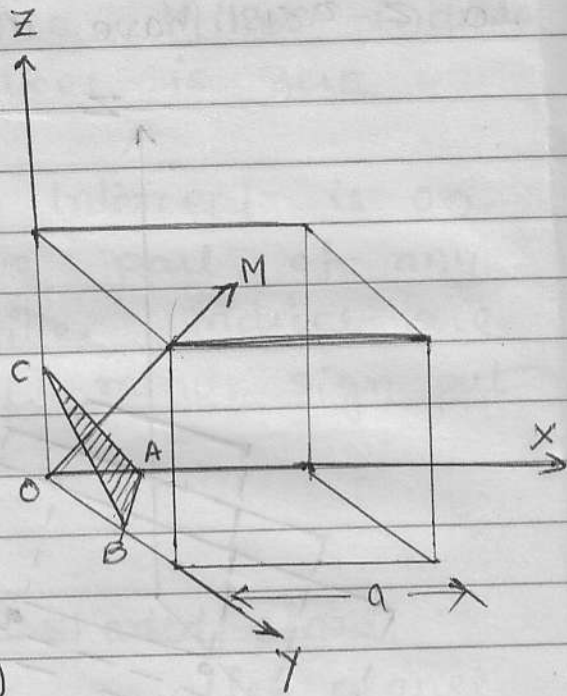


fig 3.14(a)

Consider the case of plane ABC of cubic crystal as shown in fig. This plane belongs to a family of planes whose Miller indices are hkl because Miller indices represent a set of planes. Let ON is the perpendicular drawn from origin to this plane. The distance ON represents the interplanar spacing ' d ' of the family of planes.

ice planes

Let α' , β' , γ' be angles between coordinate axes x, y, z and ON respectively.

The intercepts of planes on three axes are

$$OA = a/h$$

$$OB = a/k$$

$$OC = \frac{a}{l}$$

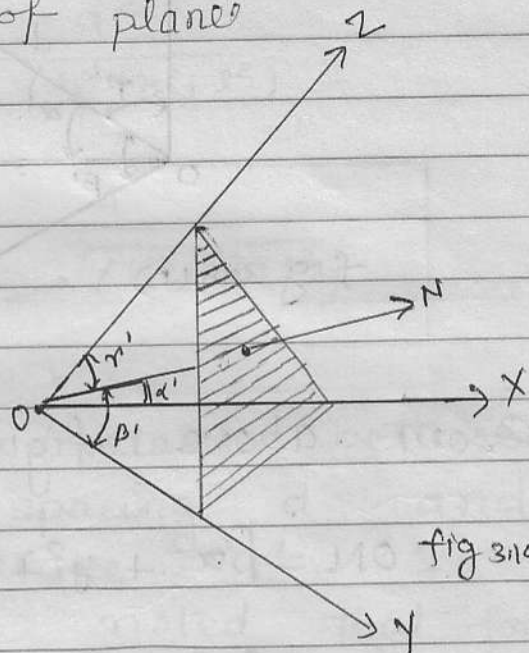


fig 3.14(b)

where ' a ' is length of cube edge. from fig we have

$$\cos \alpha' = \frac{d}{OA}$$

$$\cos \beta' = \frac{d}{OB}$$

$$\cos \gamma' = \frac{d}{OC}$$

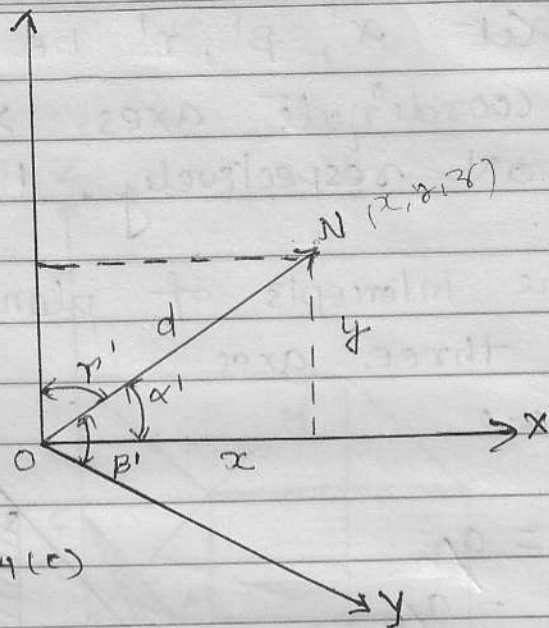


fig 3.14(c)

From above figure.

$$ON = [x^2 + y^2 + z^2]^{1/2}$$

$$d = [d^2(\cos^2 \alpha') + d^2(\cos^2 \beta') + d^2(\cos^2 \gamma')]^{1/2}$$

$$\Rightarrow \cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$$

Substituting the values of $\cos \alpha'$, $\cos \beta'$ and $\cos \gamma'$ in above equation we get-

$$\left(\frac{d}{OA}\right)^2 + \left(\frac{d}{OB}\right)^2 + \left(\frac{d}{OC}\right)^2 = 1$$

$$\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$$

$$\Rightarrow \frac{d^2}{a^2} (h^2 + k^2 + l^2) = 1$$

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

→ x

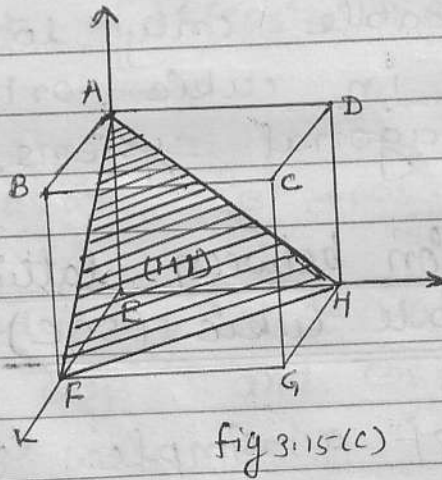
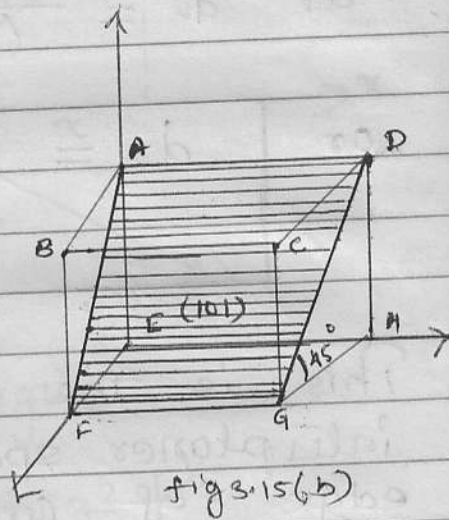
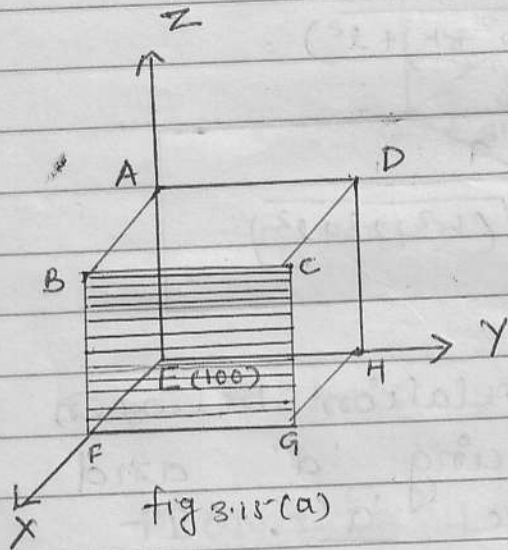
$$\text{or } d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

This is the relation between interplanar spacing 'd' and edge of cube 'a'. It should be noted that formula is applicable only to primitive lattice in cubic, orthorhombic and tetragonal systems.

Separation between lattice planes in simple cubic (SCC):

In case of a simple cubic lattice, the (100) planes cut the x-axis and parallel to y and z axis. The (110) planes

cut obliquely across x and y -axis but they are parallel to z -axis. Similarly (111) planes cut obliquely along three axes.



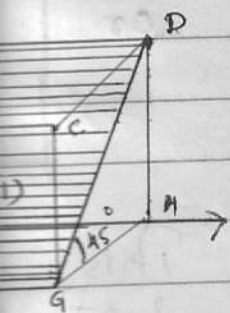
and
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in axes.

If d_{100} represents the perpendicular distance between successive (100) planes, then.

$$d_{100} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{\sqrt{1^2+0^2+0^2}} = a.$$

Similarly $d_{110} = \frac{a}{\sqrt{(1)^2+(1)^2+(0)^2}} = \frac{a}{\sqrt{2}}$

and $d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$



3.15(b)

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

or $\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \sqrt{3}$

Similarly for body centered lattice

$$\frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = 1 : \frac{1}{\sqrt{2}} : \sqrt{3}$$

For face centered lattice structure

$$\frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2}$$

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Crystal Symmetry:

Crystals possess different external symmetries which are described by certain mental operations.

A symmetry operation is one that takes the crystal into configuration identical to the initial configuration.

The crystal is said to possess a symmetry element corresponding to an operation if after performing the particular operation the crystal goes into a position distinguishable from initial position.

The most important symmetry elements are - centre, an axis, and a plane.

(i) Centre of Symmetry:

A centre of symmetry is such point in crystal that any straight line drawn through this point intersects the crystal surface at equal distance in both directions and joins the identical points (particles) in crystal. It is also called centre of inversion.

It is obvious from above definition that the centre of symmetry leads to parallel pairs of faces on opposite sides of the crystal.

(2) Axis of Symmetry :-

An axis of symmetry is a line about which a crystal may be rotated such that after definite regular rotation about this axis the crystal comes into a congruent position. It is found that crystalline solids can have 2-, 3-, 4-, 6- fold symmetry corresponding 180°, 120°, 90°, 60° rotations respectively.

(3) Plane of Symmetry :-

It is actually a mirror plane, when an imaginary plane can divide the crystal into two equal parts such that each part is the exact mirror

image of other, then crystal is said to have a plane of symmetry.

Symmetry Elements in Cubical Crystal:

(1)

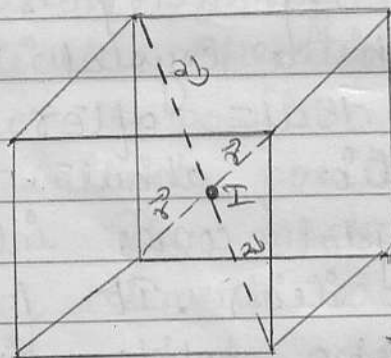


fig 3.15(a)

If the body centre point is I , and body diagonals are drawn through it, each diagonal connects identical lattice points located at equal distance and in opposite direction from I . The point I acts as a mirror point which generates the lattice point at an equal distance in an opposite direction. Therefore the

crystal
plane of

point I is the centre of symmetry
or inversion point. Thus in
cubical lattice inversion point
is located at body centre.

Cubical Crystal:

(2) Let us consider normal MN
through mid points of the
pair of opposite parallel faces
of a cube. If the cube is
rotated through 90° around the
normal MN , it comes into
self coincidence. After every 90°
rotation it goes into an
indistinguishable configuration. In
one complete rotation of 360° ,
the cube becomes indistinguishable
four times. Therefore face
normals are 4-fold symmetry.
There are three such 4-fold axes
of symmetry, MN , PQ and RS
one normal to each of the three
pairs of parallel faces.

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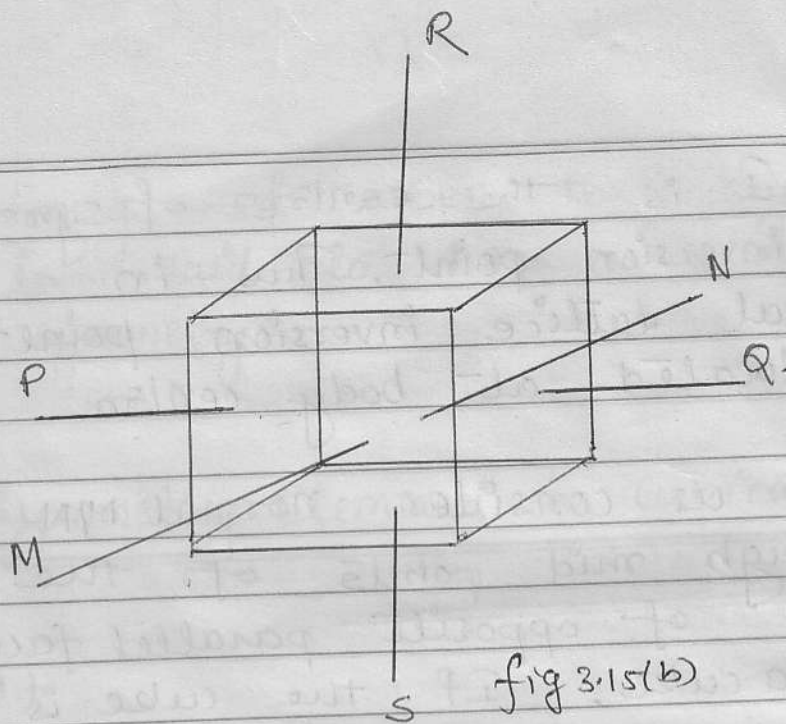


fig 3.15(b)

Let us consider the axis cd passing through the body diagonal of the cube. If the cube is rotated around the body diagonal of cube through 120° it comes into congruent position. In one full rotation, the cube becomes indistinguishable three times. Therefore body diagonal is a 3-fold axis of symmetry. A cube has four body diagonals and therefore possess four 3-fold axes of symmetry.

Next points of cube become of 9 configurations a 12 there num are

m

So

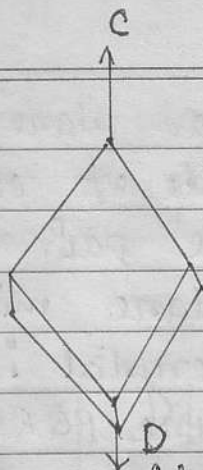
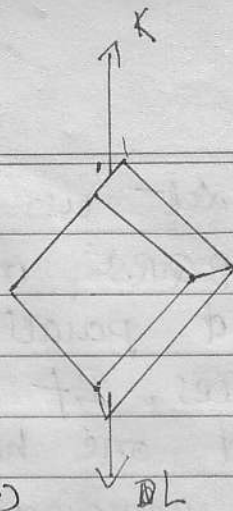


fig 3.15(c)



Next consider a normal KL at mid points of parallel edge. If the cube is rotated through 180° , it becomes congruent. In one rotation of 360° , the cube assumes indistinguishable configuration twice. Therefore KL is a 2-fold axis of symmetry. As there are 12 edges in cube, the number of 2-fold axes of symmetry are six.

The axes of symmetry in a cube are thus

2-fold axes (diad) 6

3-fold axes (triad axes) 4

4-fold axes (tetrad axes) 3

13

So there are total 13 axes of symmetry.

(B) Let us consider the plane like PQRS in the middle of cube and parallel to one pair of faces. If it is plane mirror and one half of crystal is cut and removed, the plane PQRS form the image of that half of the crystal in it. Therefore PQRS is called a plane of symmetry or mirror plane. There are three such plane of symmetry parallel to the faces of the cube.

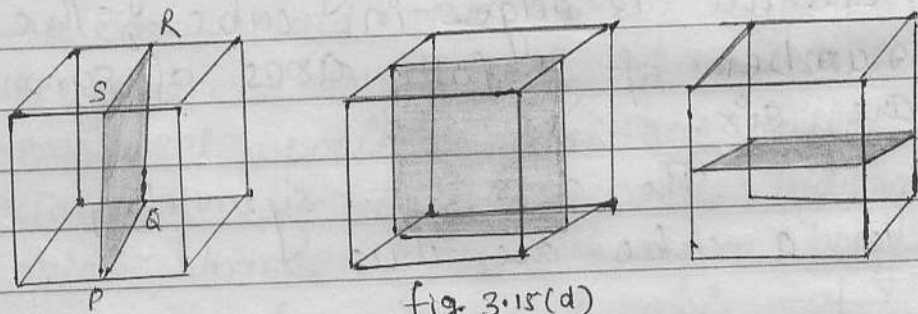


fig 3.15(d)

Further, consider the diagonal plane, KLMN in the cube. If KLMN is imagined to be a mirror, it is readily seen that the prism behind it is reflection of the prism in contact with it in its front. Thus it is also a

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mirror plane. There are six such
such diagonal mirror planes in a
cube.

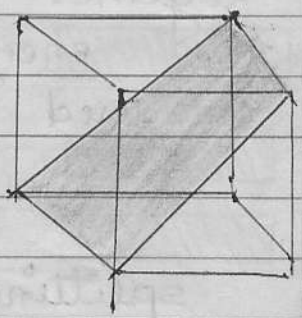
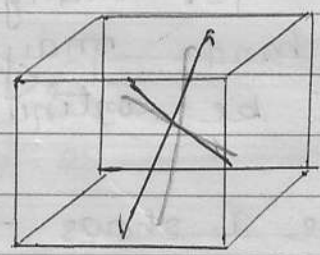
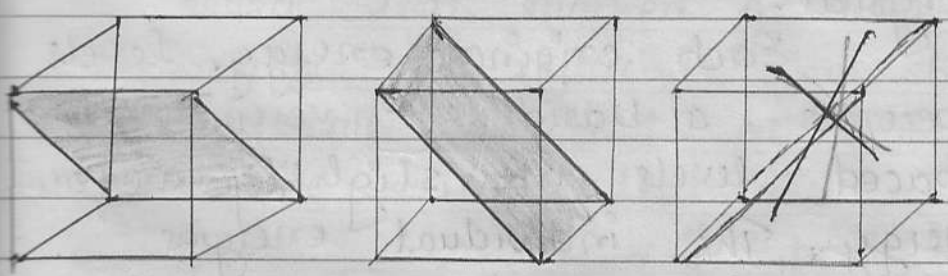
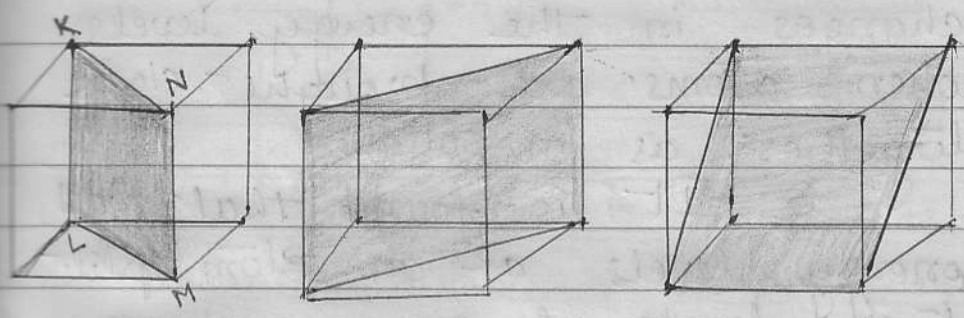


fig 3.15 (e)

Total elements of symmetry of a cubic
crystal are 23 comprising of one centre of
inversion, 13 axes of rotation, 9 mirror planes.

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Energy bands in Solids:

In case of an isolated single atom, there are single energy levels. But there are significant changes in the energy levels when atoms are brought close together as in solids.

It is found that each energy level of an atom splits into N levels of energy where N is number of atoms in the crystal.

Each original energy level becomes a band of very closely spaced levels of slightly different energy. The individual energies within the band are so close together that for many purposes the energy band may be considered to be continuous.

Figure 1 shows the splitting of K, L, and M levels as the distance between different atoms is reduced.

At first, only

Fig 3-16



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fig 3.16 (a)

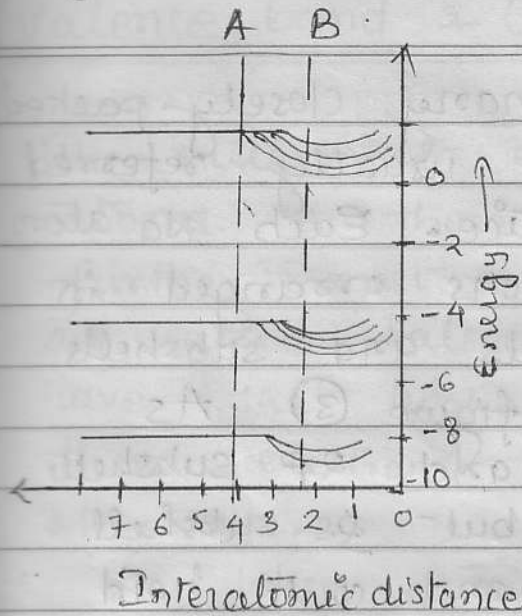
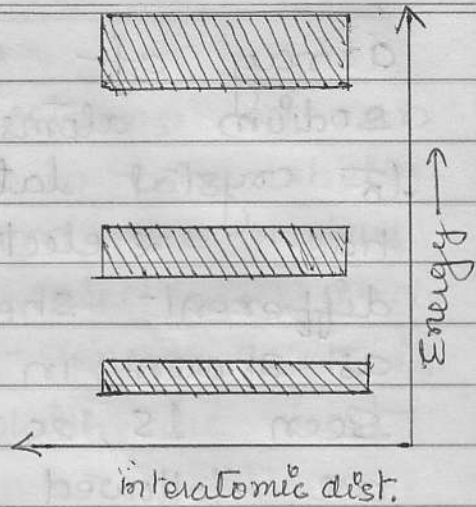


fig 3.16 (b)



valence level or M level as shown by dotted line marked A then as separation is reduced inner shells also became affected as indicated by dotted vertical line B.

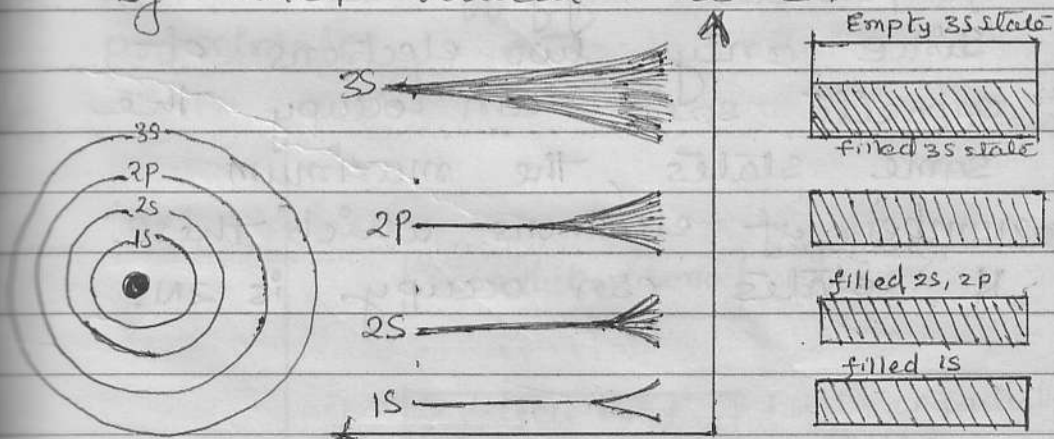


fig 3.16 (c)

Consider the case of Na crystal which consists of a ordered

array of many closely packed sodium atoms usually referred to crystal lattice. Each Na atom has 2 electrons arranged in different shells and subshells as shown in figure (3). As seen 1s, 2s and 2p subshells are followed but 3s subshell is incomplete and could hold one more electron. The electron

in each subshell occupy specific energy levels, for a

In general, in an assembly of N atoms the number of possible energy states is N .

Since only two electrons of opposite spin can occupy the same states, the maximum number of electrons which these N states can occupy is $2N$.

valence band & Conduction band

The outermost electrons of an atom i.e. those in the shell furthest most from the nucleus are called valence electrons and have the highest energy. It is these electrons which are most affected.

When a number of atoms are brought very close together as during the formation of a solid. The state of lower energy electrons orbiting in shell nearer to the nucleus are little if at all affected by this atomic proximity.

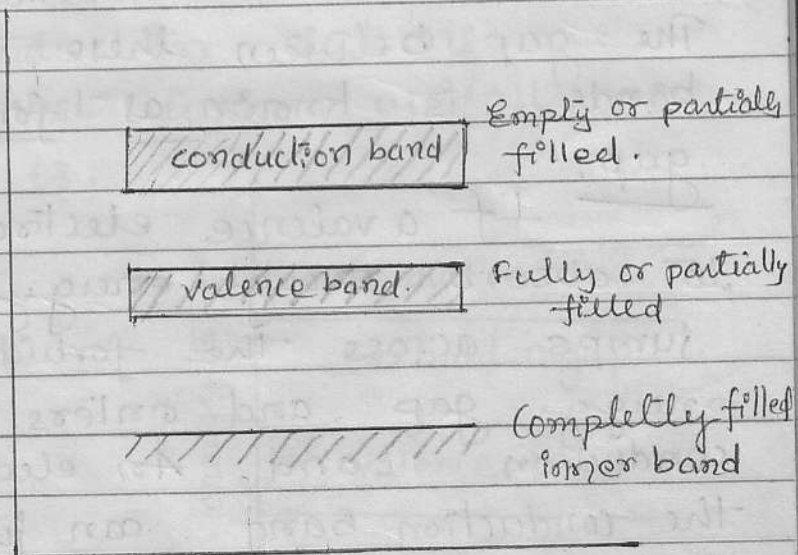


fig 3.17

The band of energy occupied by valence electrons is called the valence band and obviously highest-occupied band. It may be completely filled or partially filled by electrons.

The next higher permitted energy band is called the conduction band and may be either empty or partially filled.

The next higher permitted energy band is called the conduction band and may be either

In conduction band electrons can move freely and hence are known as conduction electrons.

The gap between these two bands is known as forbidden gap.

If a valence electron happens to absorb enough energy, it jumps across the forbidden energy gap and enters into conduction band. An electron in the conduction band can jump

Classification of Solids

back to the valence band from where it had come earlier. When an electron is ejected from valence band a covalent band is broken and positively charged hole is left behind. This hole can travel to an adjacent atom by acquiring an electron from that atom which involves breaking an existing covalent bond and then reestablishing a covalent bond by filling up the hole. To summarize the above it may be repeated -

- (i) Conduction electrons are found ~~in~~ and freely flow in conduction band.
- (ii) Conduction electrons are almost twice as fast as holes.

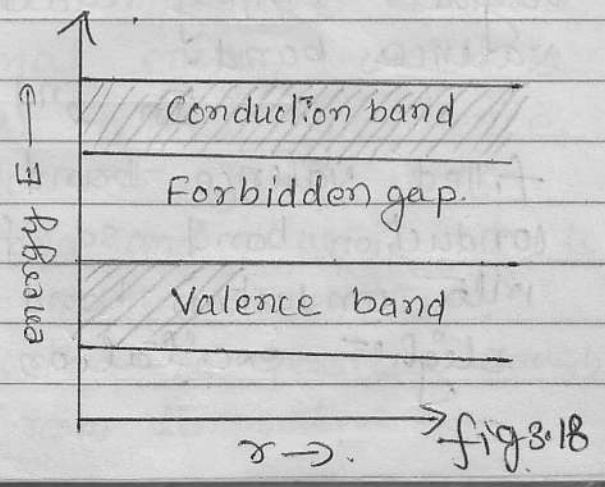


fig. 18

Classification of Solids:

Solids are classified on the basis of their band structure as

- (1) Conductors
- (2) Semiconductors
- (3) Insulators.

Conductors:

Conductors are those solids which have vacant energy states immediately above the highest filled level of valence band. This can happen in two ways.

In first case, the valence band is only half or partially filled. When an external field is applied the electrons acquire energy and hence move into higher empty states in the valence band.

In 2nd case the filled valence band overlaps conduction band so freely enters into conduction band with the slight excitation i.e. very less

amount of energy. Such solids exhibit high conductivity and hence called as conductors. In case of conductors the conductivity is completely due to free electrons.

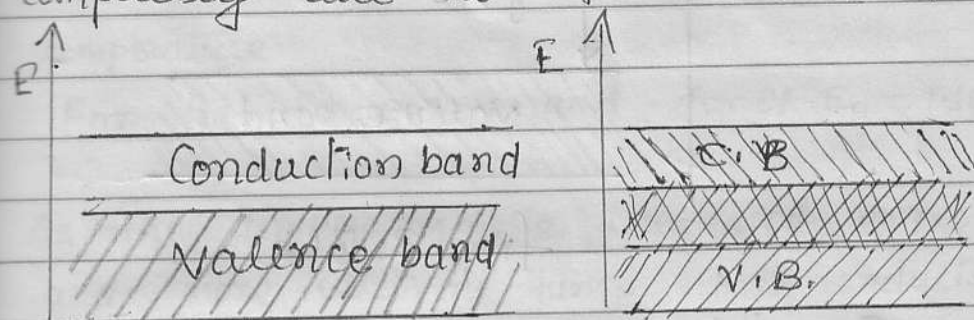


Fig 3.18(a)

Insulators: (eg wood and glass)
In case of ^{insulators} semiconductors

the energy gap is small of very large of the order of 3 eV. or more. Therefore, electrons requires large amount of energy to move to conduction band.

At room temperature electrons acquire thermal energy which is much smaller than E_g . Hence electrons do not jump into conduction band and therefore it is empty at room temperature.

Thus no conduction is possible through insulators at room temperature.

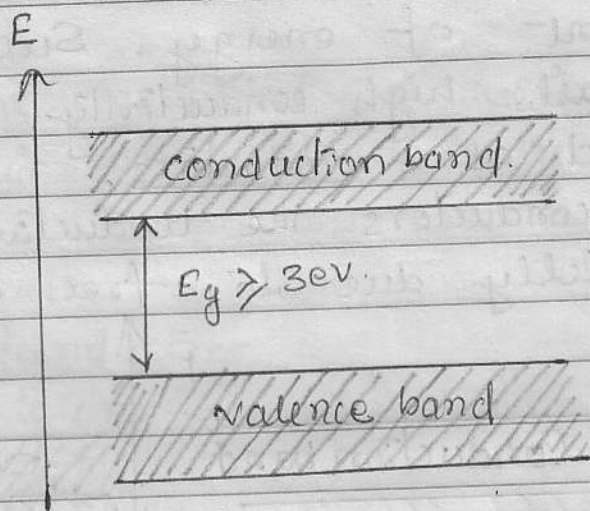


fig 3.18(b)

3) Semiconductors : (eg. germanium & silicon)

In case of semiconductors the energy gap is small of the order of 1eV for silicon and 0.7eV for germanium.

At 0K there are no electrons in conduction band and valence band is completely filled. Hence at 0K semiconductor behaves as insulators.

Since E_g is small, at room temperature some valence electrons acquire thermal energy greater than E_g . Hence these valence electrons jump into conduction band by crossing narrow

forbidden gap. Therefore at room temperature, semiconductor have partially filled valence band and partially filled conduction band and hence it behaves as conductor at room temperature

For Ge $E_g = 0.7 \text{ eV}$ and for Si $E_g = 1.1 \text{ eV}$

As the temperature is increased more and more electrons jump into conduction band. Thus conductivity increases further or resistivity decreases.

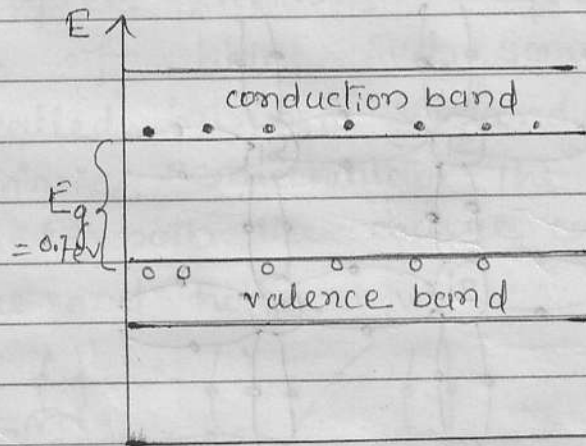


fig 3.19(c)

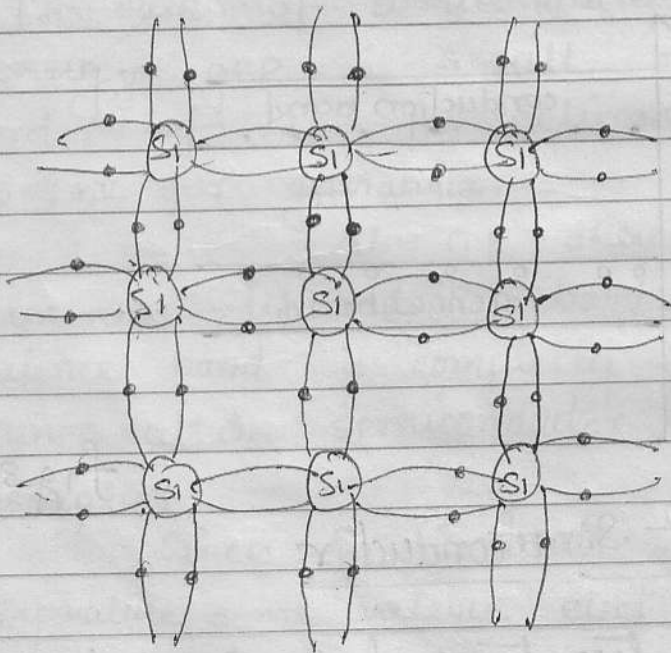
Types of Semiconductor:

There are two types of Semiconductors

- (1) Intrinsic semiconductor
- (2) Extrinsic semiconductor

Intrinsic Semiconductors :

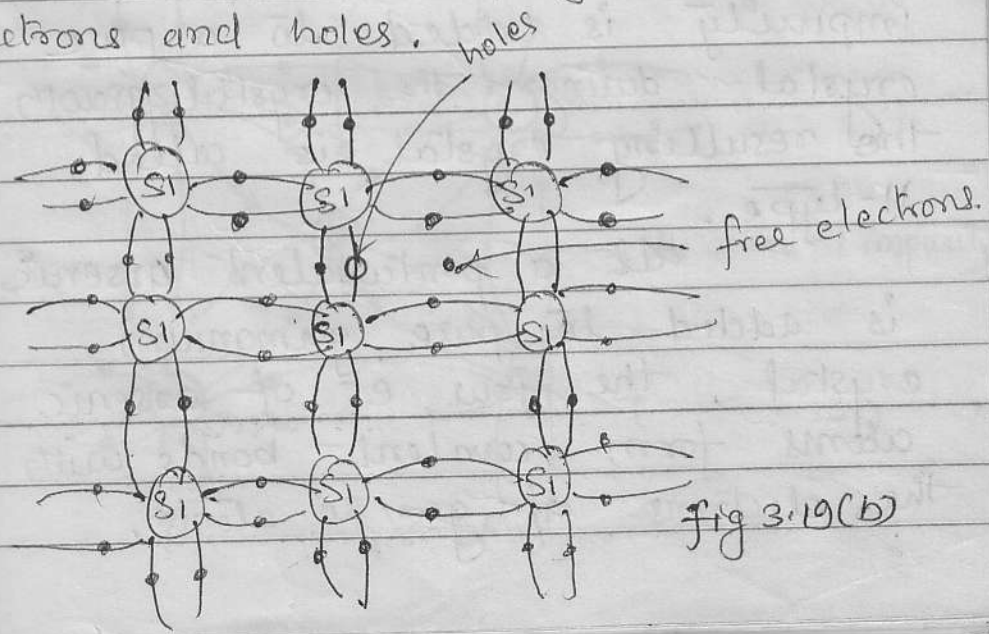
A semiconductor in an extremely poor form is known as Intrinsic semiconductor. Eg: Si and Ge. They are tetra valent atoms i.e. their outermost shell contains four electrons. Figure shows Si crystal lattice, such Si atoms are bonded covalently to four other Si atoms. Thus there are no free or conduction electrons at absolute zero (0K). Hence acts as insulator at 0K.



(Si lattice at 0°K)
fig. 3.19(a)

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Now if the temperature is increased the electrons vibration also increases. Some of valence electrons may absorb sufficient amount of energy and become free electrons. Thus electron-hole pair is created. As the temperature of semiconductor is raised from zero to $T > 0K$ no of bonds will break and conduction takes place as a result of motion of electrons and holes under the influence of external field. In pure Si or Ge the no. of free electrons is equal to no. of holes. Such semiconductors are called intrinsic semiconductor and in intrinsic semiconductor the conductivity is due to both the charge carriers ie electrons and holes.



K)

Extrinsic Semiconductors:

The electrical conductivity of pure germanium or silicon can be increased by adding some impurity in the process of crystallization.

The added impurity is very small of the order of 1 atom per million atoms of pure semiconductor. Such semiconductors are called extrinsic semiconductors.

Depending upon the type of impurity semiconductors can be divided into two classes -

- (1) N-type semiconductor
- (2) P-type semiconductors.

N-type Semiconductors:

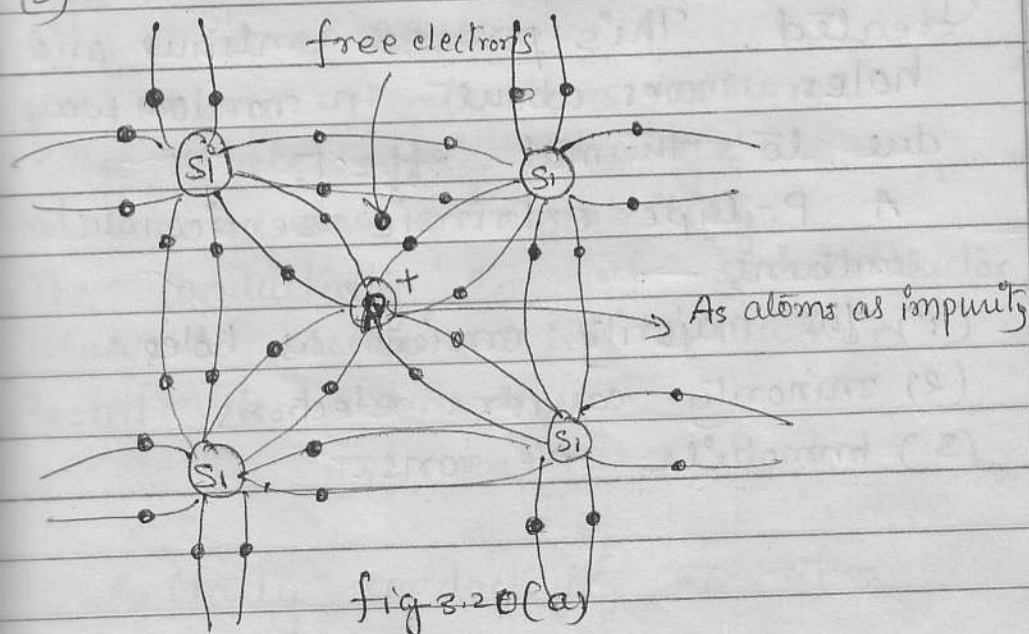
When a pentavalent-impurity is added to a pure crystal during the crystal growth the resulting crystal is called N-type.

Let a pentavalent-arsenic is added to pure germanium crystal, the four e⁻ of arsenic atoms form covalent-bonds with the electrons of ~~ger~~ Si atoms.

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fifth e^- of arsenic is not
 covalently bonded but it is loosely
 bonded to arsenic atom. By
 increasing temperature or by applying
 electric field this electron can be
 easily excited to conduction band.
 Thus every arsenic atoms contributes
 one conduction electrons with creating holes.
 Hence arsenic is called donor atoms.
 The crystal as a whole has excess of
 negative charge which are current carriers
 N-type extrinsic semiconductors have -

- (1) majority charge carriers electrons.
- (2) minority charge carriers holes.
- (3) Immobile +ve ions.



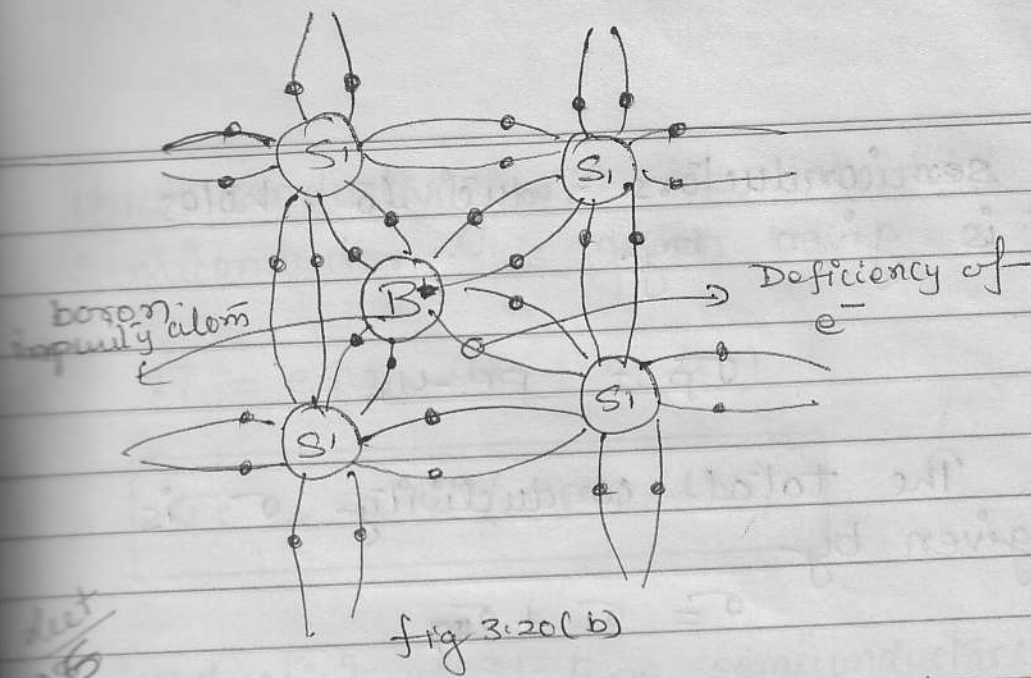
P-type Extrinsic Semiconductors

When trivalent impurity atom (like boron or aluminium) is added to pure crystal during crystal growth, the resulting crystal is called p-type extrinsic semiconductor. Let us consider boron atom is added to pure germanium or silicon crystal.

Three electrons of boron atom form covalent bonds with the valence electrons of silicon atom. There is a deficiency of one atom e^- which is called hole. Boron steals one electron from neighbouring germanium or silicon where a hole is created. This process continues and holes move about in random way, due to thermal effect.

A P-type extrinsic semiconductor contains —

- (1) the majority carriers as holes.
- (2) minority carriers electrons
- (3) immobile $-ve$ ions.



Conductivity of Semiconductor.

In a semiconductor charge carriers are both electrons and holes. On the basis of free electron theory the conductivity σ of a metal is given by

$$\sigma = ne\mu_e$$

$n \rightarrow$ no. of electrons / volume

$e \rightarrow$ electronic charge.

$\mu_e \rightarrow$ electron mobility.

The conductivity σ_n of semiconductor due to electrons in conduction band is given by

$$\sigma_n = ne\mu_e$$

Similarly conductivity σ_p of

conductivity of semiconductors due to holes is given by

$$\sigma_p = p e \mu_h$$

The total conductivity σ is given by

$$\sigma = \sigma_n + \sigma_p$$

$$\sigma = n e \mu_e + p e \mu_h$$

$$\sigma = e (n \mu_e + p \mu_h)$$

Conductivity of intrinsic semiconductors

In case of intrinsic semiconductors the number of conduction electron is equal to the number of holes

$$\text{i.e. } n = p = n_i$$

where n_i is intrinsic concentration of electron and holes in the semiconductors.

Thus conductivity σ_i of intrinsic semiconductor is given by

$$\sigma_i = e(n_i \mu_e + n_i \mu_h)$$

$$\sigma_i = e n_i (-\mu_e + \mu_h)$$

Conductivity of N-type semiconductors:

In case of N-type semiconductors the electron concentration is far greater than hole concentration i.e. hole concentration is negligibly small in comparison to electron concentration. In N-type semiconductor

$$n > p \quad \text{or} \quad n \mu_e > p \mu_h$$

$$\therefore \sigma_n = e n_d \mu_e$$

Conductivity of P-type semiconductors:

In case of P-type semiconductors the electron concentration is negligible small in comparison to