VIII. BRAGG'S LAW

Consider a ray PA reflected at atom A in the direction AR from plane 1 and another ray QB reflected at another atom B in the direction BS. Now from the atom A, draw two perpendiculars AC and AD on QB and BS respectively. The two reflected rays will be in phase or out of phase depending on the path difference. When the path difference (CB + BD) is a whole wavelength (λ) or multiple of whole wavelength ($n\lambda$), then the two rays will reinforce each other and produce an intense spot. Thus condition of reinforcement is:

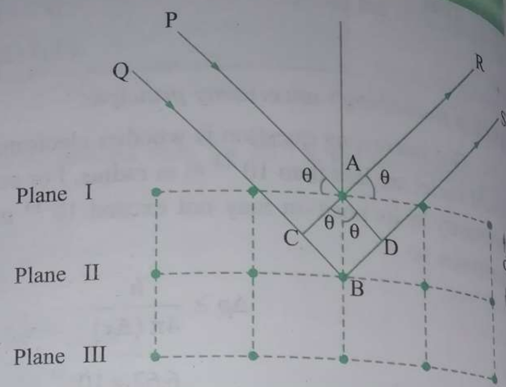


Fig. 5.5 Reflection of X-rays from lattice planes in a crystal

$$CB + BD = n\lambda$$

From Fig. (5.5), we have

$$CB = BD = d \sin \theta$$

where, θ is the angle between the incident ray and the planes of reflection (*glancing angle*). Therefore,

$$2d \sin \theta = n\lambda \tag{5.11}$$

where, d is the interplanar spacing of planes and $n = 1, 2, 3, \ldots$ stands for first order, second order, third order, ... maxima respectively. Equation (5.11) is known as Bragg's law. Different directions in which intense reflections will be produced can be obtained by giving different values to θ, *i.e.*,

for first maximum, $\sin \theta_1 = \dfrac{\lambda}{2d}$

for second maximum, $\sin \theta_2 = \dfrac{2\lambda}{2d}$

for third maximum, $\sin \theta_3 = \dfrac{3\lambda}{2d}$ and so on.

It should be remembered that the intensity goes on decreasing as the order of spectrum increases.

Thus we see that when a beam of monochromatic X-rays falls on a crystal, each atom becomes a source of scattering radiations. It has already been mentioned that in a crystal there are certain planes which are particularly rich in atoms. The combined scattering of X-rays from these planes can be looked upon as reflections from these planes. Generally, the *Bragg scattering* is regarded as *Bragg reflection*, and hence are known as *Bragg planes*. At certain glancing angles, reflections from these set of parallel planes are in phase with each other, and hence they reinforce each other to produce maximum intensity. For other angles, the reflections from different planes are out of phase, and hence they reinforce to produce either zero intensity or extremely feeble intensity.

XII. CORRECTION FOR BRAGG'S EQUATION

Let us consider the surface layer of a crystal on which an X-ray of wavelength λ (in air) is incident. Suppose θ is the glancing angle, and we take the layer immediately below the surface, the glancing angle at that layer will not θ but θ'.

The Bragg's law for the reflection at that layer is:

$$n\lambda' = 2d \sin \theta' \quad (5.1$$

where, λ' is the wavelength in the crystal.

The refractive index μ can be written as:

$$\boxed{\begin{aligned} \mu &= \frac{\sin i}{\sin r} = \frac{\cos\theta}{\cos\theta'} = \frac{\lambda}{\lambda'} \quad (5.1 \\ \text{or} \qquad \lambda' &= \frac{\lambda}{\mu} \end{aligned}}$$

Substituting this in the above equation (5.14), we get:

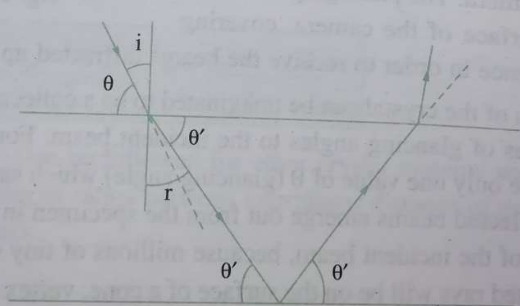


Fig. 5.8 Refraction of X-rays on layers of a crystal

Source: Solid state Physics From S.O. Pillai

$$n\frac{\lambda}{\mu} = 2d\,[1 - \cos^2\theta']^{1/2}$$

$$n\lambda = 2d\,\mu\,[1 - \cos^2\theta']^{1/2}$$
$$= 2d\,[\mu^2 - \mu^2\cos^2\theta']^{1/2}$$
$$= 2d\,[\mu^2 - \cos^2\theta]^{1/2}$$
$$= 2d\,[\mu^2 - (1 - \sin^2\theta)]^{1/2}$$
$$= 2d\,[\mu^2 - 1 + \sin^2\theta]^{1/2}$$

$$= 2d\sin\theta\left[1 - \frac{(1-\mu^2)}{\sin^2\theta}\right]^{1/2}$$

The value of $(1 + \mu)$ is approximately 2 as is μ nearly 1.

Thus
$$n\lambda = 2d\sin\theta\left[1 - \frac{1}{2}\times 2\,\frac{(1-\mu)}{\sin^2\theta}\right]$$

$$= 2d\sin\theta\left[1 - \frac{(1-\mu)}{\sin^2\theta}\right]$$

Let
$$\delta = (1 - \mu)$$

$$n\lambda = 2d\sin\theta\left[1 - \frac{\delta}{\sin^2\theta}\right] \quad (5.16)$$

We know,

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

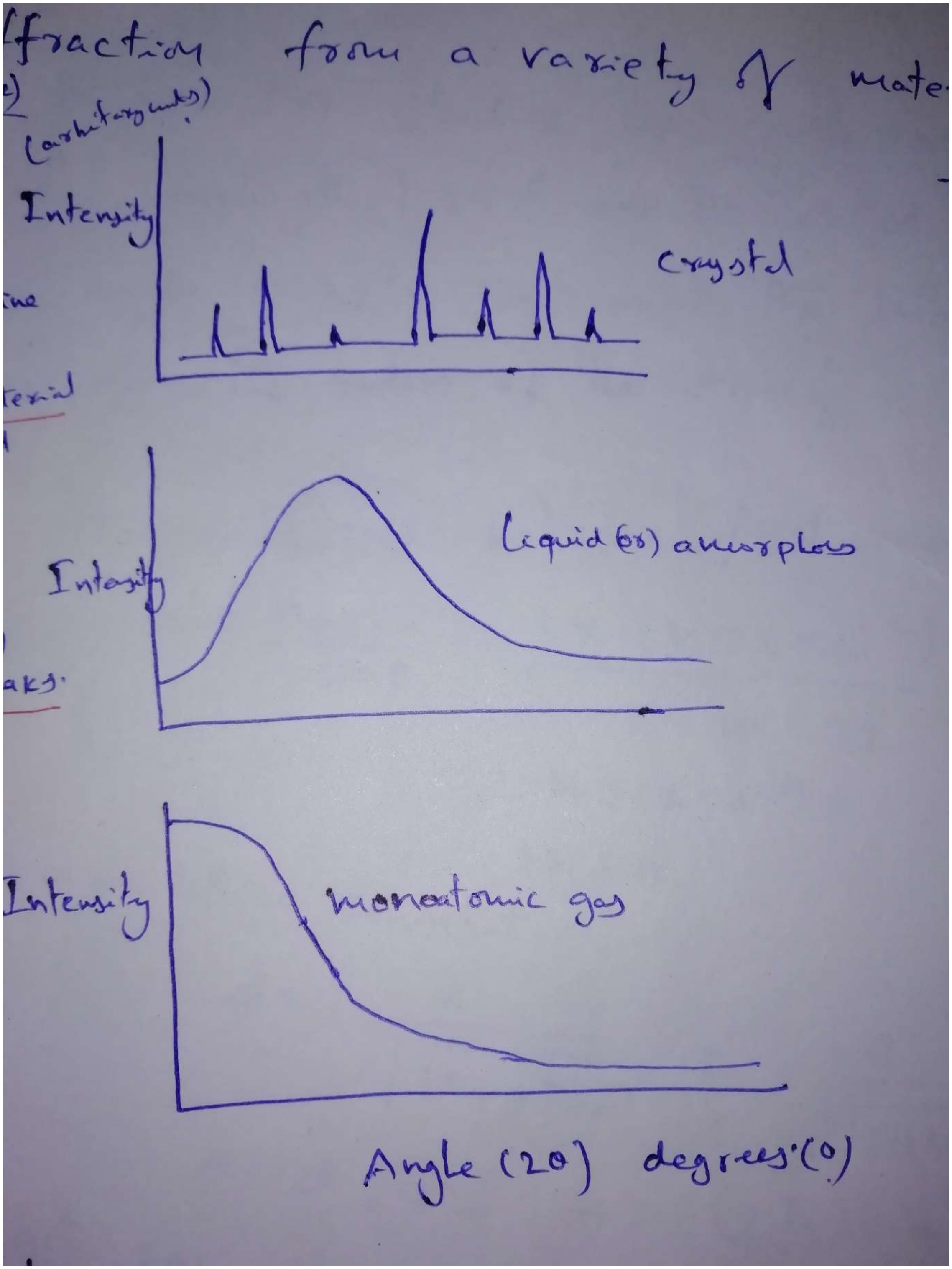
$$\sin^2\theta = \frac{n^2\lambda^2}{4d^2}$$

Substituting this in equation (5.16), we get:

$$\boxed{n\lambda = 2d\sin\theta\left[1 - \frac{4\delta d^2}{n^2\lambda^2}\right]} \quad (5.17)$$

Hence, equation (5.17) is *modified Bragg's equation.* The correction term $\frac{4d^2\delta}{n^2\lambda^2}$ decrease as increases for a given value of λ. Thus, Bragg's ordinary equation $\eta\lambda = 2d\sin\theta$ holds good for high values of n.

XRD for amorphous and crystalline material



X. POWDER CRYSTAL METHOD

The Laue's and Bragg's techniques for the investigation of crystal structures can be applied only if single crystals of reasonable size are available. But in general, large crystals, without fault are difficult to obtain. Therefore, Debye-Scherrer adopted a different technique. The specimen was taken in the form of a well powdered sample of the crystal in a thin glass capsule. The experimental arrangement is shown in Fig. 5.7(*a*).

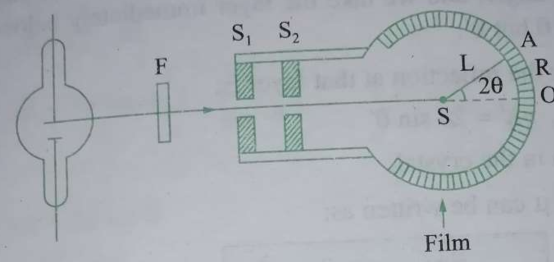


Fig. 5.7(*a*) Powdered crystal spectrometer

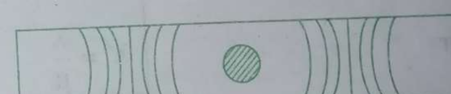


Fig. 5.7(*b*) Developed film

A narrow beam of these monochromatic X-rays suitably collimated by two lead slits S_1 and S_2, falls on the powdered specimen *S*. The specimen is suspended vertically on the axis of a cylindrical camera. The photographic film is mounted round the inner surface of the camera, covering nearly the whole circumference in order to receive the beams diffracted up to 180°.

The powder specimen of the crystal can be imagined to be a collection of random oriented tiny crystals, presenting all values of glancing angles to the incident beam. For a given wavelength and a given value of *d*, there can be only one value of θ (glancing angle) which satisfies the equation $2d \sin\theta = n\lambda$, where, $n = 1$. Such reflected beams emerge out from the specimen in all directions inclined at an angle 2θ with the direction of the incident beam, because millions of tiny crystals in the specimen are random oriented. The reflected rays will be on the surface of a cone, vertex at the specimen, base on the photographic film and having a semi-vertical angle 2θ. The traces obtained on the photographic film will be as in Fig. 5.7(*b*).

Let *L* be the radius of the cylindrical camera. The direct beam strikes the film at *O*. Suppose a spectrum with glancing angle θ is found at *A* which is at a distance *R* from *O*. Then $\theta = \frac{R}{2L}$. Using the value θ in the Bragg's equation and knowing the value of λ, *d* (spacing of the plane involved) can be calculated. The powder method has been employed in the study of microcrystalline substance like metals, alloys, carbon, fluorescent powders and other forms where single crystals are not available.

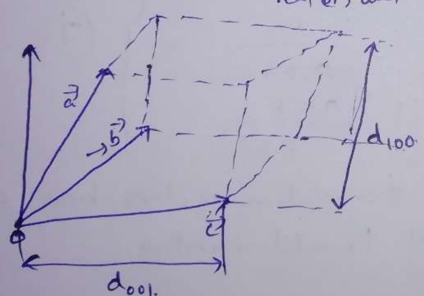
Vector algebraic discussion: (or) Reciprocal Lattice vectors:-
(or)
Relation b/n σ_{hkl} and Crystallographic Axes:-

Relation b/n fundamental reciprocal vectors and primitive translation vectors in the direct lattice.

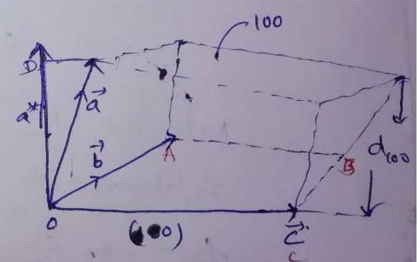
A reciprocal lattice vector, σ_{hkl} is defined as a vector having magnitude equal to the reciprocal of the interplanar spacing d_{hkl} and direction coinciding with normal to the (hkl) planes. Thus we have $\sigma_{hkl} = \frac{1}{d_{hkl}} \hat{n}$ —— (i)
→ where $\hat{n}$ is the unit vector normal to the (hkl) planes.

Consider a direct crystal lattice, whose unit cell is defined by vectors a, b and c. for example, take triclinic system
($a \neq b \neq c$ & $\alpha \neq \beta \neq \gamma \neq 90$)

a, b, c → primitive translation vectors of the direct lattice
real (or) unit vectors " "



(or)



Properties of Reciprocal Lattice:

(1) Every crystal structure has two lattices associated with it.
(or)
Every crystal structure may be imagined to be made up of two lattices (a) direct lattice (or) crystal lattice and (b) reciprocal lattice.
(Any diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal whereas the microscopic image is a map of the direct lattice.)

(2) Primitive vectors in the direct lattice have the dimensions of length. Vectors in the reciprocal lattice have the dimensions of $(\text{length})^{-1}$.

(3) Direct lattice (or) crystal lattice is a lattice in real space. The reciprocal lattice is a lattice in the reciprocal space (or) K-space or fourier space. (in the Fourier space associated with the crystal).

(4) Each point in a reciprocal lattice corresponds to particular set of parallel planes of the direct lattice.

(5) The distance of a reciprocal lattice point from an arbitrarily fixed origin is inversely proportional to the interplanar spacing of the corresponding parallel planes of the direct lattice.

6. The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of the corresponding unit cell of the direct lattice.

7. The direct lattice is the reciprocal lattice to its own reciprocal lattice. (The reciprocal of the reciprocal lattice is the direct lattice).

8. Every reciprocal lattice vector is normal to the lattice plane of the crystal lattice.

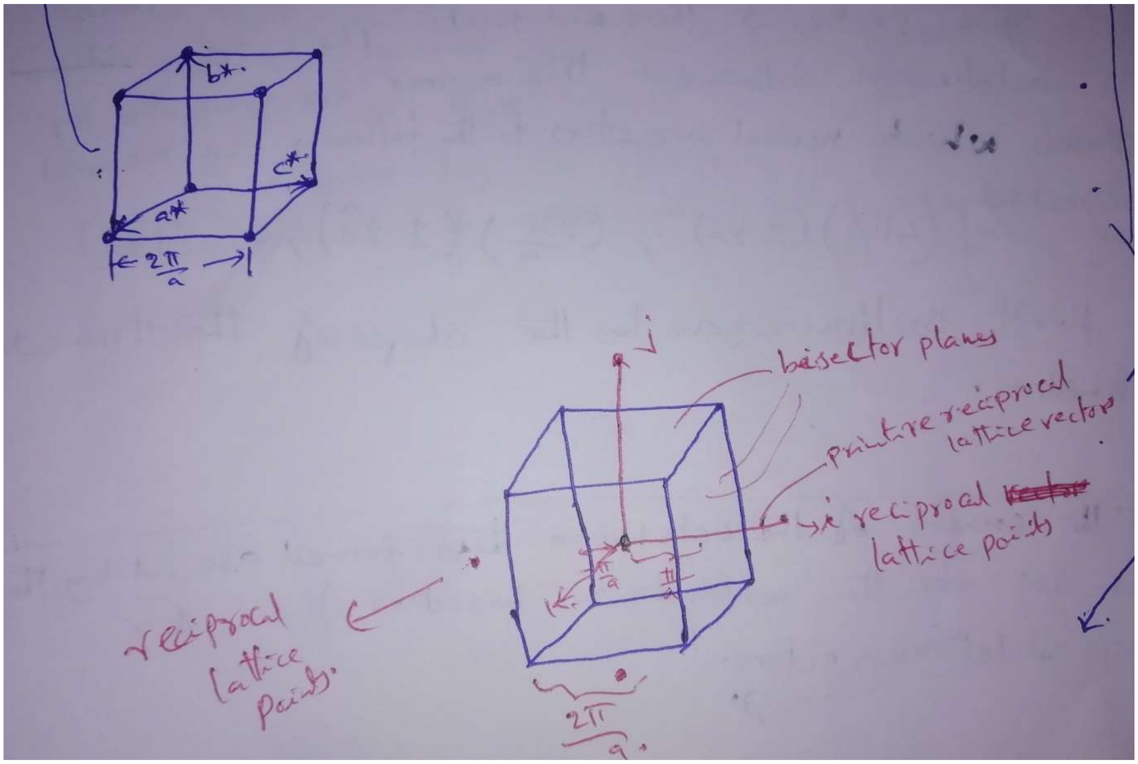
Based on the above properties, it will be interesting to prove that

(i) The RL of a simple cubic lattice is also a simple cubic lattice.
(or) SC lattice is self-reciprocal

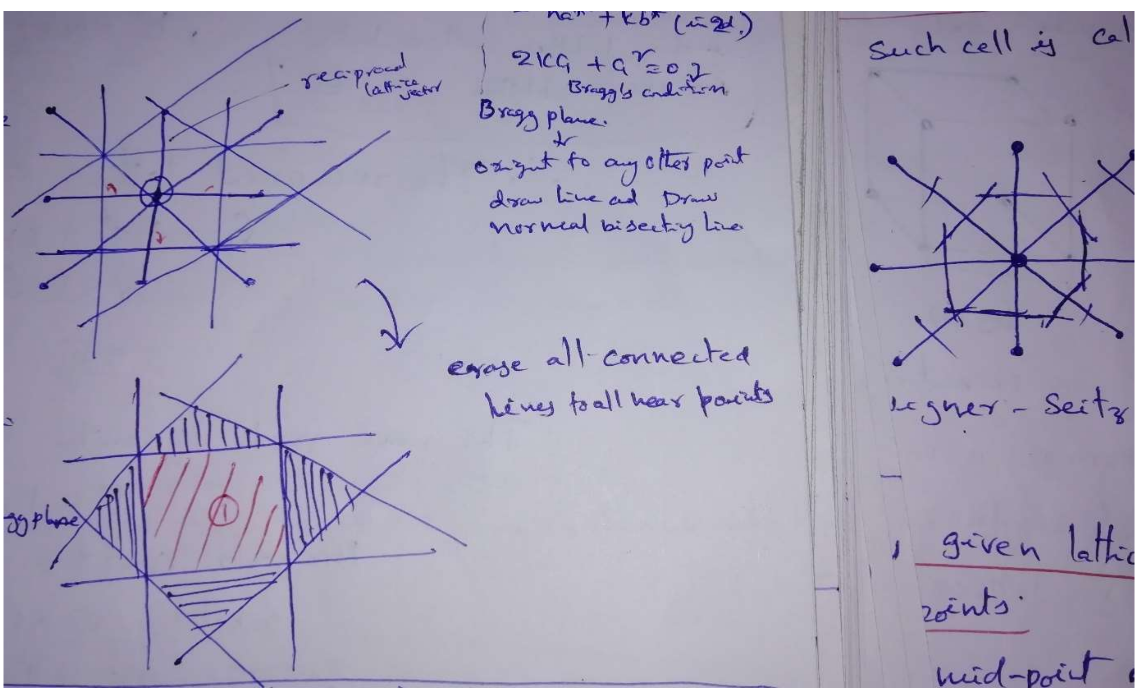
(ii) The RL of a face centred cubic lattice is a body centred cubic lattice.
(iii) The RL of a body centred cubic lattice is a face centred cubic lattice
(or) bcc and fcc lattices are reciprocal to each other.

(iv) The RL of a hexagonal close-packed lattice is a hexagonal close-packed lattice.

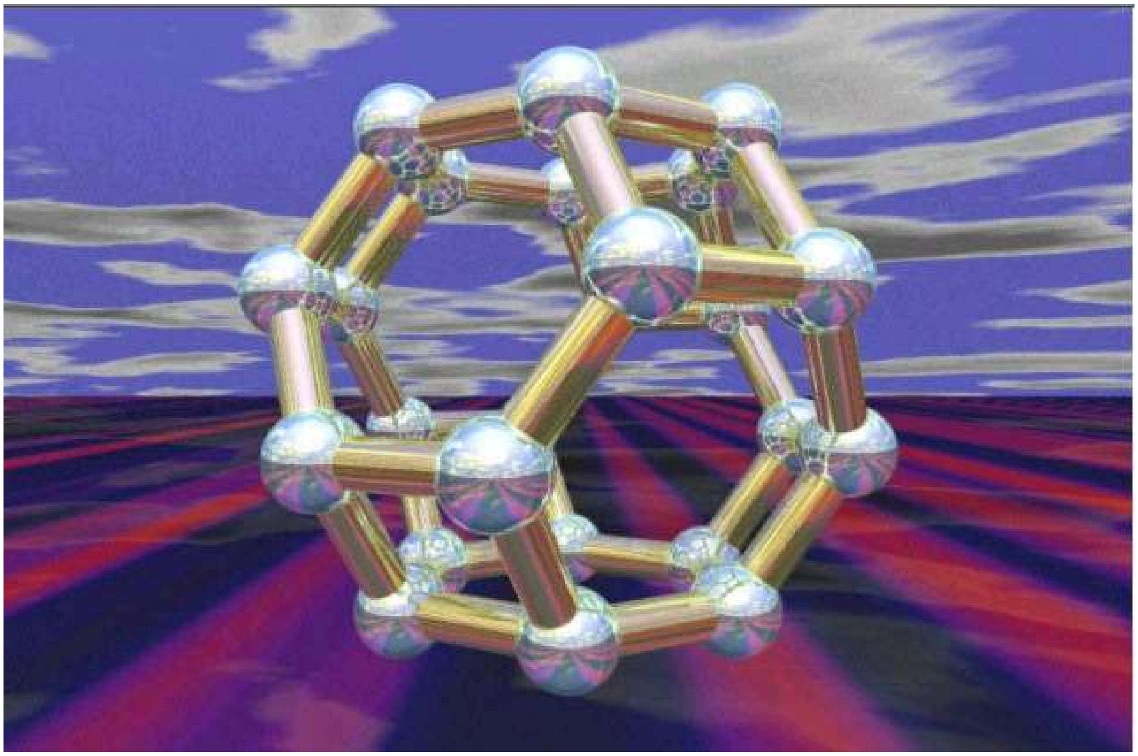
Reciprocal lattice to Simple Cubic



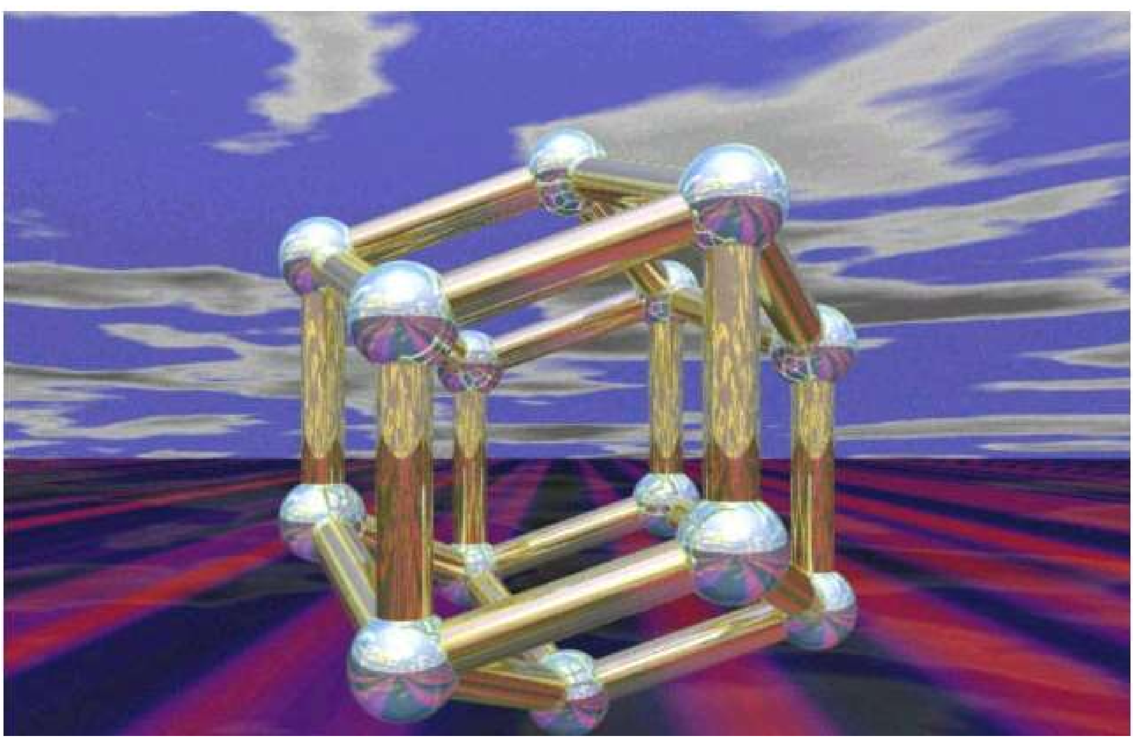
Construction of **Brillouin Zone and Wigner-Seitz cell**

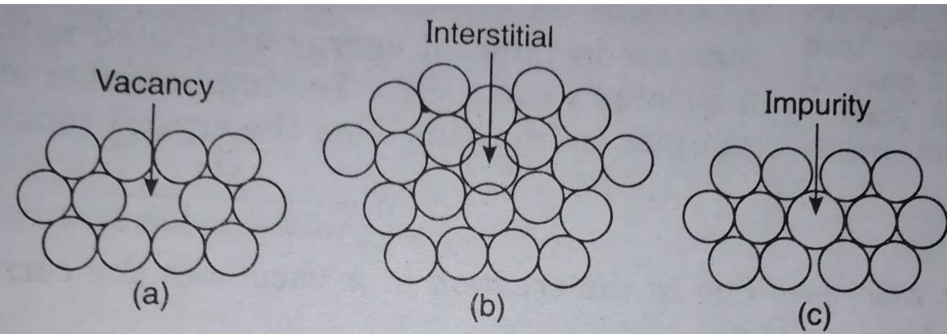


First Brillouin Zone BCC

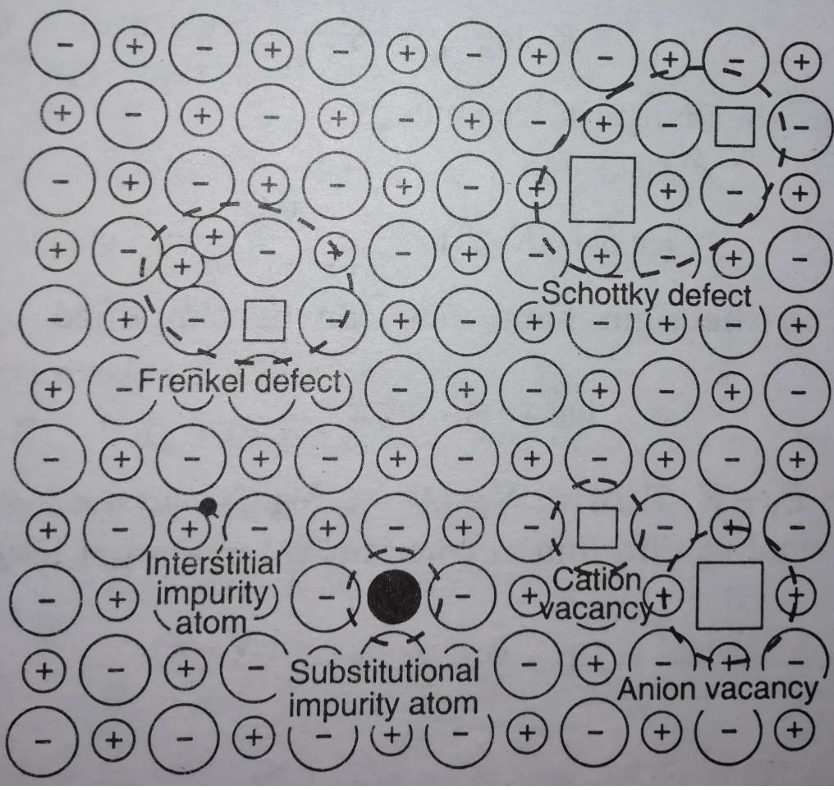


First Brillouin Zone FCC

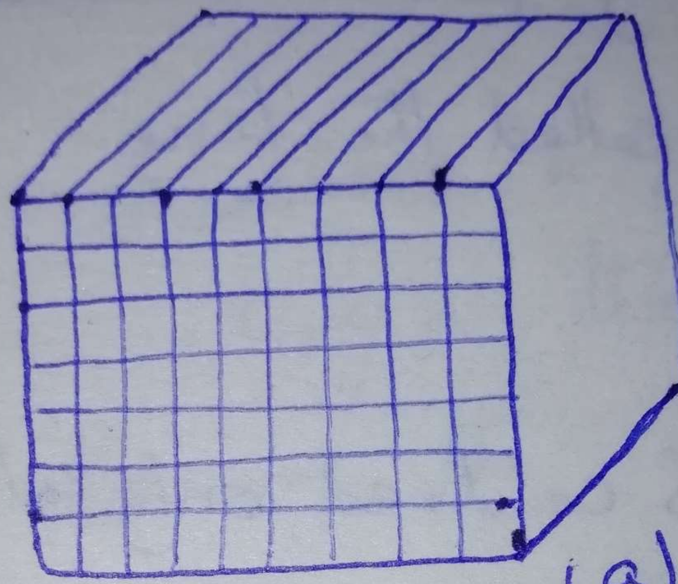




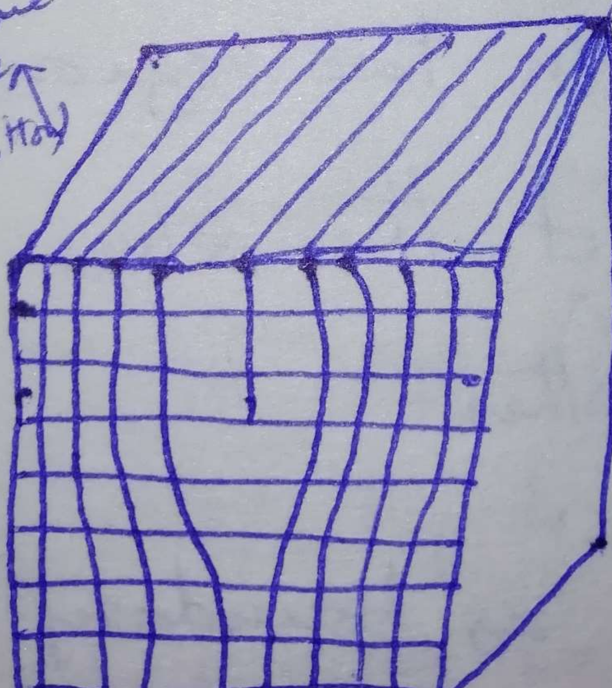
Three common point defects. (a) vacancy, (b) interstitial, (c) impurity.



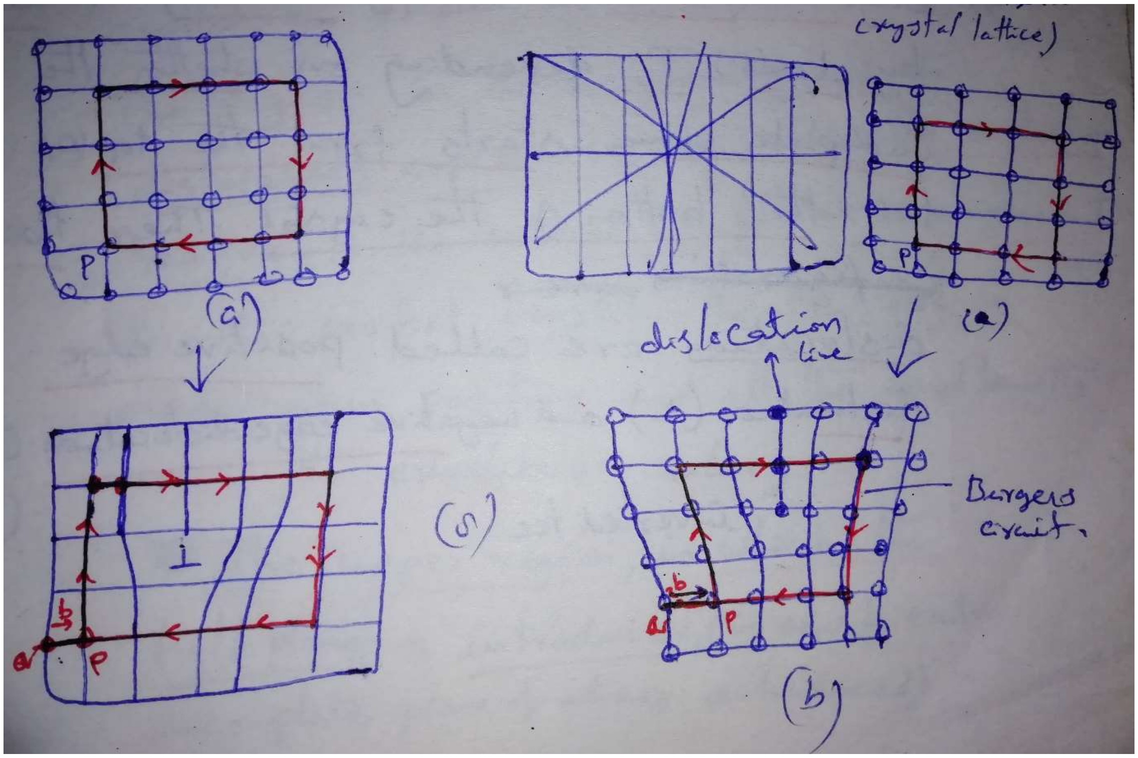
(a) Edge dislocation:-



(a)



(or)


(crystal lattice)
P
(a)
(a)
dislocation line
Burgers circuit.
b
P
(b)

econd basic type of dislocation

cation.

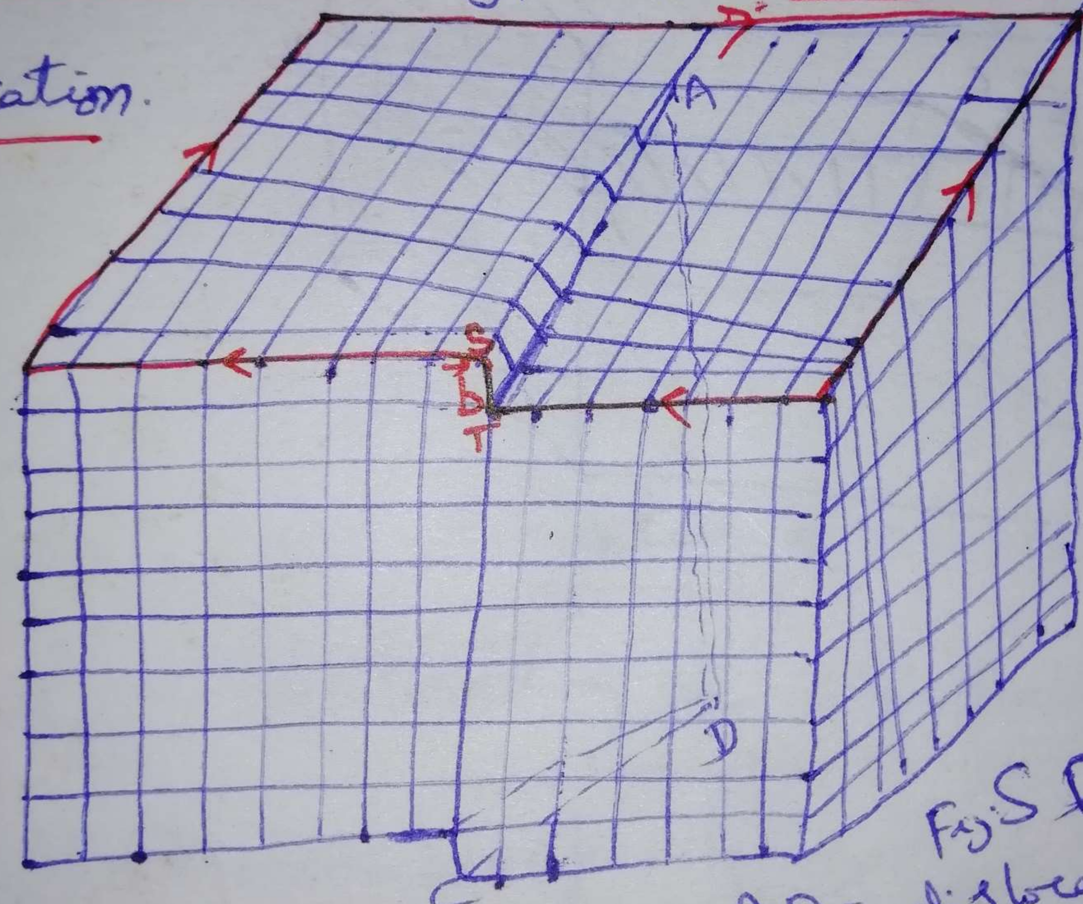


Fig: S D

AD = disloca