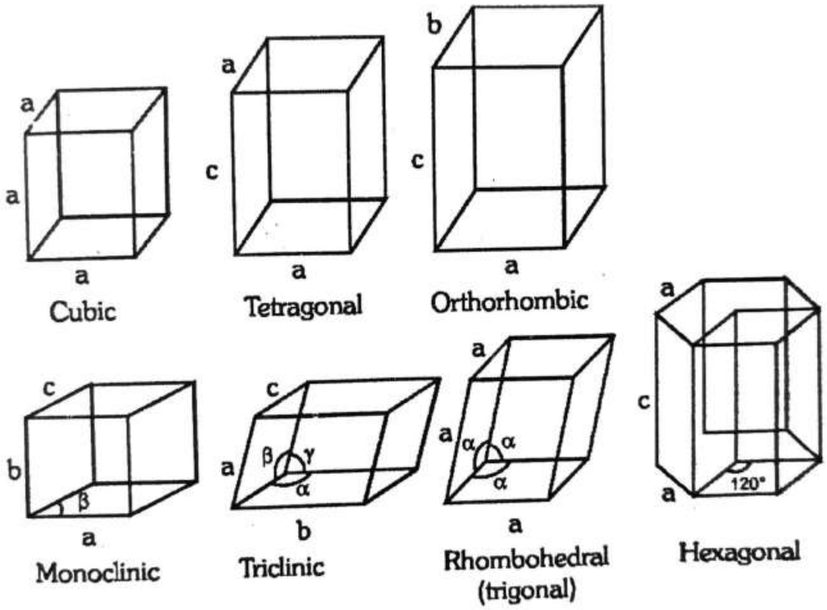
Crystal Structure

Crystal System

On the basis of symmetry, crystals can be divided into 32 classes which can again be grouped on the basis of axial ratio and the axial angles into seven crystal system. The crystals belonging to any system may differ in shape, size and elements of symmetry but their axial characteristics le axial ratio and axial angles will be the same.

The seven crystal system

System	Axial character	Minimum symmetry	Crystal class	Examples
cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Three-fold axis	5	NaCl, Ag, Cu, Au
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	four-fold axis	7	Sn(White), SnO_2, TiO_2
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	two-fold axis	3	S(rhombic), $BaSO_4$, Ga,Fe_3C
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90°, \beta \neq 90°$	two-fold axis	3	S(monoclinic), gypsum
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	three-fold axis	5	calcite, As, Sb, Bi
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	six-fold axis	7	graphite, Zn, Cd
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	none	2	$K_2Cr_2O_7I; CuSO_4, H_2O$



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Unit crystal is composed of atoms, ions or molecules as the primary building units. In a particular crystal system atoms, ions or molecules may have different arrangements. For seven crystal system we have fourteen different types of arrangement of atoms or ions in space resulting into fourteen different types of unit crystals called Bravis Lattices after the name of A. Bravis who in 1848 that all possible spatial arrangements of geometrical points to form unit crystal can be do fourteen ways. The fourteen Bravis Lattice are-

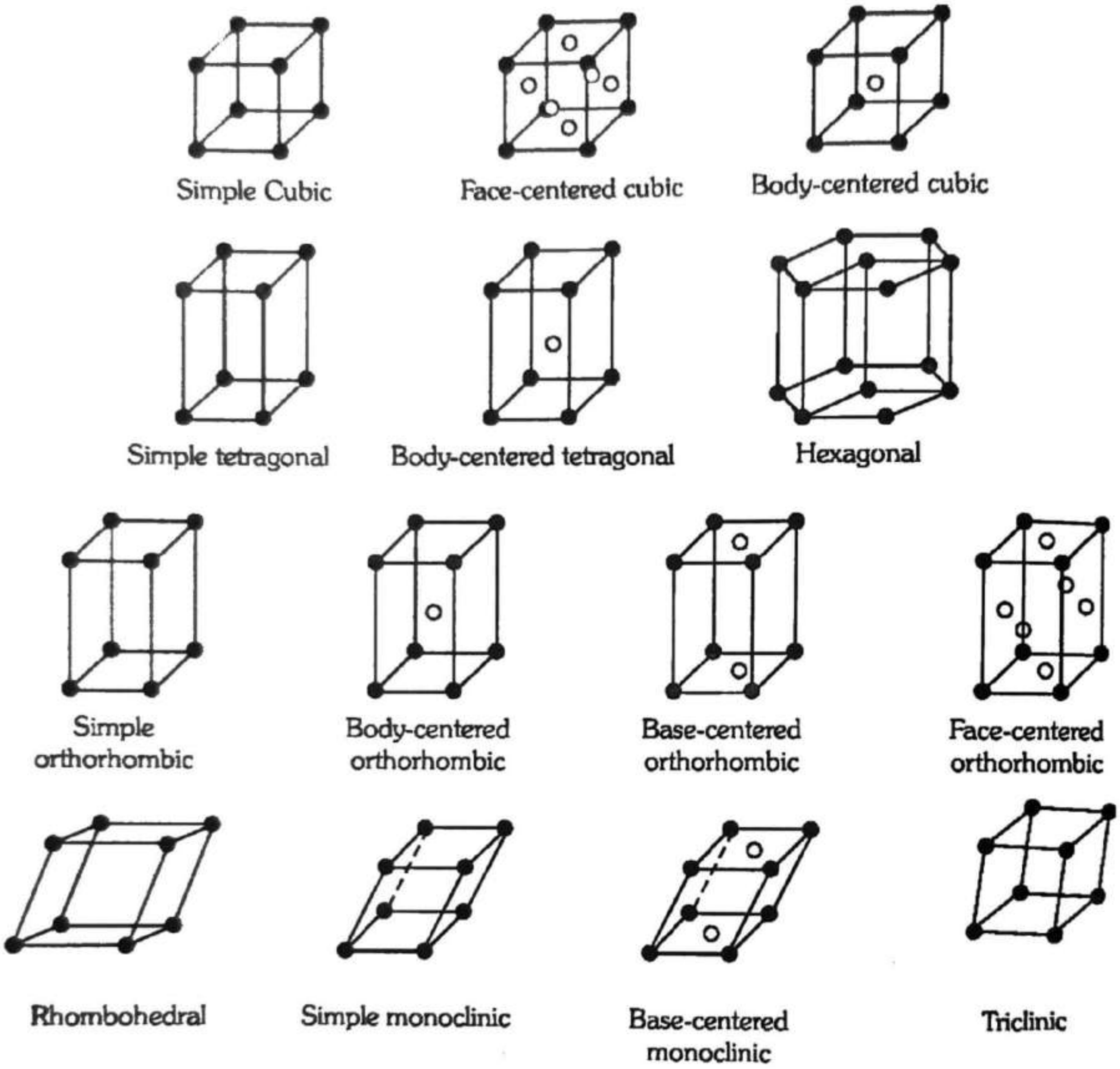

Fig 17: Fourteen Bravis Lattices

Crystal Lattice

If geometrical points are arranged at regular interval in one dimension an one dimensional lattice is produced. When points are arranged regularly in two dimension a two-dimensional lattice is produced. In two dimensional lattice if parallel lines are drawn through the lattice points in two directions (say along x- and y-axis arbitrarily chosen) then the two dimensional space is divided into large number of parallelograms where the shape of the parallelogram will depend upon the choice of drawing of parallel lines. If the geometric points are similarly arranged in three dimension a space lattice is formed. A space lattice is a geometrical abstract figure in imagination. The gap between two adjacent points along three coordinates may or may not be the same. If parallel lines are arbitrarily drawn through these points along three coordinates the space lattice is divided into finite number of identical parallelopipeds. If in place of all the geometric points the fundamental units of the crystal, called basis of the crystal are placed of all the geometric figure is called a crystal lattice. Basis may be an atom or group of atoms or ionpair and it has the same composition with that of the crystalline substance. For example in NaCl crystal the basis is the ion pair $Na^+ Cl^-$.

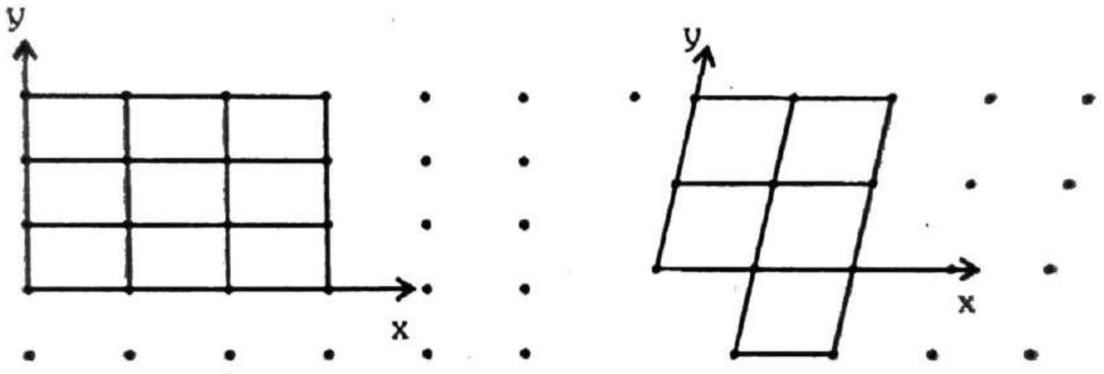

Fig.18: Two dimension regular arrangement of points.

The smallest parallelopiped in the crystal lattice is called a unit cell or unit crystal. The gap between wo adjacent points of an unit cell along x,y, or z-direction along the crystallographic axes is called primitive translation. Primitive translation along three crystallographic axes are represented by a, b and c. Therefore, the side lengths of the unit cells are a, b and c. If the lattice points are present only at the corner of the unit cell, then the unit cell is called primitive unit cell and is represented by P Body centred unit cell contains points at the corner of the unit cell and also at the centre and is labelled 1, Similarly the unit cell may be face-centred labelled F and base or side centred labelled by C. Each corner atom of a unit cell is shared equally by adjacent unit cells. Each face centred atom is shared by two adjacent unit cells and each body centred atom belongs to one unit cell only.

Interplanar Separation between hkl planes

(1) **Two dimensional lattice**: Let us consider hk planes in two dimensional lattice. The plane (hk) cuts the two crystallographic axis at A and C with intercepts a/h and a/k where a is the side length of the unit cell (fig.19). Let us draw perpendicular OD on AC from the origin. OD is the gap between the (hk) planes and is represented as d_{hk} .

The diagonal AC bisects the rectangle OABC.

Area of OABC = a/k. a/h

= a^2 / hk

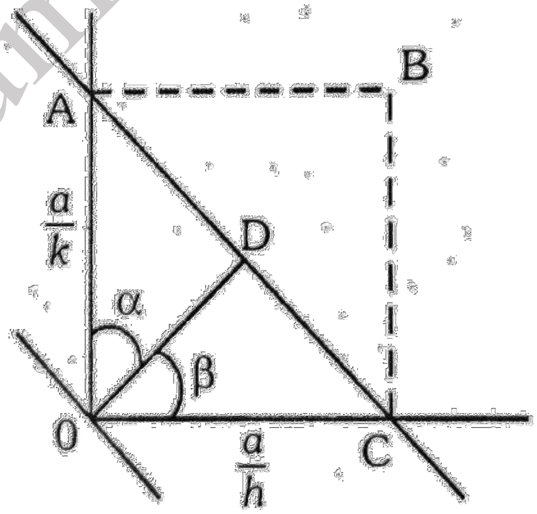

Fig.19: Separation between (hk) planes

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Again $\Delta OAC = \frac{1}{2}\cdot AC \cdot OD = \frac{1}{2}\sqrt{\frac{a^2}{h^2}+\frac{a^2}{k^2}} \times d_{hk}$

$$\therefore \quad \frac{1}{2}\frac{a^2}{hk} = \frac{1}{2}\cdot\frac{a}{hk}(h^2+k^2)^{1/2}d_{hk}.$$

$$\therefore \quad d_{hk} = \frac{a}{\sqrt{h^2+k^2}}$$

For three dimensional lattice $(hk0)$ planes are same as (hk) planes in two dimension. So,

$$d_{hk0} = \frac{a}{\sqrt{h^2+k^2}} \text{ provided the unit cell is a cube.}$$

(II) Three dimensional lattice : Let us consider an (hkl) plane nearest to the origin of the crystallographic axes. Let the plane be ABC and it makes intercepts OA, OB and OC. On the three crystallographic axis. Therefore, $OA = \frac{a}{h}$, $OB = \frac{b}{k}$ and $OC = \frac{c}{l}$ where a, b, c are primary intercepts along three axes. Let us draw perpendicular OD, on the plane ABC from the origin(fig.20). OD represents the perpendicular distance between adjacent hkl planes. Here one plane passes through the origin being parallel to the plane ABC. OD is represented by d_{hkl}. Let OD make angles α, β, γ with the three crystallographic axes.

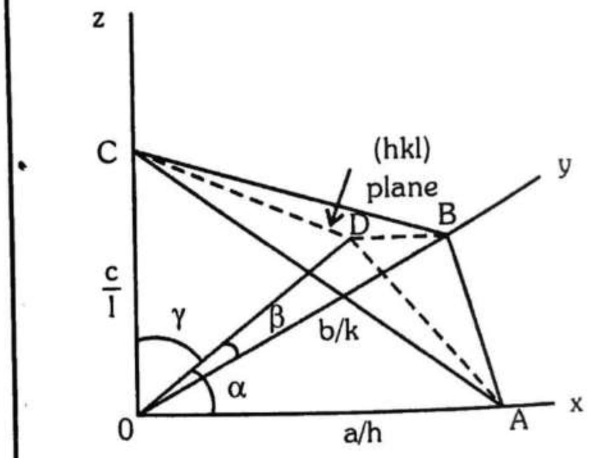

Fig : Interplaner separation (d_{hkl}) between successive (hkl) planes

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Therefore considering the right angled triangle ODA

$$\cos\alpha = \frac{OD}{OA} = \frac{OD}{a/h} = \frac{d_{hkl}}{a/h},$$

Similarly from rt.angled triangle ODB

$$\cos\beta = \frac{OD}{OB} = \frac{OD}{b/k} = \frac{d_{hkl}}{b/k}$$

and from the rt. angled triangle ODC,

$$\cos\gamma = \frac{OD}{c/l} = \frac{d_{hkl}}{c/l}$$

Now, $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

$$\therefore \quad d^2_{hkl} = \left[\frac{1}{(a/h)} + \frac{1}{(b/k)^2} + \frac{1}{(c/l)^2}\right]$$

$$\text{or,} \quad d^2_{hkl} = \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right] = 1$$

$$\text{or,} \quad d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

For cubic crystal $a = b = c$

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

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X- ray diffraction by crystal:

In the first decade of the last century it was realised that X-rays are electromagnetic waves having very short wave lengths probably of the order $10^{-8} \sim 10^{-9}$ cm . But this could not be proved by diffraction experiments since grating having 10^{8} lines per cm could not be prepared. However, in those days it was believed that crystals are formed by the ordered arrangement of atoms or ions in space Latice and they remain in closely packed manner. The interatomic separation can be roughly estimated by taking one mole crystal in the form of a cube and determining its density. If M be the molar mass of the substance and d be the density of the crystal, then the volume of the crystal = M/d Since the Crystal is taken in the form of a cube, the side length of the cube $(M/d)^{1/3}$. If the cubic lattice is formed by the atoms, then the $N_0^{1/3}$ atoms are arranged along any edge. So, the interatomic separation=$(M/d\ N_0)^{1/3}$

For NaCl crystal, $\rho = 2.173 gcm^{-3}$

So, the average gap between Na^+ ions = $\sqrt[3]{\frac{58.5}{2.173\times 6.022\times10^{23}}} = 3.55\times10^{-8}$ cm

This suggests that the distances between adjacent atoms in a crystal is of the order of 10^{-8}.So, the rows of atoms in a crystal plane can act as natural three-dimensional grating where 10^{8} limes are present per cm. In 1912 Von Laue suggested that due to ordered arrangement of atoms in crysta a crystal can be used for diffraction of X-ray. When X-rays fall on a crystal diffracted beams produced and analysis of the diffracted beam would enable one to determine the wave-length of X-ray. Laue showed theoretically that when a beam of X-ray falls on a crystal a number of diffracted beams are arranged symmetrically around the primary beam (Fig. 21)

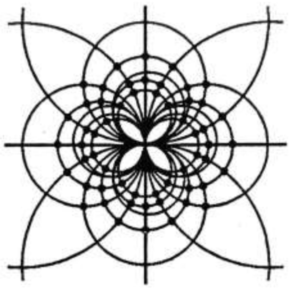

Fig. 21:Theoretical diffraction pattern (Laue)

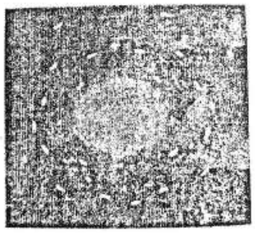

Fig. 22: Laue diagram

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If a photographic plate is placed behind the crystal, then the main X-ray beam and the diffracted beams will strike the plate and on development, the incident X-ray beam will produce a bright spa and surrounding the bright spot other spots are obtained symmetrically surrounding the main bright spot. Such photograph of diffracted beams is called Laue photograph (Fig. 22).

Laue photograph was difficult to interpret at that time since X-rays used contains radiations different wave lengths and exact arrangement of atoms in crystal was not known.

W.H. Bragg and W. L. Bragg, father and son developed a simple method to correlate interatomic spacing in the crystal with the wave length of X-ray used following diffraction of X-ray by the atoms in the crystal.