CHAPTER IV

EXPERIMENTAL AND COMPUTATIONAL TECHNIQUES.
(a) **Optical properties of crystals:**

In an anisotropic crystal the velocity of light varies with the direction of propagation. A beam of light entering such a crystal is in general divided into two rays—each polarised in planes at right angles to the other. This fact forms the basis of the optical method of studying crystals. In tetragonal, trigonal and hexagonal systems, because of symmetry there is one direction in which the aforesaid double-refraction (birefringence) does not occur. This direction is called the "optical axis" and is the same as the conventional crystallographic axis. Such crystals are called 'uniaxial crystals'. Crystals of the orthorhombic, monoclinic and triclinic systems possess two directions—not necessarily coincident with the crystallographic axes, which correspond closely to the optic-axis of uniaxial crystals. They are called 'biaxial crystals'. In these crystals there are three planes perpendicular to each other, such that one of the two extraordinary rays which can travel in any direction along these planes has a constant refractive index. These three planes are defined by three orthogonal axes along which
the refractive index has the maximum, the minimum and a
particular intermediate value. In an orthorhombic crystal
these directions are the same as the crystallographic axes.
In monoclinic crystals one of them is parallel to the
b-crystallographic axis, the other lies in the a c plane;
whereas in triclinic crystals they have no relation with the
crystallographic axes.

(b) **Examination of crystals between crossed polars:**

When examined thus, isotropic substances will remain
dark like the rest of the field whereas anisotropic substances
will appear coloured in most positions and will become dark
only in certain definite orientations. If such as substance
is examined on the rotating stage of the microscope it becomes
dark — or extinguishes in four positions at intervals of 90°
and between these extinction positions the crystal is illuminat-
ed. In the extinction positions, the traces of vibration
direction in the section of the crystal are parallel to the
planes of vibration of the polars, for in such positions light
from the polariser is not resolved in the plate but passes on
to the analyser as if no crystal were on the stage and darkness
results. If the crystal plate is an optical axial section of the crystal, extinction will be observed in all positions. However, biaxial optical axial sections do not extinguish so completely as the uniaxial ones, but are faintly and uniformly illuminated on rotation.

If the direction of extinction is parallel to the length of the crystal section, or to a single cleavage or prominent edge, it is said to be straight or parallel extinction. If it bisects the edge between two cleavages or prominent edges it is called 'symmetrical', and in the case where it is neither symmetrical nor straight it is 'oblique or inclined'. These extinction angles prove useful in the identification of crystals and in distinguishing the crystals of one substance from those of the other.

The polarising microscope also helps us to know the form, texture and purity of the crystals under study and helps us to choose suitable crystals for study by the otherwise time consuming X-ray method.

(c) Spencer's polarising microscope:

A number of types of available polarising microscopes have been described by Hartshorne and Stuart (1960)\(^1\). In my
FIGURE - 1. Polarising Microscope.
(iii) When the objective lenses are removed, care should be exercised that they do not fall down.

(iv) Finger prints on the lens, eve piece and deposition of dust should be avoided.

II. X-RAY DIFFRACTION UNIT:

The X-ray diffraction unit used in the present study is Phillips Stabilised X-ray diffraction apparatus (generator) PW 1010.

This unit is fed with smooth D.C. In addition the high tension and tube current are both stabilised in order to eliminate fluctuations in the intensity of the primary beam. High precision electronic stabilising circuits keep the tube current as well as the anode voltage within ± 0.1% of the adjusted value, independent of fluctuation of the mains upto ± 10%. With the same expenditure of energy, the average radiation output is about 30% higher in this case as compared to halfwave, rectifier system. This unit with these stabilisations give fairly constant intensity of the primary beam and is much suited for most of the diffraction work.

The tube shield, which is fitted vertically at centre
of the upper panel of the unit, consists of four windows for the X-rays to pass through, three of these windows have a disc, having five filters and one open hole, fitted over them. such as Rotation of the disc brings before the windows the desired filter or hole for white radiation. The Weissenberg camera is placed before the point-focus window. With Cu-target tube the Ni-filter is used to filter out $K_\beta$-radiation.

**Monochromatic X-rays:**

X-radiation from the machine consists of a wide band of white radiation with superimposed characteristic spectrum of $K\alpha_1$, $K\alpha_2$, $K\beta$ lines and some contaminating K or L lines from the target. Many diffraction techniques preferentially require a monochromatic beam. Although this is never obtainable with X-rays, yet various degrees of monochromatism are obtained using a single filter, balanced filters or crystal monochromators.

A single filter made of an element which has an absorption edge of wavelength just less than that of $K\alpha_1$, $\alpha_2$ doublet will absorb part of that doublet but much more of the $K\beta$ line and a good part of the white radiation of all wavelengths.
The copper and molybdenum targets:

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Filter Not to be Transmitted</th>
<th>Radiation in A°</th>
<th>Crystal window contains for Kα</th>
<th>Optimum ratings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>Kα₁</td>
<td>Kα₂</td>
<td>Kα₁</td>
<td>Kα</td>
</tr>
<tr>
<td>Cu</td>
<td>1.53\text{A}</td>
<td>1.54\text{A}</td>
<td>1.28\text{A}</td>
<td>Kα</td>
</tr>
<tr>
<td>Mo</td>
<td>0.707\text{A}</td>
<td>0.712\text{A}</td>
<td>0.631\text{A}</td>
<td>Zr, Y, Sr</td>
</tr>
</tbody>
</table>

Tables relating to the production, wavelength and intensities of X-rays are given in "International Tables for X-ray Crystallography" Vol. III, page 59-72.

X-radiation from Mo-target is for all purposes and generally useful for all crystallographic work. However, for examining organic substances usually Cu(Kα) radiation is used because of the following reasons:

(i) Almost all recordable data can be obtained with Cu-radiation because of high B-values for the light atoms as a consequence of which high sinθ-data is negligible.

(ii) Greater separation of spots in reciprocal space helps setting and avoids overlap.
However, when heavy atoms are present (heavier than Cu or Cu itself) or for low temperature work, Mo-radiation must be used.

III METHODS OF SETTING CRYSTALS:

In setting a crystal one of its principal crystallographic axis has to be brought in a position parallel to the rotation axis. In terms of reciprocal space, the setting of a crystal, therefore, means bringing a selected reciprocal lattice net perpendicular to a given direction, which is the rotation axis. The chosen direction is first set approximately parallel to the axis of rotation by the optical method. In order to get the crystal set by X-rays, the following methods are used:

(1) Oscillation method:

After setting the crystal optically, a small angle (10° - 15°) oscillation photograph is taken, keeping one of the goniometer arcs parallel to the beam for the mean position of the crystal. The zero-layer reflections are found to form a curve in case of ill-setting. The reflections at the end of the curve (if present), indicate the direction and approximate extent of correction to be applied to the arc
parallel to X-rays. After correcting the position of this arc, corrections are applied to the other arc, in a direction which helps in removing the curvature of the zero-layer line.

(ii) **Double Laue method**

In this method a Laue photograph is first taken (in unfiltered radiation), with one of the arcs parallel to the beam and on this is superimposed another Laue photograph taken after rotating the crystal by $180^\circ$ and giving half the original exposure.

The zero-layer reflections lie on one of the four possible types of curves given by Olga Veisz and W.F. Cole (1948), which indicate the direction of corrections. The extent of correction is worked out by measuring the separation of spots at $\theta = 45^\circ$ on both sides of the centre. One of the separations is equal to $\delta_\parallel + \delta_\perp$ and the other separation at $\theta = 45^\circ$ is $\delta_\parallel - \delta_\perp$ where $\delta_\parallel$ and $\delta_\perp$ are the distances of the displaced points from the ideal position of the zero-layer line for a Bragg angle $\theta$.

In addition, the position and separation of spots at $\theta = 90^\circ$ gives a good and independent estimate of the correction to be applied to the arc parallel to the X-ray beam,
which serves as a check and helps avoid errors which might occur due to slip in working out the direction of moving arcs by the above method.

Alternatively, the double Yaue method by Davies, RT. 4 (1950) can also be used. In this the arcs are at 45° to the incident beam. The separation of the zero-layer curves at the two positions of θ=45° are measured giving a positive sign if the more intense spot is the upper spot. If Δ1 and Δ2 are the separations on the left hand side and right hand side respectively, then the corrections (anti-clockwise sense, if positive) are given by:

(Figure - 2.):

Arc No. 1. \[ Δ_1 \left[ \frac{\frac{180}{\pi}}{2 \sqrt{2} \cdot R} \right] \]

Arc No. 2. \[ Δ_2 \left[ \frac{\frac{180}{\pi}}{2 \sqrt{2} \cdot R} \right] \]

Where R is the radius of the camera.

(iii) Using Weissenberg camera:

A number of modifications have been made to the methods originally described by Runn, C.W. 2 (1945) and Weisz and Cole 3 (1948), utilizing the translation possibilities of the Weissenberg-film holder by Winchell, H. 5 (1950), Jerslev 6
Figure 2. Diagramatic plan of arcs in correct orientation for the longer exposure.

Figure 3. Oscillation photographs of the unaligned crystal.
(1951) and Drassdorf, R.D. (1953) etc.

Two oscillation photographs can be made on a Weissenberg camera, one of the two exposures is made with the crystal oscillating 15° about the point at which one sonometer arc is normal to the beam and the other exposure is taken with the film-stage moved 2° or more centimeters and about a point 180° different from the first (Drassdorf, 1953). The angle of inclination of the crystallographic axis may be produced by two rotations through angles \( i_1 \) and \( i_2 \) where \( i_1 \) is the angle of rotation about the X-ray beam as an axis and in a plane perpendicular to the X-ray beam corresponding to the correction to be required to be made to the arc perpendicular to the beam, and \( i_2 \) is the angle of rotation about the intersection of the X-ray beam with the axis of rotation in plane determined by the incident beam and the axis of rotation corresponding to the correction to be applied to the arc parallel to the X-ray beam.

If \( C \) be the distance of translation of the film holder and \( A \) and \( B \) the distance of spots at an angle \( 2\theta = 90° \) (figure -3) then according to Henderson (1937):

\[
i_2 = \frac{1}{2} (A - B) \quad \text{and} \quad i_1 = \frac{1}{2} (A + B) - C.
\]
Taking camera-radius (R) into account, the correction to be applied in radians are \( \frac{i_2}{R} \) and \( \frac{i_1}{R} \) respectively.

IV **WEISSENBERG MOVING FILM CAMERA**:

The Weissenberg goniometer\(^8\) consists essentially of a goniometer head mounted on a spindle which is co-axial with a cylindrical camera. The movement of this camera is electrically coupled to the rotation of the crystal by a synchronised motor. The camera can move parallel to its axis during the rotation of the crystal.

The X-ray beam is allowed to pass through a collimator - by which fogging due to scattering from slit is minimized. Screens, which are coaxial with the camera, permit reflections only from a layer-line of the rotation photograph to fall on the moving film. Attached to one of the screens is a beam-catcher which absorbs the direct X-ray beam.

An advantage of this goniometer over the old moving-film goniometers is that all angles of reflections up to a value close to 90° can be recorded.

In this method the reflections from the various planes
present work I used the "Spencer's Polaris ing micro-
the diagram of which is reproduced as Figure 1 and which
is described briefly below:

The beam of parallel light is directed to the
polariser by the mirror, then it passes through the condenser
lens and is focussed on the stage. After passing through the
specimen it passes through the objective lenses, the analyzing
prism, eye-piece field lens and the eye-lens focussing lens.
The diagram gives the names of the parts of the Spencer's
polarising microscope. T1143.

The important precautions in handling the polarising
microscope are the following:
(i) Care should be taken that the microscope is never lifted
using any part of microscope except the
(ii) The objective lenses should never be brought in contact
with slide or the crystal. To do this the microscope should
be brought down by moving the adjustment knob, while observing
the objective lens which should not be lowered so much as to
touch the slide and the crystal. After this, correct focussing
should be obtained looking through the eye piece and gradually
rotating the knob so as to lift up the microscope from this
position.
of a zone (say h o l zone) are separated on the film because of a synchronised periodic translation of the film parallel to the rotation axis. The position of the reflections is determined by the camera characteristics, that is, the extent of translation per degree of rotation and the camera-radius. The X-ray photograph obtained represents the weighted, distorted reciprocal-lattice net perpendicular to the axis along which the crystal has been set.

In the standard Unicam Weissenberg Camera the camera-diameter is 57.3 mms. and the translation is 1 mm. for every 2° rotation of the crystal. In the normal beam photograph taken with these cameras, the axial reflections lie on lines making an angle of 63°-32', with respect to the direction of translation. These lines are separated by a distance which in millimeters is equal to half of the angle between the reciprocal axes. The general reflections lie on catenary-type of lines between the axes.

V INDEXING OF WEISSENBERG PHOTOGRAPHS:

In order to index and interpret the normal-beam zero-layer Weissenberg photograph, the Weissenberg chart is superimposed on the photograph in such a fashion that the
base-line of the chart lies on the middle of black-band running the length of the photograph (central-line), and the chart is moved side ways until its left hand sloping line lies on the straight row of spots on the left-hand side of the photograph. Spots with a common indice, say \( h = 1 \), will lie on festunes parallel to the trace of such festunes on the chart, similarly, if the chart is moved to the right till its left hand sloping line lies on the row of spots from the other axis, spots with common indice, now \( k = 1 \) etc., will lie on festunes parallel to these on the chart. Both the sets of festunes may be drawn and the indices of spots, which will lie at the intersections obtained.

If the distance between the side row of spots from one set of axial reflections and the central row of spots is less than 4.50 cms. corresponding to a reciprocal angle of less than \( 90^\circ \), the reflections in this low angle area are indexed positive and those on higher angle area side are indexed as negative (represented by bars over indices).

By the position of \( a^* \), \( b^* \), \( c^* \), \(-a^*\), \(-b^*\) and \(-c^*\), the corresponding \( h \), \( k \) and \( l \) reflections are indexed in the case of Weissenberg photographs from higher layer lines as
illustrated in the following diagram:

It will be clear that in some cases two Weissenberg photographs (with crystal rotated by 180° in one of the sets) will have to be taken to photograph all the reflections from the layer line.

VI MULTIPLE - FILM TECHNIQUE:

This technique developed by Robertson (1943), is very helpful in estimating intensity from Weissenberg moving film photographs visually.

In the cylindrical camera, three or more films are loaded—well protected from light and the photograph is taken. All the films are processed under similar conditions of developing, fixing and washing.

The visual method of estimation of intensity is quite
satisfactory for estimating the integrated intensity of reflections. This method consists of visually matching the intensity of each spot on the film with a spot of known intensity. The standard spots can be obtained with a rotating-sector. Alternatively, the set crystal itself is exposed to X-rays for different intervals of time to give graduated intensities covering the range of distinctly measurable intensities of the spots under investigation.

From multiple-film technique, it is possible to estimate all the spots. The top film will help in estimating relative-intensities of the weak and moderate spots, and the subsequent films -- for the stronger spots which cannot be estimated by single top-film. The moderate spots are used to get a "Film-factor", which helps in converting all the estimations on the same scale.

VII METHODS OF COMPUTATION OF FOURIER SERIES:

One of the most popular devices used for Fourier summations is the strip-method. By this method the Fourier summation is performed by the help of strips of cards upon which are printed numbers representing the ordinates of the various terms to be included. Essentially, this method is for
summing one dimensional series of the form:

\[
\text{(cosine)} \quad C = \sum_{h=0}^{H} A_h \cos 2\pi hx \quad \ldots \quad (A)
\]
and \( (\sin) \quad S = \sum_{h=0}^{H} A_h \sin 2\pi hx \quad \ldots \quad (B)\)

Here \( A_h \) is the amplitude.

There are three methods based on the utility of strips, viz.,
Beavers - Lipson strips method \(^{10,12}\),
Patterson - Tunell method \(^{13}\),
and Robertson's strip method \(^{14}\).

(1)(A) Beavers-Lipson strips:

This strip method relieves the computer of all the
preliminary mathematical work in computing equations (A) and
and (C). On the strips, for a particular value of \( A \) and \( h \), all
the values, likely to be needed, of \( A_h \cos 2\pi hx \) & \( A_h \sin 2\pi hx \)
are recorded for the 16 successive 'x' locations of 0/60, 1/60,
2/60 \ldots \ldots 15/60.

For example for \( A = 39 \) and \( h = 4 \), the various values
of \( A_h \cos 2\pi hx \) are printed on the strip as follows:

\[
x \quad = \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad \ldots \ldots \quad 14 \quad 15
\]

\[
39 \quad C \quad 4 \quad 39 \quad 36 \quad 26 \quad 12 \quad 4 \quad \ldots \ldots \quad 36 \quad 39
\]
Similarly for \( A = 19 \) and \( h = 6 \), the values of \( A_h \sin 2\pi hx \) for the parameter \( x \) are printed on a strip as follows:

\[
\begin{array}{cccccccccccccc}
& x = 0 & 1 & 2 & 3 & 4 & 5 &\cdots & 10 & 11 & 12 & 13 & 14 & 15 \\
19 & 5 & 6 & 0 & 11 & 18 & 18 & 11 & 0 &\cdots & 0 & 11 & 18 & 18 & 11 & 0 \\
\end{array}
\]

Thus, inorder to sum up the values of \( A_h \cos 2\pi hx \) or \( A_h \sin 2\pi hx \) for all or particular values of parameter \( x \), the corresponding strips for the particular values of \( A_h \) are collected and arranged so that the total can be performed for each value of parameter \( x \). The summation of the even values and odd values is performed separately. In case of cosine-series summation, if \( C_e \) is the value of even values of \( A \) and \( C_o \) is that for odd values of \( A \), then the Fourier synthesis for the range \( x = 0 \) to 15/60 is obtained by adding \( \Sigma C_o \) to \( \Sigma C_e \) while the range from 30/60 to 15/60 is obtained by subtracting \( \Sigma C_o \) from \( \Sigma C_e \). In case of cosine synthesis, it is symmetrical about \( \frac{1}{2} \), so this completes the synthesis.

(B) THE Patterson-Tunell method:

This method differs chiefly in the number of kinds of strips needed. Set of stencils are used which uncover only those numbers that have to be added. Strips of required
amplitudes are arranged over a board and over this an appropriate mask is placed inorder to uncover only the required values.

Patterson and Tunell method is advantageous in the sense, that a much smaller collection of strips of different kinds, is employed, since the strips are functions of $A$ only and not of both $A$ and $h$ as in the case of Breevers-Lipson method.

(C) **Robertson's strips**:

Robertson (1926) adopted a method in which there are strips for unit index only and the ordinates for all other indices are obtained from this one, by appropriate translation. By this method, it is also possible to sum two dimensional series in a direct manner.

(ii) **Optical methods of Fourier synthesis**:  

Since there is a close analogy between X-ray diffraction and Fourier synthesis on the one hand and optical diffraction and image formation on the other it is evident that the process of Fourier summation is essentially the adding of sets of fringes. This similarity between Fourier series and image found by optical instrument, is the basis of a number of
Aids for structure analysis.

(A) **Bragg's**\textsuperscript{15} photographic method:

In this method the image which is the superimposition of a number of interference fringes can be represented on a photographic paper, as would be obtained by an X-ray microscope. The image is not true one, since the background of the atomic peaks is very high. Also this method yields only qualitative results.

(B) **The Huggins masks** :\textsuperscript{16-17}

A Cinematograph-film of a set of masks representing the fringes for indices (with the right spacing and orientation) is projected on to a sheet of photographic paper. The exposure for each mask is made proportional to the structure amplitude. A Fourier synthesis is obtained on the development of the photographic paper, if the total exposure is within the range of photographic proportionality.

(C) **The X-ray microscope** -(Optical diffractometer):

If a parallel monochromatic beam of light is allowed to pass through a screen in which holes are punched to represent
the magnitude of the structure factors and their position in the reciprocal lattice section, the image formed by the emergent beam will be the Fourier synthesis of the diffraction pattern. This method is specially direct one, for Patterson synthesis, when the phases are all the same. In general application to Fourier synthesis the phase differences must be taken into account. Buerger introduced this phase shift, by placing over each reciprocal lattice hole, a mica plate so tilted as to increase the optical path.

Other modification is by Hanson, Taylor and Lipson\textsuperscript{19} (1951) in which the apertures in the screen represent only the reciprocal lattice positions, and the biaxial optical properties of mica are used to control both the amplitudes and the phases, which can only differ by integral multiples of $\pi$. Hughes and Taylor\textsuperscript{20} (1953), placed the set of equal holes, representing the reciprocal lattice, between crossed Nioles in the diffraction spectroscopic and thus introducing the phase difference.

(iii) \textbf{The Photosommateur}:

Based on the analogy between X-ray diffraction and Fourier synthesis on the one hand and optical diffraction and
image formation on the other hand, G.v. Eller constructed a versatile machine - the Photosommateur. A vertical slit source of light passing through a specially designed grating produces a sinusoidal distribution of intensity on a photographic paper mounted at the centre of a movable disc. The intensity depends on the exposure time, and the correct orientation of the Fourier terms relative to each other is achieved by rotating the disc carrying the photographic paper. The spacing is altered by varying the distance between grating and source, the grating being geared to a cursor which permits the settings to be made directly from a drawing of the reciprocal lattice mounted on the disc. The phase is introduced by an eccentric spindle which enables the grating which produces the vertical fringes to be translated horizontally by any amount up to one complete period $2\pi$.

The photosommateur at National Chemical Laboratory, Poona (India) has been sued in part of the present work. A diagram of the Photosommateur is reproduced in figure -4.

(iv) Large-Scale computing equipments:

Rapid and accurate methods of Fourier summation are provided by large scale electronic analogue machines, solely
FIGURE - 4. BEAUDOUIN - Photosommateur.
designed for crystallographic calculations and by modern digital electronic computers. Of the analogue machines, mention may be made of X-RAC and S-FAC.

On X-RAC — the electron density contour map is produced directly on a cathode ray screen from a setting of dials and switches that correspond to amplitudes and signs of the Fourier terms. While S-FAC — calculates structure of factors from the maxima of the Fourier map presented on the screen.

Punch-card methods provide a rapid means of data input. In these methods, the data is fed in the form of holes in the cards. These cards are passed through metal rollers and a series of wire brushes. The circuit is completed only through a hole in the cards depending on the particular position of the card. Such equipments can be attached to analogue machines or to digital electronic computers.
REFERENCES


6 Jerslev, H., ibid. (1951), 4, 472.

7 Drassdorf, R.D., ibid. (1953), 6, 220.


15 Bragg, W.L., Z. Krist. (1929), 70, 482.


