CHAPTER III

Experiments:

For studying the diffuse reflections of X-rays from crystals, Geiger Muller Counter method or the photographic technique is generally used.

Laval (1939) Olmer (1948) used ionization chamber for accurate measurements of the intensity of diffuse reflections. Ramchandran and Wooster (1951) applied both the photographic technique and Geiger Muller Counter method for studying diffuse spots. Sen (1949,55) used photographic technique for the detection, as well as, for the measurements of the intensities in various directions of the diffuse spots. Photographic technique is generally preferred where an overall survey of the diffuse spots is required. Because, in one photograph, one can have different directional intensities for one setting of the experimental crystal; whereas in counter technique one has to set the detecting counter in different directions for the measurements of different directional intensities.

The monochromatic beam of X-rays should be considerably intense in order to increase the contrast between the background count and the count for the very weak diffuse reflection intensities. To intensify the monochromatised beam, one can use curved crystal monochromator. But, in that case, the divergence
of the beam will be considerably high and consequently one can not record the intensity of the diffuse spot very close to relp (i.e. reciprocal lattice nodes). With plane crystal monochromator where the divergence is less, the intensity of the reflected beam being much reduced the exposure time will have to be increased to record a fairly high count. Again to avoid higher harmonics of the wavelength of X-rays, the X-ray unit should run at a low voltage. Due to this reduction of voltage, the exposure time will have to be increased further to get a considerable good count, in both the cases of diffuse spot and direct beam. As in counter diffractometry one has to record the intensities of the diffuse spot and direct beam separately, minute fluctuations in X-ray unit will involve serious error in the relative measurements of intensities of the diffuse spots and the direct beam.

In photographic technique, both the diffuse spot and the direct beam, being recorded on the same film, the stabilization of the X-ray unit is not essential, because, the fluctuations in the X-ray unit will have the same effect on both of them. With the use of plane crystal monochromator, minimisation in divergence of the beam helps one to record the diffuse spot very close to relp. The only difficulty with this method is due to the fogging of the film, the Compton scattering and the background scattering can not be very accurately measured.
In the present investigation the photographic method together with a plane crystal monochromator (fluorite-(111) plane) was used. Chakravarty (1958) determined the elastic constant $C_{44}$ of KBr with this method and found that the value of the constant agrees well with the value determined by Galt (1948) by Ultrasonic pulse method.

**Crystal Growth:**

Crystals of 1:8 dihydroxy anthraquinone were grown from a solution of the substance in Benzene by slow evaporation of the solvent at room temperature ($30^\circ$C approx). The crystals generally grow as plates with edges parallel to a- and b-axes. Flat faces are perpendicular to c-axis.

A suitable crystal of fairly good size was selected and examined under a microscope. The dimensions of the crystal were measured with the help of a powerful travelling microscope and its volume was computed. The volume of the crystal thus determined was checked up by weighing the crystal in a microbalance and dividing the weight of the crystal by density of the substance, determined by floatation method.

**Laue Photographs:**

In the present investigation the Laue photographs were taken with a cylindrical camera fabricated in the workshop. A long circular slit of length 6.5 cm. having a diameter of 0.05 cm was used. The radius of the camera obtained approximately from
the powder photographs of Aluminium is 3.75 cm. A rod passing through the axis of rotation of the camera carries a goniometer head with all its usual arrangements for making one of the axes of the crystal parallel and coincident with the axis of rotation of the camera. The camera is provided with a circular disc graduated in half degrees from which a minimum angle of rotation of 3° can be read accurately with the help of a vernier scale. The camera is provided with a screw for fixing the axis of rotation at any position.

The crystal was mounted with durofix adhesive on a fine glass rod with an aluminium tip on the head of the crystal. Then the whole assembly was rigidly mounted on the goniometer head with bee wax. The aluminium tip on the crystal here serves the following purposes.

(1) The radius of the camera and consequently the angle of scattering can be accurately determined, and (2) the relative intensities of the diffuse reflections in the different photographs can be standardised.

The crystal was set with a-axis along the camera axis and in the first photograph the incident beam was along the b-axis. In the successive photographs the beam was inclined at various angles with the b-axis.

A few Laue photographs with unfiltered Cu-radiation of x-rays at different settings of the crystal were taken. The
Laue reflections associated with the diffuse reflections, were identified from the known axial lengths and the direction cosines of the incident and the diffracted beams. But this method does not give the order of diffraction. So with the help of the reciprocal lattice net and the position of the sphere of reflection in this lattice, planes giving rise to the diffuse reflection were finally identified.

A series of Laue photographs were then taken with monochromatised x-ray beam, around Bragg-reflection positions of different planes. The experimental arrangement for taking Laue pictures with monochromatic x-rays is shown if fig- 76.

The x-ray beam being collimated through rectangular slits $S_1$ and $S_2$ are allowed to fall on the plane crystal reflector mounted on B and provided with arrangements for movements in two mutually perpendicular directions. At first the crystal face was made vertical and parallel to the directions $S_1 S_2$ and then by rotating the crystal about a vertical axis with the help of the screw $P$ it was brought to Bragg-reflection position for (111) plane of fluorite (Bragg-reflection for CuK occurs in this case at 14°6'), when the reflected beam has the strongest intensity. The reflected beam was then allowed to pass through the experimental crystal after being collimated through the slit of the Camera by adjusting the position of the Camera. The perfection of collimation was finally checked up by taking
FIG. 6

THE EXPERIMENTAL ARRANGEMENT OF TAKING
LARGE PHOTOS OF MICRO-CRYSTAL RADIATION.

L — LEAD SHIELD
B — BRASS PLATE
P — SCREW
F — FLUORITE CRYSTAL
S_3, S_4 — KNIFE EDGES
photographs with short exposures. The vertical and horizontal divergences of the incident beam were calculated by taking two photographs at 10 cm. apart with short exposure. The horizontal divergence is 12' and vertical divergence is 24'. The vertical divergences are further reduced by the small vertical dimension (about 0.1 cm) of the crystal.

To suppress $\lambda/3$ component in the monochromatic beam the tube was run at 25 kv. The time of exposure varied from 14 hrs to 40 hrs depending on the angle of deviation from the Bragg angle of the planes; structure factors of the planes and the spacing of the planes.

A few Laue photographs were taken with filtered radiation using Ni-foil as filter to record the weak scattering corresponding to large angular deviation from the Bragg reflection positions. The necessary arrangements required for this purpose is shown in the fig. 47.

When studying the scattering over a large area some of the aluminium diffraction lines get mixed with diffuse angle-of-scattering, consequently aluminium powder could not be placed at the top of the crystal. A thin aluminium foil specially prepared by mixing aluminium powder with collodion is placed near the inside collimator near the end of the slit facing the crystal. The x-ray beam after absorption is allowed to pass through the slit and fall on the crystal. There is two almost
SCHEMATIC DIAGRAM OF THE EXPERIMENTAL ARRANGEMENT OF TAKING LAUE PHOTOGRAPHS WITH FILTERED RADIATION.
semicircular openings on the two sides of the diffracted beam corresponding to the diffraction lines of Al. to pass through. The thickness of the Al-foil is adjusted to minimise the absorption of the beam and to bring down the intensity of the Al. diffraction line to a range comparable to that of the diffuse scattering. The time of exposure required to record the weak diffuse scattering varied from 20 hrs to 25 hrs.

The angle corresponding to the directions of observation were determined from the distance between two Laue spots from known planes. The orientation of the crystal is obtained from the distance between the direct beam and any known Laue spot. Thus the intensity of diffuse scattering can be plotted against the angular distance. The intensity in the different photographs can be brought to the same intensity scale from the integrated intensities of the Aluminium diffracted lines.

Measurements of Intensities:- The intensity distribution in the diffuse reflections, Aluminium diffraction lines and the incident beam were measured by the Moll recording Microphotometer. The film is mounted on a sliding carriage provided with the horizontal as well as vertical movements. Light from a straight filament lamp drawing a steady current of about 5 amp from 6 volts accumulators, was focussed on the film. The dimension of the focussed light spot can be varied to the desired size. The spot in the present case was .02 cm. in height and .005 cm.
in breadth. For the equatorial spots the film carriage was so adjusted that the scanning spot traverses through the centre of the incident beam along the equatorial line. For the 1st layer line spots the film carriage was raised or lowered through the known distance corresponding to this layer line, and the spots scanned parallel to the equatorial line.

After passing through the film the light falls on a vacuum thermopile and the current developed there is recorded by a Moll sensitive galvanometer which is mounted on a vibration-less pillar. The time of response of the combination is of the order of .25 secs. The galvanometer deflections corresponding to different densities of blackening were recorded on a photographic paper wrapped on a drum which was rotated synchronously with the translatory movement of the film. The ratio of the movement of the drum to the movement of the film was 4:1.

The distances between several lines of Aluminium recorded on the film is used to convert the distances in the photometric curve into angles of diffraction. The intensities were obtained from the photometric curve by comparing the deflection with those of a standard calibration strip following the method of Robinson (1933). The basic feature of the calibration strip is that the time of exposure is linearly proportional to the distance from the zero intensity line. The photometric curve for the calibration strip was recorded under identical photometric conditions as that
used for diffuse spots. Intensities of diffuse reflexions and the incident beam thus estimated are on the same arbitrary scale.

**Corrections to the observed intensities:**

1. **General scattering:** The measured intensities contain the contribution of intensities from other sources along with the first order thermal diffuse reflections. These are fluorescent scattering, Compton scattering, and air scattering.

   Fluorescent scattering arises due to the fact that the primary X-ray beam incident on the crystal containing shorter wavelengths (higher frequencies) than the wavelength of the K, L, M absorption edges of the chemical elements present in the crystal ionizes the atoms and gives rise to the K, L, M fluorescent radiations characteristic of the atoms. If the scattering particles containing lighter elements are irradiated by X-rays there will be a scattering with slightly greater wavelength than those of X-rays due to Compton effect. The air inside the camera will also give a gaseous type of scattering. These scattering varies slowly with the angle of diffraction and appears as a general background to the diffuse reflection. This background scattering intensities were deduced from the intensities on the two sides of the diffuse reflections where their intensities are negligible. This background scattering has been shown in each $I_d/I_o$ vs $\phi$ curve by dotted lines. The corrected intensities were obtained by subtracting the
background intensities from the total intensities.

**Divergence corrections:** The incident beam is divergent and the diffusely scattered intensity is measured over a finite solid angle. As a result, the measured value of the diffuse intensity is in effect the mean over a small element of volume surrounding the reciprocal lattice point concerned and a correction has to be applied to the measured intensities. This correction becomes important if the divergence of the incident beam is very high. In the present investigation the divergence of the incident beam is very low. These corrections were calculated in a few cases and were found to be negligible.

**Skew correction:** This correction arises due to the fact that the angles of incidence and reflection are not equal. Laval (1939) has shown that the diffuse scattered intensity is to be multiplied by a correction factor

\[ \frac{1}{2} \left( 1 + \frac{\sin i}{\sin (\phi - \theta)} \right) \]

where \( i \) = angle of incidence, \( \phi \) = total angle of scattering.

**Correction for non-equatorial reflexions:** For non-equatorial spots the intensities of the diffuse reflections are to be multiplied by \( \sec^2 \mu \), where \( \mu \) is the angle with the normal to the film at which the beam after diffraction is allowed to fall on the film.
Absorption corrections: - The intensities of the diffuse reflections are reduced due to absorption in the crystal and on account of this a correction should be applied to the measured intensities. In the present case the linear absorption coefficient of the crystal and their linear dimensions are very small, the absorption correction factor is therefore very low. Furthermore the incident beam is registered after absorption by the crystal and the intensities of the diffuse reflections are compared with this absorbed undeviated beam intensity. This automatically takes account of the absorption correction to a large extent.

Correction due to Mosacity of the Crystal: - When the points of observations lie within the mosaic spread of the crystalline Bragg reflections, the intensities are enhanced and are inaccurate. These regions are avoided in the present measurements.

Corrections for Second order diffuse reflexions: - The measured intensities include a contribution from second order diffuse reflexions due to the interactions of two phonons. This is approximately given by the expression,

\[
\frac{I_{d2}}{I_{d1}} = \frac{\lambda^3 k T}{2} \cdot \mathcal{Q} \cdot \frac{K(uvω)_{HKL}}{K(uωω)_{HKL}}
\]
Where \( K'(\lambda n \lambda m)_{hkl} \) like \( K(\lambda n \lambda m)_{hkl} \) is a function of the elastic constants. The preliminary values of the elastic constants obtained by neglecting \( I_d^2 \) are used for estimating \( I_d^2 / I_d \) and the corrected value of \( I_d \) are evaluated. Final values of \( I_d \) are obtained by the process of iteration. For points very close to the reciprocal lattice modes, the contribution from \( I_d^2 \) is negligible and therefore corrections were applied only to cases where \( I_d^2 \) was appreciable.

The corrected values of \( I_d^1/I_0 \) were finally corrected for the angle factor due to polarisation of the x-ray beam. This factor is given by the expression

\[
A^2 + B^2 \cos^2 \phi = \frac{1 + \cos^2 2\alpha \cdot \cos^2 \phi}{1 + \cos^2 2\alpha} \quad \text{for equatorial spots},
\]

and

\[
= \frac{\cos^2 \mu \cdot \sin^2 \phi + \cos^2 \phi \cdot \cos^2 2\alpha}{1 + \cos^2 2\alpha} \quad \text{for non-equatorial spots}.
\]

Where \( \alpha \) is the Bragg angle for monochromatisation of the beam and \( \phi \) and \( \mu \) are the equatorial and the normal angular components of the scattered beam.