Chapter 2

Fundamentals of crystallography

2.1 Introduction

Crystallography is the science concerned with the study of crystals. Crystallography originated as the science of the study of macroscopic crystal forms, and the term “crystal” has been traditionally defined in terms of the structure and symmetry of these forms. The environment of a particular atom in a crystal has certain arrangement, and if you look at the same kind of an atom at another place farther along by the same distance, you will find the conditions exactly the same once more. The pattern is repeated over and over again and, of course, in three dimensions. This orderly arrangement in a crystalline material is known as the crystal structure and is defined as

\[
\text{crystal structure} = \text{lattice} \ast \text{motif}
\]

Where, the lattice is a geometrical abstraction relating to the exact geometry of the crystal and motif is a special entity which concerns the ar-
rangement of the molecules. An integral part of the process of crystal structure determination is an experiment and the techniques used to collect the experimental data. The experiment consists of scattering radiation from crystalline matter, the radiations that are usually employed being X-rays, electrons and neutrons. Although all three radiations can be employed, the vast majority of structure determinations are based on X-ray diffraction data. X-ray crystallography is concerned with discovering and describing the crystal structure. This chapter will therefore be dedicated to X-ray techniques.

### 2.2 A brief history of crystallography

For many years, mineralogists and crystallographers had accumulated knowledge about crystals, chiefly by measurement of interfacial angles, chemical analysis, and determination of physical properties. There was little knowledge of interior structure. Such was the state of knowledge in 1912 when the German physicist Von Laue took up the problem. Starting from an article by Ewald, a student of Sommerfeld, he suggested the use of crystals as natural lattices for diffraction. Friedrich and Knipping, both students of Roentgen, successfully performed an experiment and obtained the remarkable result that X-rays were indeed diffracted by crystals of copper sulphate. In 1913 W. L. Bragg and M. Von Laue used X-ray diffraction patterns for deducing the structure of NaCl, KCl, KBr, and KI. The spread of knowledge stemming from X-ray crystallography was rapid and in recent years it has assumed an increasingly important role in the modern sciences because of its interdisciplinary nature.

### 2.3 X-ray diffraction

Change in the directions and intensities of a group of waves after passing through an obstacle whose size is approximately the same as the wavelength of incident waves is referred as diffraction. During the twentieth century,
different types of diffraction have been found. Neutrons and electrons, which would be considered particles according to classical mechanics, can be diffracted. The differences between X-ray, neutron and electron diffraction by crystals are such that these three techniques complement one another to a remarkable degree. Each of these techniques provides a particular stream of information which the others are incapable of yielding. Since wavelengths of X-rays are comparable with inter atomic spacing, X-ray diffraction technique is used for the investigation of the fine structure of matter. It is a tool which provides a means of finding the positions of atoms in space, and for complex structures. It is the most accurate, and sometimes the only, way of doing this. X-ray diffraction is regarded as the most powerful tool to analyse both the geometrical nature of the three dimensional array of molecules within a crystal and also the nature of the molecules themselves.

2.4 Significance of diffraction pattern

The infinite lattice will give rise to an infinite array of $\delta$ functions in the diffraction pattern. These sharp peaks will be smeared out as a result of the fact that the crystal is finite. The intensities of these smeared out peaks is determined by the motif. Thus from the diffraction patterns following general rules are arrived:

- The position of the main peaks gives information on the lattice.
- The set of intensities of all the main peaks gives information on the structure of the motif.
- The shape of each main peak gives information on the overall object shape.
2.5 Bragg’s law

A crystal is a homogeneous solid. Any atom in a crystal structure is repeated by the symmetry operations of the space group. Since the atoms are arranged periodically on a lattice, the rays scattered by them have definite phase relations between them. These phase relations are such that destructive interference occurs in most directions of scattering, but in a few directions constructive interference takes place and diffracted beams are formed. Bragg considered the crystal planes behaved as though they partially reflected the X-rays, like sheets of atomic mirrors, since angle of incidence and reflection are equal and are coplanar with the normal to the reflecting planes. Bragg’s law allows each observed diffracted beam to be uniquely labelled with three indices \((hkl)\) called Miller indices. The reflections from adjacent planes in the set give rise to interference effects which is governed by the equation

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

The above equation is called Bragg’s law. Rearrangement of Bragg equation gives

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

2.6 Reciprocal lattice and Ewald sphere

The concept of reciprocal lattice is needed in the study of X-ray diffraction by crystals. For each direct lattice, a corresponding reciprocal lattice may be postulated. For every plane in the direct lattice draw a normal from the origin of the unit cell whose length is restricted to the reciprocal of the interplanar spacing. A point is placed at the end of each limited normal, and the collection of such points constitutes a new lattice called the reciprocal lattice. The reciprocal lattice has the same symmetry as the direct lattice. The reciprocal lattice points from a true lattice involves six
reciprocal cell parameters in the most general case; three sides \(a^*, b^*\) and \(c^*\), and three angles \(\alpha^*, \beta^*\) and \(\gamma^*\). The relation between the direct and reciprocal lattices requires that \(a^*\) be perpendicular to both \(b\) and \(c\), and conversely, that \(a\) be perpendicular to both \(b^*\) and \(c^*\), and so on for the other cell constants. Here \(a, b\) and \(c\) corresponds to three sides of direct lattice. Hence, in converting from direct space to reciprocal space and vice versa, the crystal system is preserved.

The geometric interpretation of X-ray diffraction photograph is greatly facilitated by means of a construction due to Ewald, and known as the Ewald Sphere. The sphere is centred on crystal and drawn with a radius \(r \propto 1/\lambda\). Since diffraction depends on a reciprocal lattice point’s touching the surface of the sphere drawn about the center of the sphere, this sphere is known as sphere of reflection. Ewald sphere provides the mechanism for predicting the occurrence of X-ray reflections and their directions in terms of the sphere of reflection and the reciprocal lattice. The condition that the crystal is in the correct orientation for a Bragg reflection \(hkl\) to take place is that the corresponding reciprocal lattice point is on the sphere of reflection. As the crystal oscillates, an X-ray reflection flashes out each time a reciprocal lattice point cuts the sphere of reflection.

### 2.7 Data reduction

To know the positions of atoms within a unit cell, we measure intensities of the reflections from a given crystal. The measure of the total number of photons which are diffracted in the proper direction by reciprocal lattice point is termed as integrated intensity. The electron density distribution in the crystal can be analysed from these intensities. The raw data of Bragg reflections normally consist of the Miller indices \((hkl)\), the integrated intensity \(I(hkl)\) and its standard deviation \((\sigma(I))\). The relative amplitude of the diffraction spot associated with the reciprocal lattice point \(hkl\) is given by the structure factor \(F_{hkl}\). 

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2.7 Data reduction
\[ F_{hkl} = \sum_j f_j e^{-2\pi i (hx_j + ky_j + lz_j)} \]

and the relative intensity of the X-ray beam is proportional to the square of the wave amplitude

\[ I_{hkl} = |F_{hkl}|^2 \]

Here \( I_{hkl} \) represents the intensity of the scattering by a unit cell as compared to that by a single electron, and so \( I_{hkl} \) is relative, and not an absolute measure of intensity.

The measured intensity is affected by various factors Viz. Lorentz factor, Polarization factor, Temperature factor etc., for which corrections must be applied. The conversion of intensities I to “observed structure amplitudes” \(|F_0|\) or \(|F_0|^2\) and, correspondingly, of standard deviations \(\sigma I\) to \(\sigma F_0\) or \(\sigma F_0^2\) is known as data reduction.

### 2.7.1 Lorentz factor

The image of diffraction event as recorded on a photographic film arises when reciprocal lattice point touches the Ewald sphere. As crystal rotates, reciprocal lattice also rotates. X-ray reflection flashes out when reciprocal lattice point cuts the sphere of reflection. If a node is in diffracting position for a long time, the intensity of the corresponding reflection will be proportionally higher. The time a node is in diffracting position depends on the position of the node (Geometrical opportunity) and the velocity with which it sweeps through the sphere of reflection (Time opportunity). The Lorentz factor takes account of both the time opportunity and the geometrical opportunity for different reciprocal lattice points to diffract. The correction factor differs for each type of detector geometry. The Lorentz factor \(L_{hkl}\) is defined as

\[ L_{hkl} = \frac{1}{\lambda} \frac{\omega}{\nu_n} = \frac{1}{\sin 2\theta} \]

where, \(\lambda\) is the wavelength of the incident radiation, \(\omega\) is the angular velocity with which the crystal rotates, \(\nu_n\) is the velocity component perpendicular to the Ewald sphere surface and \(2\theta\) is the scattering angle appropriate to the diffraction maximum indexed as \(hkl\).
2.7 Data reduction

2.7.2 Polarisation factor

The partial polarization of X-rays on scattering causes a reduction in their intensity that varies with $2\theta$. The corrections for this, the polarization factor $P_{hkl}$, which is a function of Bragg angle is given by

$$P_{hkl} = \frac{1 + \cos^2 2\theta}{2}$$

where $\theta$ is the Bragg angle and the diffracting crystal is tacitly assumed to be ideally mosaic. Any beam from a crystal monochromator is partially polarised before it reaches the specimen. Under these circumstances, the polarization correction $P_{hkl}$ is given by,

$$P_{hkl} = \frac{(\cos^2 2\theta \cos^2 \rho + \sin^2 \rho) |\cos^n 2\theta M| + \cos^2 2\theta \sin^2 \rho + \cos^2 \rho}{1 + \cos^n 2\theta M}$$

where $\theta_M$ the angle of reflection of the monochromator crystal which is used to select the wavelength. $\rho$ is the angle between the projection of the normal to the reflecting plane on to a plane perpendicular to the incident monochromated X-rays and the plane of incidence.$^5$ When the original X-ray beam, the monochromated beam and the scattered beam all lie in the same plane this angle is equal to 0 and the polarisation factor takes the simpler form

$$P_{hkl} = \frac{\cos^2 2\theta |\cos^n 2\theta M| + 1}{1 + |\cos^n 2\theta M|}$$

The exponent $n$ depends on the characteristics of the monochromating crystal. If the crystal is assumed to be a perfectly mosaic it is equal to 2, whereas for an ideal crystal it is equal to 1.

2.7.3 Thermal effects

Atoms inside the crystal undergo thermal vibration about their mean positions even at absolute zero of temperature, and the amplitude of this vibration increases as the temperature increases. Each atom undergoes a motion such that its electron density is smeared over a small anisotropic volume,
usually regarded as a tri-axial ellipsoid in the general case. Thermal agita-
tion has the effect of smearing out the lattice planes; atoms can be regarded
as lying no longer on mathematical planes but rather in plate like regions of
ill-defined thickness. The thickness of the plate like “planes” in which the vi-
brating atoms lie is, on the average, 2u, where u is the average displacement
of an atom from its mean position. Under these conditions the reinforce-
ment of waves scattered at the Bragg angle by various parallel planes, is
not as perfect as it is for a crystal with fixed atoms and it becomes more
imperfect as the ratio u/d increases, i.e. as the temperature increases, since
that increases u, or as θ increases, since high θ reflections involve planes
of low d value. Thus the intensity of a diffracted beam decreases as the
temperature is raised, and, for a constant temperature, thermal vibration
causes a greater decrease in the reflected intensity at high angles than at
low angles. The temperature corrected atomic scattering factor \((f_j)_T\) for a
given bragg angle θ and incident wavelength λ is given by equation

\[
(f_j)_T = f_j e^{-B_j (\sin^2 \theta / \lambda^2)}
\]

where \((f_j)_0\) is the scattering factor for a stationary atom. The quantity
B is called the temperature coefficient, and its value depends on the
atom under study and the temperature at which the diffraction event takes
place. An implicit assumption in the form of the above equation is that the
thermal vibrations of the atom \(j\) are spherically symmetric. The equation
accounts for the thermal motion by introducing a negative exponential.
The term \(\sin^2 \theta / \lambda^2\) is necessarily positive, and \(B_j\) is always positive. Since
\(B_j (\sin^2 \theta / \lambda^2)\) must be dimensionless, the dimensions of \(B_j\) are \([\text{length}]^2\).
The value of \(B_j\) is given by:

\[
B_j = \frac{8\pi^2}{3} \langle u^2 \rangle
\]

where \(\langle u^2 \rangle\) represents the mean square displacement of the \(j^{\text{th}}\) atom. This
equation shows that \(B_j\) is necessarily positive.

Hence, \((f_j)_T\) is always less than \(f_j\). When θ is zero, \((f_j)_T\) equals \(f_j\). Also,
the value of the exponential decreases quite rapidly as θ increases causing
\((f_j)_T\) to fall off sharply as compared to \(f_j\).
2.7.4 Absorption correction

When X-ray beam passes through the crystal, the electric field causes electronic excitation. Due to this, the thermal energy of the electrons increases and hence the temperature of the crystal also increases. For this, energy of the incident X-ray beam is used. This attenuates the incident X-ray beam and known as the absorption. The absorption correction is the amount by which the measured intensity should be artificially boosted in order to correct for absorption and is given by

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

which is valid for every point in the crystal. Here \( \mu \) is linear absorption coefficient of the crystal, and is a property of the material considered and \( x \) is the total path length of X-rays inside crystal. It varies with wavelength of X-radiation. The wavelengths at which absorption edges occur which is indicated by sharp discontinuities in the behaviour of linear absorption coefficient are related to those X-ray energies which cause changes in the quantum states of the electrons within any atom. The linear absorption coefficient for the crystal can be calculated from the mass absorption coefficient \( (\mu_m) \) of the atoms present in the unit cell without having structural knowledge. The “International tables for X-ray crystallography” provides values of the mass absorption coefficients of the elements. From the values of \( \mu_m \) for a given wavelength, \( \mu \) can be calculated by the following equation

\[ \mu = \rho \sum g_i \mu_{im} \]

where \( g_i \) is the mass fraction of element \( i \) present in the unit cell, \( \mu_{im} \) is its mass absorption coefficient, and \( \rho \) is the crystal density.

2.7.5 Extinction

Extinction is a phenomenon which results in the attenuation of the primary beam of X-radiation when the crystal is in diffracting position, and so reduces the intensity of the diffracted beam. Extinction depends on physical
perfection of the crystal. Darwin, who first theoretically investigated the effects of “Extinction” subdivided the general attenuation of intensity due to this cause into two categories: primary “extinction” and secondary “extinction”. An excellent resume of the subject is given by Lonsdale.

2.7.6 Primary extinction

When primary X-ray beam strikes the crystal, every incident wave can suffer multiple reflections from different lattice planes at Bragg angle. The direction of the wave will be same as the diffracted beam after it suffers odd number of reflections. After an even number of reflections, the direction will be same as the primary beam. A phase lag of $\pi$ is introduced after each scattering. As a result, the primary beam is weakened by destructive interference. As the primary beam penetrates the crystal further and further, it is continuously attenuated in this manner. The same consideration holds for waves propagating along the direction of the diffracted beam. This weakening phenomenon continues through series of planes. The primary beam becomes so attenuated that it effectively “extinguished”. This phenomena is called primary extinction.

2.7.7 Secondary extinction

When an X-ray beam is incident upon a crystal, the lattice planes first encountered by the primary beam will reflect a significant fraction of the primary intensity. Therefore deeper planes receive less primary radiation. The intensity of the primary beam received by a plane is equal to that of the original beam less that which has been reflected by the planes preceding it, less any absorption in the path to it. The reduction of the intensity of the primary beam due to this kind of previous reflection is called by “secondary extinction”. This causes a weakening of diffracted intensity, mainly observable for high intensity reflections at low $\sin \theta/\lambda$ values in sufficiently perfect crystals. If the mosaic blocks are misoriented, then they do not diffract together and shielding of deeper planes is consequently reduced. Since secondary “extinction” behaves like ordinary absorption,
it is customary to consider it as adding to the ordinary linear absorption coefficient. Thus it is negligible for sufficiently small crystals.

### 2.7.8 Anomalous scattering

An electron does orbit a nucleus with a characteristic frequency. If the frequency of incident X-radiation is comparable to orbital frequency, the electron cannot be regarded as free and will not oscillate in phase with electric vector. If an atom absorbs X-rays strongly, there will be a phase change for the X-rays scattered by the absorbing atom relative to the phases of the X-rays scattered by other atoms. This is known as anomalous scattering and the atom is said to be an anomalous scatterer. The spherical symmetry and centrosymmetry are destroyed due to perturbation of electron distribution. In this case, fourier transform of atomic scattering factor $f_j$ is given by complex value

$$f_j = (f_j)_c + \Delta f' + i\Delta f''$$

where $(f_j)_c$ is the form factor calculated on the assumption of spherical symmetry and is corrected by a real part $\Delta f'$ and an imaginary part $\Delta f''$ both of which vary with the wavelength of the incident radiation, being high near an absorption edge and can be calculated theoretically.

When $f_j$ is real,

$$|F_{hkl}| = |\overline{F_{hkl}}|$$

which is the well known Friedel’s law. Since we measure intensities, Friedel’s law implies

$$I_{hkl} = I_{\overline{hkl}}$$

When an anomalously scattering atom is present, Friedel’s law breaks down and

$$I_{hkl} \neq I_{\overline{hkl}}$$

These differences in intensity may be used to determine the absolute configuration of the crystal.
2.7.9 Radiation damage

The exposure of a crystal to an X-ray beam is often harmful. Crystal decomposition triggered by exposure to X-rays is not at all an uncommon occurrence. This leads to radiation damage of the crystal. Radiation damage involves movements of atoms so that each Bragg reflection is changed in a specific way, depending on the crystal structure. This results in the decrease of the integrated Bragg reflection intensity, which is a function of the absorbed dose. Another effect is chemical damage, possibly as a result of formation of free-radicals or loss of solvent of crystallization. Further signs of radiation damage are changes in the unit cell dimensions and an increase in the crystal mosaicity, i.e., the decline of the order within a crystal with accumulated dose.\textsuperscript{8–10} This reduces extinction effects leading to higher values of some integrated intensities. The causes that lead to the changes in intensity as a crystal is exposed to higher and higher X-ray doses have been listed by Abrahams.\textsuperscript{11}

The radiation damage correction factor, $R(t, \theta)$, is defined as follows

$$R(t, \theta) = \frac{I(t)}{I(0)}.$$  

It is the inverse of the factor by which the intensity measured at time ‘$t$’ has to be multiplied to yield the intensity corrected at time zero. This correction factor is a function, not only of the time after data collection started but also of the scattering angle of the reflection $\theta$.

An efficient way to minimize radiation damage and therefore to make the application of a correction less significant is by collecting the data at low temperature.\textsuperscript{12}

2.7.10 Friedel’s law

Normally X-ray diffraction pattern from a crystal is centrosymmetric whatever the crystal class. For centric crystals, symmetry provides that reflections from $(hkl)$ and $(\bar{h}\bar{k}\bar{l})$ are indistinguishable. The structure factor corresponding to an arbitrary reciprocal lattice point $hkl$ and its centrosymmetrically related point $\overline{hkl}$ is given by
2.7 Data reduction

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

\[ F_{\bar{h}k\bar{l}} = \sum_j f_j e^{-2\pi i (hx_j + ky_j + lz_j)} \]

Since the only difference lies in the sign of complex exponential, we may assume that the atomic scattering factors \( f_j \) are real, and in this case, \( F_{\bar{h}k\bar{l}} \) is simply the complex conjugate of \( F_{hkl} \)

\[ F^*_{hkl} = F_{\bar{h}k\bar{l}} \]

The structure factors \( F_{hkl} \) and \( F_{\bar{h}k\bar{l}} \) may be represented on an argand diagram by mirror reflections in the real axis, since magnitudes of \( |F_{hkl}| \) and \( |F_{\bar{h}k\bar{l}}| \) are equal.

\[ |F_{hkl}| = |F_{\bar{h}k\bar{l}}| \]

The above equation is known as Friedel’s law. Since phases cannot be measured in X-ray diffraction experimentation, it follows that reflections from \( (hkl) \) and \( (\bar{h}k\bar{l}) \) have the same intensities.

\[ I_{(hkl)} = I_{(\bar{h}k\bar{l})} \]

The breakdown of Friedel’s law in non-centrosymmetric crystal is of extreme importance in the solution of the phase problem.

2.7.11 Determination of crystal symmetry

The symmetry of a crystal is indicated by its diffraction pattern. The systematic absences corresponding to lattice type determine the Bravais lattice, while information on screw axes and glide planes is obtained from the systematic absences. Breakdown of friedal’s law helps in identifying if a crystal is centrosymmetric or not.
2.8 The phase problem

The aim of structural analysis is to obtain the distribution of electron density in the unit cell from the diffraction data. Calculation of electron density function requires information about structure factor $F_{hkl}$. In general $F_{hkl}$ is a complex quantity and can be written as $|F_{hkl}| e^{i\phi_{hkl}}$. During the diffraction of X-rays with crystal the scattered X-ray intensity $|I_{hkl}|$ is detected by the detector from which we can get $|F_{hkl}|$. However, information on relative phases $\phi_{hkl}$ is lost. This is referred to as “Phase problem”. An attempts to find solutions to the phase problem\textsuperscript{13,14} started around 1934.

2.9 Direct methods

Estimation of relative phase angles directly from the measured intensities without any reference to prior knowledge of likely structures or isomorphous crystals are referred to as direct methods. Direct methods involve selecting most important reflections, working out the probable relationships among their phases, then trying different possible phases. For the most important combinations, fourier transforms are calculated from the observed amplitudes and trial phases, and are examined for recognizable molecular features. In direct methods\textsuperscript{15} there are two imposed constraints that restrict the relative value of phase angles.

- An electron has a finite probability of being found at any position $(x,y,z)$ in the unit cell and the electron density $\rho(xyz)$ has a positive value for $F$. However when this probability is zero, then $\rho(xyz)$ is zero. But electron density function calculated with deduced phases should never be negative.

- The electron density maps should have high values at and near atomic positions and have nearly zero values else where.
2.9 Direct methods

2.9.1 Structure invariants and semi-invariants

The goal of the direct methods is to obtain the phases directly from the observed amplitudes. From the observed amplitudes we can only obtain informations on single phases or linear combinations of phases. These relative phase combinations are independent of the choice of origin. Since their value depends only on the structure, they are called structure invariants.

Structure semi-invariants are single phases or linear combinations of phases which are invariant with respect to a shift of origin provided these changes are made subject to specific space-group symmetry constraints.

2.9.2 Unitary structure factor $U_{hkl}$

Direct methods involve the comparison of the structure factor magnitudes. The unitary structure factor $U_{hkl}$ is defined as

$$U_{hkl} = \frac{F_{hkl}}{\sum_j f_j}$$

Further, unitary atomic scattering factor, $n_j$ is defined as,

$$n_j = \frac{f_j}{\sum_j f_j}$$

Therefore

$$U_{hkl} = \sum_j n_j e^{2\pi i (hx_j+ky_j+lz_j)}$$

which is analogous to the expression for $F_{hkl}$.

2.9.3 Normalised structure factor $E_{hkl}$

In order to derive maximum information on atomic positions before determination of phase $\phi(hkl)$ the measured structure factors $|F_{hkl}|$ are modified
by eliminating fall of intensity at high scattering angle due to atomic size and vibrations, so that structure factors correspond to point atoms at rest. These structure factors are called normalised structure factors \( E(hkl) \) and are given by

\[
|E(hkl)| = \sqrt{\frac{|F(hkl)|}{\epsilon \sum_j f_j^2(hkl)}}
\]

Generally the value of \( \epsilon \) factor is taken to be unity, but is needed to account certain classes of Bragg reflections such as those with one zero index. The \( E \) values have an average value (over the entire set of data) for their square equal to unity i.e. \( < E^2_{hkl} > = 1 \). Hence the name normalised. The centrosymmetric crystals give a relatively higher number of weak Bragg reflections than non-centrosymmetric crystals.

The direct methods are classified according to the means by which structure factor magnitudes are compared as follows:

- Inequalities
- Equalities
- Probabilities

### 2.9.4 Inequalities

Historically, the first mathematical relationships capable of giving phase information were obtained, in the form of inequalities, by Harker and Kasper.\(^{16}\) in 1948 and further developed by Karle and Hauptman and others. The Harker and Kasper inequality relationship is given by

\[
U^2_{hkl} \leq \frac{1}{2} (1 + U_{2h2k2l})
\]
where \( u \) represents unitary structure factor. Rearranging above equation, we get

\[
U_{2h \ 2k \ 2l} \geq 2U_{hkl}^2 - 1
\]

This equation relates information concerning the reciprocal lattice site \( h \ k \ l \) to that for the site \( 2k \ 2h \ 2l \). The inequality is true only if \( U_{2h \ 2k \ 2l} \) is positive. Another limitation is that the use of inequalities is restricted to centrosymmetric crystals.

### 2.9.5 Equalities

The equality relationships are applicable only to the centrosymmetric crystals. We may represent the sign associated with the structure factor \( F_{hkl} \) by \( s(hkl) \). Sayre derived the following relationships between the signs of three reflections by considering a structure of identical, resolved (i.e., non-overlapping) atoms, indexed as \( hkl \), \( h'k'l' \) and \( h + h' k + k' l + l' \):

\[
s(hkl) = s(h'k'l') \cdot s(h + h' k + k' l + l')
\]

\[
s(h + h' k + k' l + l') = s(hkl) \cdot s(h'k'l')
\]

Thus, knowledge of the signs \( s(hkl) \) and \( s(h'k'l') \) permit the unambiguous determination of the sign \( s(h + h' k + k' l + l') \). For organic crystals the above equations have been shown to hold if the associated structure factors are large.

### 2.9.6 Probabilities

The use of probabilities as opposed to equalities is a more general approach although subject to errors. But if a set of signs can be identified, the errors in the electron density may be removed during subsequent refinement and we may be able to compute fourier synthesis. For a general centrosymmetric crystal the equation is as follows:

\[
s(hkl) \cdot s(h'k'l') \cdot s(h + h' k + k' l + l') \approx 1
\]
For non centrosymmetric crystals, the probability relation known as tangent formula is applicable.

If the phase angle associated with the structure factor $F_{hkl}$ is represented for concise as $\alpha_h$, then

$$\tan \alpha_h \approx \frac{\sum_{h'} |E_{h'}| |E_{h-h'}| \sin(\alpha_{h'} + \alpha_{h-h'})}{\sum_{h'} |E_{h'}| |E_{h-h'}| \cos(\alpha_{h'} + \alpha_{h-h'})}$$

The estimated phase $\alpha_h$ is thus the average taken over all the triplet reflections involving $h'$.

### 2.10 Structure solution with fourier synthesis

#### 2.10.1 Calculation of electron density maps $\rho(xyz)$

With respect to the X-ray diffraction from a crystal, the equation expression for $\rho(xyz)$ is given by

$$\rho(xyz) = \sum_{h,k,l} F(hkl) e^{-[2\pi i (hx_j + ky_j + lz_j)]}$$

$$\rho(xyz) = \frac{1}{V} \sum_{h,k,l} |F(hkl)| e^{-[2\pi i (hx_j + ky_j + lz_j)]} e^{i\phi(hkl)}$$

The electron density which originally generated the diffraction pattern is obtained by adding together all the diffracted beams, with their correct amplitudes and phases which include the correct relative phases of the waves relative to the original incident beam and an extra phase shift appropriate to each geometrical position of atoms relative to the unit cell origin. The L.H.S above equation is also called electron density map.
2.11 Structure refinement

There are many stages in the overall scheme of a crystal structure analysis which can give rise to errors in the structure factors $F_{hkl}$. The inaccuracies inherent in the observed structure factor magnitudes and phases, coupled with series termination errors, imply that the first derived electron density map is not an accurate representation of the true structure.

Hence the structural model obtained by direct method is often incomplete and in most cases it represents a crude first approximation of the real structure. The errors accumulated in many stages of data collection and structure analysis must be removed before getting the final electron density map. The process of obtaining atomic parameters that are more precise than that obtained from initial model, is referred to as refinement of the crystal structure. It is an essential, integral and most vital part of any crystal structure analysis. In order to improve the agreement between the observed structure factors, $|F_{hkl}|_o$ and those calculated from the determined model, $|F_{hkl}|_c$, the positions $x$, $y$ and $z$ and the atomic displacement (thermal) parameters $B$, derived for each atom in a preliminary model are adjusted. The progress in improving this agreement is usually monitored by a residual index, $R$, defined as

$$R = \frac{\sum ||F_{hkl}|_o - |F_{hkl}|_c|}{\sum |F_{hkl}|_o}$$

The $R$ value is measure of the precision of the results of the refinement. If $R$ value is high, the derived structure is most likely incorrect. The refinement procedure takes place in four stages:

1. *The derivation of the trial structure:* This is deduced from the first calculated electron density using the observed structure factor magnitudes with the evaluated phases. Preliminary three dimensional atomic coordinates of atoms in crystal structures are usually derived from electron density maps by fitting atoms to individual peaks in the map. This is a crude model of the true structure. From the trial structure we may build a proposed molecular model which must be chemically realistic.
2. Cyclic Fourier refinement:

A set of structure factors including the thermal effects are obtained from the trial model. The sequence of repeated Fourier synthesis using freshly calculated phase angles with the originally observed structure factor magnitudes followed by recalculations of the structure factors from the newly defined electron density map is referred to as cyclic Fourier refinement. The cyclic Fourier refinement process primarily gives us better values of the phases and allows us to draw an electron density map with more accurately located atomic sites.

3. Difference Fourier synthesis: As a result of several cycles of cyclic Fourier refinement, we derive a consistent set of phases. Hence further Fourier refinement is no longer helpful. Because the value of the residual is unchanged on further cycles. The value of residual does not reduce further, indicating the presence of some errors in phases, the structure factor magnitudes, the temperature corrections, or as a result of series termination error. Having obtained a more reliable set of phases, we perform Fourier synthesis using the quantities \(|F_0| - |F_c|\). This gives a difference Fourier map which refines the correct model still further. Also, this enables the identification of missing atoms and refinement of thermal parameters.

4. Least squares refinement: Least squares refinement is statistical treatment of data. Here a model which represents the best fit with the observed data is obtained. In the most sophisticated treatment, three positional and six thermal parameters are fitted for each atom. The applicability of refinement techniques depends on the size of the structure to be solved and validity of each method.

2.1.1 Results derived from the refined structure

The complete model of the structure with all hydrogen atoms is obtained after successful completion of the refinement process. From this model, one can derive informations about bond lengths, bond angles, torsion angles, estimated standard deviations and ring conformations.
2.11.2 Bond lengths and angles

The distance between two atomic nuclei that are joined together by some type of electronic bonding is referred as bond length. Bond lengths are the average or equilibrium bond lengths due to thermal motion of atoms. If two atoms at \( x_1, y_1, z_1 \) and \( x_2, y_2, z_2 \), lie in a unit cell that has edges with lengths \( a, b \) and \( c \) and interaxial angles of \( \alpha, \beta \) and \( \gamma \), the square of the distance \( r \) between these two atoms is

\[
r^2 = [(x_1 - x_2)a]^2 + [(y_1 - y_2)b]^2 + [(z_1 - z_2)c]^2 + [2ab \cos \gamma (x_1 - x_2)(y_1 - y_2)] + [2ac \cos \beta (x_1 - x_2)(z_1 - z_2)] + [2bc \cos \alpha (y_1 - y_2)(z_1 - z_2)].
\]

The internuclear bond angle, \( \angle ABC \), is the angle between the bonds \( A-B \) and \( B-C \) formed by three atoms \( A, B \) and \( C \), connected in that order. If the length of \( A-B = l_1 \), \( B-C = l_2 \) and \( A-C = l_3 \), then the angle \( A-B-C = \delta \) may be calculated from the formula

\[
\cos \delta = \frac{l_1^2 + l_2^2 - l_3^2}{2l_1l_2}
\]

2.11.3 Estimated standard deviations

The estimated standard deviation (e.s.d.) of the geometric quantity of interest is used to assess the precision of a structure determination. Estimated standard deviations are obtained from the least squares refinement. The more precisely a measurement is made, the smaller is the e.s.d. of that measurement.

**Estimated standard deviations of bond lengths**

For two atoms, \( A(x_A, y_A, z_A) \) and \( B(x_B, y_B, z_B) \), \( \sigma_{x_A} \) is the e.s.d. of \( x \) for atom \( A \), and \( \Delta x = x_B - x_A \). The required e.s.d. values are obtained by least squares refinement. The e.s.d. of the bond distance between \( A \)
and B is:

\[ \sigma_r^2 = \frac{1}{ \sigma^2 } \left[ \left( \sigma_{xA}^2 + \sigma_{xB}^2 \right) (\Delta x + \Delta y \cos \gamma + \Delta z \cos \beta)^2 \right] + \left[ \left( \sigma_{yA}^2 + \sigma_{yB}^2 \right) (\Delta y + \Delta x \cos \gamma + \Delta z \cos \alpha)^2 \right] + \left[ \left( \sigma_{zA}^2 + \sigma_{zB}^2 \right) (\Delta z + \Delta x \cos \beta + \Delta y \cos \alpha)^2 \right] \]

Estimated standard deviations of inter bond angles

The e.s.d. of the angle between the bonds A-B and B-C is calculated by:

\[ \sigma_\theta = \left\{ \frac{\sigma_A^2}{(AB)^2} + \frac{\sigma_B^2(AC)^2}{(AB)^2(BC)^2} + \frac{\sigma_C^2}{(BC)^2} \right\}^{1/2} \]

where \( \sigma_A, \sigma_B \) and \( \sigma_C \) are the e.s.d.s of the positions of atoms A, B and C.

2.11.4 Torsion angles

A torsion is the extent of the twist of constituents about a bond. The steric relationships across single bonds and the ring geometry is described by torsion angle. It will indicate if the bonds to the substituted groups are eclipsed, staggered or intermediate between these. For four atoms A, B, C, D, in sequence the torsion angle \( \omega(ABCD) \) is defined as the angle between the normals to the planes ABC and BCD(Fig. 2.1). By convention, \( \omega \) is positive if the sense of rotation from BA to CD, viewed down BC, is clockwise, otherwise it is negative(Fig. 2.1). The sign of a torsion angle does not change by rotation or translation, and is reversed by reflection or inversion.
2.11.5 Ring conformations

A ring containing single bonds, could have different conformations which can be described by a potential energy curve having minima and maxima corresponding to ring conformers and transition states. Classical examples of degenerate conformations are the envelope (E) and twisted (T) conformations of cyclopentane and the boat (B) and twist-boat or twisted (T) conformations of cyclohexane.

\[
B_{2g} : \phi_c(i) = z_i = 6^{-1/2}q_3 \cos[3\pi(i - 1)/6] = 6^{-1/2}q_3(-1)^{(i-1)} \\
E_{2a} : \phi_{B,T}(i) = z_i = 3^{-1/2}q_2 \cos[4\pi(i - 1)/6 + \phi_2]
\]

where \(\phi_2\) is a phase angle having values of 0, 60, 120, 180, 240 or 300° for the pure B conformations and 30, 90, 150, 210, 270 or 330° for the pure T conformations. The characterising parameters \(q_3, q_2, \phi_2\) are more generally identified as the \(N - 3\) generalised puckering coordinates.

The conformations of a six-membered ring in terms of the parameters \(q_3, q_2\) and \(\phi_2\) and the \(N - 3\) possible conformations remain characterised as the three C, B and T conformers.
2.11.6 Combined figure of merit or CFOM

Direct method requires an initial set of phases to determine structures. This can be achieved by introducing a large number of permutable phases which are used to generate different phase sets. Figures of merit are usually used to screen the set of solutions, prior to computing Fourier transforms ($E$ map). Since one or more figures of merit are available for each type of structure combined figure of merit is effective in finding the correct solution.

2.12 Instrument used

The imaging plate is an area detector, qualitatively similar to the photographic film but operating on entirely different principles. The image plate is essentially a storage phosphor. When the plate is exposed to X-rays the image is temporarily stored in the phosphor coating. The radiation energy of X-ray photons can be stored by the phosphor for fairly long periods. The latent image formed is then excited by stimulation with a He-Ne laser producing light of 633nm. The light of wavelength 390nm is generated and irradiated from the plate areas which were previously hit by the X-ray photons with an intensity proportional to that of the original X-rays. The phenomenon is called photo stimulated luminescence. The photo stimulated luminescence released upon the laser is collected into the photomultiplier tube through the light collection guide and is converted to electric signals. An amplifier/ADC unit converts the analogue photomultiplier signal into digital form and is stored in the hard disc and used by image display software. On exposure to visible radiation, the image plate is restored to its initial condition and can be be used repeatedly.

2.12.1 Process of IP

The image plate is a flexible sensor in which bunches of very small crystals of photo stimulable phosphor of barium fluorobromide containing a trace amount of bivalent europium as a luminescence center, formulated as BaFBr:Eu$^{2+}$, are uniformly coated on a polyester support film. The
BaFBr:Eu$^{2+}$ is an ionic crystal (grain size is about 5 micrometer) having a tetragonal structure, and Ba is replaced with Eu$^{2+}$ ion to create a solid solution. The ability of this phosphor to act as an image storing device relies on the presence of the Eu$^{2+}$ dopant. During the preparation of these crystals a large number of vacancies are created at the sites of fluoride and bromide (or iodide) negative ions, and these vacancies are essential to the process.

When a X-ray photon strikes the imaging plate, Eu$^{2+}$ ions are ionized further to Eu$^{3+}$ and the “detached” electrons are raised to the conduction band. When so excited, the electrons are trapped at the vacancies which are inherently present in the crystal, and colour centers of metastable state are formed. Hence, the imaging plate changes color at the sites on which incident scattered radiation is falling.

The colour centers are known as F centers and are caused by the absence of halogen anions from their designated position in the BaFBr lattice. The resulting F$^+$ centers are long life traps into which electrons having enough energy to enter the conduction band may fall.

When the exposure has been completed, the diffraction pattern has been temporarily recorded on the imaging plate. The plate is then scanned by a He-Ne laser, and the trapped electrons are released, fall down to the valence band, and recombine with Eu$^{3+}$ to become excited Eu$^{2+}$. This transition is accompanied by a release of energy, which corresponds to the emission of blue light.

The intensity of luminescent light is proportional to the number of F-centers containing trapped electrons. The number of F centers trapped by electrons from the excitation process is proportional to the X-ray doses received. The luminescence is detected by a photomultiplier tube and then converted to digital signal. The coordinates of the diffraction spots and the intensity of the luminescence are recorded online in a computer and constitute the required set of data.

The raw spiral image is then corrected against a calibration image and converted to a Cartesian coordinate system. A separate calibration image is set up for each plate using a flood field from an Fe$^{55}$ radioactive source.
and is used to correct all images recorded by the plates.

When the scanning process has been completed, the imaging plate is exposed to visible light, which erases all the remaining traces of color centers and the plate is suitable for further use.

The factors contributing to possible errors in the measurement of diffraction intensities are summarised below along with estimates of the size of errors.

The calibration image formed by illumination with a uniform flood field typically displays variation in sensitivity of about 10% due to inhomogeneity and imperfections in the plate surface. Use of the image files as a correction to subsequently measured flood field images demonstrated that this correction procedure introduced an uncertainty which was on an average much less than the statistical noise in the data.

The X-rays absorption efficiency of the BaFBr:Eu$^{2+}$ phosphor is 100% for X-rays energies below 12000 eV and falls off to only 85% with 20000 eV photons.

The Image plate has a very large linearity range, and an excellent quantum efficiency, and is therefore a convenient and very fast detector of X-rays diffraction patterns.

The DIPLabo image plate diffractometer as a whole and the goniostat and the X-rays tube are shown in the figures 2.2 and 2.3 respectively.
2.12 Structure refinement

Figure 2.2: DIPlabo Image Plate System.

The procedure for data collection involves mounting the crystal and aligning it with the aid of a CCD Camera. The mechanical assembly in this case comprises of a kappa goniostat. The goniometer carrying the crystal is mounted on an arm that can rotate about the $\kappa$ axis, which forms an angle of $50^\circ$ with the main instrument axis as shown in the figure 2.4. The advantage of this system is that it is less cumbersome than the Eulerian cradle and thus rotations that would cause collisions or would produce diffracted beams that would be blocked by the $\chi$ circle in the conventional four-circle diffractometer are still measurable. In the traditional approach, one collects the data first and then starts analysing the results. This strategy has a risk that there may be a gross inefficiency in the setup of the experiment, for example: the data set may be incomplete, the reflections may overlap, the zones may overlap, a large percent of the reflections may be overloaded, etc. Data collection is therefore performed as a highly interactive process. Immediate data processing provides fast feedback during data collection. The image plate detector radius is 12 cm. The length and width of the
Figure 2.3: Goniostat and X-ray tube of DIPlabo Image Plate.

Figure 2.4: Schematic diagram showing the $\kappa$ geometry goniostat.
image plate are 44.266 cm and 24.00 cm respectively. The oscillation range for data collection is set to 5° by default. The analysis and reduction of single crystal diffraction data consists of seven major steps. These are:

- Visualization and preliminary analysis of the original, unprocessed, diffraction pattern.
- Indexing of the diffraction pattern.
- Integration of the crystal and detector parameters.
- Integration of the diffraction maxima.
- Finding the relative scale factors between measurements.
- Precise refinement of crystal parameters using the entire data set.
- Merging and statistical analysis of the measurements related by space group symmetry.
References


