CHAPTER I

X-RAY DIFFRACTION AND CRYSTAL STRUCTURE
(A) **DIFFRACTION OF X-RAYS BY CRYSTALS:**

M.v.Laue\(^1\) (1912) was the first to suggest, that X-rays, if they have short wave length of the same order as the interatomic distances in crystals, will be diffracted by crystals. White - X-radiation passing through a crystal of zinc-blend and falling on a photographic film gave a diffraction pattern consisting of spots. Such photographs came to be known as "Laue photographs".

Although, M.v.Laue worked out the conditions for obtaining X-ray diffractions from crystals, the credit for first explaining the phenomenon in a simple way, as being due to reflection from sets of parallel planes in the crystal, goes undoubtably to W.H. Bragg\(^2\) (1913) who along with his students also did a lot of pionnering work in applying the technique of Z-ray diffraction to the determination of crystal structures.

Niggli\(^3\) (1919) showed how the space group of a crystal could be determined by extinctions. He described the positions of the symmetry elements in the 230 space groups and gave the coordinates of equivalent points in general and special positions.
Debye and Scherrer\textsuperscript{4} (1916) devised the powder-photographic method, by which the range of crystals which could be examined was immensely increased. Further development was the rotating crystal methods, using single crystal and the indexing of such photographs. The correct indexing of these photographs was first suggested by Bernal, J. D.\textsuperscript{5} (1926), who introduced the famous Bernal-Charts. Weissenberg\textsuperscript{6} (1924) introduced the cylindrical moving film camera in which the difficulties of overlap of reflections and of assigning indices to the reflections are overcome by an improved moving film technique.

de Jong and Bouman\textsuperscript{7} (1938) introduced a precession camera method in which an undistorted photograph of the reciprocal lattice is obtained.

During the last 15 years the power of X-ray diffraction method in solving complicated structures has increased due to the introduction of high speed digital computers, and complicated structures like proteins, haemoglobin, etc., have been solved.
THE INTENSITY OF DIFFRACTION BY A CRYSTAL:

Since crystals rarely approach the condition of a 'perfect crystal', the X-ray reflection by a crystal face cannot be measured by comparing the incident and reflected beam. This difficulty is overcome by a device employed by W.H. Bragg. If the crystal reflects an amount I₀ per second when set at the angle θ, and the incident radiation measured in the same way is I₀ per second, the integrated intensity  \( f(hkl) \) is defined as:

\[
f(hkl) = \int_{\theta - \epsilon}^{\theta + \epsilon} \frac{I_\theta}{I_0} \, d\theta.
\]

The limits \( \theta + \epsilon \) and \( \theta - \epsilon \) are chosen at a sufficient interval on either side of the mean angle of reflection \( \Theta \) to ensure that the reflections from the different blocks in the mosaic crystal are taken into account.

Now, if \( E \) be the energy of radiation, then for a rotating crystal:

\[
E = \int_{\theta - \epsilon}^{\theta + \epsilon} I_\theta \frac{d\theta}{\omega} \quad \text{where } \omega \text{ is the angular velocity,}
\]

\[
= \rho \frac{I_0}{\omega}.
\]

Thus \( \rho = \frac{E \omega}{I_0} \).
It was derived that:

$$E = \frac{I_0}{\omega} \frac{n^2 \lambda^4 e^4}{\omega^2 c^4} \cdot \frac{1 + \cos^2 \theta}{2 \sin \theta} \frac{|F|^2}{dV}$$

where

$$Q = \frac{n^2 \lambda^4 e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 \theta}{2} \frac{1}{\sin^2 \theta} |F|^2$$

here:
- \(e\) = charge on the electron,
- \(m\) = mass of the electron,
- \(c\) = velocity of light,
- \(\lambda\) = wavelength of X-radiation,
- \(n\) = number of unit cells per unit volume (i.e., one cubit centimeter),
- \(\omega\) = rate of rotation of the crystal,
- \(dV\) = the volume of the crystal,
- \(F\) = the factor representing the resultant scattering by a single unit cell.

**Formulae for diffraction by a mosaic crystal or an ideally imperfect crystal:**

The fact that the X-ray diffraction spot is spread on both sides of \(\theta\) corresponds to width of lines in case of diffraction from gratings, by analogy this spread is proportional to the number of building blocks (number of diffracting lines in case of a line grating).
As it is impossible to set an absolutely perfect crystal, so the alternative is to use a crystal which is ideally imperfect that is one which is comprised of small blocks such that "each block is a perfect crystal but the adjacent blocks are not accurately fitted together". Quantitative measurements have a definite meaning when made with a crystal in this state.

For the aforesaid mosaic crystal the formula for the intensity of the integrated reflection has been deduced by Darwin and Ewald and is:

\[
\rho(hkl) = \frac{1}{2\mu(hkl)} \cdot \frac{n^2 \alpha^4 \lambda^3}{m^2 c^4} \cdot \frac{1}{\sin 2\theta} \cdot \frac{1 + \cos^2 2\theta}{2} \cdot F(hkl)^2
\]

where \(\mu\) is the linear absorption coefficient of X-rays in the crystal and \(F(hkl)\) is the structure amplitude appropriate to the diffracted beam. The factor \(\frac{1 + \cos^2 2\theta}{2}\) is the polarisation factor.

**Measurements of integrated intensity**:

The peak intensity of a X-ray spot can be determined easily either by photographic film or by quantum counters,
but the measurement of integrated intensity is more difficult
as the X-ray intensity \[ \int_{-\pi}^{\pi} \frac{I_0}{\theta} \text{d}\theta \] is greater in the central region and lighter towards the edges. That is, each of the spots has different intensity in different regions and these intensities must be added to make up the total "integrated intensity".

The following methods are employed for the determination of the integrated intensity. A comparison of some of these methods has been made by Robertson, J.M. and Dawton, R.H.V.M. (1941). 9

I Photometer - trace method:

This method is employed to obtain integrated intensities from powder photographs with the help of a recording photometer.

II Density - wedge method:

This method is based on the ability of human eye to make a fairly good estimate of the integrated intensity by visual comparison and is one of the most satisfactory and neat ways of determining integrated intensities. In this method the density on the photograph is matched with a known density, e.g., a location on a density "wedge". This
equality can be judged by eye or by means of a photocell arrangement.

III Density transforming method:

This method is devised by Robertson and Dawton. In this the image of the spot to be photometered is projected on to an aperture in a screen and the light from a small area of reflection is allowed to reach photocell whereby measuring the intensity.

The other methods are: (a) The Astburg $\alpha$-ray method, (b) Photometry based on scattering, (c) Positive film photometry, (d) The Plateau method.

(C) RECIPROCAL LATTICE:

The concept of reciprocal lattice, first applied by Ewald, P.P. (1921), sums up the relationship between a structure and its X-ray diffraction pattern and is consequently an alternate way of describing a structure.

In case of X-ray diffraction by crystals, the reflections can be treated as reflections by the sets of parallel planes in the crystal; and the representations of these planes and their interplanar spacings in two-
dimensions gives difficulty. In order to make the representation easier, we consider only the perpendicular to the plane to define a set of planes, which has got one dimension less than the plane. The direction of the normals will automatically indicate the direction of the plane, whereas the length of the normal is assumed to be related in a reciprocal way to the interplanar distance $d_{hkl}$ (length of the normal is usually taken as $\frac{\lambda}{2d_{hkl}}$ and is equal to $\sin \theta$ according to the Bragg's law). The resulting construction is consequently referred to as "the reciprocal lattice".

The reciprocal lattice is constructed by representing each set of planes $(h k l)$ of the original lattice by a point $h k l$, such that the line joining the point to the origin is normal to the planes, and its distance from the origin is inversely proportional to the spacing $d_{hkl}$ of the planes. All the multiples of $h k l$, by such construction, lie upon a new lattice, which is called the reciprocal lattice. [see figure 1(a)].

This concept of reciprocal lattice provides one of the most important tools available in the study of X-ray diffraction by crystals.
Figure 1(a) Construction of a reciprocal lattice.

Figure 1(b) A general triclinic cell.
Relationship between reciprocal and real lattice:

The direct cell edges and angles are represented by unstarred letters \( a, b, c, \alpha, \beta, \gamma \), and to designate the corresponding reciprocal cell elements, the starred letters \( a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^* \), are used. The following relations are obtained for the real lattice and reciprocal lattice:

\[
\begin{align*}
a^* &= \frac{1}{d(100)} & a &= \frac{1}{d^*(100)} \\
b^* &= \frac{1}{d(010)} & b &= \frac{1}{d^*(010)} \\
c^* &= \frac{1}{d(001)} & c &= \frac{1}{d^*(001)}
\end{align*}
\]

In a general triclinic cell [figure 1(b)] the volume \( V \) of the cell is 

\[
V = \text{base} \times \text{altitude} = ab \sin \gamma \times d(001)
\]

\[
\therefore d(001) = \frac{V}{ab \sin \gamma}
\]

Hence:

\[
\begin{align*}
a^* &= K \frac{bc \sin \alpha}{V} & a &= K \frac{b^* c^* \sin \alpha^*}{V^*} \\
b^* &= K \frac{ac \sin \beta}{V} & b &= K \frac{a^* c^* \sin \beta^*}{V^*} \\
c^* &= K \frac{ab \sin \gamma}{V} & c &= K \frac{a^* b^* \sin \gamma^*}{V^*}
\end{align*}
\]

( where \( V^* = 1/V \) ).
The volume of a triclinic cell, in terms of its own dimensions \( a, b, c \), and \( \alpha, \beta, \gamma \), is:

\[
V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}
\]

\[
= abc \sqrt{\sin^2 \alpha + \sin^2 \beta + \sin^2 \gamma - 2 + 2 \cos \alpha \cos \beta \cos \gamma}
\]

Also

\[
\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}
\]

\[
\cos \beta^* = \frac{\cos \gamma \cos \alpha - \cos \beta}{\sin \gamma \sin \alpha}
\]

\[
\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}
\]

In case of a monoclinic cell:

(i) \( a^* = K/a \sin \gamma \), \( b^* = K/b \sin \gamma \), \( c^* = K/c \)

\[
\alpha^* = \beta^* = 90^\circ, \quad \gamma^* = 180^\circ - \gamma
\]

or

(ii) \( a^* = K/a \sin \beta \), \( b^* = K/b \), \( c^* = K/c \sin \beta \)

\[
\alpha^* = \gamma^* = 90^\circ, \quad \beta^* = 180^\circ - \beta
\]

( where \( K = \text{reciprocal constant} \) ).
The relations for triclinic cell elements and those for the direct cell elements have been listed by Buerger, M. J. M. J., in table 20 and 21 and in "International tables for X-ray crystallography" volume I.

(D) FACTORS AFFECTING INTENSITY OF THE DIFFRACTED BEAM:

(i) Lorentz factor:

Lorentz, H. A., first gave a factor which was in its particular form applicable to Laue method. This factor is concerned with the specific motion of the crystal, which is a uniform rotation about an axis at right angles to the X-ray beam.

In the equation:

\[ E = \frac{I}{\omega} \cdot \frac{n^2 \lambda^3 e^4}{m^2 c^4} \cdot \frac{1}{\sin 2\theta} \cdot p \frac{1}{F^2} dV \]

the factor \(1/\sin 2\theta\) is known as Lorentz factor.

(ii) Lorentz - Polarisation factor:

Normally, it was assumed, for simplicity, that the electric vectors of all the X-rays impinging on the electron are confined to single direction, in other words, it means that the incident X-ray beam is plane polarised. But, in
actual practice, unpolarised X-ray beam is used, which implied that the azimuth of electric-vector assumes all directions. Thus, after reflection by the crystal, the effective amplitude of the radiation, consists only of the components of these azimuths after reflection. By this phenomenon, the intensity of the X-ray beam deflected by an angle $2\theta$ is reduced by a factor $p$, known as the polarisation factor. The value of this factor $p$ is given in the equation for the total intensity of the reflected beam as:

$$p = \frac{1 + \frac{1}{2} \cos^2 2\theta}{2} = \frac{1 + \cos^2 2\theta}{2}.$$ 

The Lorentz factor ($L$) taken along with the polarisation factor ($p$) is called the Lorentz–polarisation factor ($LP$).

Effects of these factors can be removed by the following two methods:

1. By the process of recording — so that $|F|^2$'s are actually measured instead of $E$'s.

2. By multiplying $1/Lp$ — as obtained from calculation, tabulation or charts based on instrumental coordinates or upon reciprocal lattice coordinates — to the measured $E$'s.
(iii) Extinction of X-rays:

In case of perfect crystals, a reflected X-ray beam is at a correct angle to be reflected back into the direct beam by a second reflection from the same stack of planes. Since each reflection produces a phase change of $\pi/2$, the doubly reflected beam and the direct beam will differ in phase by $\pi$ and will interfere and so decrease its intensity. Similarly the singly and triply reflected X-ray beams will differ in phase by $\pi$, and interfere decreasing the intensity of the reflected beam. These effects are called primary extinctions and are difficult to allow for, unless the degree of perfectness of the crystals is known. Fortunately, most crystals behave as ideally imperfect crystals (Darwin 1914, 1922) for which extinction is negligible except when:

(i) structure factor $|F|$ is large,
(ii) spacing $d$ is large, and
(iii) order of reflection is small.

One of the ways to eliminate the effect is by dipping the crystal in liquid-air. The consequent stress induces
imperfections. The presence or absence of primary extinction can be determined by the divergent-beam X-ray technique. However, since only a few reflections having large $|F|$'s and large $d$'s may suffer from primary extinction, it is customary in X-ray crystallography to omit these when computing the residual $R$-factors and also to substitute in Fourier synthesis the computed values of the $|F|$'s for the observed values for such reflections.

(iv) **Tunnel Factor or the Rotation Factor**:

In case of equi-inclination Weissenberg method, when the reflecting plane does not contain the axis of rotation, that is, when the diffraction spot does not lie on the equatorial line of the photograph, the angular velocity of the plane, $\omega$, is effectively decreased to $\omega'$, ($\omega'$ is the angular velocity about an axis perpendicular to the plane containing the incident and reflected beam).

Previously, the correction for this velocity was called the Rotation factor and was defined as:

$$D = \frac{\omega'}{\omega}$$

But the above equation does not hold good for general cases.
Ott\textsuperscript{16}, (1924) and later Cox and Shaw\textsuperscript{17} (1930) have given the value of rotation factor for normal-beam rotating crystal as:

\[ D_{\perp} = \sqrt{\frac{\sin^2 \chi - \sin^2 \Theta}{\cos \Theta}} \]

where \( \chi \) is the angle between the rotation axis and the normal to the crystal plane.

Tunell\textsuperscript{18} (1932) evaluated for the equi-inclination arrangement, the value of \( D \) as:

\[ D = \frac{\sqrt{\cos^2 \mu - \cos^2 \Theta}}{\sin \Theta} \]

where \( \mu \) is the angle of tilt of the Weissenberg camera axis from its usual position which is perpendicular to the beam.

(v) The temperature factor:

Due to the temperature effect, there is a thermal motion of atoms about their mean positions, which makes the electrons of each atom to sweep out or effectively occupy a larger volume than they would occupy if the atom were at rest. Consequently, there is greater interference between waves diffracted from the various parts of the atom particularly for high \( \sin \Theta \) -values. This phenomenon causes the \( f \) - curves of the atom to fall off more rapidly with \( \sin \Theta / \lambda \) than for the same atoms at rest.
Assuming the atomic vibration to be isotropic, Waller, L. (1927) showed that:

\[ f = f_0 e^{-\left(\frac{B \sin^2 \theta}{\lambda^2}\right)} \]

The quantity \( B \) is called the temperature coefficient and its value is given by:

\[ B = 8 \pi^2 \bar{u}_L^2 \]

where \( \bar{u}_L^2 \) is the mean-square-displacement normal to the reflecting plane of the atom from its mean position.

In terms of the Debye - characteristic temperature --

\[ R = \frac{6 \hbar^2 T}{m k \theta^2} \cdot \varphi \left( \frac{\theta}{T} \right) \]

In general the vibrations of the atoms are not isotropic since vibrations along certain directions are restricted due to bonding and packing environments of the atom. An anisotropic temperature-factor \( (T) \) is usually represented as:

\[ T = \exp \left\{ -\alpha_1 \hbar^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 \hbar k + \alpha_5 kl + \alpha_6 hl \right\} \]

(vi) **Absorption of X-rays:**

As a X-ray beam passes through a crystal, it is absorbed by the crystal and thereby it loses its energy. In tiny crystals this phenomenon of absorption is much more than
ordinarily appreciated, and its effect can only be omitted in case of rough work. Due to the complications in application of correct correction in actual practice, only approximations are used, as the absorption of X-rays is a function of the shape of the crystal and the relation of the direct and diffracted beams to this shape.

When an X-ray beam penetrates a slab of the crystal of thickness \( t \), the intensity \( I \), of the original wavelength transmitted, is related to the incident intensity \( I_0 \), by the relation:

\[
I = I_0 \cdot e^{-\mu t}
\]

where \( \mu \) is termed the 'linear absorption coefficient'. As the absorption coefficient depends on the mass traversed, the equation can be written as:

\[
I = I_0 \cdot e^{-\frac{\mu}{\rho} \cdot pt}
\]

where \( \frac{\mu}{\rho} \) is the "mass-absorption coefficient" and \( pt \) is the mass per square centimeter of the absorbing material i.e., density.

The absorption-coefficient plays an important part in X-ray analysis and in case of absolute measurements, its value should be determined. In most of the cases, the
correction for absorption is applied treating the crystal as cylindrical or spherical according to the shape of the given crystal which may be needle shaped or equidimensional lump. Absorption correction becomes unnecessary if one works with a spherical or cylindrically ground and mounted crystal of a small size (optimum diameter for best results being $2/\mu$ cms.).

The linear absorption coefficient, $\mu$, can be calculated from the mass-absorption coefficients ($\mu/\rho$, listed in the "International tables for X-ray crystallography" Vol. III, p. 162) of the individual elements according to the formula:

$$\mu = \text{density} \cdot \left[ \beta_A \left( \frac{\mu}{\rho} \right)_A + \beta_B \left( \frac{\mu}{\rho} \right)_B + \beta_C \left( \frac{\mu}{\rho} \right)_C \right]$$

where $\beta_A$ is the fraction by weight of element A in the compound $AB\,C$ and so on.

In case of rubidium para-nitrobenzoate dihydrate, for copper Kα radiation, density of compound 1.88 gm./c.c.; the value of mass-absorption coefficient is:

For $Rb = 117.0, \, C = 4.6, \, N = 7.52$

$H = 0.435$ and $O = 11.5$ (from "International tables for X-ray crystallography" Vol. III, p. 162).
Rb \((\text{C}_7\text{H}_4\text{NO}_4) \cdot 2\text{H}_2\text{O}\) \quad \text{Mol. Wt.} = 287.63 .

\[ \mu = \frac{1.88}{287.63} \left\{ \left( 85.48 \times 117.0 \right) + \left( 7 \times 12 \times 4.6 \right) + \left( 8 \times 0.435 \times 1.0 \right) \\
+ \left( 14 \times 7.52 \right) + \left( 6 \times 16 \times 11.5 \right) \right\} \text{ cm}^{-1} \]

\[ = \frac{1.88}{287.63} \times 11600.32 \text{ cm}^{-1} = 75.8 \text{ cm}^{-1} \]

(E) **STRUCTURE FACTORS AND THE ATOMIC COORDINATES:**

The wave scattered from the \(j\)th atom of a unit cell is described in amplitude and phase by the term 
\[ f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]
where \(f_j\) is the atomic scattering factor for the \(j\)th atom at the appropriate value of \(\sin \Theta\), and \(x_j\), \(y_j\) and \(z_j\) are its fractional coordinates viz., \(x/a\), \(y/b\) and \(z/c\). In general, the effective scattering from plane \((h k l)\) of a crystal, will be the sum of scattering from all the atoms, viz.,

\[ F_{hkl} = \sum_{j=1}^{n} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

The factor \(F_{hkl}\) is a complex quantity. Its direction and magnitude are determined by the phase and the amplitude of the scattered wave respectively. Since, this factor depends on the arrangement of matter in the crystal, that is, on its crystal structure, the factor is commonly called the structure
factor. This complex resultant is characterised both by an amplitude $|F_{hkl}|$ and a phase constant $\phi$. It can be represented as:

$$|F_{hkl}| = \sqrt{A^2 + B^2} \quad \text{and} \quad \phi_{hkl} = \tan^{-1} \frac{B}{A}$$

The atomic scattering factor designated as "f" represents the scattering power of the atom as compared to that of a single, free electron. f-values can be calculated on the basis of the electron density distribution function for the atom. Such calculations of atomic - scattering factors are listed in "International Tables for X-ray crystallography" Vol. III (1960) - page 202-206.

Since $|F_{hkl}| = \sqrt{A^2 + B^2}$ and $\phi_{hkl} = \tan^{-1} \frac{B}{A}$

where

$$A = \sum_{j=1}^{n} f_j \cos 2\pi (hx_j + ky_j + lz_j) \quad \text{and}$$

$$B = \sum_{j=1}^{n} f_j \sin 2\pi (hx_j + ky_j + lz_j)$$

Hence the magnitude of the structure factor, called the "structure amplitude, $|F_{hkl}|$ is given by the equation:

$$|F_{hkl}| = \sqrt{\left(\sum_{j=1}^{n} f_j \cos 2\pi (hx_j + ky_j + lz_j)\right)^2 + \left(\sum_{j=1}^{n} f_j \sin 2\pi (hx_j + ky_j + lz_j)\right)^2}$$

which is a function of the atomic coordinates in the cell.
\[ A = \frac{j^{\text{in}}}{j_{\text{org}}} f_j A_j \]

\[ B = \frac{j^{\text{in}}}{j_{\text{org}}} f_j B_j \]

**FIGURE - 2.** Direction and magnitude of structure factor - \( F(hkl) \)
Phase angle of the structure factor $F(hkl)$ can be given (figure 2) as:

$$
\tan \phi_{hkl} = \frac{\sum_{j=1}^{n} f_j B_j}{\sum_{j=1}^{n} f_j A_j}
$$

$$
\cos \phi_{hkl} = \frac{\sum_{j=1}^{n} f_j A_j}{|F_{hkl}|}
$$

$$
\sin \phi_{hkl} = \frac{\sum_{j=1}^{n} f_j B_j}{|F_{hkl}|}
$$

When $B = 0$, the phase angle becomes 0 or $\pi$. This amounts to assigning a sign to the structure-factor. Specifically, when $\phi_{hkl} = 0$, $F_{hkl}$ is positive and when $\phi_{hkl} = \pi$, $F_{hkl}$ is negative.

(F) **ELECTRON DENSITY AND STRUCTURE FACTOR:**

If the electron density at the point $(x, y, z)$ is $\rho(x, y, z)$, the amount of scattering material in the volume element $Vdxdydz$ is $\rho Vdxdydz$ and the structure factor equation is:
\[ F_{hkl} = \iiint_V \rho(xyz) \exp \left( \frac{2\pi i}{\lambda} (hx + ky + lz) \right) \, dx \, dy \, dz \] \quad (1)

Since a crystal is periodic in three dimensions, it can be represented by a three-dimensional Fourier series, by which the density function \( \rho(xyz) \) may be represented in the general form:

\[ \rho(xyz) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} K(h'k'l') \exp \left( \frac{2\pi i}{\lambda} (hx' + ky' + lz') \right) \]

where \( K(h'k'l') \) is the Fourier coefficient.

Therefore,

\[ F_{hkl} = \iiint_{V} K(h'k'l') \exp \left( \frac{2\pi i}{\lambda} (hx + ky + lz) \right) \exp \left( \frac{2\pi i}{\lambda} (hx' + ky' + lz') \right) \, V \, dx \, dy \, dz \]

Integral of this, over a single complete period is zero, only if \( h = -h' \), \( k = -k' \) and \( l = -l' \). Under these conditions:

\[ F_{hkl} = \iiint_{V} K(h'k'l') \, V \, dx \, dy \, dz \]

Thus the coefficients of the Fourier series \( K \), representing the electron density are directly related to the corresponding structure factors, for the corresponding crystal plane, and

\[ \rho(xyz) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F_{hkl} \exp \left\{ \frac{-2\pi i}{\lambda} (hx + ky + lz) \right\} \]

\[ \ldots (2) \]
The close resemblance between equation (1) and (2) in terms of the transform-theory can be stated by saying that in equation (2) we see that the electron density distribution at the point \( x, y, z \) is the Fourier transform of the structure factors \( F_{hkl} \); whereas in equation (1) we see that the structure factors \( F_{hkl} \) are the inverse Fourier transforms of the electron-density-distribution \( \rho(xyz) \) (Figure -3. ).

In order to get the values of \( \rho \), from the above equation, it is necessary to specify a location, such as \( (x_1, y_1, z_1) \) where this value is required; substituting this value of \( x_1, y_1 \) and \( z_1 \) in the right hand side of the above equation, we get \( \rho(x_1y_1z_1) \) as the result of a triple summation over all values of \( h, k, \) and \( l \). In other words, the computation implied by the above Fourier summation is a discrete process which applies to a discrete point in space.

In all the above considerations, the three dimensional space is represented by a group of parallel planes, spaced by the sampling interval not contained in the plane. In other words, the three dimensional distribution of electron density is regarded as sampled along a sequence of parallel planes. Contours connecting points of equal electron-density are drawn on each of these planes to obtain a clear presentation.
FIGURE 3. Image formation and Fourier transform.
(G) **SYMMETRY AND MISSING REFLECTIONS:**

Important informations regarding the symmetry of the crystalline lattice is sometimes obtainable from the missing reflections. Some such clues are listed below. However, in some cases the required information about the symmetry is not obtainable from the missing reflections alone and the space group can not be determined unambiguously without taking recourse to other tests. In particular, the X-ray pattern in a number of cases does not provide conclusive evidence of presence or absence of centres of symmetry. An evidence from (i) study of pyro-electric\textsuperscript{20} and piezoelectric\textsuperscript{21} effects, and/or (ii) distribution of intensities\textsuperscript{22,23} is proved extremely useful.

**Clues from the missing reflections:**

1. **Face centring:** If (001) plane is face centred then all \(h \quad k \quad l\) reflections having \(h + k = \text{odd}\) are missing.

2. **Body centring:** In case of body centring \(h \quad k \quad l\) reflections with \(h + k + l = \text{odd}\) are missing.

3. **Repeat distance along an axis halved:** say if repeat distance along \(x - \text{axis}\) halved then \(h \quad k \quad o\) is missing when \(h = \text{odd}\).
4. Glide plane and screw axes: Two fold screw axes give rise to systematic absence of odd values of \( h, k \) or \( l \) in the group \( h o o \), \( o k o \) and \( o o l \). Glide planes parallel to the axis are responsible for systematic absences in the groups \( h k o \), \( h o l \) and \( o k l \).

5. Sometimes systematic absences may arise out of the symmetry of the molecule if it is situated at special points in the lattice as in \( s \)-bisnitroaminoethane or due to statistically symmetrical arrangements.
REFERENCES

   Nature Wissenschaften April (1922).


   Dawton, R.H.V.M.


   ibid, (1922), 43, 806-29.


