CHAPTER I

FUNDAMENTALS OF X-RAY DIFFRACTION AND CRYSTAL STRUCTURE DETERMINATION
1. DIFFRACTION OF X-RAYS BY CRYSTALS AND CRYSTAL STRUCTURE

Three dimensional periodic arrangement of atoms or group of atoms or unit motif in an ideal crystal may be described by a collection of points which forms the "SPACE LATTICE". It provides a basis for the theory of X-rays, electron and neutron diffraction by the crystal. The foundation of the crystal structure analysis by X-rays originates from the revolutionary discovery of diffraction of X-rays by crystals by Von Laue in 1912.

In the plane wave approximation if \( \vec{s}_0 \) be the unit vector along the direction of incidence and \( \vec{s} \), the unit vector along the direction of scattering then according to Laue's kinematical theory of diffraction intensity maxima occurs when the following conditions are satisfied.

\[
\frac{\vec{s}}{\lambda} \cdot \vec{a}_i = h, \quad \frac{\vec{s}}{\lambda} \cdot \vec{a}_2 = k, \quad \frac{\vec{s}}{\lambda} \cdot \vec{a}_3 = l
\]

where \( \vec{s} \) is the external bisector of \( \vec{s}_0 \) and \( \vec{s} \), \( \lambda \) the wavelength of the incident monochromatic X-rays, \( a_i \) \( (i = 1, 2, 3) \) define the crystal lattice and \( h, k, l \) are triple integers. These conditions are known as Laue equations. Bragg (1913) pointed out that the three Laue equations \( (1.a) \) have simple geometrical interpretation and the diffraction maxima may be interpreted as a specular reflection from a stack of parallel lattice planes. Interpretation of diffraction problems is simplified in terms of reciprocal lattice which is generated by \( \vec{b}_j \)'s \( (j = 1, 2, 3) \) that are obtained from the primitive translational vectors \( \vec{a}_j \)'s defining the space lattice by the relation

\[
\vec{a}_i \cdot \vec{b}_j = \delta_{ij}
\]

where \( \delta_{ij} = 1 \) for \( i = j \)

\( = 0 \) for \( i \neq j \)
A reciprocal lattice vector defined by \( \vec{\sigma}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 = \vec{H} \) where \( h, k, l \) are integers has two important properties; namely the vector \( \vec{\sigma}_{hkl} \) is normal to the Miller plane (hkl) in the space lattice and \( |\vec{\sigma}_{hkl}| = \frac{1}{d_{hkl}} \), where \( d_{hkl} \) is the interplanar spacing. The Laue equations have a simple form of representation in reciprocal lattice and these are equivalent to a single condition.

\[
\vec{s} = \vec{\sigma}_{hkl} \quad \text{(1.c)}
\]

The equivalence of the two vectors given by (1.c) means that \( \vec{s} \) is also perpendicular to the plane (hkl) so that \( \vec{s}_0 \) and \( \vec{s} \) make the same glancing angle \( \theta \) with the (hkl) plane and

\[
|\vec{s}| = |\vec{s} - \vec{s}_0| = 2 \sin \theta
\]

Since

\[
|\vec{s}| = |\vec{\sigma}_{hkl}| = \frac{1}{d_{hkl}}
\]

\[
\frac{2 \sin \theta}{\lambda} = \frac{1}{d_{hkl}}
\]

If \( n \) be a common factor of the triple integers, the above equation is expressed as

\[
2 d_{hkl} \sin \theta = n \lambda \quad \text{(1.d)}
\]

which is the well known Bragg's law.

By observing the positions of diffraction maxima, information regarding the unit cell parameters may be obtained. In general a unit cell contain large number of atoms located at different positions with respect to corner of a cell.
When we consider coherent scattering from a crystal block of dimension \( N_1a_1, N_2a_2, \) and \( N_3a_3 \) along the directions \( \vec{a}_1, \vec{a}_2, \vec{a}_3 \) respectively (\( N_1, N_2, N_3 \) have integral values), according to Laue's kinematical theory the intensity of the diffraction pattern is given by

\[
J = I_e \sum_{j=1}^{n} \sum_{m=1}^{n} f_j f_m^* \exp \left( 2\pi i \frac{\vec{s}}{\lambda} \cdot (\vec{r}_j - \vec{r}_m) \right) I_0 \left( \frac{\vec{s}}{\lambda} \right)
\]

\[
= I_e G(\frac{\vec{s}}{\lambda}) G(\frac{\vec{s}}{\lambda}) I_0(\frac{\vec{s}}{\lambda})
\]

where \( f_j \) is the atomic scattering factor of the \( j \)th scatter and \( \vec{r}_j \) (\( j = 1, 2, 3 \ldots \ldots n \)), the position vector of the \( j \)th atom with respect to the corner of the cell and

\[
G(\frac{\vec{s}}{\lambda}) = \sum_j f_j \exp(2\pi i \frac{\vec{s}}{\lambda} \cdot \vec{r}_j)
\]

is known as the Fourier transform of one unit cell content and

\[
I_0(\frac{\vec{s}}{\lambda}) = \frac{\sin^2 N_1 \pi \vec{s} \cdot \vec{a}_1}{\sin^2 \frac{\pi a_1}{\lambda} \cdot \vec{s}} \frac{\sin^2 N_2 \pi \vec{s} \cdot \vec{a}_2}{\sin^2 \frac{\pi a_2}{\lambda} \cdot \vec{s}} \frac{\sin^2 N_3 \pi \vec{s} \cdot \vec{a}_3}{\sin^2 \frac{\pi a_3}{\lambda} \cdot \vec{s}}
\]

is known as the Laue interference function and \( I_e \) is the intensity scattered by a classical electron. \( J \) attains a maximum value when

\[
\vec{a}_1 \cdot \frac{\vec{s}}{\lambda} = h, \quad \vec{a}_2 \cdot \frac{\vec{s}}{\lambda} = k \quad \text{and} \quad \vec{a}_3 \cdot \frac{\vec{s}}{\lambda} = l
\]

which is equivalent to \( \frac{\vec{s}}{\lambda} = \vec{h}(H) \) and

\[
J_{\max} = I_e |F(H)|^2 N^2
\]

where \( N = N_1N_2N_3 \) is the total number of unit cells in the crystal block and \( F(H) \) is called crystal structure factor i.e value of the Fourier transform of one unit cell content at the reciprocal lattice node \( hkl(H) \).
Because of the mosaicity of a crystal, divergence of the incident X-ray beam and nature of the Laue interference function, one is not in a position to measure $J_{\text{max}}$. In practice one measures the total intensity of a crystal reflection as the crystal plane passes through reflection position with the crystal mounted on a goniometer head rotating very slowly with angular velocity $\omega$. This quantity known as integrated reflection is given by

$$\rho(H) = N^2 \lambda^3 \left( \frac{e^2}{mC^2} \right)^2 |F(H)|^2 L_p B G A \Delta v \quad (1.f)$$

where $(e/m)$ the specific charge of the electron; $C$ - the velocity of light in vacuum; $L_p$ - the Lorentz-polarisation factor; $B$ - the attenuating factor due to photo-electric absorption of the incident and scattered beam; $A$ - attenuation factor due to primary and secondary extinction of the observed intensity; $G$ - the correction term for anomalous scattering if any and $\Delta v$ - the volume of the crystal fully bathed in the incident X-ray beam of wavelength $\lambda$. Eqn. (1.f) is used to find $|F(H)|$.

1.1 Crystal Structure Factor

The crystal structure factor is the ratio of the total amplitude of X-rays scattered by all the atoms in the unit cell in the direction of the spectra $(H)$ to that scattered by an electron situated at the corner of the unit cell in the same direction under identical conditions and it has the form

$$F\left(\frac{3}{\lambda}\right) = \sum_{j=1}^{n} f_j \exp 2\pi i(hx_j + ky_j + lz_j) \quad (1.g)$$
or in the shorter form

$$F(H) = \sum_{j=1}^{n} f_j \exp\left(2\pi i H \cdot \vec{r}_j\right) \quad (1.h)$$

where $f_j$ is the atomic scattering factor, $(x_j, y_j, z_j)$ are the fractional coordinates of the $j$th atom and $H$ is the position of the node $(hkl)$ in reciprocal space; $n$ being the number of atoms in the unit cell.

1.2 Electron Density and Crystal Structure Factor.

The structure of a crystal on the atomic scale is best understood by considering it as a continuous distribution of electron charge density $\rho(\vec{r})$, reaching maxima at the atomic centres and minima elsewhere. In such representation the crystal structure factor $F(H)$ is expressed as

$$F(H) = \int \rho(\vec{r}) \exp\left(2\pi i H \cdot \vec{r}\right) dv \quad (1.i)$$

The integral is taken over whole volume $V$ of the unit cell. Since $\rho(\vec{r})$ is a triply periodic function in a direct lattice, it can be expressed as triple Fourier series and it may be written as

$$\rho(\vec{r}) = \sum_{H} C(H) \exp\left(-2\pi i H \cdot \vec{r}\right) \quad (1.j)$$

When $C(H)$'s are the complex amplitude of the Fourier waves.

The development of the lattice spectra can also be described as interaction between the incident monochromatic X-ray wave and each component of the sinusoidal distribution of scattering matter [given by eqn. (1.j)] which gives two spectra in the positive and negative first order corresponding to a spacing equal to the wavelength of a
Fourier wave and thus for each component of the Fourier wave, there are spectra of the type $hkl$ and $\bar{h}\bar{k}\bar{l}$.

The co-efficient $C(H)$ of the Fourier series $(l,j)$ is related to the crystal structure factor $F(H)$ by $C(H) = \frac{F(H)}{V}$ where $V$ is the volume of the unit cell. Therefore

$$\rho(\vec{r}) = \sum_{-\infty}^{+\infty} \frac{F(H)}{V} \exp(-2\pi i \vec{H} \cdot \vec{r}) \quad (1.k)$$

The structure factor $F(H)$ is in general, a complex quantity and can be expressed as

$$F(H) = A(H) + iB(H)$$

where

$$A(H) = \sum f_j \cos 2\pi (hx_j + ky_j + lz_j)$$

$$B(H) = \sum f_j \sin 2\pi (hx_j + ky_j + lz_j)$$

the summation being over all the $n$ atoms in one unit cell, and can be written as

$$F(H) = |F(H)| \exp i\Phi(H) \quad \text{where} \quad |F(H)|^2 = A(H)^2 + B(H)^2$$

and $\Phi(H)$ called the phase angle is given by

$$\Phi(H) = \tan^{-1} \frac{B(H)}{A(H)}$$

The factors $A(H)$ and $B(H)$ take different forms for different space groups.

1.3 Phase Problem.

If one could have a large number of $F(H)$'s available equation(1.k) which represents the electron density in direct space can be computed
for the electron density function leading to the location of atomic positions in the unit cell. But from diffraction experiments only the numerical magnitude of the structure factors \( F(H) \)'s can be obtained and the knowledge about their phases are lost during the process of experiment. So if the phase of the structure factors can be determined by some means, the Fourier series \( (l,k) \) can be summed up and the structure can be determined univocally. Thus the whole problem of finding a crystal structure from the observed intensity data reduces to one of determining the phases of various reflections, the phase being proved to be the greatest hurdle set before the crystallographers. This phase problem has been a constant source of investigation by many workers. Several methods have been developed to tackle the phase problem. These may be classified as follows:

a) Trial and error method.
b) Patterson vector method.
c) Heavy atom method.
d) Isomorphic replacement method.
e) Anomalous dispersion method.
f) Direct methods.

The principle of methods which were used in the present structural investigations have been discussed in some detail whereas the other methods have just been outlined briefly in the following sections.
1.3.1 THE TRIAL AND ERROR METHOD

The trial and error method was the principal procedure in the early decades of the development of structure analysis. A model of the structure is postulated from the prior knowledge of the morphology, physical properties, chemical formula, standard bond lengths and angles and the space group symmetry. The orientation of a ring or a chain molecule about one of the crystallographic axes can be determined from the weighted reciprocal lattice (Robertson, 1945; Roychoudhury, 1973). Sometimes it is possible to gain important information about the orientation of the molecule from only a few intensities if these are outstandingly large, and for planar molecule, even one outstandingly intense reflection can give clue to the structure. The structure of hexamethyl benzene was solved by Lonsdale (1929) by this way. The orientation of a planar molecule can sometimes be obtained from magnetic susceptibility measurement. Once the orientation is known a few models of the arrangement of the molecules in the unit cell with respect to the symmetry elements can be built up from packing considerations of the molecules in the unit cell. For each model, the structure factors ($F_C$) for certain important reflections are calculated and these are compared with the observed structure factors ($F_O$) of those reflections and if they agrees roughly, the procedure can be extended for other reflections.

As the correct solution is approached a better agreement between $F_C$ and $F_O$ is achieved with small displacement of atoms. One of the objective criteria for checking the trial structure is described by a quantity, called "Residual" which is broadly defined by

$$R = \frac{\sum |(F_O - F_C)|}{\sum |F_O|}$$
where summation is taken over all the reflections. If $R$ is less than a certain value, the trial structure may be assumed to be correct. Accepting the phases of the structure amplitudes given by the postulated model in this way a reasonably accurate atomic coordinates can be obtained from successive Fourier synthesis of electron density.

The optical transform method developed by Lipson & Taylor (1964) based on the analogy between optical and X-ray diffraction is useful for checking a trial structure.

At present though the trial and error method is hardly used, its basic idea - comparing and fitting the calculated and observed structure factors are still used. The quantity $R$, called residual or its modified form is still widely used as a criterion of the correctness of the postulated or determined structure and as a method of estimating the progress of its refinement.

1.3.2. THE PATTERSON VECTOR METHOD

We have seen that lack of knowledge of the phases of structure factors prevents us directly computing an electron density map and hence the positions of the atoms in the unit cell.

A.L. Patterson (1934) suggested as an aid to structure determination, the use of a function $P(\vec{r})$, known as Patterson density function with squares of the structure factors as Fourier coefficient which are directly proportional to the observed intensities and independent of phase angle.
A Patterson function is defined as

\[ P(\mathbf{r}) = P(uvw) = \iiint \rho(xyz) \rho(x+u, y+v, z+w) \, dx \, dy \, dz \]

which is the integral product of the electron density at a point \( x, y, z \) and at another point within the unit cell separated from the former by a distance \( \mathbf{r}'(u,v,w) \). The product will have small value in general but it may have an appreciable value if \((u,v,w)\) are the components of \( \mathbf{r}_{mn} \) the vector distance between two atoms in the structure.

This function can be represented by a triple Fourier series

\[ P(\mathbf{r}) = \frac{1}{V} \sum_H |F(H)|^2 \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) 
= \frac{1}{V} \sum_H \sum_{m,n=1}^{N} f_m(H) f_n(H) \exp(-2\pi i \mathbf{H} \cdot (\mathbf{r} - \mathbf{r}_{mn})) 
= \sum_{m,n=1}^{N} P_{mn}(\mathbf{r} - \mathbf{r}_{mn}) \]

where \( P_{mn}(\mathbf{r}) = \frac{1}{V} \sum_H f_m(H) f_n(H) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \) represents a single Patterson peak for a pair of atoms marked \( mn \). The height of the peak depends on the atomic number of the \( m \)th and \( n \)th atoms only. The Patterson map would have \( N^2 \) peaks out of which \( N \) numbers are concentrated as a large peak at the origin and the remaining \( N(N-1) \) peaks are distributed centrosymmetrically throughout the unit cell. The light pair of atoms will give a peak of small height at a vector distance \( \mathbf{r}_{mn} \) from the origin. The largest peak occurring at the origin will generally mask the peak of small heights and when there are pair of heavy atoms in the structure, the corresponding peaks are generally well resolved and \( \mathbf{r}_{mn} \) may be found out for that pair. For centric structures for a pair of atoms having co-ordinates \( \mathbf{r}_i \) and \( \mathbf{r}_j \), there is a similar pair at \( -\mathbf{r}_i \) and \( -\mathbf{r}_j \). They produce single peaks at \( \pm 2\mathbf{r}_i, \pm 2\mathbf{r}_j \) and double
peaks at $\pm (r_i - r_j)$ and $\pm (r_i + r_j)$. When a molecule contains a large number of atoms (organic structures), the resolution of Patterson peaks becomes poorer and the interpretation of the Patterson function becomes difficult, since all the short vectors which occur between 1.20Å and 1.55Å are over-crowded near the origin. Despite the over-crowded nature of Patterson map, useful information can frequently be derived from it to solve crystal structures. Several modifications of the Patterson function have been attempted to improve the resolution of Patterson peaks.

Harker (1936) showed some useful informations about the location of atomic positions could be obtained from certain section of Patterson map containing peaks due to pair of atoms related by symmetry element of the crystal space group. These sections are known as Harker sections. For example in the space group $P2_1/\bar{1}$, the equivalent positions are $x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z$. The peaks due to pair of atoms related by the screw axis lie in the plane $u\frac{1}{2}w$; that means the position of the peak will give directly the $x$ and $z$ coordinates of the atoms involved in the symmetry operation. The peaks due to pair of atoms related by glide plane lie along the line $0 v \frac{1}{2}$, which gives the $y$ coordinate of the atom.

1.3.3. HEAVY ATOM METHOD

If a crystal contains a heavy atom or a small number of heavy atoms together with other light atoms and if scattering power of the heavy atoms dominate the intensities then Patterson peaks due to the interaction between the heavy atoms stand out strongly against a background of overlapping smaller peaks due to all the other interatomic
vectors and immediately the positions of the heavy atoms may be ascertained from the Patterson function or Harker sections.

Once the heavy atom and hopefully a few light atoms are located from the Patterson map, considering the contribution of the atoms located the phases of the structure factors can be calculated. Then associating these calculated phases with the corresponding observed structure factors (F₀)’s, a Fourier map is computed. A few more atoms are readily located and then these are included for calculation of phases for the next Fourier synthesis. The process is repeated until the complete phasing model is built up.

For most successful use of this method the ratio of sum of the squares of the atomic number of the heavy atoms to that of light atoms should be nearly equal to one.

Sometime it is not possible to determine the phases of reflections with certainty from the contribution of the heavy atom only, particularly in the case of organic crystals having one heavy and a large number of light atoms. On the otherhand when the atom is very heavy compared to the others in the structure, its dominance becomes too great and the comparison of F₀ and Fc becomes relatively insensitive to the positions of the light atoms. Thus uncertainty in the light atom coordinates increases; and in extreme cases the light atoms may not be found out at all.

The success of the heavy atom technique led many workers to solve the organic structures by incorporating deliberately some heavy atoms in the molecules. However, this method has some limitations.
1.3.4 ISOMORPHOUS REPLACEMENT METHOD

When two crystalline materials differing only in that one atom or group of atoms, in one material is replaced by another atom or group in the other, have same space groups and have diffraction patterns of similar appearance, such structures are said to be isomorphous.

This method which has wide application for determining the crystal structures of large molecules, e.g., isomorphous salts of alkoloids, derivatives of Penicillin and protein structures, is based on the changes in the structure amplitudes of two or more isomorphous compounds with a replaceable heavy atom resulting from replacement of one atom by another. These changes can be utilised since from a knowledge of the position of the replaceable atom, its contribution to a particular structure factor may be decisive to determine the phase quite conclusively. The applicability of the method is restricted to centrosymmetrical structures.

1.3.5 ANOMALOUS DISPERSION METHOD

This method is based on the use of the anomalous scattering properties of certain atoms whose absorption edges are close to the wavelength of the incident radiation. Due to this dispersion effect, the scattering factor of an atom becomes complex and for non-centrosymmetric structures intensities scattered from hkl and h̅k̅l are different violating the Friedel's law. From these differences in intensities the phase change can be determined. By the use of phase change produced by anomalous scattering Bijvoet et al (1951) were able to deduce absolute configuration of atom of an optically active molecule in the crystal.
and corroborated Emil Fischer's conventions of the tartaric acid molecule. Further use of anomalous scattering for phase determination was made by Ramachandran (1956) and Raman (1958). This method in conjunction with the isomorphous series method, has been of great help in determining protein structures.

1.3.6. DIRECT METHODS

Methods which make it possible to determine exactly or with some probability the phases \( \phi(H) \) of reflection from a certain set of \( |F_0(H)| \) values are called direct and a review of all such methods has been nicely presented by Woolfson (1971).

The main characteristics of direct methods are that these are cast in the form of a mathematical problem which, once formulated, may be solved by a sequence of steps in which any decision is purely a mathematical one. The first step in direct methods was made by Harker and Kasper (1948) who derived inequality relationships between structure factors and showed that these relationships were capable of giving phase information, but these could only give a solution for simple centric structures. Karle and Hauptman (1950) from the condition that electron density is everywhere positive, derived inequality relationships of a general type. The next impetus to the development of direct methods was initiated by Sayre (1952) leading to the discovery of simple probability relationships between phases of structure factors. Simultaneously Cochran (1952) and Zachariasen (1952), from a slightly different point of view also arrived at the same probability relationships. All these methods
could be applied to centrosymmetric structures. Cochran (1955) showed that the general values phases for non-centrosymmetric structures are also related. During the next decade a number of more-or-less involved methods were proposed for applying sign relationships. Subsequently Karle and Karle (1964, 1966) showed that a comparatively simple approach, the symbolic addition method could be applied even to complex structures. A variant of the method is also applicable to non-centrosymmetric structures. A different technique of applying phase relationships developed by Germain, Main and Woolfson (1971), has been fully automated and quite complex structures can now be solved with computer programs.

The procedure evolved has gain convenient applicability through MULTAN, a set of programs written by them.

A systematic account of the development of the direct methods is beyond the scope of this brief review. We shall present here certain basic principles, together with some working formulas and shall then outline the procedure of phase determination adopted in the well known program package MULTAN (1978, version) which has been utilised in some part of the present work.

1.3.6a. Harker- Kasper inequalities: Unitary structure factor.

Using Cauchy's inequality, Harker and Kasper (1948) deduced some useful inequality relations between magnitudes and phases of unitary structure factors. One of the obvious difficulties in applying the inequalities to \( F_0(H) \)'s is the falling off their magnitude due to decrease in the values of the atomic scattering factors with increasing angle of diffraction; the latter again is due to the effect of finite
atomic size and the thermal motion of the atoms. It causes uncertainties in obtaining reliable phase information. To avoid this Harker and Kasper defined unitary structure factor as

$$U(H) = \frac{F(H)}{\sum_{j=1}^{N} f_j}$$

where \(f_j\) is the atomic scattering factor of the \(j\)th atom which includes temperature effect and \(N\) the total number of atoms in the unit cell. Its value lies between -1 and +1 and have the same phase as that of \(F(H)\).

Representing the sign of \(U(H)\) by \(S(H)\), the general expression for the inequality relationship for a centrosymmetric space group (viz. \(P\bar{1}\)) may be written as

$$[|U(H)| + |U(H')|]^2 \leq [1 + S(H)S(H')S(H+H')]U(H+H')||[1 + S(H)S(H')S(H-H')||U(H-H')|]$$

This relationship shows that the sign of one or both the triple sign products is positive if \(U(H)'s\) are sufficiently large.

As stated earlier the Harker - Kasper inequalities, has limited applications.

1.3.6b. Sayre's Equation and Probability Methods.

Sayre derived an equality relation between structure factors for a structure composed of equal atoms which are fully resolved from one another. If the electron density is squared, its distribution remains unchanged in the sense that it is still composed of equal resolved peaks in the same position as before. Thus if "\(f\)" is the
scattering factor of each of the atoms and "g" that of squared atom. Sayre derived the relation for $H$th reflection

$$F(H) = \theta(H) \sum_{H'} F(H') F(H-H')$$

where $\theta(H) = f(H)/V g(H)$, $V$ being the volume of the unit cell. This is an exact relation involving measured magnitudes and phases for structures with identical atoms and valid for both centrosymmetric and noncentrosymmetric cases.

Multiplying both sides of Sayre's equation by $F(-H)[=F(H)]$ we get

$$|F(H)|^2 = \frac{f(H)}{V g(H)} \sum_{H'} F(-H) F(H') F(H-H')$$

The series on the right hand side adds up to a positive sum. If three particular magnitudes $|F(H)|, |F(H')|$ and $|F(H-H')|$ are large, the corresponding product is likely to be a dominating term of the series—large and positive. So we may have the probability relation

$$\phi(-H) + \phi(H') + \phi(H-H') \approx 0$$

which for centrosymmetric structure reduces to

$$S(H) S(H') S(H-H') \approx +1$$

This equation is commonly known as triple product sign relationship and it is the basis for most of the current direct methods of determination of phases.

Cochran (1952) and Zachariasen (1952) also derived at the same probability relationship from different point of view.

Cochran (1955) calculated the probability $P[\phi(HH')]$ of
\[ \psi_{HH'} = \psi(-H) + \psi(H') + \psi(H-H') \] which is given by

\[ P[\psi_{HH'}] = \frac{\exp[K(HH') \cos(\psi_{HH'})]}{2 \pi I_0 K(HH')} \]

where \( K(HH') = 2\sigma_3^2 \sigma_2^{-5/2} \left| E(H) E(H') E(H-H') \right| \); \( \sigma_m = \sum_{j=1}^{N} Z_j^m \)

and \( I_0 \) is the modified Bessel function of zero order.

Woolfson (1955) obtained an expression for probability of triple product sign relationship which is commonly used and can be applied for structures with non-equal atoms.

1.3.6c. The Hauptman and Karle Approach.

Karle and Hauptman (1950) from the idea of constraint of non-negative electron density derived an inequality in a general determinantal form, from which a large variety of different inequalities can be derived.

Karle and Hauptman favoured the use of a normalised structure factor \( E(H) \) in place of unitary structure factor \( U(H) \).

Where \( E(H) \) is defined by the relation

\[ E^2(H) = \frac{|F(H)|^2}{\epsilon \sum_{j=1}^{N} f_j^2} \]

where \( \epsilon \) is a small integer and division by \( \epsilon \) brings all the reflections to a common basis and makes

\[ \langle |E(H)|^2 \rangle = 1 \]
It has been observed that in the presence of symmetry axes, and planes average intensity of special classes of reflections (e.g. those with one or two indices zero or with two equal indices etc) is enhanced by a factor \( e \) with respect to that of the general hkl reflections. \( e \) is unity for general reflections and may assume values like 2, 4 etc for special class of reflections depending on the nature of symmetry.

Since the atomic form factor curves have approximately similar shape for all atoms, we may assume \( f_j = z_j \hat{f} \), where \( \hat{f} \) is a common shape factor and \( z_j \) is the atomic number of the \( j \)th atom in the structure, and so we may write

\[
E(\vec{H}) = \sum_{j=1}^{N} z_j \exp(2\pi i\vec{H} \cdot \vec{r}_j) / \left[ e \sum_{j=1}^{N} z_j \right]^{1/2}
\]

and this expression is commonly used for the calculation of \( E(\vec{H}) \).

Normalised structure factors thus represent scattering from stationary point atoms. It is in general an approximation for a structure containing different types of atom and exact for structures containing similar atoms. The normalised structure factors have statistical properties which are often useful to distinguish centrosymmetric and non-centrosymmetric structures.

Some of the basic Karle and Hauptman formula for centrosymmetric cases are

\[
\Sigma_1 = S[ E(2H) ] \approx S[ E^2(\vec{H}) - 1 ]
\]

\[
\Sigma_2 = S[ E(\vec{H}) ] \approx S[ \sum_{H'} E(\vec{H}') E(\vec{H} - \vec{H}') ]
\]
relationship can indicate either a positive or negative sign for $E(2H)$ depending upon the magnitude of $E(H)$. If both $E(H)$ and $E(2H)$ have large values, the sign of $E(2H)$ has the probability of being positive. The relationship $\Sigma_2$ is a modified form of Sayre's equation.

1.3.6d. Choice of Origin.

In order to define a crystal structure completely, it is necessary to specify the atomic positions with respect to a point chosen as origin of reference. This entails setting up a system of axes in the crystal with clearly defined origin. The crystal symmetry usually determines the directions of the axes but not their absolute position and there will be in general, alternative choice of origin location.

Such choice is made in an obvious way when the structure is solved by interpretation of the Patterson function. However, when the structure is solved by phase determination, it is necessary to examine how the real space choice of origin position may be carried out in reciprocal space.

The magnitudes $|F(H)|$ are obviously independent of our choice of origin, but its phases $\theta(H)$ are very much dependent on origin locations. Quantities which remain unaltered for any arbitrary change of origin are called "structure invariants".

The unit cell of a centrosymmetric structure contains eight non-equivalent centres of symmetry each of which can be considered as an origin of reference. With one of centre of symmetry at $(0, 0, 0)$, there are others located at $(\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The change of sign of structure
factors due to change of origin occur in such a way that all members of one parity group change together. A parity group is a set of \( hkl \) which are odd or even in the same way. The indices \( hkl \) can have eight parity groups like eee, oee, eoe, eeo, ooe, eoo, eoo and ooo where e stands for even and o stands for odd. The members of the parity group with all indices even do not change sign with change of origin within the chosen eight positions. The quantities which remain unchanged when the origin is shifted only in the restricted way allowed by the space group symmetry, are called "structure seminvariants". Thus \( \Phi(2H) \) i.e. phase for a reflection with all even indices is a structure seminvariant and hence eee reflections cannot be used for origin definition. If three structure factors with indices \( H, H' \) and \( H + H' \) are chosen such that the vector sum of the three indices gives parity eee, then the product of three such structure factors (called linearly dependent) is also structure invariant. We have to assign arbitrary signs (+++ say) to three reflections from different parity groups which are not linearly related to define a unique origin in case of structures having primitive lattices. When an origin defining reflection is a systematic absence due to the lattice centring that reflection is not needed. This always results in one less origin defining reflections in the case of \( A, B, C \) and \( I \) lattices and usually only one reflection is needed to define the origin in the case of \( F \) centred lattices.

Origin definition in non-centrosymmetric space groups can be carried out using exactly the same logic as that of described for centrosymmetric space groups. However, an additional matter must be considered. The structure, being non-centrosymmetric, may exist as
one of two enantiomorph form or if it contains mirrors or glides, the axes may be left or right handed. In either case, the effect on the phases is the same. It means that by inverting the structure through the origin all phases $\phi(H)$ changes to $-\phi(H)$. Thus both origin and enantiomorph must be defined to determine explicit phases for the reflections. The problem can be simplified by considering not individual phases, but a combination of phases whose value is independent of origin position, i.e. a structure seminvariant. Its value will change sign upon change of enantiomorph but will be unaffected by change of origin. This gives a very simple rule for enantiomorph definition, that is, to restrict the phase of a structure seminvariant to the range 0 to $\pi$ rather than $\pi$ to 2$\pi$.

1.3.6e. Important Relationships for Phase Determination and Procedure in MULTAN.

The MULTAN Package program consist of four different programs NORMAL, MULTAN, EXFFT and SEARCH.

The program NORMAL, preceding MULTAN program package, brings the input intensity data to an absolute scale using a Wilson plot or a Debye plot (ref. section 4). $|E|$ the normalised structure factor values are then calculated and a requisite number of $|E|$ values, generally 8 to 10 per non-hydrogen atom in one asymmetric unit, are saved on the output file for utilisation of phase determination procedure of MULTAN. Fifty smallest $|E|$ values are also saved for calculation of the figure of merit to be discussed later.

For centrosymmetric structures $\phi(H)$ the phase of $E(H)$ may be either 0 or $\pi$ i.e. $S[E(H)]$ is either + or --, and the phase relationships
are set up using the following $\Sigma_2$ relation (Karle and Hauptman, 1950; Hauptman and Karle, 1953)

$$S [E(H)] \approx S \left[ \sum_{H'} E(H') E(H-H') \right]$$

where $H'$ indicates a restricted summation involving $r$ large $E$ values.

The probability that $E(H)$ is positive, is given by Cochran and Woolfson (1955).

$$P = \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2 \frac{-3/2}{|E(H) E(H') E(H-H')|}$$

where $\sigma_n = \sum_{j=1}^{N} Z_j$.

If all the $N$ atoms of the unit cell are equal, $\sigma_3 \sigma_2 = N^{-3/2}$. Hence the probability of a correct sign assignment increase for large $E$'s and hence such are used initially.

The corresponding relation for non-centrosymmetric case is (Karle and Hauptman, 1950; Karle and Karle, 1964, 1966)

$$\hat{\phi}(H) \approx \langle \hat{\phi}(H') + \hat{\phi}(H-H') \rangle_{H'}$$

A special case of the $\Sigma_2$ relation where the reflections $H'$ and $H-H'$ are the same or equivalent, is used in MULTAN, under the name $\Sigma_1$ relation. Obviously, the phases generated by $\Sigma_1$ relation are for reflections with even-even-even indices.

The approximate phases obtained have to be refined by the well known tangent formula (Karle and Hauptman, 1956).
\[
\tan \hat{\phi}(H) = \frac{\sum_{H'} E(H') E(H-H') \sin [\hat{\phi}(H') + \hat{\phi}(H-H')]}{\sum_{H'} E(H') E(H-H') \cos [\hat{\phi}(H') + \hat{\phi}(H-H')]}.
\]

A quantity \(\alpha(H)\) which gives a measure of the reliability with which the phase \(\hat{\phi}(H)\) may be determined was defined by Karle and Karle (1966) as

\[
\alpha^2(H) = \left[ \sum_{H'} K(HH') \cos \{\hat{\phi}(H') + \hat{\phi}(H-H')\} \right]^2 + \left[ \sum_{H'} K(HH') \sin \{\hat{\phi}(H') + \hat{\phi}(H-H')\} \right]^2
\]

where

\[
K(HH') = 2 \sigma_2 \sigma_2 E(H) E(H') E(H-H')\]

For calculation of \(\alpha(H)\), both \(\hat{\phi}(H)\) and \(\hat{\phi}(H-H')\) have to be known. But in MULTAN an estimation of \(\alpha(H)\) is required before any of the phases has been determined. For this purpose, Germain, Main and Woolfson (1970) deduced an expression for \(\alpha(H)_{\text{est}}\) and in practice the following equation is used

\[
\alpha(H)_{\text{est}} = \sum_{H'} K(HH') \frac{I_1(K(HH'))}{I_0(K(HH'))}
\]

where \(I_0\) and \(I_1\) are modified Bessel function and

\[
\frac{I_1(K)}{I_0(K)} \approx 0.5658 K - 0.1304 K^2 + 0.010 K^3
\]

is used for computation in the range \(0 \leq K \leq 6\); for \(K > 1\) the function is essentially 1.

The phases determined by \(\Sigma_1\) relation for a number of reflections with all even indices having largest probabilities (at least \(> 0.95\)) are accepted as "reflections with known phases" for inclusion in the starting set of reflections.
The best reflections to define the origin and enantiomorph (where necessary) are then found out by the principle of convergence. This is done by calculating $\alpha(H)_{\text{est}}$ for all the reflections and then discarding the reflection with lowest $\alpha(H)_{\text{est}}$ together with all the phase relationships to which this reflection contribute. Such a procedure changes the value of $\alpha(H)_{\text{est}}$ for all the reflections and are therefore updated and once more the reflection with smallest $\alpha(H)_{\text{est}}$ is eliminated. If the process of elimination prevents the origin from being defined then that reflection is retained and the reflections with next smallest $\alpha(H)_{\text{est}}$ is eliminated. The process must converge to a small group of reflections which are linked together with a large number of strong $\Sigma_2$ relationships.

Phases are arbitrarily assigned to maximum of three reflections with proper parity out of this group to define the origin. One reflection is required to define the enantiomorph (in case of non-centrosymmetric structure only). The reflection with known phases, as mentioned before, are now added to these small group of reflections obtained by the method of convergence.

The rest of the reflections are assigned different combination of phases to obtain different starting sets. For $n$ number of such reflections in centrosymmetric cases, $2^n$ number of starting sets are obtained. This is because of the fact that in centrosymmetric structure phases may be either 0 or $\pi$.

In non-centrosymmetric cases, instead of any value ranging from $-\pi$ to $+\pi$, certain discrete values of phases are assigned to these reflections. A special reflection, according to its type, may have one or other of a pair of values like $(0, \pi)$ or $(\pm \frac{\pi}{2})$, where a
general reflection is given or other of the quadrant values
\((- \frac{3\pi}{4}, \pm \frac{3\pi}{4}\).

Using each of these starting sets, phases are determined
for all reflections of chosen E's saved in the outfile of NORMAL, with
the help of a weighted tangent formula.

\[ \tan \phi(H) = \frac{\sum_{H'} Q(HH') \sin[\phi(H') + \phi(H-H')] \cdot T(H)}{\sum_{H'} Q(HH') \cos[\phi(H') + \phi(H-H')] \cdot T(B)} \]

where \(Q(HH') = W(H') W(H-H') E(H') E(H-H') / (1 - U(H)^2)\)

and \(W(H) = \tanh \left[ N^{-1/2} \frac{|E(H)|}{\{T^2(H) + B^2(H)\}^{1/2}} \right] \)

\(N\) being the number of atoms in the asymmetric unit. Thus
we obtain a number of complete of phased E's, a number of probable
solutions to our problem.

It is advantageous to have some figure of merit associated
with each set of phases determined in order to judge their relative
plausibilities. These are absolute figure of merit (M), \(\Psi\) and
residual R. One such measure could be \(Z = \sum \alpha(H)\), defining \(\alpha(H)\)

\[ \alpha(H) = 2N^{-1/2} |E(H)|^{2} \begin{pmatrix} T(H) + B(H) \end{pmatrix}^{1/2} \]

which gives \(W(H) = \tanh \left[ \alpha(H) / 2 \right] \)

Using values of \(\alpha(H)_{\text{est}}\), we get the expectation value of \(Z\) as \(Z_{\text{exp}}\).

When there is no self-consistency in the contributions
to \(\alpha(H)\) the random expectation value of its square is found to be
\[<\alpha^2(H)_{\text{rand}}> = \sum_{H'} K^2(HH')\]

whence
\[Z_{\text{rand}} = \frac{\sum <\alpha^2(H)_{\text{rand}}>}{\sum <\alpha^2(H)_{\text{rand}}>}^{1/2}\]

The absolute figure of merit is defined as
\[M = \frac{Z-Z_{\text{rand}}}{Z_{\exp}-Z_{\text{rand}}} \]
and which is a measure of internal consistency among \(\Sigma_2\) relationship. The absolute figure of merit is clearly zero for random phases and unity if sum of all the \(\alpha(H)\) is equal to its expectation value.

\[\psi_0\] Figure of merit was first used by Cochran and Douglass (1955) and is defined by
\[\psi_0 = \sum |\sum E(H') E(H-H')|\]
where the inner sum is over the phases determined and the outer sum is over a number of reflections for which \(E(H)\) is zero or very small (a number of such reflections stored in the output file of NORMAL, for the calculation).

For correct set of phases \(\psi_0\) should be small.

A third figure of merit is the residual, proposed by Karle and Karle (1966) is based on Sayre's equation.

For each \(E(H)\) in the set, one calculates
\[E(H)_{\text{calc}} = K \sum_{H'} E(H') E(H-H')\]
where \(K\) is a constant chosen to give
\[\sum |E(H)|^2_{\text{obs}} = \sum K |E(H)|^2_{\text{calc}}\]
The residual is then defined as

\[ R = \frac{\sum |E(H)|_{\text{obs}} - |E(H)|_{\text{calc}}}{\sum |E(H)|_{\text{obs}}} \]

A combined figure of merit \( C \), defined as follows, is found to be more effective than either \( M \), or \( R \) taken separately.

\[ C = \frac{M - M_{\text{min}}}{M_{\text{max}} - M_{\text{min}}} + \frac{(\psi_0)_{\text{max}} - \psi_0}{R_{\text{max}} - R_{\text{min}}} + \frac{R_{\text{max}} - R}{R_{\text{max}} - R_{\text{min}}} \]

where the weights \( W_1, W_2, W_3 \) are generally chosen as unity.

The set with highest combined figure of merit is chosen first for obtaining an E-map. Often a set with lower value of the combined figure of merit provides the correct solution. The program EXFFT is used for computation of the E-map and SEARCH finds out the peaks in the map, calculates distances and angles and helps one to decide whether the model obtained is physically reasonable or not.

Quite often, only a part of the asymmetric unit is revealed in the E-map. In such a case there is a provision to input the known atomic positions in NORMAL for preparation of an input file for computation of a weighted Fourier synthesis by EXFFT and use SEARCH as before to complete the phasing model.
2. MEASUREMENT OF INTENSITIES OF X-RAY REFLECTIONS FROM SINGLE CRYSTALS

There are two avenues of approach available for the measurement of X-ray intensities. One method is based on the use of the fact that X-rays can affect photographic film or plate having an emulsion of AgBr and a few per cent of AgI producing blackening on development. The degree of blackening is related to X-ray intensity incident upon the film. The blackening can be measured using a microphotometer or by eye estimation. This is known as photographic method.

The other method is based on the use of the fact the X-ray photon can produce photo electron which ionises gases whose magnitude is measured by G-M Counter diffractometer. In the following sections the photographic method and the counter diffractometer method which have been used in the present investigation have been described briefly.

2.1. Photographic Method

Single crystals of suitable dimension were used to record photographically the different crystal reflection by moving film technique - Weissenberg method. For recording all the observable reflections normal beam zero layer photographs and equi-inclination photographs for upper layers were taken about different crystallographic axes using multiple film technique and nickel filtered CuKα (λ = 1.5418 Å) radiation. The integrated intensities of all the reflections were measured visually from the blackening produced on the diffraction photographs. Relative estimation of intensities were made by systematic comparison of the observed reflections against a graded
intensity scale which was prepared by selecting an intense reflection from the same crystal recorded in the zero layer photograph.

The graded intensity strip had a scale of intensity from 1 to 30, the weakest spot being barely visible. To estimate the intensities of spots recorded, the film was placed on an illuminated viewer and graded intensity strip was placed over it. The reflection is viewed through the background of the strip and is compared with reference spots until a perfect match is found or until found to lie between two consecutive values. An eye estimated interpolated value was assigned to the intermediate value.

In the multiple film technique, any spot which would rate greater than 30 on the top film, its intensity was estimated from a lower film where it would appear less dense by film factor. The film factor is determined by estimating intensities of some common spots which have values less than 30 in two successive films and taking average ratio of the same. Exposure time varying from 30 hours to 30 minutes was necessary to record all the crystal reflections, while estimating the intensities of spots due allowance was given for the variation of spot shape in different photographs. All the estimated intensities were then put on a same scale by using the film factor and the intensity measured on the top film.

2.2 Counter Method: Using a Four Circle X-ray Diffractometer.

Using an Enraf-Nonius CAD-4 automatic single crystal diffractometer, the intensities of X-ray reflection from a single crystal were collected by an $\omega - 2\theta$ scan with graphite-monochromated MoK$\alpha (\lambda = 0.71073\text{Å})$. 
radiation. For each reflection, the scanning range was divided into 96 steps of which the middle 64 steps covered the reflections and the first and last 16 steps give the measurements of the background. The scan speed was 20.1166/n degree per minute, n varying from 8 to 24. For every intense reflections, an attenuator was set with an attenuation factor 18.741. During data collection crystal stability and its orientation was monitored by periodically (after every 50 measurements) measuring the intensities of three standard reflections. There was no evidence of crystal deterioration in the present investigations.

The measured value of intensity is given by

$$I_{\text{raw}} = \frac{A}{n} (C - R \cdot B)$$

where C = total count, R = ratio of scan time to background counting time ( = 2.0 for CAD-4), B = total background count, n is an integer varying from 8 to 24, A = attenuation factor ( = 18.741 for MoKα radiation). The standard deviation of the raw intensity on the basis of counting statistics is given by

$$\sigma(I_{\text{raw}}) = \frac{20.116 \cdot A \cdot \frac{1}{n} \cdot \frac{1}{C + R^2 \cdot B}}{2}$$

Applying the Lp correction (discussed in section 3) to the $I_{\text{raw}}$ and $\sigma(I_{\text{raw}})$ we get $|F_0|^2$ and $\sigma(I_{\text{cor}})$ respectively.

Thus $\sigma(I_{\text{cor}}) = \sigma(I_{\text{raw}})/Lp$

The standard deviation of $F_0$ based on counting statistics may then be taken as

$$\sigma(F_0) = \sigma(I_{\text{cor}})/2F_0$$
3. PHYSICAL AND GEOMETRICAL FACTORS AFFECTING THE OBSERVED INTENSITY

When evaluating the magnitude of structure factor from the integrated intensity of a reflection, certain physical and geometrical factors affect the diffracted intensity. These are enumerated below.

3.1. Polarisation Correction

It arises out of the state of polarisation of the incident X-ray beam. The characteristic X-ray emanating from the X-ray tube is unpolarised. The scattered intensity being a function of the angle between the electric vector of the incident beam and the direction of scattering, an average value of the said function has to be considered when the beam is unpolarised. For such cases the polarisation factor \( p \) for a crystal reflection \( hkl \) is given by

\[
p = \frac{1}{2} (1 + \cos^2 \theta_{hkl}) \quad \text{where} \quad \theta \quad \text{is the Bragg angle}.
\]

But for a crystal reflected monochromatic beam used for collection of intensity data the polarisation factor for the reflection takes the form

\[
p = PF \cdot \frac{\cos^2 \theta_m + \cos^2 \theta_{hkl}}{1 + \cos^2 \theta_m} \cdot \frac{\cos 2 \theta_m + \cos^2 \theta_{hkl}}{1 + \cos 2 \theta_m}
\]

where \( PF \) = a constant depending on the perfection of the monochromator crystal \( (\approx 0.5 \text{ in our experiment}) \)

\[
\theta_m = \text{Bragg angle for monochromator crystal (graphite) for the}
\]

\[
= 6.1^\circ \text{ for MoK}_\alpha \text{ radiation}
\]

The raw intensity data I collected is corrected for polarisation
factor and the corrected intensity is given by

\[ I_{\text{cor}} = I/p. \]

3.2 Lorentz Correction.

This factor a geometrical one, depends solely upon the experimental arrangement for recording the intensity of a crystal reflection. When a crystal sweeps through reflecting position with a rotatory motion, linear velocity with which the corresponding reciprocal lattice point cuts the sphere of reflection depends on the distance of the reciprocal lattice node \((hkl)\) from the axis of rotation. Thus for different reflections the time spent during observation of each reflection would be different. This factor known as the Lorentz factor is given by

\[ L = \frac{\sin^2 hkl}{\sin^2 hkl (\sin^2 hkl - \sin^2 \mu)^{1/2}} \]

for equi-inclination Weissenberg photography.

where \(\mu\) is the equi-inclination setting angle.

For single crystal diffractometer the intensity data collected by \(\omega-2\theta\) scan the corresponding expression is

\[ L = \frac{1}{\sin^2 hkl} \]

the correction factor being \(L^{-1}\).
3.3 Spot Shape Correction.

Another correction factor becomes necessary when the intensity data are visually estimated from Weissenberg photographs. Due to the characteristic geometry of the Weissenberg method, spots recorded in the upper level photographs are extended in one half of the film and contracted in the other half. When visual estimation of intensity of these spots are made by comparison with a calibrated strip prepared using a zero layer spot, proper correction should be applied for the effect of variation of area of the blackened spots. Philips (1954, 1956) showed that reliable correction factor could be calculated only for extended spots; the factor for a crystal reflection hkl being

\[ W = 1 + \frac{180}{\pi} \cdot \frac{\left\{ \left[ \frac{2}{(4 - \xi^2) / \bar{\xi}} \right] - 1 \right\}^{1/2}}{2R_1 / (4 - \xi^2)^{1/2} + R_2} \]

where \( \xi \) and \( \bar{\xi} \) are cylindrical coordinates for the reciprocal lattice node hkl, \( R_1 \) and \( R_2 \) are the camera radius and the first pinhole-to-crystal distance respectively. For the Weissenberg camera (Unicam S35) used in our experiment the values of \( R_1 \) and \( R_2 \) are 28.65 mm and 75 mm respectively. The visually estimated intensities of the extended spots (\( I_E \)) is therefore corrected by the equation:

\[ I = W I_E \]

3.4 Absorption Correction.

When an X-ray beam passes through a material a part of it is absorbed, causing an attenuation of the transmitted beam. For a crystal with appreciable absorption the diffracted beams in different directions traverse unequal path lengths inside the crystal and consequently suffer different degrees of attenuation. Calculation of
the correction factor is best achieved by shaping the crystal in the form of a sphere and the second best is a cylindrical form. The correction factor may be minimised by using a more penetrating X-radiation such as MoKα so that linear absorption coefficient \( \mu \) becomes low. The main difficulty of finding absorption correction for a crystal actually arises from the shape anisotropy of the crystal.

3.5 Extinction Correction.

Besides photo electric absorption effect, an additional attenuation of diffracted beam occurs when the crystal is set at the Bragg angle for a reflection. This additional attenuation is of two kinds, which are known as primary and secondary extinctions.

Primary extinction arises due to dynamic interaction between the primary and reflected waves when a Bragg reflection condition is satisfied. It causes the wave propagated in the initial direction weakened as the beam penetrates deeper and deeper into the crystal. It is particularly significant for strong reflection having low glancing angles but it can be practically neglected for a sufficient small mosaic blocks of an ideally perfect mosaic crystal.

Secondary extinction effect of observed intensities in mosaic single crystal arises because the deeper layer of mosaic crystal blocks in correct orientation, receive an incident intensity of lower strength since as a part of the initially incident beam is reflected by the upper tiny crystals which are also in correct orientation for the Bragg position. Also the reflected beam from the lower blocks may be further attenuated due to partial re-scattering of this reflected beam from the upper blocks.
which are correctly oriented to reflect it back. The secondary extinction effect is also more pronounced for spots of high intensity at low glancing angles \( (\text{Sin} \theta / \lambda) \).

Some empirical method of extinctions correction of the observed intensities are available for practical purpose. In the present investigation these extinction effects were neglected.

3.6 Anomalous Scattering

When the frequency of the incident radiation is far removed from the natural absorption frequencies of the atoms in the crystal, the atomic scattering factor is independent of wave length of radiation used and is a real quantity. This is generally the case for light atoms for the radiations commonly used in X-ray diffraction experiments but often it is not true for heavier atoms. When the wave lengths of the incident X-rays beam lies near an absorption edge of an atom in the scattering element, an anomalous phase change occurs during scattering by electrons associated with such an absorption edge and it causes the atomic scattering factor to be incident frequency dependent and a complex quantity. This is expressed by \( f = f_o + \Delta f' + i \Delta f'' \)

where \( f_o \) is the normal scattering factor, \( \Delta f' \) is a real component of the correction term (usually negative) and \( \Delta f'' \) is the imaginary component. The effects are more pronounced for long wave length X-radiation used and the correction terms \( \Delta f' \) and \( \Delta f'' \) which arises from anomalous scattering are almost independent of \( \text{Sin} \theta \).

In our study of the Sm complex using MoK\( \alpha \) radiation, the Sm atom was considered as an anomalous scatter and its modified form factor, a complex quantity was taken into account.
3.7 Temperature Factor

Atoms in crystals are in a state of thermal motion in which all the atoms are vibrating about their mean position with an amplitude which increases as does the temperature of the solid. The frequencies of vibrations of atoms are low as compared with that of X-rays. For this reason we may imagine that at any instant of time, the diffraction pattern is produced as that of a 'frozen' crystal in which all the atoms are stationary and displaced by some distance from their mean positions. The total observed intensity is the time average obtained at successive instants. The electron density $\rho(\vec{r})$ defines scattering and the function $W(\vec{r})$ gives the time average distribution of centres of atoms about their mean positions. The atomic scattering factor without temperature effect is given by

$$f_a(S) = \int \rho_a(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) \, d\vec{r}$$

where $|\vec{S}| = 2 \sin \theta$ and $f(S)$ is the Fourier transform of $\rho_a(\vec{r})$.

Assuming spherically symmetric distributions of electron density, $f_a(S)$ in spherical coordinates is given by

$$f_a(S) = \int_0^\infty 4\pi r^2 \rho_a(r) \frac{\sin \frac{4\pi \sin \theta}{\lambda} r}{4\pi \sin \theta} \, dr$$

But due to thermal effect, $\rho_a(\vec{r})$ is modified by $W(\vec{r})$ and modified electron density $\rho_{ar}(\vec{r})$ around an atomic centre is given by convolution of two functions $\rho_a(\vec{r})$ and $W(\vec{r})$.

$$\rho_{ar}(\vec{r}) = \rho_a(\vec{r}) * W(\vec{r})$$
The Fourier transform of $\rho_{ar}(\vec{r})$ gives the atomic scattering factor with temperature effect and it is equal to the product of the Fourier transform of $f_a(\vec{r})$ and $W(\vec{r})$. The Fourier integral of function $W(\vec{r})$ describing the thermal motion is precisely the temperature factor denoted as

$$f_T(S) = \int W(\vec{r}) \exp(2\pi i\vec{S} \cdot \vec{r}) \, dv$$

The smearing out factor $W(\vec{r})$ depends on many factors and generally it is anisotropic. But in the first approximation one can assume it to be isotropic.

Spherical symmetric vibrations are described by the Gaussian distribution with r.m.s. amplitude $(\overline{u^2})^{1/2}$ of the atoms from their equilibrium position so that

$$W(\vec{r}) = (2\pi\overline{u^2})^{-3/2} \exp(-\overline{r^2}/2\overline{u^2})$$

and the corresponding temperature factor is

$$f_T(S) = \exp(-B \sin^2 \theta / \lambda^2)$$

where $B = 8\pi^2 \overline{u^2}$. For anisotropic temperature effect,

$$f_T(S) = \exp - \left[ 2\pi^2 \left( \overline{u_1^2 S_1^2} + \overline{u_2^2 S_2^2} + \overline{u_3^2 S_3^2} \right) \right]$$

where $S_{x_i}$ are the projections in a reciprocal space of vector $\vec{S}$ on the axes which are parallel to the principal axes $x_i$ of the ellipsoid.
of thermal vibrations. The above equation may be written as

\[ f_T(S) = \exp \left[ -\left( \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl \right) \right] \]

where \( \beta_{ij} = \frac{\mathbf{b}_i \cdot \mathbf{b}_j \cdot B_{ij}}{4} \), \( \mathbf{b}_i \) being the \( i \)th unit vector of the reciprocal lattice and \( B_{ij} \) are expressed in \( \text{Å}^2 \). This form is used in this investigation. The equivalent isotropic temperature factor (\( B_{eq} \)) was calculated from the equation

\[ B_{eq} = \frac{B_{11} + B_{22} + B_{33}}{3} \]

A quantum of incident radiation (photon) can exchange energy and momentum with the travelling waves which represents the normal modes of vibration of the crystal and whose energies are quantized and are known as phonons. X-ray photon scattered with emission or absorption of one phonon is known as first order scattering process. For higher order scattering process, the photons are scattered with emission or absorption of two or more phonons. Such interaction between all phonons and X-ray photons results in a phenomenon known as "Thermal Diffuse Scattering" which gives rise only background intensity around Bragg reflection positions. Because of complexity of the problem, such correction is normally neglected in the crystal structure analysis.

4. ESTIMATION OF OVERALL TEMPERATURE FACTOR AND ABSOLUTE SCALING OF INTENSITY DATA.

The observed intensities of reflections corrected for the different factors are obtained in an arbitrary scale. These may be put
to an absolute scale by the methods of internal standards or by statistical methods. The latter is widely used now a days. According to Wilson (1942) for a random distribution of N atoms in the unit cell, the average value of the absolute intensity $|F|^2$ is given by

$$\langle |F|^2 \rangle = \frac{2}{N} \sum_{j=1}^{2} f_j^2$$

A procedure based on this fact enables the estimation of a common isotropic value of $B$ for all the atoms together with a scale factor $K$ to bring the observed intensities ($|F_0|^2$) to an absolute scale. The entire observed reciprocal space is divided into concentric zones with small variation of $\frac{\sin^2 \theta}{\lambda^2}$, $\langle |F_0|^2 \rangle$ is determined for each of them and $\sum f_j^2$ is calculated using mean value of $\frac{\sin^2 \theta}{\lambda^2}$ for each zone.

Now since, $\langle |F_0|^2 \rangle = K \langle |F|^2 \rangle$

and

$$\sum_{j} f_j^2 = \sum_{i} f_j^2 \exp (-2B \frac{\sin^2 \theta}{\lambda^2})$$

Hence we get,

$$\ln \left( \frac{\langle |F_0|^2 \rangle}{\sum f_j^2} \right) = \ln K - 2B \frac{\sin^2 \theta}{\lambda^2}$$

The plot of $\ln \left( \frac{\langle |F_0|^2 \rangle}{\sum f_j^2} \right)$ against $\frac{\sin^2 \theta}{\lambda^2}$ called Wilson plot, is a straight line, its slope and its intercept with the Y-axis gives the values of $B$ and scale factor $K$ respectively.

In the above process a random distribution of atoms in the unit cell is assumed. When groups of atoms of known geometry (for example a benzene type six-membered ring etc.) is present in the
in the structure the information may be included in the expression for average intensity, although the positions and orientations of such groups are unknown. When G groups of known geometry are present, the Kth of which contains M_K atoms, we may write using scattering formula of Debye (1915).

\[
\langle |F| \rangle^2 = \sum_{K=1}^{G} \sum_{i=1}^{M_K} \sum_{j=1}^{M_K} r_{ij} f_i f_j \frac{\sin 2\pi r_{ij} \sin \theta}{\lambda} \text{mean} + \sum_{j=1}^{N} f_j^2 \frac{\sin 2\pi r_{ij} \sin \theta}{\lambda} \text{mean}
\]

where \( r_{ij} \) is the distance between the \( i \)th and \( j \)th atoms of the \( K \)th group and \( \frac{\sin \theta}{\lambda} \text{mean} \) is as stated before. The plot obtained in this manner, known as Debye plot, gives a better straight line fit for obtaining \( B \) and \( K \).

Another method is based on a \( K \) curve. For each zone of \( \frac{\sin^2 \theta}{\lambda^2} \) mentioned above, \( K \left( \frac{\sin \theta}{\lambda} \text{mean} \right) \) is computed as

\[
K \left( \frac{\sin \theta}{\lambda} \text{mean} \right) = \frac{\sum e^{2} \sum_{i=1}^{N} f_{i}^{2} \left( \frac{\sin \theta}{\lambda} \text{mean} \right)}{\sum |F|^{2} \left( \frac{\sin \theta}{\lambda} \text{mean} \right)}
\]

where \( e \) is a small integer depending on space group. A least square procedure is used to fit a best smooth analytical function usually

\[
\ln K = A + B \left( \frac{\sin \theta}{\lambda} \right)^{C}
\]

to the experimental points. The curve is the same as that of Wilson plot for \( C = 2.0 \).

Using any of the above methods, intensity data may be brought to an absolute scale and the value of overall isotropic temperature factor could be estimated.
5. **REFINEMENT OF THE STRUCTURE**

The methods of structure determination so far outlined can give only the approximate co-ordinates of the atomic positions of the structure and help to build up a model of a stereochemically meaningful structure. The correct structure may be obtained as closely as possible within the limit of experimental accuracy by refining the atomic co-ordinates and their thermal parameters along with a scale factor. The basic idea behind the refinement is to determine a set of atomic co-ordinates for which the calculated structure factors $F_c(H)$ agree fairly well with $F_o(H)$, the structure factors which are obtained after applying necessary correction factors. The most common method of assessing the agreement is by calculating the residual $R$ (ref. sec. 1.3.1) defined by

$$
R = \sum \frac{|(|F_o| - |F_c|)|}{\sum |F_o|}
$$

the summation being over all the reflections. Evidently, the lower the value of $R$, the better is the agreement. Alternative use of a weighted residual $R_w$ defined by Hamilton is given by

$$
R_w = \left[ \sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2 \right]^{1/2}
$$

where $w$ is the reciprocal of the variance of $F_o(H)$.

The "goodness of fit" $S$ is defined by

$$
S = \left[ \sum w (|F_o| - |F_c|)^2 / (m - p) \right]^{1/2}
$$
where \( m \) is the number of observations used in least squares and \( p \) the total number of parameters.

All the parameters \( p_j \) (\( j = 1,2,3, \ldots \ldots n \)) describing the structure are refined by using the well known principle of least squares. The function to be minimised is

\[
D = \sum w (|F_0| - |F_c|)^2 = \sum w (\Delta F)^2
\]

where the summation is over all the observed reflections and \( w \) is the weight of an observation which estimates the reliability of each observation.

To obtain the minimum the following \( n \) normal equations formed by taking derivatives of \( D \) , are to be solved

\[
\sum w \frac{\delta |F_c|}{\delta p_j} \Delta F = 0, \quad j = 1,2,3, \ldots n \quad (6a)
\]

But since \( F_c \)'s are transcendental functions of \( p_j \)'s the equations are non-linear. If we assume that our trial parameters \( p = (p_1,p_2,p_3 \ldots \ldots p_n) \) need small shifts \( \epsilon = (\epsilon_1,\epsilon_2,\epsilon_3, \ldots \ldots, \epsilon_n) \) to reach the respective correct values, we may expand \( \Delta F(\ p+\epsilon \) ) by Taylor Series and retain only the first-order terms.

\[
\Delta F(\ p+\epsilon \) = \Delta F(p \) + \sum \frac{\delta |F_c|}{\delta p_j} \epsilon_j \quad (6b)
\]

Substituting (6.b) in (6.a) we get

\[
\sum \left[ \sum w \frac{\delta |F_c|}{\delta p_1} \cdot \frac{\delta |F_c|}{\delta p_j} \right] \epsilon_j = \sum w \Delta F \frac{\delta |F_c|}{\delta p_j} \quad (6c)
\]
Here \( n \) equations corresponds to \( j = 1, 2, 3, \ldots, n \).

The solution of these equations give the best value of the parameters \( p_j \) in the least square sense.

The above equations can be written in matrix form

\[
[A] \begin{bmatrix} \epsilon \end{bmatrix} = [V]
\]

where the \( n \times n \) matrix \( A \) has elements

\[
a_{ij} = \sum_{hkl} w \frac{\delta|F_c|}{\delta p_i} \frac{\delta|F_c|}{\delta p_j}
\]

and the \( j \)th component of the \( n \) dimensional vector \( V \) is

\[
V_j = \sum_{hkl} w \Delta F \frac{\delta|F_c|}{\delta p_j}
\]

The shift \( \epsilon \) can be calculated using the relation

\[
[\epsilon] = [A]^{-1} [V].
\]

Thus the matrix \( [A] \) must be inverted and post multiplied by the column matrix \( [V] \) to obtain the quantities \( \epsilon_j \). By using these new corrections to the parameters, the calculation is repeated for several cycles until there is no significant change in the parameters between the successive cycles.

The standard deviations of the refined parameters are obtained from the corresponding diagonal elements of the inverse matrix by using the formula.

\[
\sigma(p_i) = \left[ b_{11} \left( \sum_{hkl} w (\Delta F) / (m-n) \right) \right]^{1/2}
\]
where $b_{ii}$ is the $i$th diagonal element of $[A]^{-1}$. $m$ is the number of observations and $n$ the number of parameters to be refined. The element $b_1$ of the matrix $[A]^{-1}$ is not, in general, the reciprocal of the corresponding element $a_{11}$ of the matrix $A$, but there is indeed an inverse relationship between them. With an increase in $m$, $a_{11}$ increases in magnitude and there is a corresponding decrease in $b_{ii}$. So with a large number of intensity data, the estimated standard deviations of the parameters become small. Furthermore, improved quality of data—implying smaller $\sigma(F_0)$—would of course lower the value of $\sigma_1$.

The $ij$th element of the inverse matrix, $(b_{ij})$, is a measure of the interdependence or correlation of parameter $p_i$ and $p_j$. The correlation coefficient is defined as

$$c_{ij} = \frac{b_{ij}}{(b_{11}b_{jj})^{1/2}}$$

The correlation coefficients can range from 0 to ±1, the latter values indicate complete dependence, in which case one of the two parameters should be eliminated from the process of refinement. Values of $c_{ij} < 0.2$ do not present any difficulty, but refinement may be seriously impaired due to presence of large correlations which may exist between scale and thermal parameters, between the positional parameters of an atom when interaxial angles differ appreciably from $90^\circ$, and between parameters of atoms related by exact or approximate symmetry elements not included in the space group. In such cases a judiciously chosen group of parameters are kept fixed during one cycle of refinement and are varied in subsequent cycle when some other parameters are kept fixed.
With a large number of parameters to be refined using a corresponding large set of intensity data by full matrix process, the calculation of all the matrix elements and hence building the matrix of derivative products requires two much storage and computing time. In such cases, the block-diagonal approximation may be used conveniently. In this procedure, the diagonal elements and only those off-diagonal elements which involve correlation between the scale and overall temperature factor and those between the parameters of the same atom, are retained and all the other elements are dropped. These latter would, hopefully, not represent any large correlations and thus would have negligible effects anyway. The matrix now has non-zero elements in blocks about its diagonal, - a 2X2 block for the scale and overall temperature factor, a 4X4 block for each isotropically vibrating atom, and a 9X9 block for each of the anisotropically vibrating atom. Although the use of such a matrix provides much economy in terms of computer usage, the shifts calculated with block-diagonal approximation are not accurate enough. It is the usual practice to apply only a fraction (say 0.7) of the calculated shift to the parameters. This may often necessitate more cycles of calculation before a convergence is reached.

6. DIFFERENCE FOURIER SYNTHESIS

A Fourier function of very useful importance is the so called difference Fourier where the coefficients are the quantities \(|F_o| - |F_c|\) calculated on the basis of some rough model by summing up the following series

\[
\Delta \rho(\text{xyz}) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} \Delta F \exp \left[i \phi_c - 2\pi i (hx + ky + lz)\right].
\]
where $\phi_c$ is phase of the $F_c$. It is a valuable tool for correcting the positions of atoms already present, for locating any new atoms (for example water molecule, in the present study) and also for locating the positions of H atoms at later stage.

7. IMPORTANT RESULTS DERIVED FROM THE REFINED STRUCTURE

The most important results to be derived from refined structure are the distances between bonded atoms, the angles between pair of bonds and the equation of the mean plane passing through a group of atoms.

7.1 Interatomic Distances and Angles and their Standard Deviations.

In the computer program used for all such calculations, the fractional co-ordinates $x(x, y, z)$ with respect to crystallographic axes are transformed into co-ordinates $X(x, y, z)$ Å with respect to the orthogonal coordinates system whose X-axis is coincident with the crystallographic a-axis, Y-axis lies in the ab-plane and the Z-axis is in the C* direction. These transformed co-ordinates are given by

$$\begin{bmatrix} X \\ \end{bmatrix} = \begin{bmatrix} U \end{bmatrix} \begin{bmatrix} x \\ \end{bmatrix}$$

where

$$\begin{bmatrix} U \end{bmatrix} = \begin{bmatrix} a & b \cos \gamma & c \cos \beta \\ 0 & b \sin \gamma & -c \cos \alpha \sin \beta \\ 0 & 0 & c \sin \alpha \sin \beta \end{bmatrix}$$

The calculations of interatomic distances and angles using the orthogonal coordinate system is very simple and need not be discussed here. The standard deviations of the calculated distances and angles are obtained in the following way.
If $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ are the e.s.d's of the fractional coordinates $(x,y,z)$ of an atom, we take a symmetric matrix

$$
\begin{bmatrix}
\sigma^2(x) & \sigma(x) \sigma(y) \cos \gamma & \sigma(x) \sigma(z) \cos \beta \\
\sigma(x) \sigma(y) \cos \gamma & \sigma^2(y) & \sigma(y) \sigma(z) \cos \alpha \\
\sigma(x) \sigma(z) \cos \beta & \sigma(y) \sigma(z) \cos \alpha & \sigma^2(z)
\end{bmatrix}
$$

as the variance matrix with respect to the crystallographic axes.

The variance matrix $P_s$ with respect to the orthogonal axes is given by

$$
[ P_s ] = [U] [P_o][U^T]
$$

For an atom with variance matrix $P_s$ the variance in a direction with direction cosines $L (= l,m,n)$ is given by

$$
\sigma^2 = [L][P_s][L^T]
$$

Now for interatomic distance $AB$ between atoms A and B having variances $\sigma^2(A)$ and $\sigma^2(B)$ respectively in the direction of the bond, the variance according to Cruickshank and Robertson (1953) is expressed as

$$
\sigma^2(AB) = \sigma^2(A) + \sigma^2(B)
$$

which simplifies to $\sigma^2(AB') = 4\sigma^2(A)$ in case of the distance between two symmetry related atoms.

The variance in a bond angle $\theta$ between two bonds of lengths $AB$ and $AC$ is given by
\[ \sigma^2(\theta) = \frac{\sigma^2(B)}{AB} + \sigma^2(A) \left[ \frac{1}{AB^2} - \frac{2\cos\theta}{AB \cdot AC} + \frac{1}{AC^2} \right] + \frac{\sigma^2(C)}{AC} \]

where \( \sigma^2(B) \) and \( \sigma^2(C) \) are the variance of the atom B and C in the directions at right angles to AB and AC respectively, and \( \sigma^2(A) \) is the variance of A in the direction of the centre of the circle passing through B, A and C. When A and B are related by symmetry,

\[ \sigma^2(\theta) = \sigma^2(A) \left[ \frac{1}{(AB/2)^2} - \frac{2\cos\theta}{AB \cdot AC/2} + \frac{1}{AC^2} \right] + \frac{\sigma^2(C)}{AC^2} \]

In our calculation of standard deviations for bond angles it is assumed that the variances of the atomic-co-ordinates are spherically symmetric, so that

\[ \sigma^2 = \frac{1}{3} \left[ \sigma^2(ax) + \sigma^2(by) + \sigma^2(cz) \right] \]

7.2 Mean Plane

In orthogonal system of co-ordinates, equations of a plane is

\[ lx + my + nz - p = 0 \]

where \( l, m, n \) represents the direction cosines of the normal to the plane satisfying the condition \( l^2 + m^2 + n^2 = 1 \) and \( p \) is the distance of the plane from the origin. The distance of a point \((X_1, Y_1, Z_1)\) from the above plane is \( p_1 = lx_1 + my_1 + nz_1 - p \)

The equation of the mean plane through a group of \( N \) atoms is obtained by minimising the quantity
where the weight $W_i = \frac{1}{\sigma_i^2} = 3/ \left[ \sigma^2(x_i) + \sigma^2(y_i) + \sigma^2(z_i) \right]$

The condition $\frac{\partial R}{\partial p} = 0$ gives

$$1 \sum W_i x_i + m \sum W_i y_i + n \sum W_i z_i - p \sum W_i = 0$$

or

$$1 \bar{x} + m \bar{y} + n \bar{z} - p = 0$$

where $\bar{x} = \frac{\sum W_i x_i}{\sum W_i}$, $\bar{y} = \frac{\sum W_i y_i}{\sum W_i}$, $\bar{z} = \frac{\sum W_i z_i}{\sum W_i}$, showing that the mean plane passes through the centroid $(\bar{x}, \bar{y}, \bar{z})$ of the group of $N$ atoms.

Now if $R$ is expressed as

$$R = \sum W_i \left[ 1(x_i - \bar{x}) + m(y_i - \bar{y}) + n(z_i - \bar{z}) \right]^2$$

the condition $\frac{\partial R}{\partial l} = \frac{\partial R}{\partial m} = \frac{\partial R}{\partial n} = 0$ give three linear homogeneous equations in $l, m, n$ which are solved by a procedure described by Blow (1960).

Thus equation of the mean plane referred to orthogonal axes is given by

$$1X + mY + nZ = 1\bar{x} + m\bar{y} + n\bar{z}$$

The deviations $p_i (i=1$ to $N$) of the $N$ atoms from the mean plane may therefore be calculated. We can also calculate

$$\chi^2 = \sum_{i=1}^{N} \frac{p_i^2}{\sigma^2(p_i)} \quad \text{where} \quad \sigma^2(p_i) = \frac{1}{\sigma^2(x_i)} + \frac{m^2}{\sigma^2(y_i)} + \frac{n^2}{\sigma^2(z_i)}.$$
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