UNIT- II

BONDING IN SOLIDS and X-RAY DIFFRACTION

The strength of chemical bond is measured by the energy required to dissociate a solid into isolated atoms or molecules and the energy is generally known as cohesive Energy. For example it is 7.8 eV/mole, for NaCl and 0.078 eV/~~atom~~ atom for argon. The large difference in the cohesive energy indicates that chemical bonds of very different nature are involved.

* Inter Atomic Forces and Types of Bonding

The interatomic forces exist amongst the atoms of a crystal and are responsible for holding the atoms together to form solid structures.

(a) Some attractive forces must be present between the atoms and molecules of a solid which hold them together.

(b) Some repulsive forces must also be present between the atoms or molecules since a large external pressure is needed to compress a solid to any appreciable extent.

Consider a pair of atoms which is capable of forming a stable chemical bond in the solid state. When seperated by a large distance from each other, each atom of the pair may be considered to be free from the influence of the other atoms and hence the potential energy, U, of the system may be arbitrarily taken as zero. As the distance between the atoms is decreased, they start interacting with each other resulting in a change of potential energy of the system. The atoms exert the following two types of forces on one another:

(i) The attractive forces arising from the interaction of the negative electron cloud of one atom with the positive nuclear charge on the other. Its magnitude is proportional to some power of the interatomic distance r.

(ii) The repulsive forces which come into existance when the distance between the atoms is decreased to such an extent that their electronic clouds start overlapping. The repulsion between the positively charged nuclei also contributes to the repulsive forces. The magnitude of the total repulsive force is also proportional to some power of r.

Since the attractive forces decreases the potential energy of the system and the repulsive forces increase it, the net energy of the system is equal to the algebric sum of these two categories and is written as

$$U = U_{att.} + U_{rep.}$$

$$U = -\frac{A}{r^m} + \frac{B}{r^n} \qquad \text{———} (1)$$

where A, B, m and n are constants which depend on the nature of the participating atoms; A and B are known as attraction and repulsion constants respectively. The Eq. (1) indicates that the magnitude of both attractive and repulsive energies increase with decrease in interatomic distance. Generally, $n > m$ which indicates that the increase in repulsive energy is faster than the increase in attractive energy particularly for very small values of interatomic distance. The repulsive forces are known as short range forces.

The variations of the attractive energy, repulsive energy and total energy versus interatomic distance are shown in below Fig. 1.

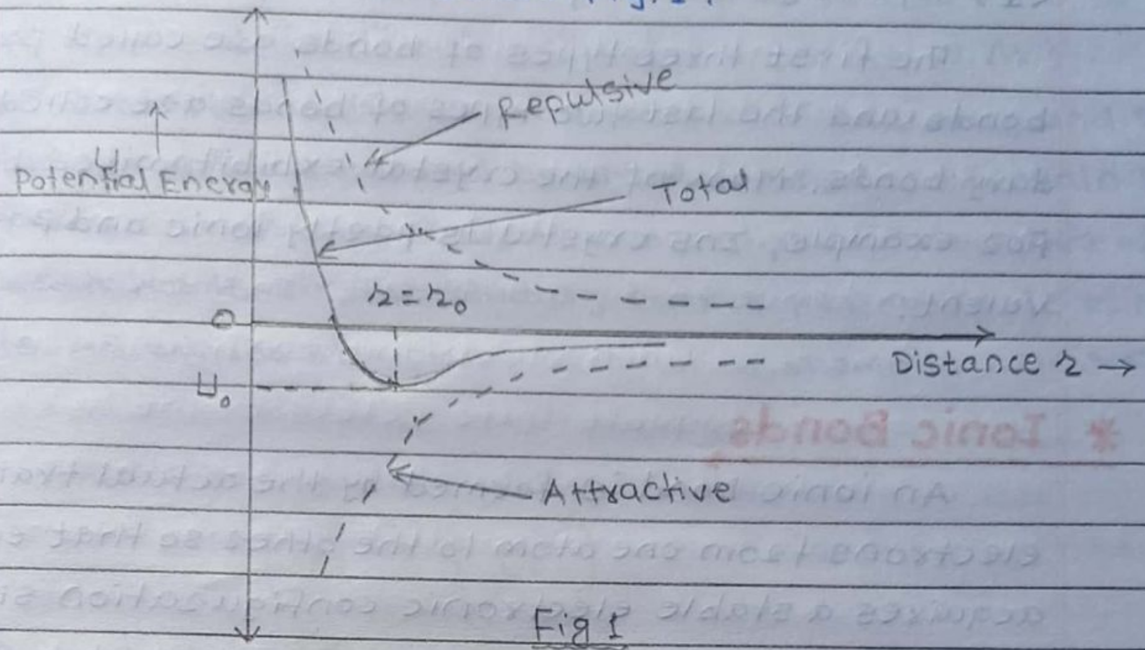


Fig I

The total energy first decreases gradually as the atoms approaching to each other, attains a maximum value for the interatomic distance r equal to r_0 and then increases rapidly as the value of r is decreased further. The interatomic distance r_0 at which the energy of the system becomes minium is known as the equilibrium distance and signifies the formation of a stable bond.

The nature of the crystal formed depends upon the nature of interactions between atoms or bonds. These bonds may be broadly classified into the following five main categories:

⟨I⟩ Ionic Bonds (transfer of valance electrons)

Ex- Nacl, Cscl, Cao etc

⟨II⟩ Covalent Bonds (Sharing of valance electrons)

Ex- Ge, Si, Ga, As, diamond etc

⟨III⟩ Metallic Bonds (free nature of valence electrons)

Ex- Ag, Cu, Na, Ni etc

⟨IV⟩ Van de Waals forces (electrons remain associated with original molecules), as in solid nitrogen

<V> Hydroge Bonds, as in ice

The first three types of bonds are called primary bonds and the last two types of bonds are called secondary bonds. Many of the crystal exhibit mixed bonding. For example, ZnS crystal is partly ionic and partly covalent.

* Ionic Bonds

An ionic bond is formed by the actual transfer of electrons from one atom to the other so that each atom acquires a stable electronic configuration similar to the nearest inert gas atom. The atom which loses an electron becomes electropositive and one which gains an electron becomes electronegative. The ions arrange themselves in such a way that the coulomb's attractive forces among the oppositely charged ions dominate over the Coulomb's repulsive forces among the ions of the same sign. Thus the source of cohesive energy which binds the ions together is mainly the coulomb's electrostatic interaction. The crystals resulting from this type of bonding are called ionic crystals. The cohesive energy of the ionic crystal is, therefore, quite large, it is of the order of 5 to 10 eV.

A good example of ionic crystals is the crystal of NaCl. The electronic configurations of Na and Cl atoms are as follows -

$Na : 1s^2\ 2s^2\ 2p^6\ 3s^1$

$Cl : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

After the transfer of an electron from 3s orbital of Na to 3P orbital of Cl, the configurations becomes

$Na^+ : 1s^2 2s^2 2p^6$ (same as Ne)

$Cl^- : 1s^2 2s^2 2p^6 3s^2 3p^6$ (same as Ar)

Each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions to maintain the charge neutrality. Thus the co-ordination number of each ion is six. The binding energy per molecule of NaCl is 7.8 eV. The structure of NaCl is shown in below Fig. 1.

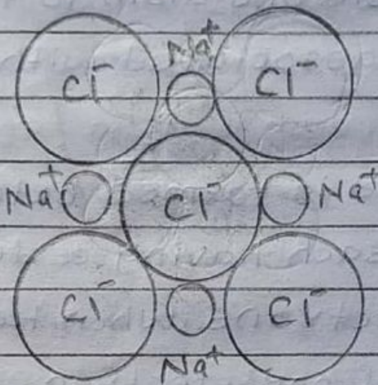


Fig. 1

Some other examples of ionic crystals are LiF, KCl, Al_2O_3 etc

Characteristics of Ionic Bond

<1> Ionic crystals have large binding energy so these are hard and have relatively high melting and boiling points.

<2> They are transparent to visible light.

<3> At normal temperatures, these are poor conductors of electricity but the conductivity increases with increase in temperature.

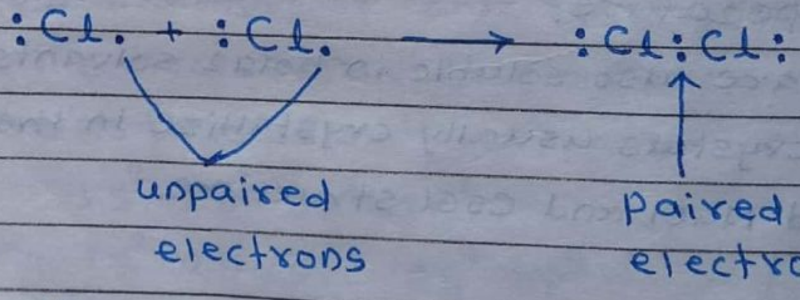
<4> These are also soluble in polar solvants such as water.

<5> Ionic crystals usually crystallize in the relatively close-packed NaCl and CsCl structure.

* Covalent Bonds

A covalent bond is formed by an equal sharing of electrons between two neighbouring atoms each having incomplete outermost shell. The atoms do so in order to acquire a stable electronic configuration in accordance to the octet rule. In the covalent bond the atoms have such electronic configurations that they cannot complete their octets by the actual transfer of electrons from one atom to the other. Hence there is no charge associated with any atom of the crystal.

A covalent bond is formed between similar or dissimilar atoms each having a deficiency of an equal number of electrons. When two atoms, each having a difficiency of one electron, come so close that their electronic shells start overlapping and each atom transfers its unpaired electron to the common space between the atoms. The sharing is effective if the shared electrons have opposite spins. In such a case the atoms attract each other and a covalent bond is formed. The formation of a covalent bond between two chlorine atoms to produce Cl_2 molecule is as below



Similarly, a water molecule is produced because of the formation of covalent bonds between oxygen atom and two hydrogen atoms.

$$2H\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\cdot \longrightarrow H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$$

If each participating atom has deficiency of two electrons, the atoms may combine to form a double covalent bond. The formation of oxygen molecule is an example of double covalent bond. In this case, each atom contributes two electrons to the common space.

Characteristics of covalent Bond

<1> The covalent bond is a strong bond
<2> The covalent bonds are strongly directional in character.
<3> The crystals having purely covalent bonding are very hard and brittle.
<4> These have high melting and boiling points.
<5> These exhibit low conductivity at ordinary temperature which increases slightly with increase in temperature.
<6> They are dielectrics.
<7> covalent crystals are typically semiconductors.
<8> They are transparent to long wavelengths but opaque to shorter wavelengths.

The other examples of covalent crystals are Si, Ge, α-Sn, etc.

* Metallic Bonds

Metallic bond is formed by the partial sharing of the valence electrons by the neighbouring atoms. Unlike the case of covalent bond, the sharing in metallic bond is not localized. Hence metallic bond may also be considered as delocalized or unsaturated covalent bond.

In metallic crystals free electrons are present. The outstanding characteristic of metal is its high electrical conductivity. The atoms in the metals contribute their valence electrons to form a common pool of electrons which has freedom to move any where in the framework of positive ion cores. This common pool of electrons is also known as the free electron cloud or gas and acts as a mobile glue to bind all the ion cores together through electrostatic attraction. The bond so formed is called the metallic bond.

Consider the case of sodium which is an alkali metal. Each sodium atom has an electronic configuration of $1s^2 2s^2 2p^6 3s^1$, i.e it contains one unpaired electron in the 3s orbital. This electron is loosely held in sodium and may be called valence or conduction electron. When two sodium atoms approach each other, their 3s orbitals being to overlap and one electron-pair bond is formed provided the electrons have opposite spins. Now, the 3s orbital being full, if a third sodium atom approaches the pair, the valence electron of this atom may occupy the 3p state without violating the Pauli's exclusion principle This is favoured by the fact that the energy difference between 3s and 3p orbitals is very small. Thus the third sodium atom can also be form an electron-pair bond, with either of the two Na atoms.

The below Fig.1 shows the wave functions of the valence electron in a sodium crystal. The wave function is not disturbed near the ion core but in the outer region it is considerably flattened and squeezed in the neighbouring valence electrons. Since the distribution of electrons in a vol-

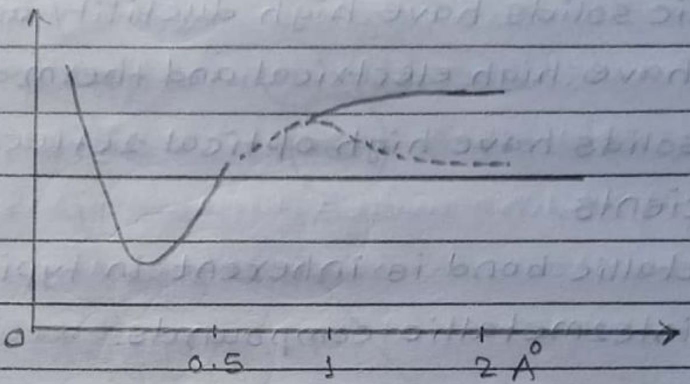


Fig.1 wave function of valence electron 3s wave function.

ume element $4\pi r^2 dr$ is given by $|\psi|^2 4\pi r^2 dr$, over 90% of the electron distribution is in this flat region. The potential energy of the electron is obviously lowered because the average electron distribution is now close to the nucleus. The kinetic energy being proportional to

$$\left|\frac{h}{2\pi}\frac{\partial\psi}{\partial r}\right|^2$$

is also reduced because of a smaller ~~∂r~~ $\left(\frac{\partial\psi}{\partial r}\right)$ in the flattened region. The reduction in the total energy constitutes a bond between atoms in a metallic crystal

Due to delocalized nature of valence electrons, the metallic bond is much less directional than covalent bond. Hence metals prefer to form close-packed structures, i.e either fcc or hcp structures. There exist certain exceptional cases too. For example, alkali metals like Na and K form bcc structure which is ~~tr~~ attributed to their low melting points.

Characteristics of Metallic crystals:

<1> The metallic bond is weaker than ionic or covalent bond.

<2> The binding energy ranges from 1 to 5 ev per bond

<3> The melting and boiling points of metallic solids are lower than ionic or covalent solids.

<4> Metallic solids have high ductility and malleability.

<5> These have high electrical and thermal conductivities.

<6> These solids have high optical reflection and absorption coefficients.

<7> The metallic bond is inherent in typical metals and many intermetallic compounds.

* Hydrogen Bond

When a covelent bond is formed between a hydrogen atom and a highly electronegative atom, such as an atom of oxygen, fluorine, chlorine, etc., the shared electron pair gets attracted more towards the electronegative atom than the hydrogen atom. Thus the electronegative atom acquires a slight negative charge and the hydrogen atom acquires an equal amount of positive charge. The molecule so formed is said to be polarized behaves like a permanent dipole. A number of such dipoles get attracted to one another due to the coulombic force of attraction. The interaction between the oppositely charged ends of permanently polarized molecules each containing a hydrogen atom is called the hydrogen bond.

The positively charged hydrogen atom can interact more strongly with the negative ends of other molecules as compared to any other positively charged atom. Thus hydrogen bonds are stronger than dipole bonds.

The exist~~ange~~ence of hydrogen bonding among water molecules is illustrated in below Fig.1

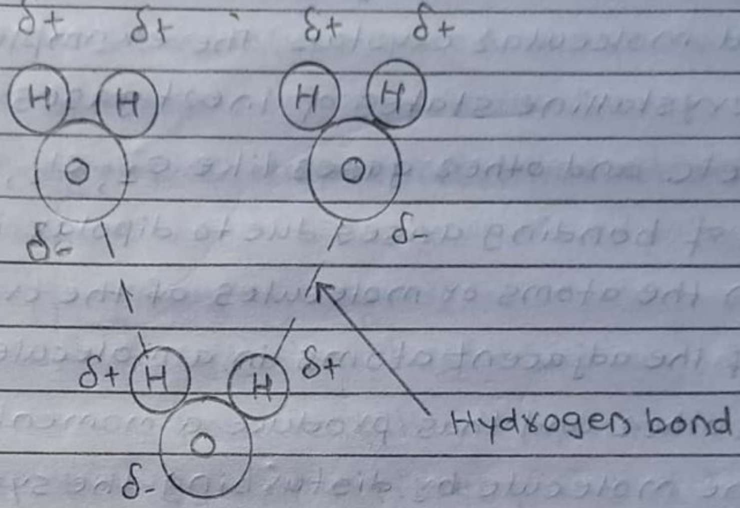


Fig.1. Hydrogen bonding among water molecules

Characteristics of Hydrogen Bond

⟨1⟩ Materials exhibiting hydrogen bonding possess high melting and boiling points compared with molecular solids.

⟨2⟩ The binding energy of water or ice is about 0.5 ev.

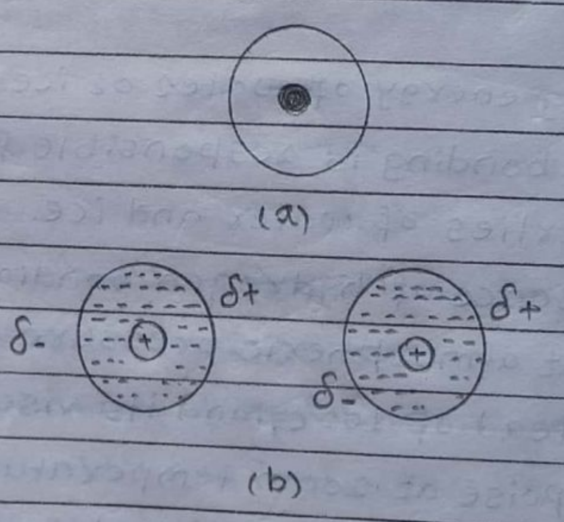
⟨3⟩ Hydrogen bonding is responsible for the striking physical properties of water and ice.

⟨4⟩ In the absence of hydrogen bonding, the boiling point of water at atmospheric pressure would have been -80°c instead of 100°c, and its viscosity much lower than 0.01 poise at room temperature.

⟨5⟩ Hydrogen bond is directional in character.

* Van der Waal's Bonds

Van der Waal's bonding exist in atoms or molecules which have their outermost shells completely filled and hence have no tendency to gain, lose or share valence electrons with other atoms or molecules in the solid. The crystals resulting from this type of bonding are called molecular crystals. The examples of such solids are crystalline states of inert gases, such as He, Ne, Ar, etc and other gases like O_2, Cl_2, CO_2, CH_4, etc. This type of bonding arises due to dipolar interaction between the atoms or molecules of the crystal. The electrons of the adjacent atoms in a molecule tend to repel each other and thus produce a momentary polarization in the molecule by disturbing the symmetry of the electronic distribution. Due to the disturbance in the electron cloud of an atom, the centres of the positive and negative charge distributions no more coincide and an electronic dipole with a non-zero dipole moment is generated as shown in below Fig. 1.



(a)

(b)

Fig. 1

This dipole is not a parmanent dipole and keep oscillating with the movement of electron cloud around the nucleus. The electric field originating from this imbalance of charge induces a dipole moment in a neighbouring atom in such a way that atom gets attracted to it. Similarly, the electric field of the second dipole produces another dipole ~~induced~~ by incuding dipole moment in a neighbouring atom, and so on. This type of dipole induced dipole interaction is called Van der Waals bond or dispersion bond.

The energy of dispersive interaction is given by

$$U_d = -\frac{3}{4}\alpha^2 \cdot E_i \frac{1}{r^6}$$

where α is the polarizability of particles, E_i is the ionization energy of particles, and r is the seperation of particles.

Characteristics of Van der Waals Bonds

⟨1⟩ The Van der Waals bond is the weakest bond of all the types.

⟨2⟩ The structures formed by this bonding are poorly stable.

⟨3⟩ These bonds have low melting points and boiling points.

⟨4⟩ It is non-directional in character.

⟨5⟩ Due to these bonds the inert gases can be liquified at very low temperatures.

⟨6⟩ The energy released during the formation of Van der Waals bonds is of the order of 0.1 eV per bond only.

⟨7⟩ These have low mechanical strength and deformability.

(8) These solids are also poor conductors of heat and electricity.

(9) These solids are transparent to electromagnetic radiation up to the far ultraviolet region.

* X-Ray Diffraction

When an atomic electron is irradiated by a beam of monochromatic x-rays, it start vibrating with a frequency equal to that of the incident beam. since an accelerating charge emits radiations, the vibrating electrons present inside a crystal become source of secondary radiations having the same frequency as the incident x-rays. These secondary x-rays spread out in all possible directions. The phenomenon may also be regarded as scattering of x-rays by atomic electrons. If the wavelength of incident radiations is quite large compared with the atomic dimensions, all the radiations emitted by electrons shall be in phase with one another. The incident x-rays have the same order of wavelength as that of the atomic dimensions hence the radiations emitted by electrons are, in general, out of phase with one another. These radiations may undergo constructive or distructive interference producing maxima or minima in certain directions.

* The Bragg's Law

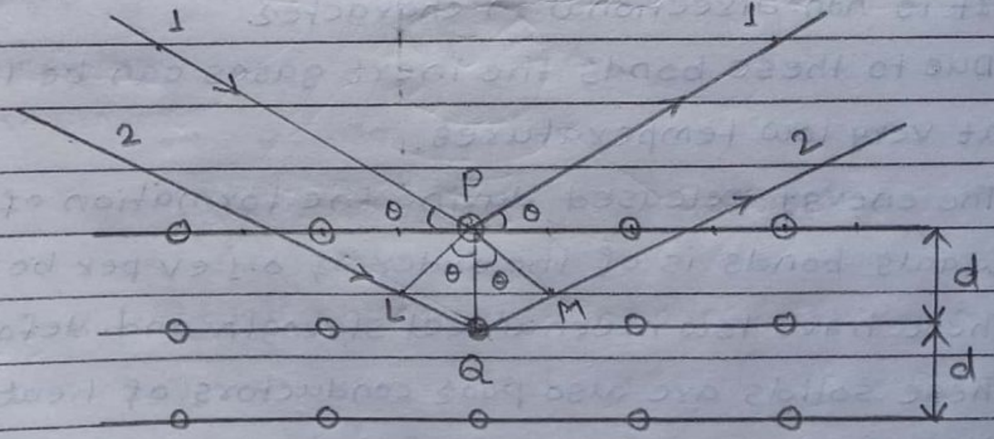


Fig. 1 Bragg's reflection of x-rays from the atomic planes.

In 1912, W.H. Bragg and W.L. Bragg put forward a model which generates the conditions for diffraction in avery simple way. They pointed that a crystal may be divided into various sets of parallel planes. Braggs derived a simple mathematical relationship which serves as a condition for the Bragg reflection to occur. This condition is known as the Bragg's law.

Consider a set of parallel atomic planes with interplanar spacing d and having Miller indices (h,k,l). Let a parallel beam of x-rays of wavelength λ be incident on these parallel planes at a glancing angle θ. Consider two such rays 1 and 2 which strikes the first two planes and get partially reflected at the same angle θ in accordance with the Bragg's treatment as shown in above Fig 1. Let PL and PM be the $\perp$rs drawn from the point P on the incident and reflected portions of ray 2 respectively. The path difference between rays 1 and 2 is, given as

$$(LQ + QM)$$

From triangle PLQ	From ΔPMQ
$\sin\theta = \frac{LQ}{PQ}$	$\sin\theta = \frac{QM}{PQ}$
$\therefore \sin\theta = \frac{LQ}{d}$ $(\because PQ = d)$	$\sin\theta = \frac{QM}{d}$ $(\because PQ = d)$
$\therefore LQ = d\sin\theta$	$\therefore QM = d\sin\theta$

$$\therefore \text{path difference} = LQ + QM$$
$$= d\sin\theta + d\sin\theta$$
$$= 2d\sin\theta$$

For constructive interference of rays 1 and 2, the path difference must be an integral multiple of wavelength λ i.e.

$$\boxed{n\lambda = 2d\sin\theta}$$

where n is an integer. This equation is called the Bragg's law. The diffraction takes place for those values of d, θ, λ and n which satisfy the Bragg's condition.

The intensity of the reflected lines decreases with increase in the value of n or θ. The highest possible order is determined by the condition that $\sin\theta$ cannot exceed unity. Also, since $\sin\theta \leq 1$, λ must be $\leq d$ for Bragg reflection to occur. Taking $d \approx 10^{-10}$ m, we obtain $\lambda \leq 10^{-10}$ m or 1 Å. X-rays having wavelength in this range are preferred for analysis of crystal structures.

* Laue's Method

An experimental arrangement used to produce Laue's patterns is shown in below Fig. 1.

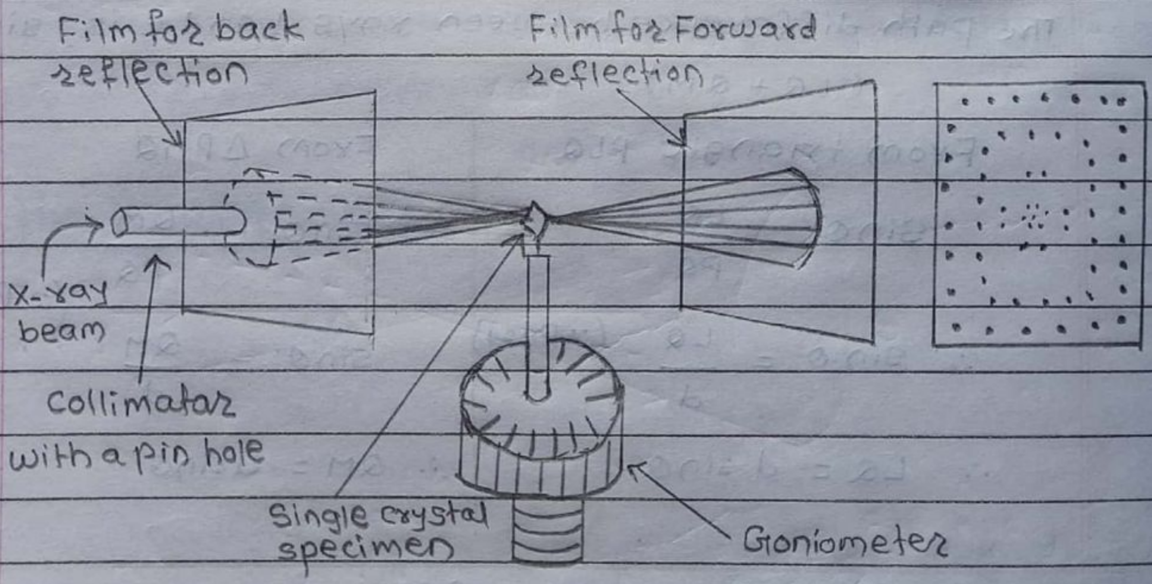


Fig. 1 A flat plate camera used in Laue's diffraction method

It consists of a flat plate camera which contains a collimator with a fine hole to obtain a very fine beam of X-rays. The sample is placed on a goniometer which can be rotated to change the orientation of the single crystal. Two flat photographic films are used, one for receiving the transmitted diffracted beam and the other for receiving the reflected diffracted beam for back reflection experiments. such experiments are performed particularly when there is excessive absorption of x-rays in the crystal

Initially, a single crystal specimen having dimensions of the order of 1mm x 1mm x 1mm is held stationary in the path of white x-rays having wavelengths ranging from 0.2 to 2Å. Since the crystal contains a number of sets of parallel atomic planes with different interplanar spacings, diffraction is possible for certain values of λ and d which satisfy the Bragg's condition. Thus diffraction spots are produced on the photographic films as shown in above Fig. The crystal can be rotated with the help of goniometer to change its orientation with respect to the incident beam. By doing so, the diffraction condition may be satisfied for a new set of atomic planes and hence a different type of pattern may be obtained on the photographic film. The symmetry of the crystal is reflected in each pattern

The Laue's method is mostly used to determine the crystal symmetry. The symmetry of the Laue's pattern also helps to orient the crystals for various solid state experiments. Another application of the Laue's method is the determination of imperfections or strains in the ~~crys~~ crystals. An imperfect or strained crystal has atomic planes which are not exactly plane but are slightly curved.

sharp diffraction spots

streaking on Laue's photographs is called *asterism*.

2.3.2 Rotating Crystal Method

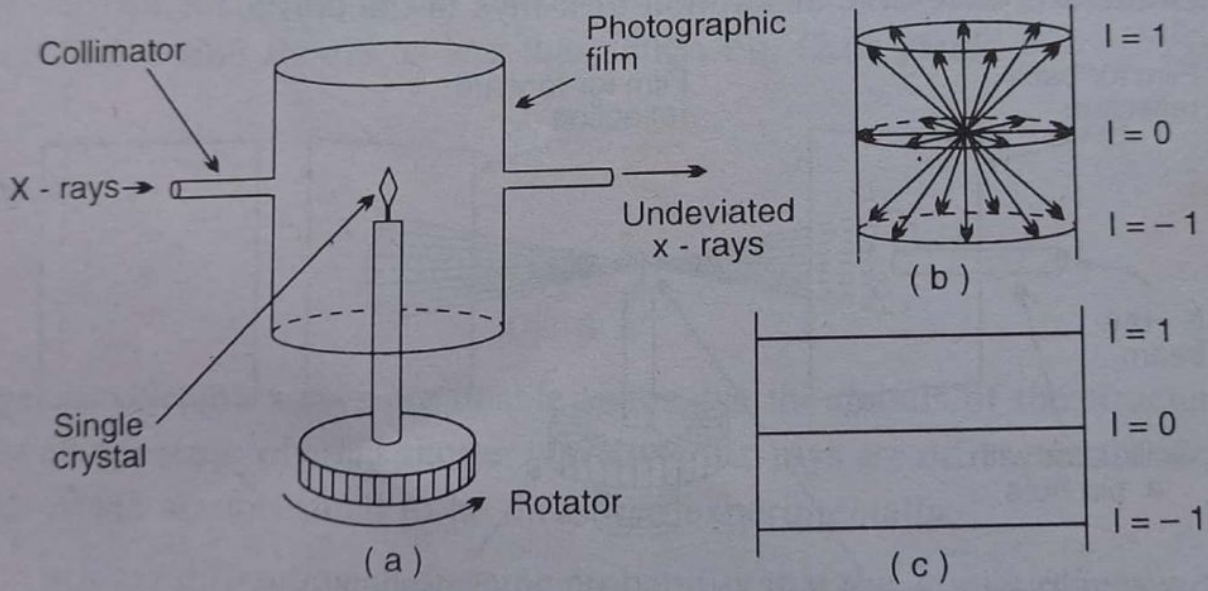


Fig. 2.6. *(a) Apparatus for rotating crystal method*
(b) Cones of scattered x-rays corresponding to reflections from (hkl) planes.
(c) Layer lines produced after flattening the photographic film.

In this method, a monochromatic beam of x-rays is incident on a single crystal mounted on a rotating spindle such that one of its crystallographic axes coincides with the axis of rotation which is kept perpendicular to the direction of the incident beam. The single crystal having dimensions of the order of 1mm is positioned at the centre of a cylindrical holder concentric with the rotating spindle as shown in Fig. 2.6. A photographic film is attached at the inner circular surface of the cylinder.

The diffraction takes place from those planes which satisfy the Bragg's law for a particular angle of rotation. The planes parallel to the axis of rotation diffract the incident rays in a horizontal plane. However, reflections cannot be observed for those planes which always contain the incident beam. The planes inclined to the rotation axis produce reflections above or below the horizontal plane depending upon the angle of inclination. The horizontal lines produced by diffraction spots on the photographic film are called *layer lines.* If the crystal is positioned such that its **c**-axis coincides with the axis of rotation, all the planes with Miller indices of the type ($hk0$) will produce the central layer line. Likewise, the planes having Miller indices of the type ($hk1$) and ($hk\bar{1}$) will produce the layer lines above and below the central line respectively, and so on. These layer lines are shown in Fig. 2.6c. The vertical spacing between the layer lines depends on the distance between the lattice points along the **c**-axis. Hence the distance **c** can be measured from the photographic film. Similarly, one can determine the translation vectors **a** and **b** on mounting the crystal along **a** and **b** axes respectively. Thus the dimensions of the unit cell can be easily determined.