1 Crystal structure

classification of solids on the basis of structure.

· Crystalline solid.-

* Definate geometrical shape.
long range ordered arrangement
- sharp M. P.
- Anisotropic
(Different physical prop. in different direction)
- Give plane surface when cut with knife.
- It has symmetry

eg NaCl, Iron

Amorphous solid.

- No definate geometrical shape
- short range ordered arrangement or no order
- Do not have sharp m. p.
- Isotropic
i.e Identical value of property in all directions
- Give rough surface when cut with knife.
- Do not have any symmetry

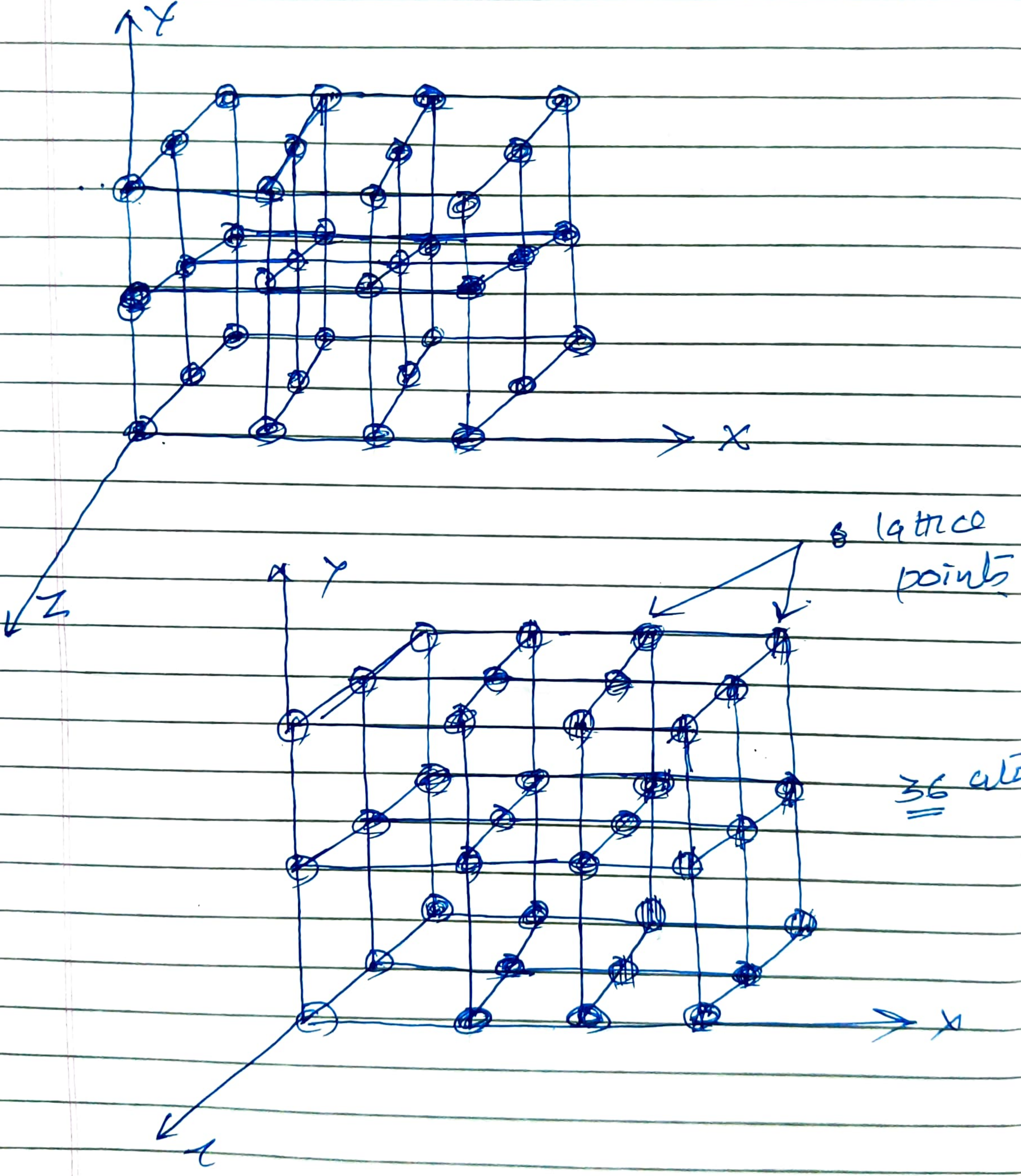
eg- Glass, Pitch

SPACE LATTICE.

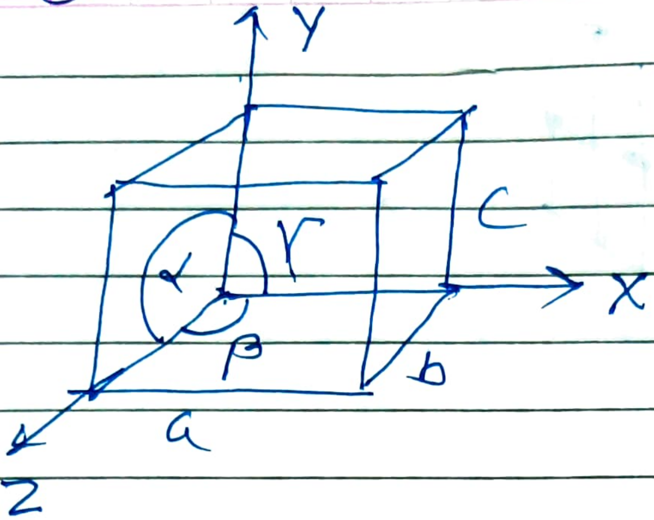
The arrangements of lattice points (atoms, molecules or ions) in three dimensional space is known as space lattice.

Unit cell - The smallest repeating pattern of lattice points which represents the structure of solid is known as unit cell.

a <u>space lattice</u>



ⓑ unit cell.



Bragg's Equation -

In 1913 W.L & W.H. Bragg found that the crystal spacing (Interplanar distance) can be determined by using X-ray of single wavelength.

& this shows that

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

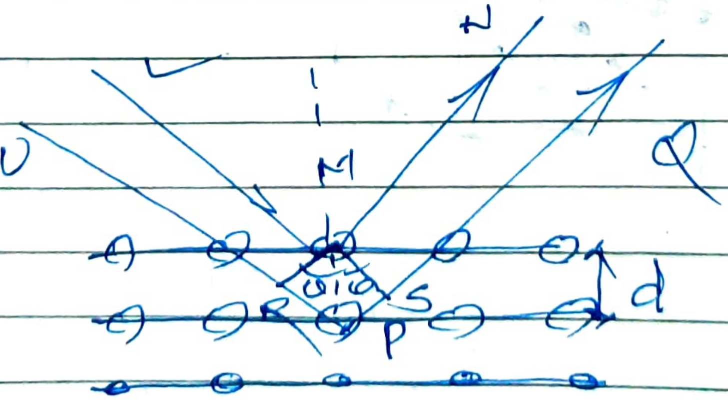
where n - order of diffraction

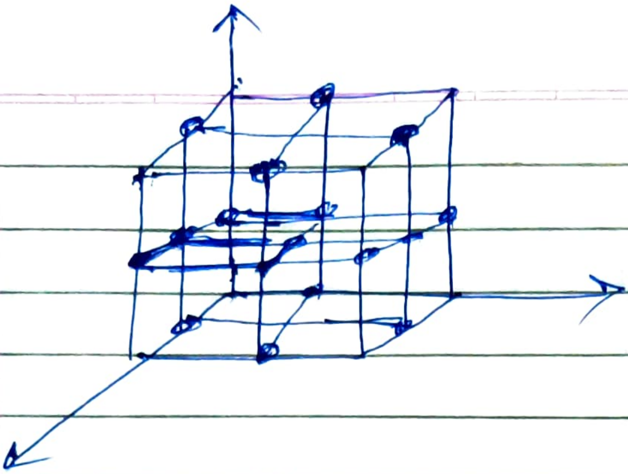
λ - Wavelength of X-ray

d - Interplanar distance

θ - diffraction angle

This is Know as Braggs equation.





A Na Cl

I Na^+ Cl^-

M NaCL constituent ~~particles~~

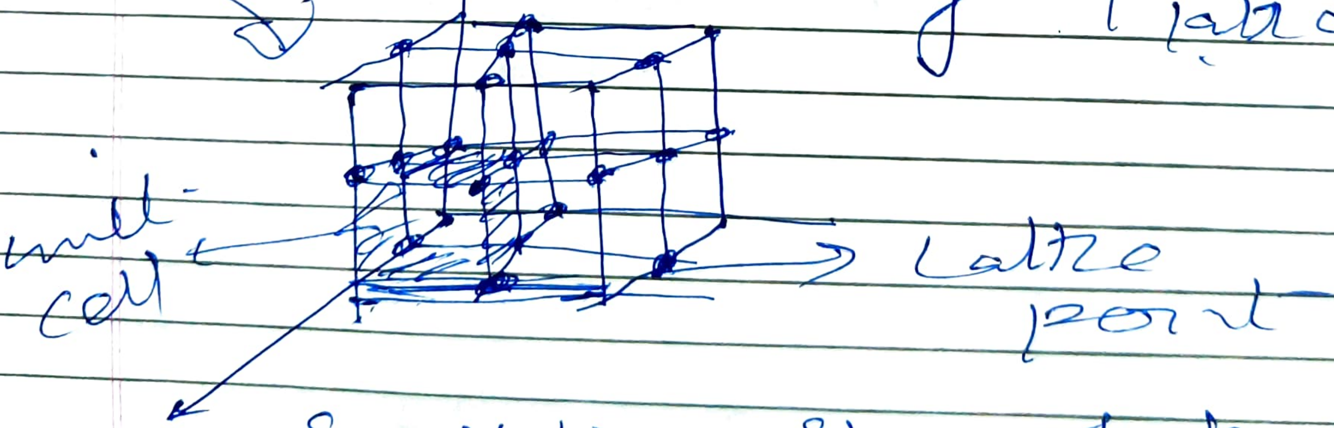
2D / crystal lattice / space lattice

3D lattice
crystal

space lattice / crystal

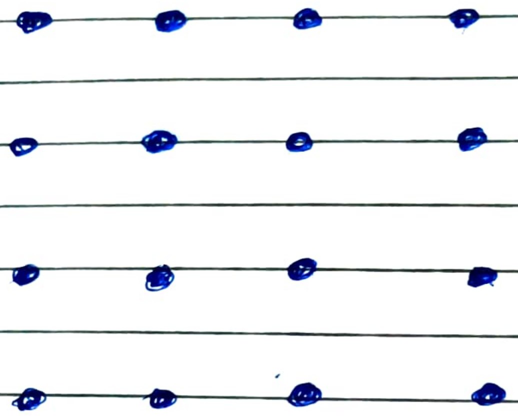
Room – unit cell

Building – space lattice



Smallest portion which repeat again & again which makes space lattice is the unit cell

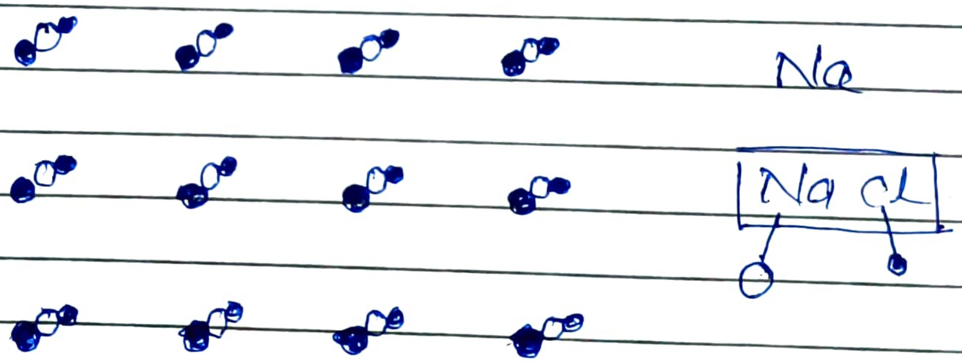
Crystal structure
(Solid state)



Crystal
↓
Solid
↓
Atom
↓
periodical.

lattice - Regular arrangement in space.

Crystal structure = Lattice + Basis



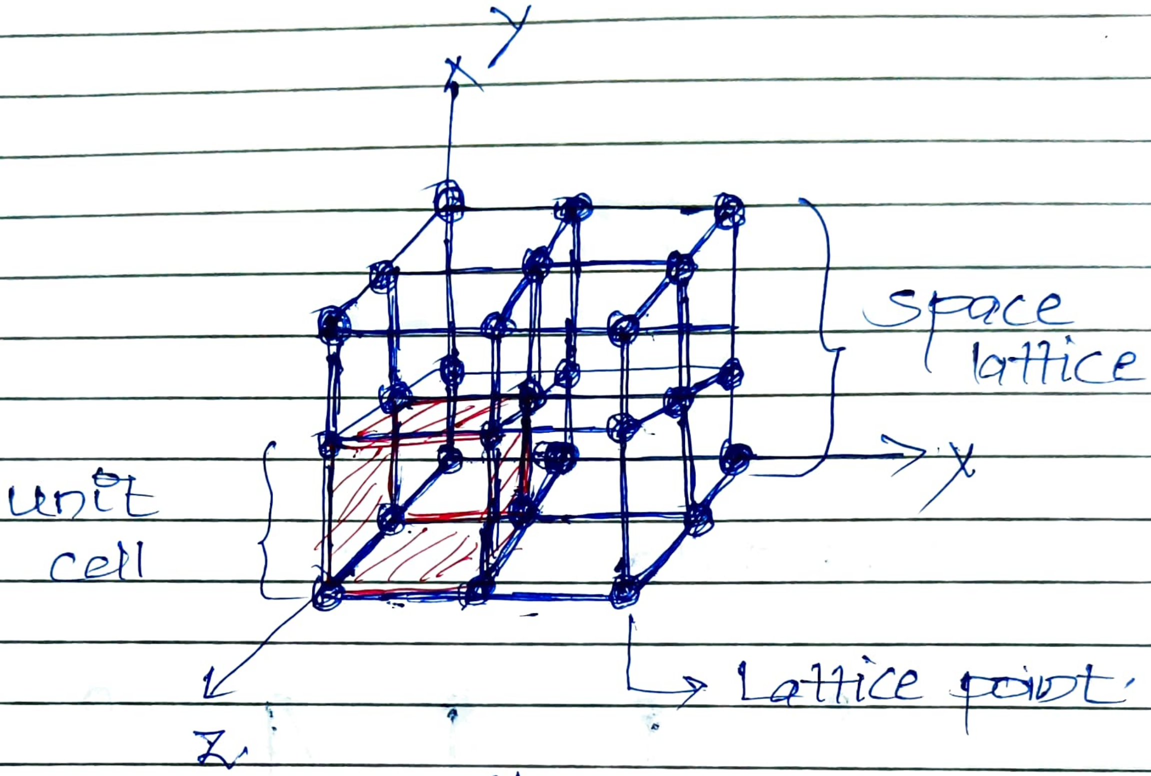
Lattice + Basis ⟶ crystal structure

✓ Lattice - periodic arrangement of point in space

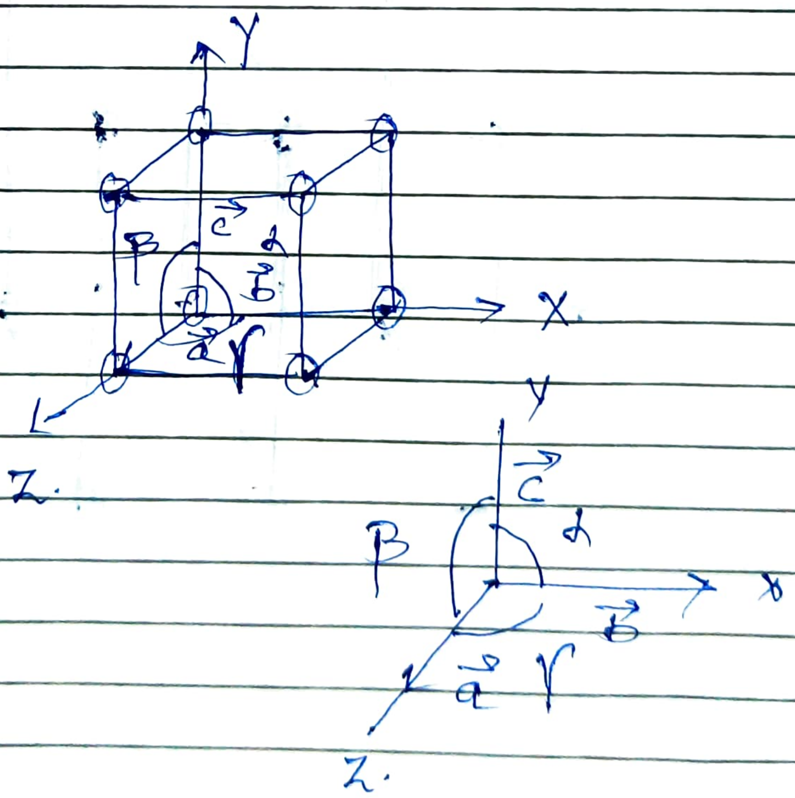
Basis — Atoms or group of atoms —
Na Na Cl

- associate with every lattice point, is called Basis.

3 Dimensional lattice

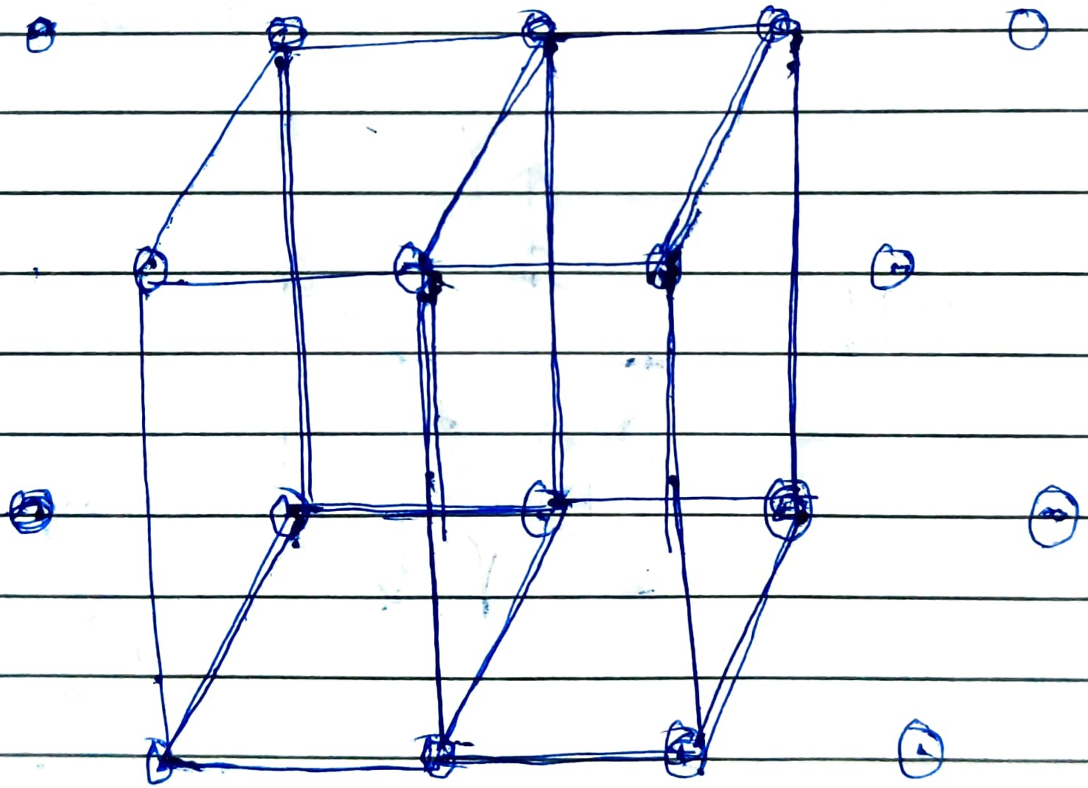


Unit cell

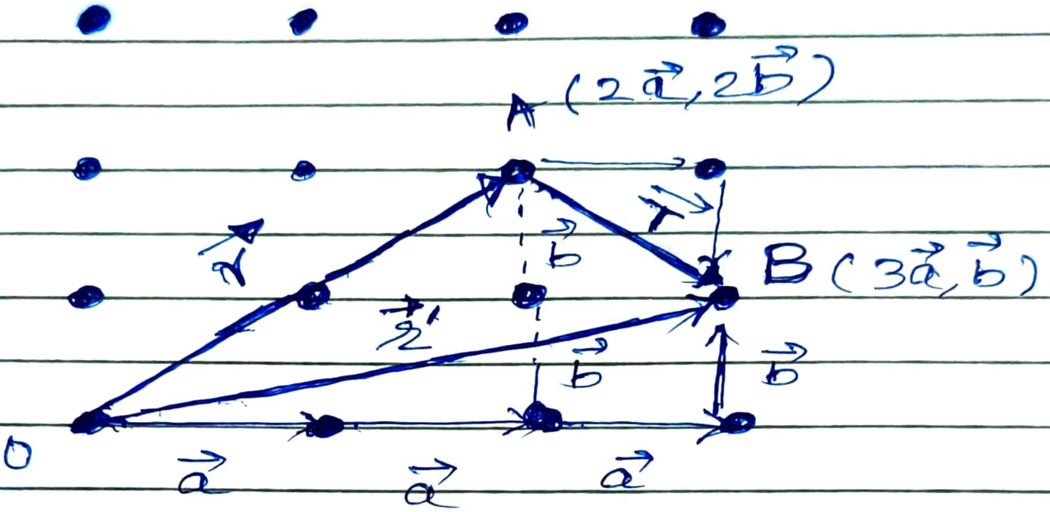


Unit cell - Smallest portion which repeat again and again to make space lattice.

3 Dimensional lattice



Translational vector ($\vec{T}$)



$\vec{OA} + \vec{AB} = \vec{OB}$ (Triangle law)

$\vec{r} + \vec{T} = \vec{r'}$

✓ $\vec{r} = 2\vec{a} + 2\vec{b}$ (value of position vector

$\vec{T} = 1\vec{a} - 1\vec{b}$ ✓

$\vec{r'} = 2\vec{a} + 2\vec{b} + 1\vec{a} - 1\vec{b}$

$= 3\vec{a} + \vec{b}$

In general

$\vec{T} = n_1\vec{a} + n_2\vec{b}$

$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{C}$

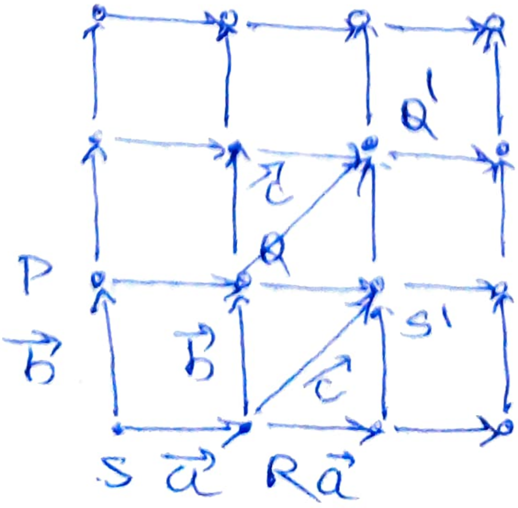
$n_1, n_2 = 1, 2\ 3 - - - -$

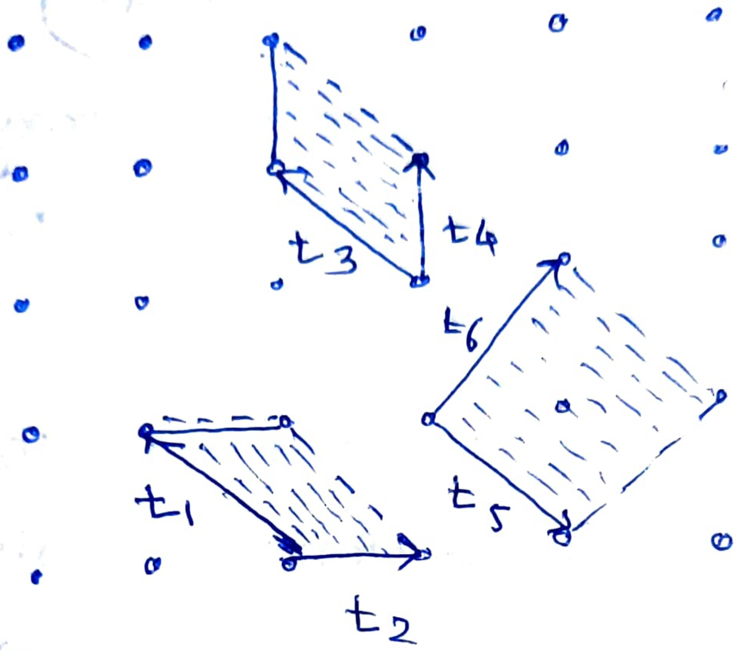
$\vec{a}, \vec{B}$ primitive vectors

$n_1, n_2, n_3 = 1, 2, 3 \ldots\ldots$

Unit cell. (primitive cell)

In a crystal lattice unit cell may be chosen in any convenient way. A parallopiped formed with lattice point only at the corner is called unit cell. This done by selecting the region of crystal defined by three translation vectors $\vec{a}, \vec{b}, \vec{c}$ which when translated by an integral multiple of vectors produce a similar region of crystal this region is called as unit cell. Unit cell can be defined by any of the possible way PQRS,





If the pair of translation such as t_1, t_2 or t_3, t_4 are chosen they are said to defined a primitive cells. So called because it contains only one lattice point at corner. Thus we can defined unit cell as a smallest unit cell in volume defined by the vectors. If instead, translation like t_5 t_6 are chosen they contains lattice point at the place other than corner is called non primitive cell or multiple cell.

Two dimensional lattices

S.No.	Lattice type	conventional cell	axes & conventional cell
1	Oblique	Parallogram	$a \neq b : \phi = 90^\circ$
2	Square	Square	$a = b : \phi = 90^\circ$
3	Hexagonal	60° rhombus	$a = b : \phi = 120^\circ$
4)	Primitive rectangular	Rectangle	$a = b : \phi = 90^\circ$
5)	Centre rectangular	Rectangle	$a \neq b : \phi = 90^\circ$

Three dimensional lattices

System	no of lattices	lattice symbols	Restriction on conventional unit cell axes and angles
) Cubic	3	P or SC I or bcc F or fcc	$a = b = c$ $\alpha = \beta = \gamma = 90$
) Tetragonal	2	P, I	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
3) Orthorhombic			

The space lattice

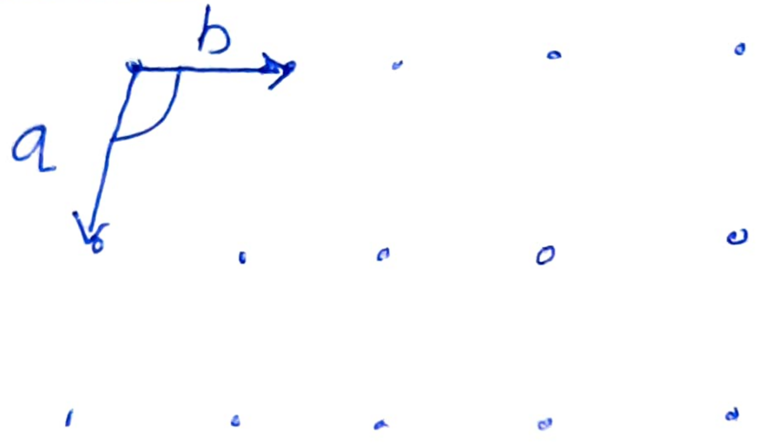
A space lattice is defined as an infinite array of points in three dimension in which every points has surrounding identi~~cte~~cal to that of every other point in the array.

consider two dimensional square array of points in Fig. By repeated translation of two vectors $\vec{a}$ and $\vec{b}$ we can generate square array. The magnitude of $\vec{a}$ and $\vec{b}$ are equal and taken to be unity. The angle between them is 90°. The $\vec{a}$ and $\vec{b}$ are fundamental translational vectors that generate array. The array can be extended infinity.

Fig

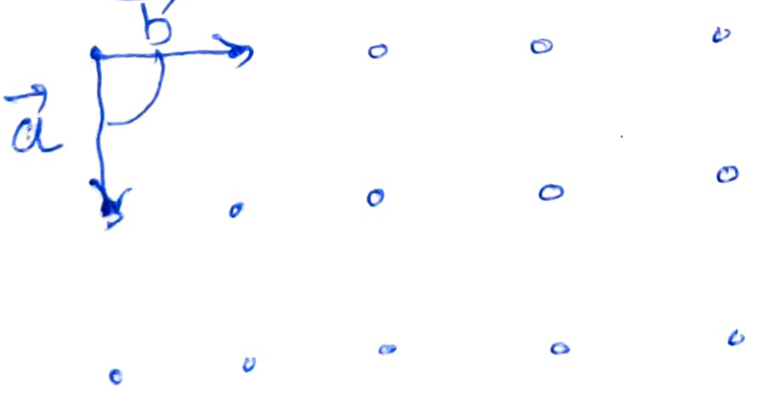
There are five type of Bravais lattices in two dimension.

i) Oblique lattice [redacted], [redacted]



$|a| \neq |b|$, $\phi = 90^\circ$, Oblique lattice is invariant under the rotation of π and 2π about any lattice points

ii) Square lattice

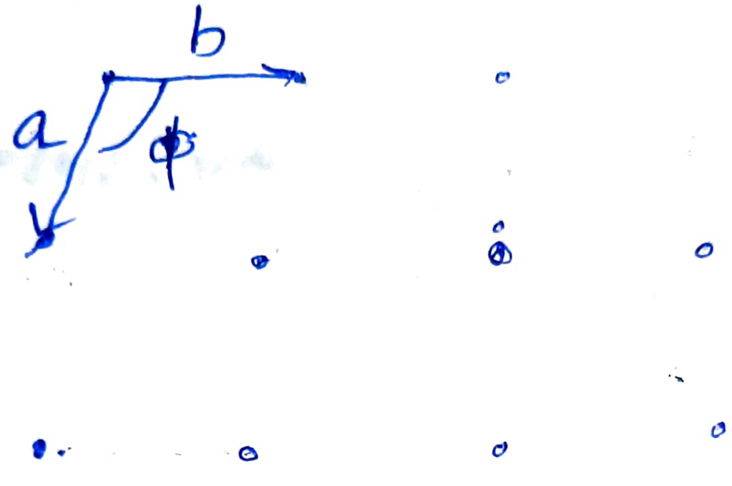


$|a| = |b|$

$\phi = 90^\circ$

III) Hexagonal lattice

six



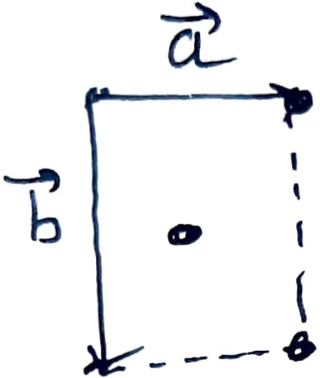
$|a| = |b| \quad \phi = 120^\circ$

This lattice is invariant under the rotation of $2\pi/6$ about an axis through lattice point and normal to the plane

(IV) Rectangular lattice

$|a| \neq |b|, \ \phi = 90^\circ$

(v) centred rectangular lattice

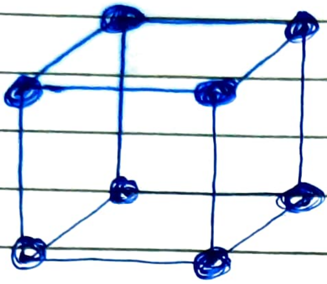


For this lattice

$a \neq b, \ \phi = 90^\circ$

Types of unit cell.

① Premitive unit cell.
Simple cubic (SC)



$a = b = c$

$\alpha = \beta = \gamma = 90^\circ$

co-ordination number is 6

The total no. of atom in SC unit cell. is one

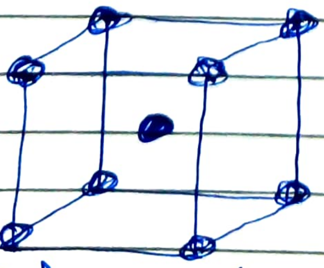
$$= 8 \times \frac{1}{8} = 1$$

Each corner atom is shared by eight unit cell. Hence share of each corner atom to the unit cell is one eighth of an atom.

Hence effective no. of lattice points in simple cubic 1

(ii) centered unit cell
(Non premitive unit cell.)

ⓐ body center cubic (bcc)



co-ordination number = 8

The number of atom per unit cell in bcc structure

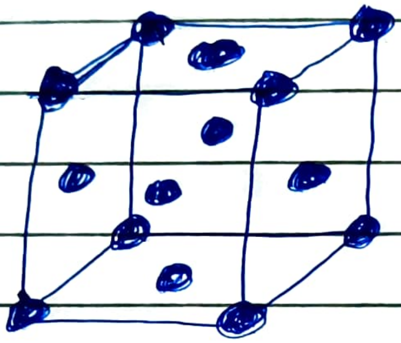
$$= 8 \times \frac{1}{8} + 1$$

$$= 1 + 1 = 2$$

No. of atoms per unit cell is 2

(b) Face Centered cubic structure.

FCC



Each corner atom is shared by 8 surrounding unit cells and each of face centered atom is shared by two surrounding unit cell

Thus total no. of atoms in FCC structure is

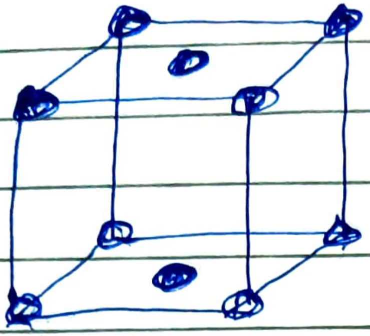
$$\cancel{8} \times \frac{1}{\cancel{8}} + \overset{3}{\cancel{6}} \times \frac{1}{2}$$

$$1 + 3 = 4$$

No. of atoms per unit cell 4

co-ordination number is 12

ⓒ End center Cubic



No. of lattice points per unit cell in end center cubic is

$$= 8 \times \frac{1}{8} + 2 \times \frac{1}{2}$$

$$= 1+1 = 2$$

No. of lattice points in unit cell of end center cubic structure is two

Crystal system

The arrangement of lattice points in a Unit cell is called crystal system.
There are seven types of crystal systems.
CTORHMT

Cubic
Tetragonal
Orthorhombic
Rhombohedral
Hexagonal.
Monoclinic
Triclinic

1) **Cubic**
$a = b = c$, $\alpha = \beta = \gamma = 90^\circ$
Maximum symmetry elements
9 planes, 13 axes,
eg - $NaCl$, KCl, ZnS diamond Alum

2) Tetragonal,
$a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

max. symm. ele - 5 planes
5 axes

eg - TiO_2, SnO_2

3) Orthorhombic
$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$
3 plane, 3 Axes
eg - KNO_3, $BaSO_4$, K_2SO_4

4) Monoclinic
$a \neq b \neq c$, $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$
1 plane 1 axis

eg monoclinic Sulpher, $KClO_3$
$CaSO_4, 2H_2O$ $Na_2B_4O_7 10H_2O$

5> Triclinic
$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma = 90°$
No plane no-axis

eg $CuSO_4 5H_2O$, H_3BO_3 $K_2Cr_2O_7$

6> Hexagonal
$a = b \neq c$, $\alpha = \beta = 90°$
$\gamma = 120°$

7 plane, 7 axes,

eg ZnO, CdS, HgS SiC AgI

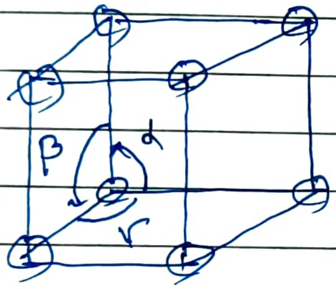
7> Rhombohedral
$a = b = c$, $\alpha = \beta = \gamma \neq 90°$
7 plane, 7 Axes,

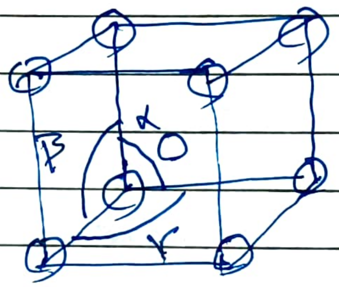
eg $NaNO_3$, quartz ($CaCO_3$)

Bravais lattice -

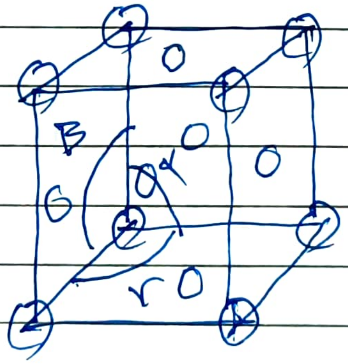
On the basis of position of lattice points in the unit cell. All the seven crystal system can be devided into 14 different arrangement. these are known as Bravais lattices. These 14 Bravais lattices as shown in the Figure.

✓ ① Cubic Space lattices



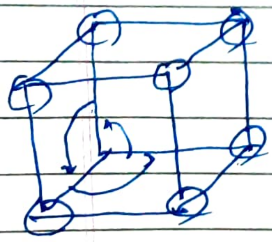


simple or primitive body centered



Face-Centered

② Orthorhombic Space lattices.



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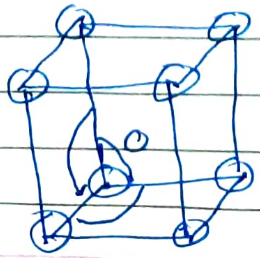
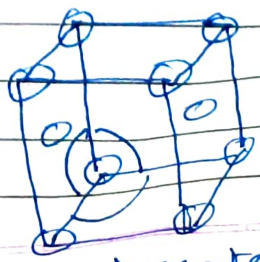
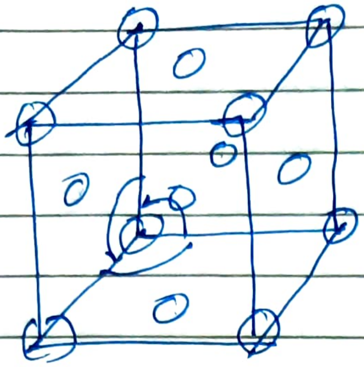


bcc



End centered.



FCC.

3) Tetragonal & monoclinic space ~~systems~~. lattices

P, 2 types

BCC - 1

~~Face~~ End centered — 1

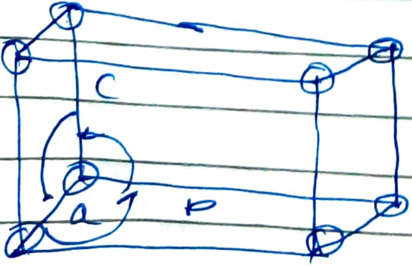
Total — 4,

P — 1+1 = 2

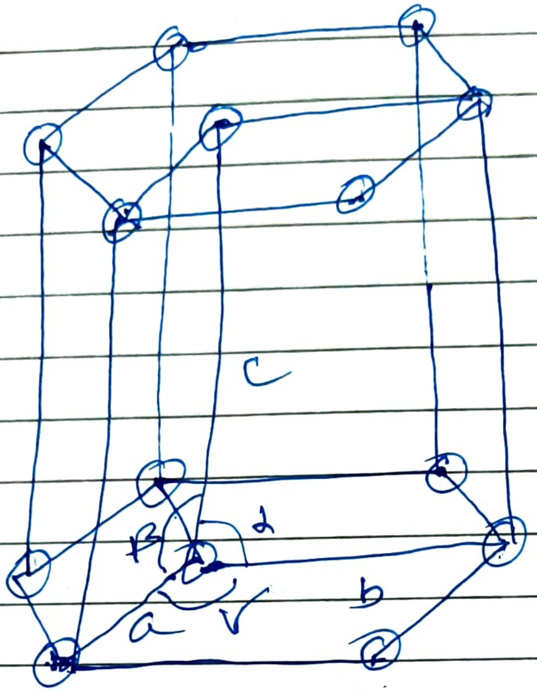
BCC — 1

End centered } — 1

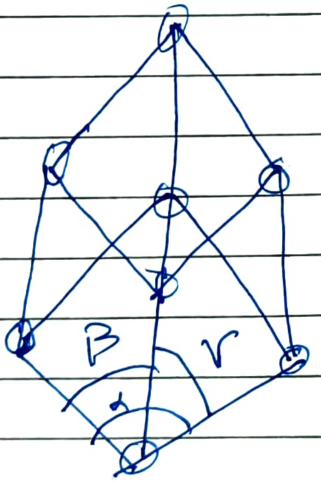
④ Triclinic Hexagonal & Rhombohedral



Triclinic



Hexagonal



Rhombohedral

Crystal system	No. of space lattices (Bravais lattices)	Lattice type
1 Cubic	3	Simple bcc, FCC
2. Orthorhombic	4	simple, bcc endcentered & FCC
3 Tetragonal	2	Simple bcc
4 Monoclinic	2	simple & end centered
5 Triclinic	1	simple (primitive)
6 Hexagonal	1	" "
7 Rhombohedral	1	" "

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No. of atoms per unit cell
(Unit cell content)

(i) A point lies at the corner of a unit cell is shared among eight unit cells and, therefore, only one eighth of each such point lies within the given unit cell. 1/8

(ii) A point along an edge is shared by four unit cells and only ~~[illegible]~~ one fourth of it lies within any one cell. 1/4

(iii) A Face centered point is shared by two unit cells and only one half of it is present in a given unit cell 1/2

iv) A body centered point lies within the unit cell and contributes one complete point to the unit cell. '1'

Contribution of lattice point per unit cell

Type of lattice point	Contribution to one unit cell
Corner	1/8
edge	1/4
Face center	1/2
body center	1

Ⓥ Total no. of constituent Units per Unit cell

$= \frac{1}{8} \times$ occupied corner $+ \frac{1}{4} \times$ occupied edge centers $+ \frac{1}{2} \times$ occupied Face centers $+$ occupied body center.

* Types of cubic Unit cell

It is of Five types

① SC or primitive
2) bcc
3) FCC ④ End FCC
⑤ Edge center cubic

Miller Indices

Miller Indices are ~~the~~ a set q integers (h, K, l) which is used to described a given plane in a crystal. Miller indices q a face q a crystal are inversly propor-tional to the intercepts q that face on various axes.

Reciprocal q the Weiss coefficients and multiplying through the smallest number will express all the reciprocals as integers.

The actual ~~pract~~ lattice in a crystal q a given kind consist q a unit-cell q that kind all over in 3 Dimensional space. As already mentioned, there can only be a maximum q 32 elements q symmetry (Pt-72): combining these with 14 Bravais lattices there can be 230 different arrangement known as Space groups.

Ex — Calculate the Miller Indices q crystal planes which cut through the crystal axes at.

① 2a, 3b c

a	b	c
2	3	1
$\frac{1}{2}$	$\frac{1}{3}$	1
$\frac{1}{2}\times 6$	$\frac{1}{3}\times 6$	6
3	2	6

hence miller indices are (326)

(ii) (a, b, c)

1 1 1

1 1 1

1 1 1

Hence miller indecies are (111)

③ 6a, 3b 2c

a b c

6 3 2

$\frac{1}{6}$ $\frac{1}{3}$ $\frac{1}{2}$

$\frac{1}{6} \times 6$ $\frac{1}{3} \times 6$ $\frac{1}{2} \times 6$

1 2 3 hence miller indecies are (123)

④ 6a 3b 3c

a b c

6 3 3

$\frac{1}{6}$ $\frac{1}{3}$ $\frac{1}{3}$

$\frac{1}{6} \times 6$ $\frac{1}{3} \times 6$ $\frac{1}{3} \times 6$

1 2 2

hence miller indecis are (122)

⑤ $2a, -3b, -3c$

$a \quad b \quad c$

$2 \quad -3 \quad -3$

$\frac{1}{2} \quad -\frac{1}{3} \quad -\frac{1}{3}$

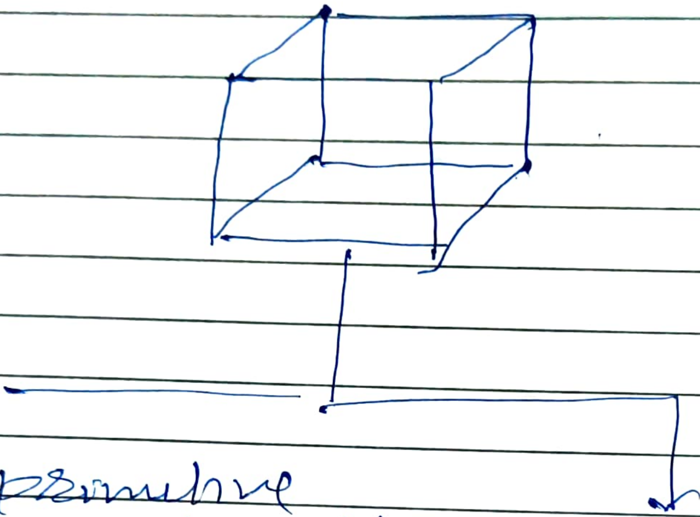
$\frac{1}{2} \times 6, -\frac{1}{3} \times 6, -\frac{1}{3} \times 6$

$3 \quad -2 \quad -2$

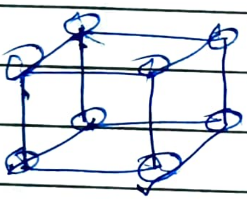
hence Miller Indices are $(3\bar{2}\bar{2})$

Unit cell

smallest portion which repeats again and again to make space lattice



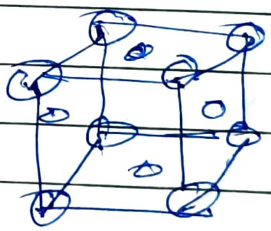
primitive unit cell



Those unit cell in which constituent particles at the corner are present

eg SC

non primitive unit cell



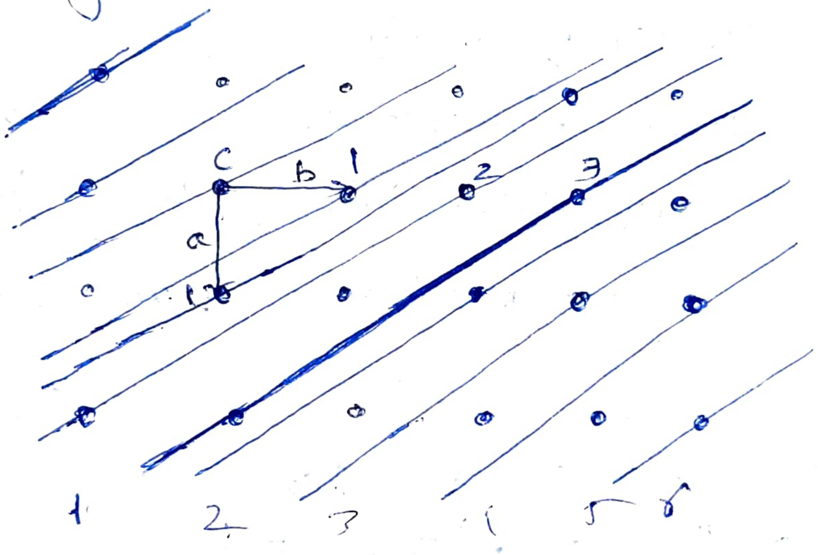
Those unit cell in which constituent particles are present at corner as well as some other position

eg bcc, FCC, end center cubic

I

Representation of planes : Miller Indices.

It is frequently necessary to consider a plane passing through a space lattice. Since it is the plane which are determined by x-rays diffraction. In order the make designation uniform of choosen plane the following procedure has been adoped.



① Determined the interceptor of the plane along a, b, c in terms of lattice constant The axis may be primitive or non primitive

2) Invert the intercepts i.e write the number as their reciprocals

3) devide the coefficient by their gretest common divisor

For Ex -

consider the plane drawn in Fig. which shows a view of space lattice along c and a set of planes that are parallel to c so that they are also seen in edge view.

consider the plane shown by heavy line we tabulated as follows

	Indexing procedure	a	b	c
1	Determined intercept	2	3	∞
2)	Note their reciprocal,	$1/2$	$1/3$	$\frac{1}{\infty} = 0$
3)	clear fraction	$\frac{1}{2} \times 6$,	$\frac{1}{3} \times 6$	0×6
		$= 3$,	2	0

the resulting integers are called Miller indices of plane and are conviniently ~~choosen~~ closed in parentheses [h k l] The meaning of this indices is that a set of parallel planes [h, k l] cut a axis into h part, b axis into k parts and c axis into l parts.

For the plane whose intercepts are 4, 1, 2, their reciprocals are $\frac{1}{4}, 1, \frac{1}{2}$ and clear the fraction.

$\frac{1}{4}\times4,\ 1\times4,\ \frac{1}{2}\times4$

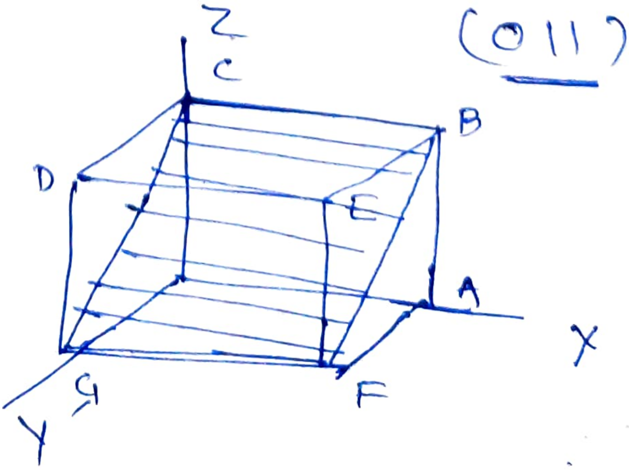
$(1\ 4\ 2)$

For an intercept at infinity the corresponding index is zero.

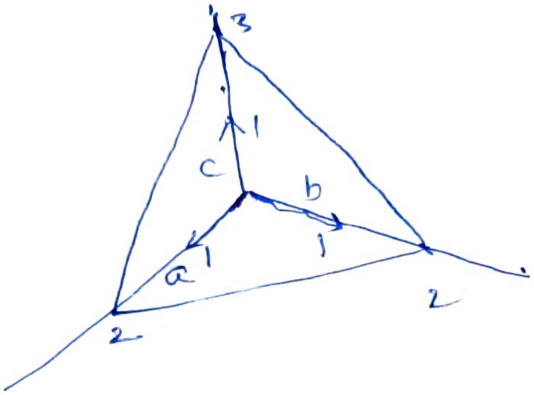
The indices of some important planes in the cubic crystals are. The indices (hkl) may denote single plane or sets of parallel planes. If the plane cut an x-axis on the negative side of origin the corresponding index is negative indicated by placing a minus sign above the index.

The cube faces of crystals are (100)

(011)



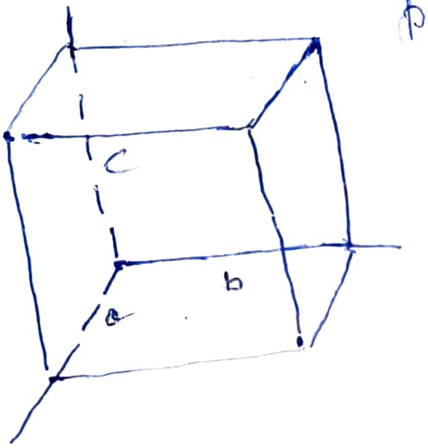
Miller Indices.



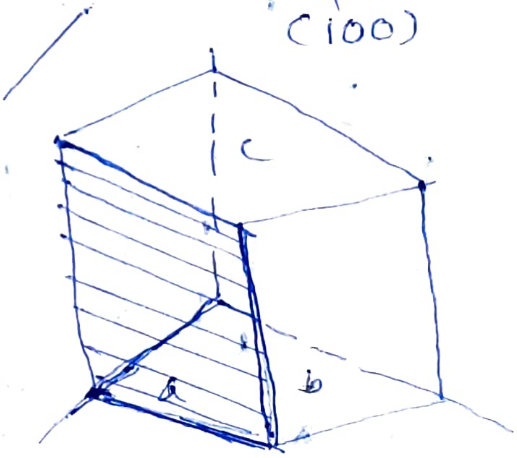
a b c
Plane (100)

Index zero represent the plane parallel to axis c and b.

①

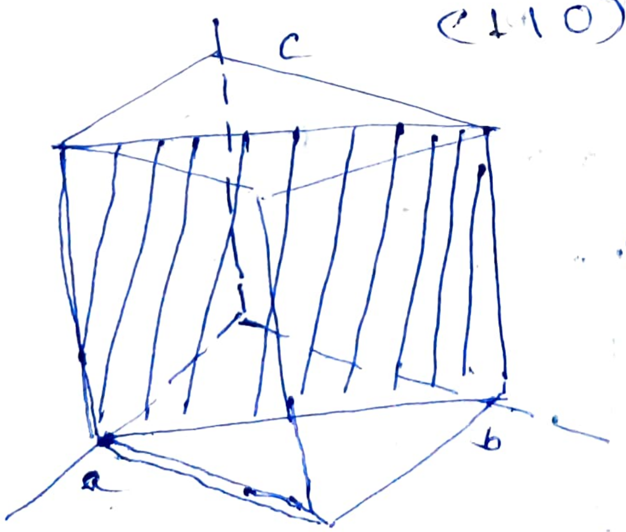


a
(100)



a b c
(110)

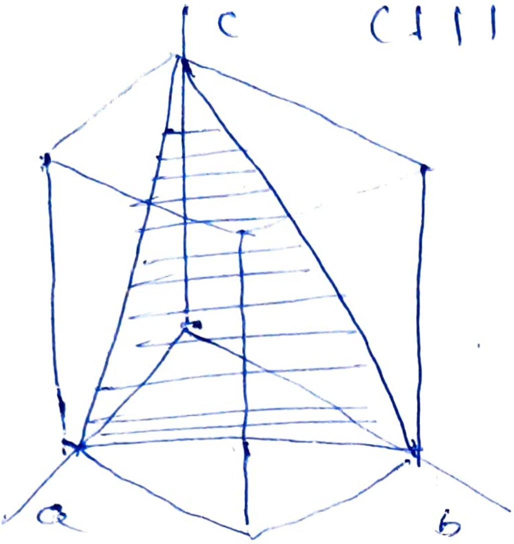
②



plane parallel to c

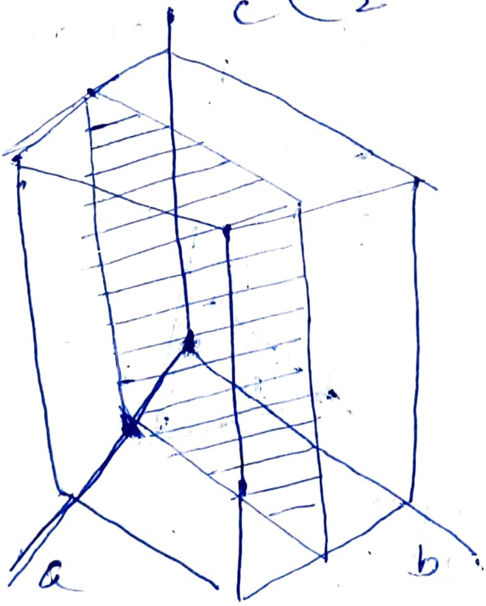
α	2		2	3	6
β	γ3		1	3	3
			1	1	1

$\begin{matrix} a & b & c \\ (1 & 1 & 1) \end{matrix}$ ③

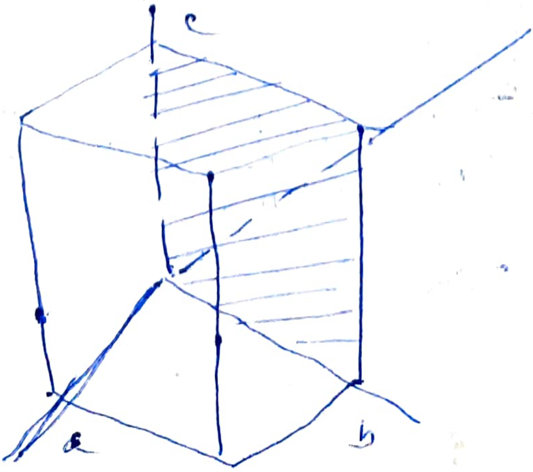


$\begin{matrix} a & b & c \\ (2 & 0 & 0) \end{matrix}$

$(\frac{a}{2}\ 0\ 0)$ [illegible]



$(\bar{1}\ 0\ 0)$ ⑤



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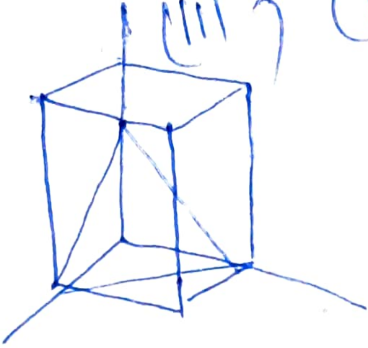

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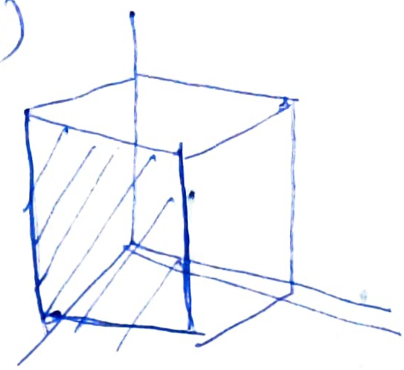

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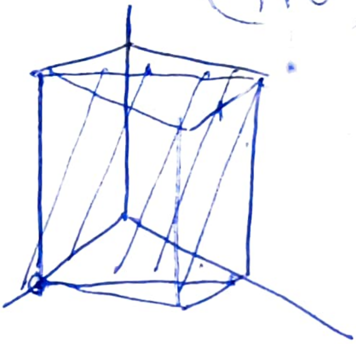
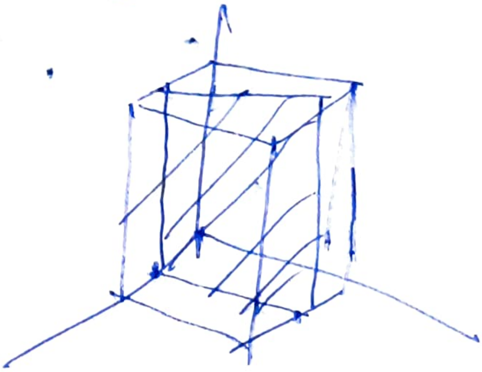
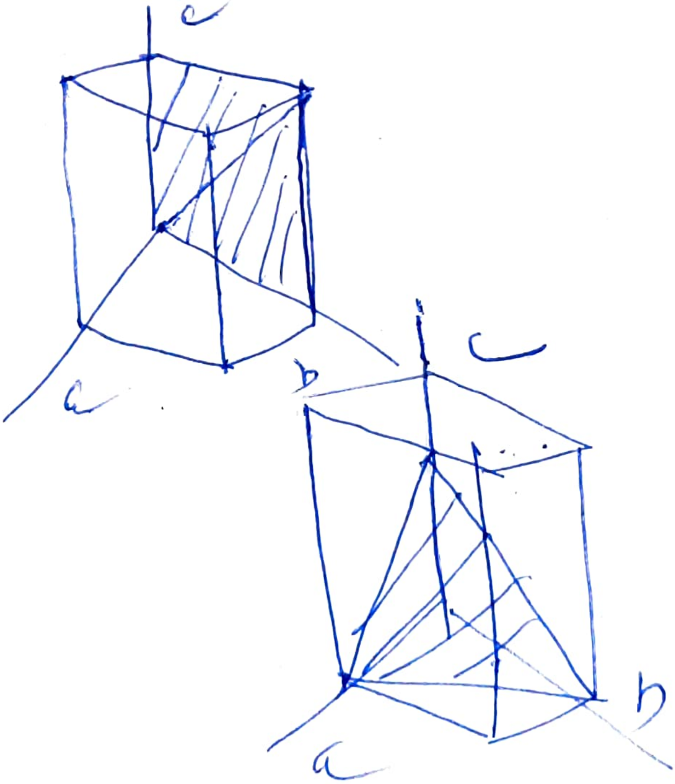


(200)



$(\bar{1}00)$



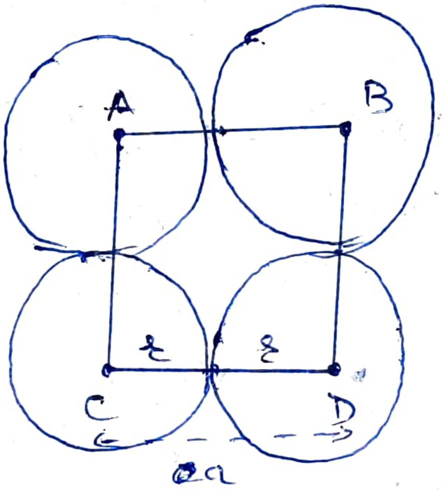
Atomic radius -

Atomic radius is defined as half the distance between neighbour in a crystal of pure element. Usually it is expressed in terms of cube edge a.

We shall calculate the relation between the atomic radius (r) and lattice parameter a in the following three cases.

① Simple cubic (s.c. lattice).

Fig -



The simple cubic lattice shown in fig. There are eight corner atoms is a member of eight cell. From the fig.

$$2r = a$$

$$\text{or } r = a/2$$

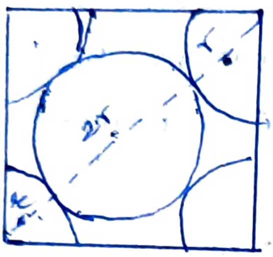
② Face centre cubic (F.C.C) lattice.

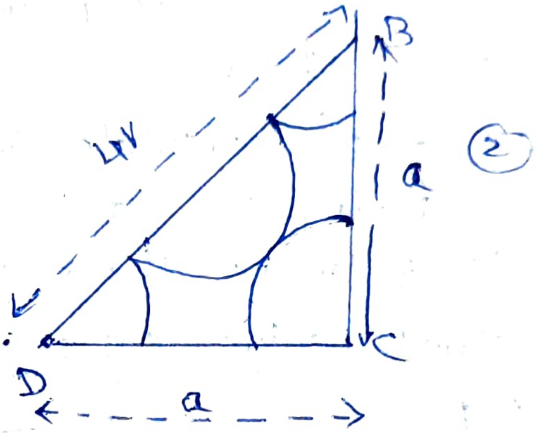
It has eight corner atoms and each one of this atom is a member of eight cell enclosing the corner. There are six face centre atoms each is a member of two cell on ~~eight~~ its either

Side eg. Nacl. crystal

Fig ① Front view of F.C.C structure unit cell ② cut view.

①





From Fig ②

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

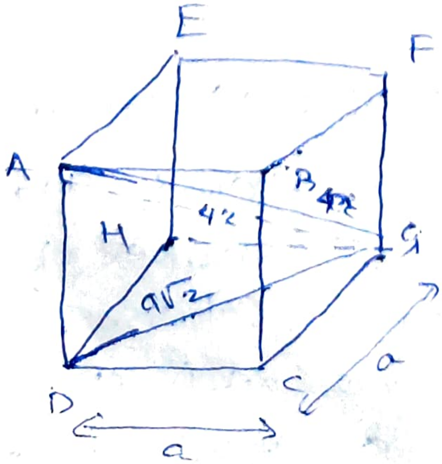
$$(4r)^2 = a^2 + a^2$$

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

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

③ B.C.C lattice –

In the unit cell of BCC lattice there are 8 atoms at corner each forming a number of eight cell and there is one atom per cell at body centre the unit cell shown in Fig



$$(AG)^2 = (AD)^2 + (DG)^2$$

$$4r^2 = (AD)^2 + (DC)^2 + (CG)^2$$

$$= a^2 + a^2 + a^2$$

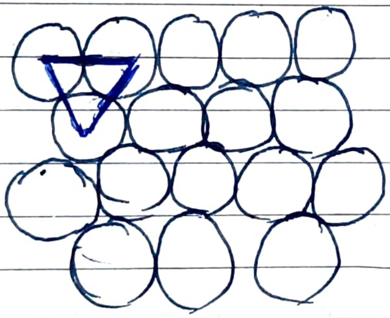
$$r = \frac{\sqrt{3}\,a}{4}$$

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

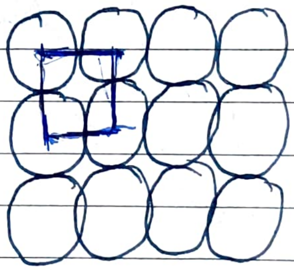
Closed packed structures

In order to understand the packing of atoms, molecules or ions in crystals, let us consider the packing of hard sphere of equal size in three dimensions. There can be number of possible arrangements but one in which maximum available space is occupied will be economical. Such an arrangement is called closest packing. Hence, the closer the packing the greater is the stability of packed system.

If a number of sphere of equal size are put in a container and shaken, it is observed that they pack themselves in two common ways, as shown in fig.



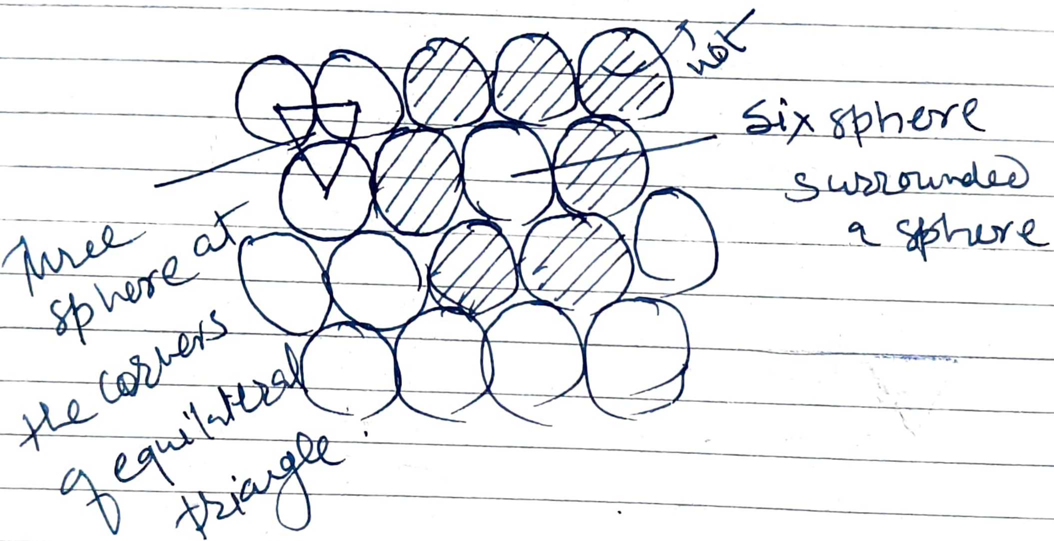
Arrangement I



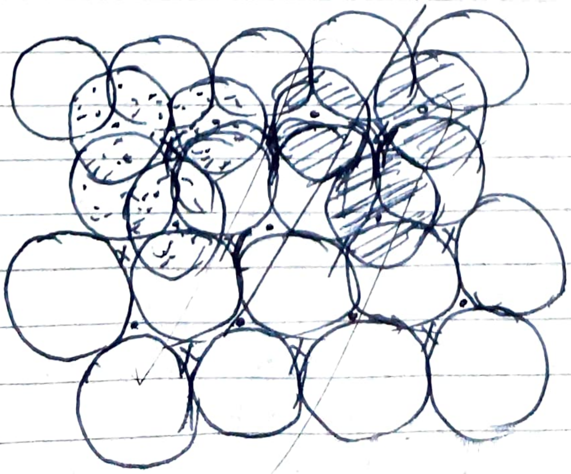
Arrangement II

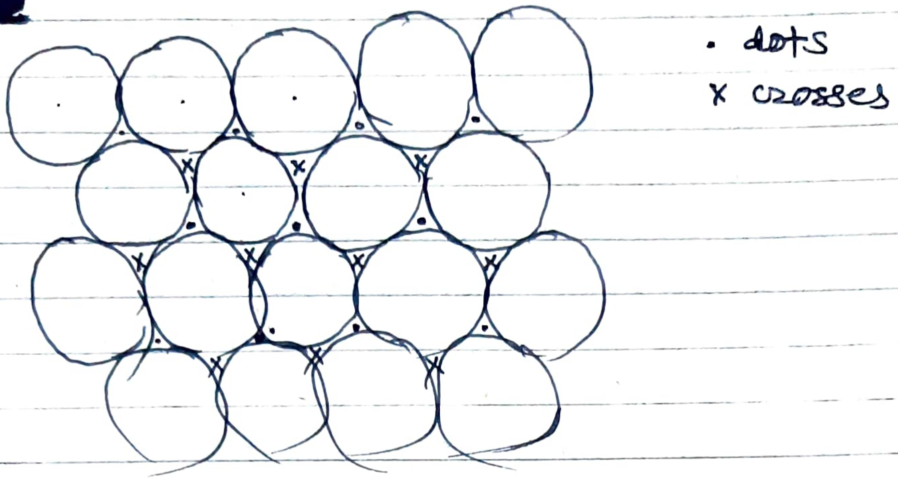
A comparison of two ways of packing of spheres shows that in arrangement I the spheres are more closely packed than the arrangement II. It has been calculated that in the first arrangement 60.4% of available space is occupied by the spheres. The remaining 39.6% of the space is empty and is called void volume. In the second arrangement only 52.4% of the space is filled and 47.6% of the space is empty. Thus the arrangement I is more economical and it represents a close packing of spheres.

It can be seen that in the close packing arrangement; the sphere arrange ~~ment~~ themselves in such a way that their centres are at the corners of an equilateral triangle. Each sphere is in contact with six other similar sphere shown shaded. The number of nearest neighbours with which a given sphere is in contact is called co-ordination number. Thus the co-ordination number of each sphere packed in above manner is six.



The arrangement can be extended in three dimensions by placing other closest packed layer on the top of hollows (or voids) of the first layer. Let us label first layer as a A layer.



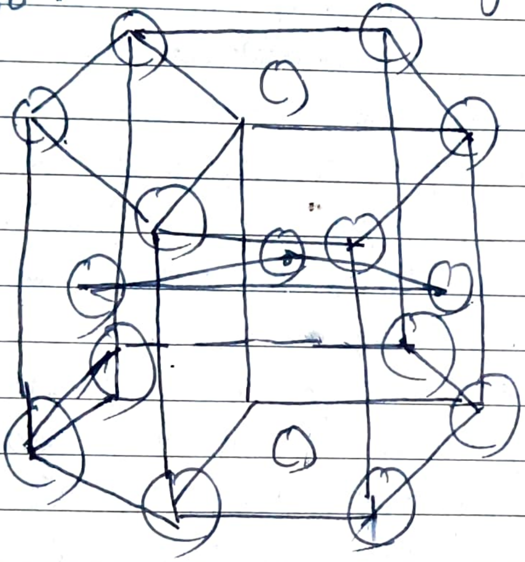


~~Let~~ There are two types of hollows in the first layer which are marked by dots (·) and crosses (x). All the hollows are equivalent but spheres of second layer may be placed either on hollows which are marked by dots or on other set of hollows marked by crosses. It may be noted that it is not possible to placed the sphere on both types of hollows. In this way, half of the hollows remain occupied while building the second layer. Let us place the spheres on hollows marked by dots to make the second layer which may be labelled as a B layer.

When we come to packing of third layer there are two alternatives ways. one way ~~to~~ is to put the spheres of third layer on the hollow of second layer. when the spheres of third layer are placed on the hollows of second layer, it is observed that each sphere of third layer (shown dark sphere) lies directly above those in the first layer. This arrangement continued indefinitely in the —

same sequence is represented as ABABABA........

This arrangements of layers on examination, is found to represents hexagonal close packing symmetry or hcp. This means that the structure has one six fold axis of symmetry. The same appearance is repeated on rotating the crystal through an angle of 60°.



The second way to pack spheres in the third layer is to place them over unoccupied hollows of the first layer marked by crosses. This will ~~gives~~ give a different type of close-packed arrangement. However it can be shown that now the sphere in ~~first layer~~ fourth layer will be corresponds ~~to~~ with those in first layer. This arrangent of stacking, if continued indefinitely is represents ABCABC - - - - -

This resulting arrangements has cubic symmetry and consequently it is referred to as cubic close packing of sphere and it is commonly ~~is~~ abberviated as ~~k~~ ccp. A closer study of ~~ccp~~ ABCABC ---- system of close packing also shows that there is a sphere at the centre of each face of the unit cube and hence this structure also known as Face centre cubic structure (FCC)

5

Roll/Exam No. 6

Shri Chhatrapati Shivaji College Omerga

Tq. Omerga Dist. Osmanabad.

(Arts, Science and Commerce)

Examination 200

Class .... Divi. ....

Paper No. ....

Subject ....

Section ....

No of Supplements ....

Date / /

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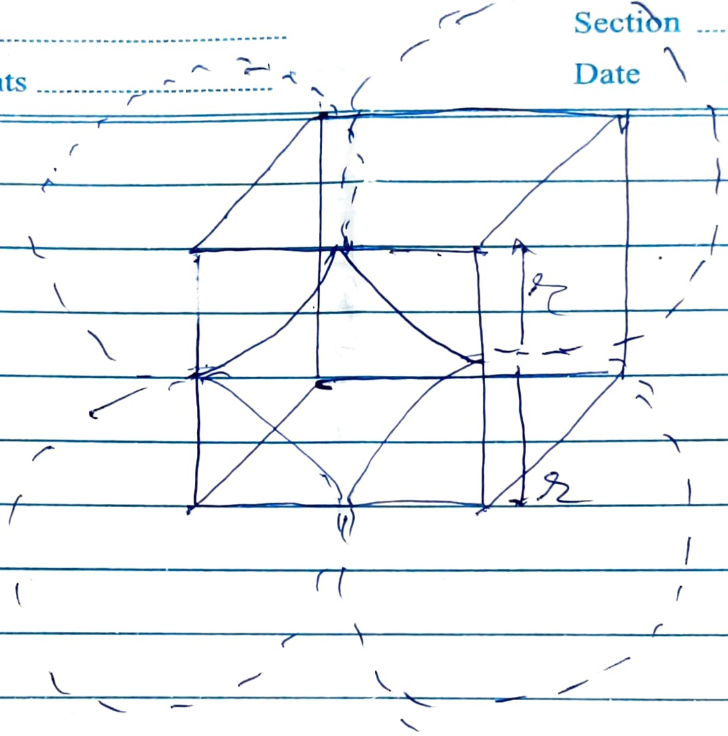


Total no. of atoms in one unit cell will be

$$\frac{1}{8} \times 8 = 1$$

i.e effective no. of lattice points in simple cubic cell is one

S.C. is primitive

Nearest neighbour distance $2r = a$

co-ordination number $N = 6$

nearest neighbour distance is $2r = a$

lattice constant $a = 2r$

No of atom per unit cell, $n = \frac{1}{8} \times 8 = 1$

Number of lattice points $= 1$

volume of all atoms in a unit-cell

$v = 1 \times \frac{4\pi}{3} r^3$

Q.No.						Q.No.					

volume of unit cell $V = a^3 = (2r)^3$
Hence the packing factor or density of packing of this structure is

$$PF = \frac{v}{V} = \frac{4\pi r^3}{3a^3}$$

$$= \frac{4}{3}\frac{\pi r^3}{(2r)^3}$$

$$= \frac{4}{3}\frac{\pi \cancel{r^3}}{8\cancel{r^3}}$$

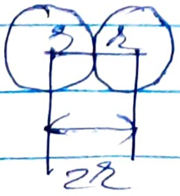
$$= \frac{\cancel{4}\pi}{6\,\cancel{24}} = \frac{\pi}{6} = 0.52$$

$$= 0.52 \times 100$$

$$= \underline{\underline{52\%}}$$

eg - Polonium

✓ Co-ordination Number (N)
✓ Nearest Neighbour distance (2r)
r - radius of atom.



✓ Atomic Radius (r) - Half distance between nearest neighbour

8

Atomic packing Factor

Space occupied by atom in unit cell is known as atomic packing Factor

i.e It is ratio of volume of atoms occupying unit cell to the vol. of unit cell relating to that structure.

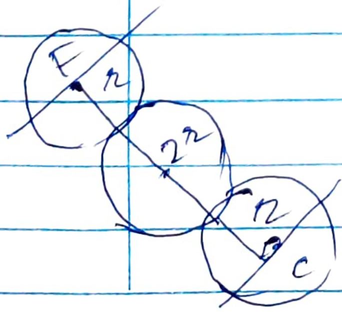
(ii) Body center cubic (bcc) structure.

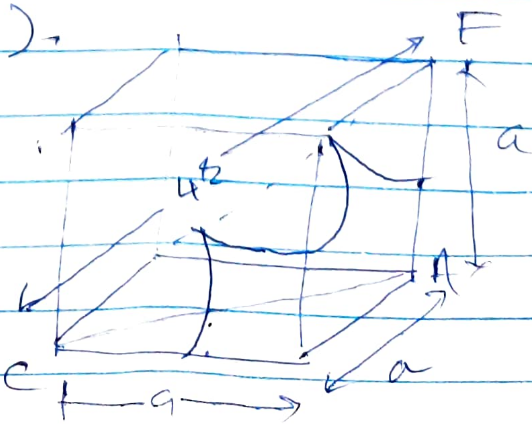
eg Li, Na, K & Cr elements like

No. of atoms per unit cell

$$= \frac{1}{8}\times 8 + 1 = 1+1 = 2$$

Corner atoms do not touch each other but touches body center atom along body diagonal. Hence coordination number is 8 (Eight).





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Q.No.						Q.No.					

calculation of lattice constant can be made with the help above Fig.

$(AC)^2 = a^2 + a^2 = 2a^2$

$(FC)^2 = (AC)^2 + (AF)^2$

$= 2a^2 + a^2 = 3a^2$

$(FC)^2 = 3a^2$

$\therefore \quad FC = 4r$

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

$a^2 = \frac{(4r)^2}{3}$

$a^2 = \frac{16r^2}{3}$

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

$4r = a\sqrt{3}$ devide by 2 throughout

$\frac{\overset{2}{\cancel{4}}r}{\cancel{2}} = \frac{a\sqrt{3}}{2}$

$2r = \frac{a\sqrt{3}}{2}$

Now we shall calculate packing factor from the following data

Divi.

Paper No.

ct

Section

Supplements

Date / /

co-ordination number = 8

Nearest neighbour distance

$$2r = \frac{a\sqrt{3}}{2}$$

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

No. of atoms per unit cell $= \frac{1}{8} \times 8 + 1 = 2$

vol. of all atoms in unit cell

$$v = 2 \times \frac{4\pi}{3} r^3 \; \cancel{a} = \frac{8\pi}{3} r^3$$

vol. of unit cell $V = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$

$$= \frac{64 r^3}{3 \times \sqrt{3}}$$

∴ atomic packing factor

$$APF = \frac{v}{V} = \frac{\frac{8\pi}{3} r^3}{\frac{64 r^3}{3\sqrt{3}}} = \frac{\cancel{8}\pi . \cancel{r^3} \cancel{3}\sqrt{3}}{\cancel{3} \; \underset{8}{\cancel{64}} \cancel{r^3}}$$

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Q.No.

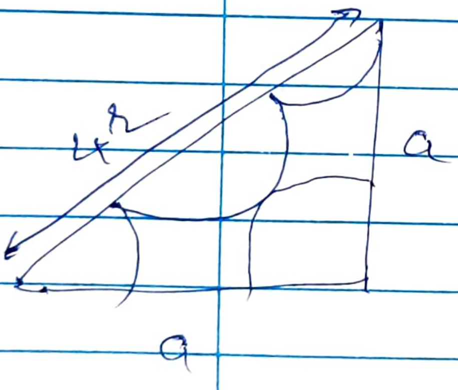
$= \frac{\sqrt{3}\pi}{8} = 0.68$ or 68%

(iii) F.C.C.

Total No. of atoms in F.C.C. unit cell.

$\frac{1}{8}\times 8 + 6\times\frac{1}{2} = 1+3 = 4$

$N = 6$ ✓



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

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

$a^2 = \frac{16r^2}{2}$

lattice const. ✓ $a = \frac{4r}{\sqrt{2}}$

No. of nearest neighbour

~~2r~~ $4r = a\sqrt{2}$ devide by 2 throughout

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

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

No. of atoms per unit cell = 4

vol. of all atoms in a unit cell

$$v = 4 \times \frac{4\pi}{3} r^3$$

vol. of unit cell $V = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$

$$= \frac{64 r^3}{8} = \frac{64 r^3}{\sqrt{4\times 2}}$$

$$V = a^3 = \frac{64 r^3}{2\sqrt{2}}$$

$$\therefore APF = \frac{v}{V} = \frac{\frac{16}{3}\pi \cancel{r^3}\, 2\sqrt{2}}{64 \cancel{r^3}}$$

$$= \frac{\cancel{32}\,\pi\sqrt{2}}{3\ \cancel{64}\,2}$$

$$= \frac{\pi\sqrt{2}}{6} = \frac{3.14 \times 1.4142}{6}$$

$$= \frac{4.4405}{6} = 0.7400 = 74\%$$

2.8 SYMMETRY ELEMENTS IN CRYSTALS

The crystal can be carried out into itself by several operation depending upon the various symmetries its unit cell posses. The important symmetries which a crystal posses are (i) translational symmetry (ii) centre of symmetry (iii) planes of symmetry and (iv) axes of symmetry.

(a) **Translational Symmetry:** Every single crystal can be repeated by translation operation of its basis by lattice vectors. Thus all crystal have translational symmetry.

(b) **Centre of Symmetry:** A lattice point can be represented by a vector $\bar{\gamma}$ drawn from an arbitrary chosen point origin. If the chosen point is such that the space lattice is brought into itself by translating every lattice point from its position $\bar{\gamma}$ to $-\bar{\gamma}$ then point is called centre of inversion or centre of symmetry. The corresponding operation is called inversion and symmetry which the space lattice as inversion symmetry.

(c) **Plane of Symmetry:** Some space lattice have one or more imaginary planes passing through it such that the portion on two sides of the plane are exactly alike *i.e.* one side is the mirror image of the other side. Such planes are called mirror plane and the corresponding symmetry as reflection symmetry. Excepting triclinic crystal system all others have one or more planes of symmetry.

(d) **Axis of Symmetry:** Axis of symmetry is an imaginary line passing through the crystal lattice such that if crystal is rotated about this line it will present the same appearance more than once during the complete rotation. For example if a cubic lattice is rotated by 90° about an axis normal to one of its face at its mid point, then it acquires a position which is exactly similar to the original position. Similar axis can be found for other crystal lattices. In general if successive rotation about the axis by an amount ϕ eventually leads to the superposition of the crystal lattice such that

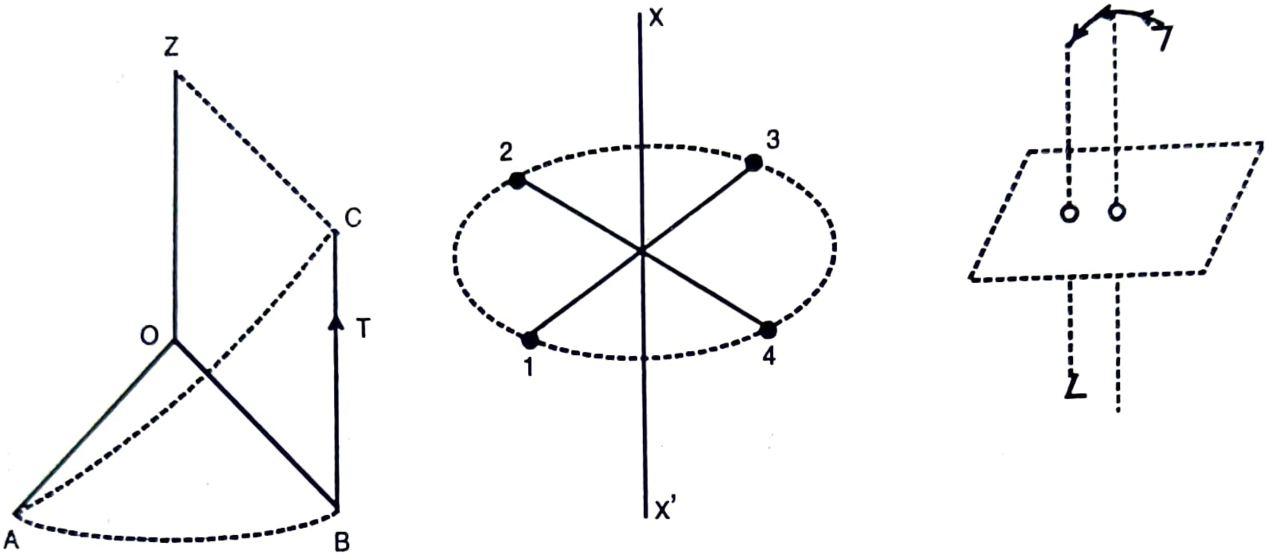
$$\phi = \frac{360}{n}, \text{ with } n = 1, 2, 3, 4 \text{ to } 6$$

then the rotation angle ϕ is called through of axis and the axis itself is called n fold axis of symmetry. If $n = 1$, then crystal has to be rotated by 360° to achieve self coincidence. In this case axis is called identity axis. If $n = 2$ axis is called two fold axis or diad axis. For $n = 3$ axis is called three fold axis or triad axis and in this case crystal achieves congruence after every 120° rotation. There are four axis in a cube. If $n = 4$, ϕ become 90° and the axis is termed as tetrad axis or four fold axis. No crystal posses five fold axis. For $n = 6$, ϕ become 60° and the axis is called hexad axis.

The basic requirement during symmetry operation is that (i) the crystal space should be filled up without any vacant site. (ii) After performing the symmetry operation the crystal has to retain its translational symmetry. These two conditions are not fulfilled by a five fold axis of symmetry. It can be easily seen that crystal space can not be fulfilled by closed packed pentagons.

Besides these common symmetries or symmentry elements there exist some other symmetries. Some of these are:

(e) **Screw Axis:** A proper rotation combined with a translation parallel to the rotation axis is equivalent to screw motion. If such operation leads to superposition, then the lattice is said to posses symmetry element called screw axis. In illustration of operation is shown in Fig. 2.13. In this figure point A is brought to B by rotation of θ°, if B is translated by amount T parallel to rotation axis it reaches point C. The point C is equivalent to a screw motion from A to C.



(a) Screw Axis (b) Four fold roto-inversion axis. (c) Two fold roto-reflection axis.

Fig. 2.13. (a) Screw Axis (b) Roto-inversion axis (c) Roto-reflection axis

(f) **Roto-Inversion Axis and Roto-Reflection Axis:** These are some axis of rotation in crystal lattice such that rotation does not lead to superposition of the basis (motif). Such a rotation leaves a right handed motif in left handed and vice-versa.

In such a case, an inversion or reflection may lead to proper superposition or identical lattice. Thus we have roto-inversion operation, which is a simple hybrid operation that combines a rotation with inversion. The corresponding symmetry element is called roto-inversion axis. A roto-reflection symmetry is another hybrid operation which combines a rotation with reflection. The corresponding symmetry element is called roto-reflection axis. Symmetry elements of different crystal system are listed in Table 2.4.

Table 2.4. Symmetry elements of different crystal system

Crystal system	Cs	Sp	DP	DA	TA	TeA	Hex A
Triclinic	No	No	No	No	No	No	
Monoclinic	0	0	0	1	0	0	0
Orthorhombic	-	-	-	3	0	0	0
Rhombohedral	-	-	-	-	-	1	0
Tetragonal	-	-	-	-	1	-	-
Cubic	1	3	6	6	4	3	0
Hexagonal	-	-	-	-	-	-	1

Cs-Centre of symmetry, SP-straight plane, DP-diagonal plane

DA-Diad axis, TA-Triad axis, TeA-Tetrad axis, Hex A-Hexad Axis

For any crystal there may be a number of *planes of symmetry, a number of axis symmetry* but there could be *only one point of symmetry.*

Symmetry Operations

Symmetry operation refers to any movement of a body, such that after the movement has been carried out, every point of the body is coincident with an equivalent point (or perhaps the same point) of the body in its original position.

The four principal operations carried out for repeating a figure are :

(*i*) Translation operation.
(*ii*) Rotation operation.
(*iii*) Reflection operation across a line in two dimensions or plane in three dimensions.
(*iv*) Inversion through a point.

1.8 Point Groups and Crystal Systems

The sets of symmetry elements found in a particular crystal were designated as *point groups* and these are used for the purpose of classifications. Crystals having the same point groups symmetry belong to the same *crystal class.*

Since the proper and improper rotational axis are restricted to 1, 2, 3, 4 and 6 only so only 32 point groups are possible, and these constitute 32 crystal classes.

Seven Crystal Systems

For a given lattice, there is, in principle, an infinite number of ways in which the three basis vectors *a*, *b* and *c* might be chosen. The choice of the most suitable unit vectors is based on symmetry. If there are no symmetry elements, the three vectors chosen are the shortest ones in three different planes. The morphological study of crystals of different symmetries showed that they could be classified into seven crystal systems based on the presence of certain rotation axes. The results are listed in Table 1.2.

Absence of Five-fold Rotation Axis in Crystals

In the crystal classification shown in Table 1.2, it can be seen that there is no crystal system in which five-fold rotation axis is present. This is due to the fact that in crystals only those rotation axes are allowed which are consistent with the translational symmetry.

centred unit cell. So, again, this does not lead to a new type of tetragonal lattice.

Thus, it can be concluded that is a tetragonal crystal system, only two distinct lattices exist: (*i*) primitive space lattice, and (*ii*) body-centred space lattice.

Space Groups

Just as only certain symmetry operations can be combined with the 5 two-dimensional lattice, the combination of the 14 Bravais lattice with *translations*, *screw axis* and *glide planes* result in 230 different three-dimensional crystal patterns. These are known as *space groups*. Every crystal belongs to one of these space graphs which completely specifies its symmetry.

Every space group is *isomorphic* with a point group and morphological examination of the external symmetry of a crystal will yield only the point group. This means that screw axes gives the some external symmetry as simple rotation axes and the glide planes give the same external symmetry as mirror planes. The actual determination of space group of crystals can be done with the help of diffraction technique.

The determination of the structure of a crystal is simplified if the space group is known because, if the symmetric portion of the unit cell is determined experimentally, the rest of the structure may be obtained through symmetry.

The number of point groups and space groups associated with different seven crystal systems are shown in Table 1.5.

1.11 Crystal Cleavage and Development of its Faces

It is possible to correlate the development of faces in a crystal with the planes that pass through lattice points as shown in Fig. 1.21.

Theoretically, it is possible to draw an infinite number of planes through various lattice points. Any one of these planes can represent a crystal face, however, only a few of these faces are actually observed to develop. It is possible to explain this, qualitatively, on the basis of energy involved in atoms, ions on molecules in a crystal. A regular pattern of these units in a crystal results in the maximum interaction and thus minimum energy. Thus, *a crystal face with a large surface density would result into more interaction vis-a-vis minimum energy and hence would show a greater probability to form a crystal face.*