CHAPTER -3

EXPERIMENTAL

3.1 X-RAY SOURCE AND ITS WHITE RADIATION

A sealed chiraina x-ray tube with a copper target was used as a source for x-rays. The operating voltage was kept at 30 KV and the tube current at 5 mA. The x-ray tube was operated by a control power supply unit supplied by Radon House, Calcutta. One requires the white radiation to record the absorption edge. The intensity distribution of white radiation is shown in Fig. 3.1. The integrated intensity is given by

\[ I = KC V^2 Z \]  \hspace{1cm} (3.1)

where

- \( K = \) Constant
- \( C = \) Tube current
- \( V = \) Voltage applied across the tube
- \( Z = \) Atomic no. of the target element

The Duane and Hunt limit \( \lambda_{min} \) is given by the rule

\[ h\nu_{max} = eV \]  \hspace{1cm} which leads to the working formula.

\[ \lambda_{min} (A^0) = \frac{12.93}{V(KV)} \]  \hspace{1cm} (3.2)

The intensity is maximum at \( \lambda_{max} \). Generally for a coolidge tube

\[ \lambda_{min} = \frac{2}{3} \lambda_{max} \]  \hspace{1cm} (3.3)
Thus the position of $\lambda_{\text{max}}$ can be controlled by $\lambda_{\text{min}}$ which in turn depends upon the voltage applied in KV.

It is always convenient to record the spectra by operating the x-ray tube at such a voltage that $I_{\text{max}}$ lies in the neighbourhood of the absorption edge. Thus, if the wavelength of the absorption edge has been roughly estimated, one can easily calculate the optimum operating voltage for the x-ray tube. It is always advisable to use the flat horizontal part of the continuous spectra (Fig. 3.1) as a background for absorption because if the wavelength of absorption edge lies in the slope region of the white radiation, the shape of the absorption edge gets distorted as shown in Fig. 3.2 (a,b,c). Fig. 3.2 (a) shows the shape of undistorted x-ray absorption edge. Fig. 3.2 (b) and Fig. 3.2 (c) shows the shape of absorption edge (distorted) when the absorption edge lies on the slope which is higher or lower energy side of the flat horizontal part of the continuous spectra (Fig. 3.1) respectively. For this reason, we have already taken care to avoid the slope regions and have used the flat part of the white radiation as a background.

Another aspect of white radiation which deserves mention here is the polarization of this radiation. Fig. 3.3 shows the direction of the cathode ray beam, the direction of observation for the x-ray beam and the plane formed by them, so that $I_1$, and $I_1$ to the intensities in the x-ray
Fig 3.1 Intensity distribution in the continuous X-ray spectrum at a constant potential.
Fig. 3.2 A plot of the absorption curve at the different slope region of the continuous X-ray spectrum.
beam corresponding to their E vector parallel and perpendicular to the plane of paper. It is found that \( I_1 > I_{11} \) and polarization \( P \), defined by

\[
P = \frac{I_1 - I_{11}}{I_1 + I_{11}}
\]

is nearly 47 percent in case of thin target. Thus more intensity will enter the spectrum if the reflecting planes of the dispersing crystal in the x-ray spectrograph lie parallel to \( I_1 \) than if they are perpendicular to \( I_1 \) direction. The polarization effects are important when

(1) Thin targets are used in the x-ray tube;
(2) Recording are done by counters;
(3) The absorbers are single crystals;

In the present case, the recording is photographic, the target used is very thick and the absorber are made up of amorphous powder. Under such circumstances the polarization effects are not significant for us.

3.2 THE X-RAY SPECTROGRAPH AND RECORDING THE SPECTRA

3.2.1 The x-ray Spectrograph

In a x-ray spectrograph, the phenomenon of Bragg reflection of x-rays is used for dispersing the radiation. If a photon of momentum \( \vec{p}_1 \) is incident at an angle \( \phi \) on a single crystal lattic plane with spacing 'd' (Fig. 3.4), one can resolve \( \vec{p}_1 \) into components \( p_{1x} \) and \( p_{1z} \), i.e., along
and normal to the surface. The scattered photon momentum \( \vec{p}_2 \) can be likewise resolved into \( p_{2x} \) and \( p_{2z} \). Here \( p_{2x} = p_{1x} \) but \( p_{1z} = -p_{2z} \). Thus, for reflection

\[
\Delta p_x = 0 \quad \text{and} \quad \Delta p_z = 2p_{2z} = 2p_1 \sin \phi
\]

Total change in momentum is \( 2p_1 \sin \phi \). Using quantization rule,

\[
\int \vec{p} \, d\mathbf{q} = nh, \quad \text{we have}
\]

\[
\oint p_z \, dz = p_z \, d = n_z h
\]

or

\[ p_z = \frac{n_z h}{d} \quad (3.5) \]

\[ \therefore \Delta p_z = \Delta n_z \frac{h}{d}, \quad \Delta n_z = 1, 2, \ldots, n. \]

\[ 2p_1 \sin \phi = \frac{nh}{d} \]

but \[ p_1 = \frac{h}{\lambda} \]

\[ 2d \sin \phi = n \lambda \quad (3.6) \]

This is known as Bragg's reflection condition. Thus, a given wavelength \( \lambda \) can be reflected only as a given set of angles \( \phi \) whose values are decided by 'd' of the lattice planes.

In spectrograph containing a plane crystal (Fig. 3.5), the crystal is kept oscillating in order to reflect one wavelength after another turn by turn. This method is wasteful in time at which \( \phi \) is at appropriate angle for Bragg condition.
M. de Broglie (1) developed a new method of photographing simultaneously a large range of x-ray spectrum using a slightly divergent beam of x-rays incident on a convex bent sheet of mica M as shown in Fig. 3.6. The sheet thus offers a family of angles to the incident beam and a range of wavelengths is reflected simultaneously on the recording film kept at P. This was later used successfully by several workers (2,3,4). This spectrograph, however, does not have focussing characteristic as developed in later designs.

We shall discuss the focussing devices in bent crystal spectrograph, since this is what we used in our work. The idea of focussing the spectrograph is originally due to Cauchois: (5) in transmission geometry and due to Johann (6) in reflection setting.

3.2.2 Principle of the Bent Crystal Spectrograph

Consider a thin crystal sheet which is plane and has one of the lattice planes normal to the surface. If the crystal sheet is cylindrically bent about the appropriate axis (Fig. 3.7) the planes will also be bent as shown in Fig. 3.7. For a parallel beam of x-rays incident on the convex side, the bent planes will offer a family of continuously varying Bragg angles such that the reflected beams for different wavelengths will be focussed at varying points on the Rowland circle. We now discuss this focussing in detail.
Fig. 3.6 Schematics of the spectrograph setup by De-Broglie.
Fig. 3.7 Figure showing the inclination of the crystal planes on bending the crystal
(a) Plane crystal
(b) Bent crystal
Not all sets of lattice planes are inclined at different angles to the surface. We shall include these in our discussion below. We shall discuss the transmission and reflection geometries simultaneously.

The important feature of Cauchois mounting shall be mentioned here. Although the x-ray beam coming out of the x-ray tube is a divergent beam, only the convergent part of the beam is used in transmission focusing as is illustrated in Fig. 3.8. One needs then a broad source of x-rays whose linear dimensions are greater than the opening provided by the crystal holder.

In Johann (6) mounting the divergent beam is used as such. In practice it is not necessary to keep the source on the Rowland circle. The source can be put closest to the crystal and Bragg's condition will automatically choose only those rays that come effectively from an imaginary point on Rowland circles (Fig. 3.9). Here the cylindrically bent planes parallel to the surface (or slightly inclined to the surface) are effective in focusing.

Johansson (7) ground the quartz crystal first to radius R and then bent it (Fig. 3.10). This provides some extra crystal planes effective only near the outer zones of the bent crystal and the result is that the focusing is now sharper. In recent years, some workers have used spherically bent mica sheets instead of cylindrically bent once. We shall
Fig. 38 Focussing by a bent crystal on reflection by a the transverse planes.
Fig. 3.9 Johann setting or reflection mounting.

Fig. 3.10
not dwell into the details of these techniques. In the end we mention a new idea due to the Weinsthein (8) about a focusing spectrograph Fig. (3.11).

When cylindrical mica sheet M inside a Brass cylinder B reflects an annular cone of x-rays, different wavelengths $\lambda_1$, $\lambda_2$, etc. get focused at point $P_1$, $P_2$ etc. on the axis of the cylinder. A counter moves on cylinder axis and records relative intensities. This instrument gives a very high intensity in the spectrum but its setting is a different problem.

3.2.3 **Geometry of Bent Crystal Spectrograph**

We now describe the details of Cauchois and Johann types of geometries (Fig. 3.12).

TT' is the crystal surface of the bent crystal (mica), set of planes BB', used for Bragg's reflection in Johann type, makes an angle $\ell$ with the crystal surface. In transmission case, the reflecting plane CC' makes an angle $\gamma$ with the normal to the crystal surface. Thus for any given plane $\gamma$ and $\ell$ have been so defined that the following relations hold

$$\ell \leq \pm 90^\circ$$
$$\gamma \leq \pm 90^\circ$$
and $\ell + \gamma = 90^\circ$ (see in Fig. 3.13) \hspace{1cm} (3.7)

The crystal holder is so set that the incident rays make
Fig. 3.11
Fig. 3.12 Schematics of bend crystal reflection.
Fig. 3.13 Inclined plane indicating the angle with respect to the surface (TT) and \( T \) with respect to the normal.
an angle $\Psi$ with the reflecting plane (Johann setting is shown by dotted line). Reflected rays will also make an angle $\Psi$ with the plane CC' or BB' in the respective geometries. The incident beam are so chosen that both the reflected beams coincide. This has been done so for the sake of generalisation.

In OAP(Fig. 3.12) $\angle POA = \Theta$, i.e., angle which the arm of the plate holder and the centre of the crystal make with the centre of the focal circle. If the film does not lie on the focal circle, but instead is so kept so as to receive the reflected rays perpendicular. Clearly, the plate holder is to be turned by an angle $\phi$. Now for this setting the Bragg's relation

$$2d \sin \Psi = n \lambda$$

will be defined.

The different angular position of the plate holder arm and crystal holder are given in Table- 3.1.
TABLE 3.1
Angular position of the crystal holder and plate holder in Cauchois and Johann setting.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Crystal holder setting</th>
<th>Angle ( \theta )</th>
<th>Plate holder (rays falls perpendicularly) ( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission</td>
<td>( \psi - \gamma )</td>
<td>( \theta = 180 - 2\phi ) ( = 180 - 2(\psi + \tau) ) ( (\psi + \tau) )</td>
<td></td>
</tr>
<tr>
<td>Reflection</td>
<td>( \psi - \ell )</td>
<td>( \theta = 180 - 2\phi ) ( \phi ) at film is ( \phi = 90 - (\psi + \ell) ) ( \phi = 90^\circ - (\psi + \ell) )</td>
<td></td>
</tr>
</tbody>
</table>

3.2.4 Dispersion

It is the ratio of wavelength differences of two neighbouring lines and their distances \( \Delta S \) (in mm) on the photographic plate. From Fig. 3.12, we have

\[
\Delta S_f = R. \Delta \theta \tag{3.8}
\]

\( \Delta S_f \) - distance of the neighbouring line if the film lies on the focal circle.

we know,

\[
\theta = 180 - 2\phi
\]

\[
\Delta \theta = -24\phi
\]

Hence \( \Delta S_f = 2 RA\phi \) \( \tag{3.9} \)
In order that the rays fall perpendicularly on the film, the plate holder should be turned by an angle $\phi$. The $\Delta S_{1}$ is only the cosine projection of $\Delta S_{r}$. Hence

$$\Delta S_{1} = 2 R \cos \phi \Delta \phi$$

(3.10)

Now the angular element should satisfy the Bragg's relation

$$2d \sin \psi = n\lambda$$

The differentiation of it gives

$$\psi = \frac{n \Delta \lambda}{2d \cos \psi}$$

(3.11)

There are the formula which states the dispersion for transmission as well as for the reflection case. When

$$\tau = \rho = 0$$

$$\phi = \psi$$

$$\frac{\Delta \lambda}{\Delta S_{r}} = \frac{\Delta \psi}{n \cdot 2 R \Delta \psi}$$

$$= \frac{d}{nR} \cos \psi$$

(3.12)

we shall now apply this to special cases.

3.2.4 (a) Dispersion in the Transmission Method of Cauchois

Here we want to consider the reflection not from a plane perpendicular to the surface but from an oblique plane CC' which is inclined at an angle $\tau$ with the normal to the surface. From Fig. 3.12 one derives

$$\psi = \phi - \tau$$

(3.13)

$$\Delta \psi = \Delta \phi$$

(3.14)
From equation 3.9, 3.11 and 3.14, it follows
\[ \Delta S_f = 2R \frac{n}{2d \cos \psi} \Delta \lambda \]

From this, we got for the dispersion on the focal circle as
\[ \frac{\Delta \lambda}{\Delta S_f} = \frac{d}{nR} \cos \psi^* \quad (3.15) \]

If the film is kept perpendicular to the reflected radiation it follows from equation 3.10, 3.11, 3.13 and 3.14.
\[ 2S_1 = 2R \cos (\psi + \tau) \frac{n}{2} \frac{1}{d \cos \psi} \Delta \lambda \]

and, therefore, the dispersion is
\[ \frac{\Delta \lambda}{\Delta S_1} = \frac{d \cos \psi}{nR \cos(\psi + \tau)} \quad (3.16) \]

for plane having \( \tau = 0 \)
\[ \frac{\Delta \lambda}{\Delta S_1} = \frac{d}{nR} \quad (3.17) \]

which shows a constant dispersion:

3.2.4 (b) **Dispersion in Reflection Method of Johann**

The spectra are obtained from the oblique lying planes like BB' (Fig. 3.12) which make an angle \( \ell \neq 0 \) with the surface TT'.

* For \( \cos \psi \) occurring in equation 3.15, we can use
\[ 2d \sin \psi = n \lambda \]
\[ \cos \psi = \left(1 - \frac{n^2 \lambda^2}{4d^2}\right)^{1/2} \]

Hence equation (3.15) becomes
\[ \frac{\Delta \lambda}{\Delta S_f} = \frac{d}{nR} \left[1 - \left(\frac{n \lambda}{2d}\right)^2\right]^{1/2} \]
From Fig. 3.12 and Table 3.1
\[ \psi = 90^\circ - (\phi + \varphi) \]
Hence \( \Delta \psi = \Delta \phi \) since \( \lambda \) is constant \( (3.18) \)

Here, again, only the absolute value of \( \Delta \psi \) is of interest.

From equation 3.9, 3.11 and 3.12, it follows
\[ \Delta S_f = R \frac{n}{d \cos \psi} \Delta \lambda \]

and from this, the dispersion on the focal circle is
\[ \frac{\Delta \lambda}{\Delta S_f} = \frac{d}{nR} \cos \psi \quad (3.19) \]

when the film is perpendicular in the reflected radiation it follows equations 3.10, 3.11 and 3.18.
\[ \Delta S_\perp = 2R \cos[90^\circ - (\psi + \varphi)] \frac{n}{2d \cos \psi} \Delta \lambda \]

and the dispersion is
\[ \frac{\Delta \lambda}{\Delta S_\perp} = \frac{d}{nR} \frac{\cos \psi}{\sin(\psi + \varphi)} \quad (3.20) \]

In the end it may be once more remarked that the obliquity of the planes influences the dispersion on the focal circle both in reflection and in transmission.

3.2.5 On the Error in Focussing Due to oblique Planes

A reflection from a plane oblique to the surface shows a greater focussing error. Consideration for the reflected radiation will be made first and then the cases of transmission and reflection methods will be discussed. As shown in Fig. 3.14 all the beams which make an angle \( \phi \) with
the normal to the face AN (i.e., radial lines), will be enveloped by a circle of radius \( r = 2R \sin \phi \). The reflected radiation therefore will not collect on the focal circle, but will cut it many times.

Proof: In Fig. 3.14

\[ MK = 2R \]

Hence \( KF = 2R \sin \phi = r \)

Let a tangent be drawn from a point A on the crystal to the circle \( r \).

Triangles \( AKF_A \) and \( MKF \) are congruent because

\[ AK = MK = 2R \]
\[ \angle AFA = \angle MKF = \frac{\pi}{2} \]

and \( FK = FA \), \( K = r \)

Hence \( \angle A = \angle M = \phi \) \hspace{1cm} (3.21)

Hence every tangent from a crystal point to circle \( r \) makes, with radius \( R \), an angle \( \phi \). Conversely, a line making an angle \( \phi \) with \( R \) and drawn from the crystal will be tangent to a circle \( r \). As Fig 3.15 shows (for oblique planes \( \phi \) is larger, i.e., we have \( \phi + \gamma \) instead of \( \phi \)) these diffused lines have an increased broadening with increased \( \phi \).

With the help of equation

\[ \psi = 90^\circ - (\phi + \rho) \]

and

\[ \psi = \phi - \gamma \]
Fig 3.14 The Caustic circle.
Fig. 3.15 Variation in defocusing at large angles of diffraction.
It can be understood that it is enough to work with longer wavelengths in the reflection method and with shorter ones in the transmission. The reason of it is quite clear in Fig. 3.16 (a) and 3.16 (b), as \( \lambda \) increases \( \psi \) also increases. In reflection, as \( \psi \) increases we approach the central line AB (Fig. 3.16). In transmission, the situation is quite opposite. It is clear that in the reflection method the sharp boundary exists towards longer A side and in transmission towards shorter A side. This minor asymmetry was undetectable with the present apparatus. With the bending of the crystal, all the planes which are oblique take the shape of a logarithmic spiral. Due to small thickness of the crystal they can be regarded as straight line so that this deformation does not influence the line shape.

In transmission method, in the photographs from planes having the same 'd' but different \( \phi \), the results were different. Independent of angle \( \phi \), the planes with small angle \( \gamma \) (nearly perpendicular) show better lines than those with greater \( \gamma \). Carlson (9) and Cauchy (10) discussed these phenomenon. They showed that 'd' of an ideally elastic crystal is so deformed that the rays reflected from both the front and back sides of the crystal cut on the focal circle. This happens only for the plane perpendicular to the surface. For oblique planes they act either before or after the focal circle. As mentioned earlier, the broadening of
Fig. 316 Tailing of lines in transmission and reflection geometries.
Fig. 3.17 Diffraction by a bent thick crystal.
the lines could be visualised for planes having higher \( \gamma \) values. Apart from extreme cases, this determination in the line shape is so small that concerned planes can be used for the spectroscopic studies without any loss in the true shape and position of the lines.

3.2.6 The Bending Mechanism

At the beginning of the discussion on erroneous focussing, Cauchois (10) calculated the influence of thickness on the sharpness of the spectral line under the supposition that in the crystalline sheet every microscopic crystallite is not deformed, only its orientation is changed so that the angle between the atomic planes inside the small crystallite and the normal to the plane which passes through the center of the crystallite remain unchanged. Such a change manifests itself as a breakage at the surface of the microscopic crystals and also as slips along the transmission direction. A result that follows from this superposition is that the lattice constants retain their normal values throughout and hence the radiation reflected by a deep lying layers will all go parallel shown with the dotted line in Fig. 3.17. This means a broadening of the spectral lines on the focal circle by an amount.

\[
e \tan \phi = (\text{see Fig. 3.18}) \quad (3.22)
\]

for oblique planes having \( \phi = \alpha \) it is

\[
e \tan (\phi + \alpha) \quad (3.23)
\]

where \( e \) is the thickness of the crystal.
Carlsson (9) considered the whole crystal as an isotropic medium deformed under the elastic bending. For the passage of a given radiation, the atomic distances vary along the depth linearly and have the largest value at the outer surface and least at the inner one. Naturally the normal will belong to the plane in between which is hence undeformed.

**Case 1**

For \( \alpha = 0 \)

Let EE (Fig. 3.17) be the plane with normal lattice constant 'd' on one side of this plane E'E' with the deformed lattice constant \( d \) and \( \delta d \).

The strain \( \frac{\delta(d)}{d} \) is directly proportional to the thickness of the crystal \( e \) and inversely proportional to the curvature, i.e., \( 2 \pi \) which we take as diameter of the focal circle.

**For the ideal case**

\[
\frac{\delta(d)}{d} = \frac{e}{2\pi r}
\]

We now take the radiation of monochromatic wavelength having a glancing angle \( \phi \) with EE. We calculate the change \( \delta \phi \) corresponding to the change in lattice constant. Bragg condition ends to

\[
2d \cos \phi \delta \phi + 2 \sin \phi \delta d = 0
\]
Using equation 3.23 this leads to
\[ |\delta \phi| = \frac{e \sin \phi}{2 r \cos \phi} \]  \hspace{1cm} (3.25)

We now search for the converging point

In \( \triangle ABC \) (Fig. 3.19)

\[ BC = e \sin (\phi - \delta \phi) \]

\[ = e \sin \phi \text{ (for } \delta \phi \ll \phi \text{)} \]

since \( AB \ll AA' \), Hence

\[ BF \approx AF = 2r \cos \phi = x \text{ (say)} \]  \hspace{1cm} (3.26)

Hence the focus lies on the focal circle. Thus the crystal thickness has no effect on the focussing from the planes with \( \alpha = 0 \).

**Case 2**

For \( \alpha \neq 0 \)

In this case, the numerator \( BC \) (Fig. 3.19) is equal to \( e \sin (\phi + \alpha) \) instead of \( e \sin \phi \). Now in equation 3.25 multiply denomenator and numerator by \( \sin (\phi + \alpha) \),

\[ |\delta \phi| = \frac{e \sin (\phi + \alpha)}{2 r \sin (\phi + \alpha) \tan \phi} \]

From Fig. 3.19

\[ \delta \phi = \frac{BC}{BF} = \frac{e \sin (\phi + \alpha)}{BF} \]

so now the x-ray will be focussed at

\[ x = \frac{2r \sin (\phi + \alpha)}{\tan \phi} = BF \]  \hspace{1cm} (3.27)
Fig. 3.19 Calculation of the effect of crystal thickness on the focussing.
For $\alpha = 0$

$$x' = \frac{2r \sin \phi}{\tan \phi} = 2r \cos \phi$$

Thus there is no mistake in generalization. The instrument used by us is shown in Fig. 3.20. It is a transmission spectrograph of Cauchois type fabricated in our Institute workshop with variable radius of curvature. It can accommodate crystal holder having radii ranging from 20 cm to 30 cm. We used a crystal holder of 30 cm radii and recorded the spectra with plate holder kept normally to the diffracted rays.

3.2.7 **Choice of Mica Crystal and its Orientation**

One has to select out a very transparent sheet of mica free from visible precipitated impurities. The sheet should be optically plane and free from scratches. The sheet should be at about 0.2 mm thick. On bending, such a sheet between the slabs of a crystal holder, a cylindrical surface can be formed. The reflection from such a surface can be tested optically and the proper bending ensured. Before bending, the mica crystal is to be suitably oriented. Fig. 3.21 shows the Laue diagram of mica. We have used [100] planes in our work. The different planes of mica together with their inclination, at values and relative luminosities are given below.
<table>
<thead>
<tr>
<th>Zone</th>
<th>Plane (hkl)</th>
<th>( \alpha ) (degrees)</th>
<th>( d ) (A(^\circ))</th>
<th>Luminosity (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>203</td>
<td>-31°38'</td>
<td>0.205</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>-27°54'</td>
<td>0.763</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>405</td>
<td>-23°26'</td>
<td>1.165</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>607</td>
<td>-23°51'</td>
<td>0.790</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>010</td>
<td>101</td>
<td>-19°36'</td>
<td>2.440</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>305</td>
<td>-15°06'</td>
<td>0.834</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>403</td>
<td>-12°45'</td>
<td>1.263</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>402</td>
<td>-5°30'</td>
<td>1.289</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>302</td>
<td>-10°22'</td>
<td>0.846</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>201</td>
<td>-5°30'</td>
<td>2.578</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>301</td>
<td>0°34'</td>
<td>0.863</td>
<td>157</td>
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<td></td>
<td>401</td>
<td>1°55'</td>
<td>1.294</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>501</td>
<td>4°24'</td>
<td>0.861</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>9°17'</td>
<td>2.556</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>9°17'</td>
<td>1.278</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>601</td>
<td>14°2'</td>
<td>0.838</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>401</td>
<td>16°21'</td>
<td>1.243</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>301</td>
<td>18°36'</td>
<td>0.818</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>22°57'</td>
<td>2.337</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>302</td>
<td>27°1'</td>
<td>0.769</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>403</td>
<td>28°57'</td>
<td>1.134</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>33(\overline{1})</td>
<td>-0°29'</td>
<td>1.498</td>
<td>276</td>
<td></td>
</tr>
<tr>
<td>44(\overline{1})</td>
<td>1°40'</td>
<td>2.246</td>
<td>92</td>
<td></td>
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<tr>
<td>110</td>
<td>8°4'</td>
<td>4.480</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>031</td>
<td>0</td>
<td>1.503</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>010</td>
<td>0</td>
<td>4.510</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

After recording the Laue pattern, the crystal and the photograph are superimposed on each other in the orientation in which the recording was made. The desired reflection is identified and the corresponding Laue spot (L) is joined to the central spot (O) Fig. 3.22. Thus direction OL is marked on the crystal by a pencil as AB. This direction is to be kept normal to the axis of the bending cylinder.

3.2.8 Mounting the Crystal

The crystal mount consists of two rectangular blocks (Fig. 3.23) cut to have a convex surface P of one and a concave surface Q of the other matching in their radius of curvature. In our case the radius of curvature chosen was 30 cm. The blocks were made of aluminium metal in order to reduce the scattering of x-rays. The cylinder surface are lapped using a fine emery powder so that they become smooth. Both the blocks contain a central opening which is rectangular in shape. This is provided for the passage of x-rays. The mica
Fig. 3.22 Illustrating the orientation of the mica sheet using a laue pattern.
crystal is put in between these blocks with AB (Fig. 3.24) parallel to the length of the blocks and gently pressed by the screws provided for this purpose.

3.2.9 Setting of the Spectrograph

Though there are many reflecting planes in the mica crystal, the most useful ones are [100], [201], [402]. In this work all the spectra were recorded using the [100] planes of mica. Table 3.3 gives all the information about the Bragg's angle, the mica lattice plane used and its inclination to the surface normal also the resultant inclination of the crystal and the plate holder are given in Table 3.3.

**TABLE - 3.3**

Data for setting the spectrograph for Germanium and Selenium K-absorption edge.

For 100 plane of the mica crystal \((\alpha = 9^\circ 17')\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength of K-absorption edge mA°</th>
<th>Angle of crystal ((\Theta + \alpha))</th>
<th>Angle of plate 2 ((\Theta + \alpha)) holder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>1116.58</td>
<td>12°36'</td>
<td>3°19'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45°46'</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>979.74</td>
<td>11°3'</td>
<td>1°46'</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40°40'</td>
</tr>
</tbody>
</table>

For proper alignment of the spectrograph with respect to the x-ray beam it is kept in such a way that at the zero-zero setting of the crystal and the plate holder the most-intense part of the x-ray beam passes normally through the centre of the plate holder. This is achieved by moving the
Fig. 3.23 Crystal holder block.

Fig. 3.24 The bent crystal.
base of the spectrograph and levelling the instrument by means of the three screws provided below the base.

3.2.10 Focussing

The angle of diffraction used by us are not high and so the errors due to caustic circle do not interfere with our setting. The focussing of the spectrograph can be improved by sliding the plate holder forward or backward so that it should be on the Rowland circle (Fig. 3.25). The standard test for the focussing is to resolve the MoK\textsubscript{1,3} doublet in the second order spectrum. This should be attained for both \( \varphi + \theta \) and \( \varphi - \theta \) settings of the crystal.

3.2.11 Reducing the Background Intensity

Divergent x-ray beam incident on a crystal strikes the metallic periphery of the opening (e.g. at the point P and Q etc. Fig. 3.26). The side walls of the opening thus become a source of scattered radiation that reaches the recording film and gives an unwanted background.

If a suitable aperture is kept in the path of incident radiation [AB in Fig. 3.26], it is possible to eliminate the scattering due to the metallic part of the crystal holder. This reduces considerably the background. The scattering at crystal surface cannot be avoided. A reduction in background intensity increases the contrast in absorption edge.
Fig. 3.25 Showing (a) the correct (b) the wrong position of the rowland circle.
Fig. 3.26 Use of aperture (AB) to stop the scattering from the metallic boundaries of the opening in the crystal holder.
3.2.12 **Optimum Condition for Getting the Best Spectra**

In order to obtain good absorption spectra from the point of view of contrast and microphotometric work it is necessary to work under certain optimum conditions. These conditions are discussed below:

3.2.12 (a) **High Tention**

We are well familiar that due to the application of an unnecessary high voltage across the x-ray tube the details of the absorption spectra get disturbed. According to Sandstrom (11), a good absorption spectrum is obtained when the value of the high voltage does not exceed 1.5 times the excitation potential of the energy level from which the photoelectron is ejected. In the course of this work the x-ray tube was operated at voltage between 25 to 30 KV. The tube current was at 5 mA.

3.2.12 (b) **Thickness of the Absorber**

The need for using absorber with optimum thickness, in order to obtain good absorption spectra, has been discussed by earlier workers. It has been shown by Sandstrom (12) that the theoretical optimum thickness of the absorbing screen is given by the formula

\[ X = 2.3 \frac{\log \mu_1 - \log \mu_2}{\mu_1 - \mu_2} \]  

(3.28)

where \( X \) is the mass of the absorber in gm cm\(^{-2}\)
$\mu_1, \mu_2$ - Mass absorption coefficient on the short and long wavelength side of the absorption edge respectively.

The coefficients of absorption $\mu_1$ and $\mu_2$ were determined in our case from the curves of Jonsson (13) (given by Cauchois (14)). The values of $\mu_1$ and $\mu_2$ along with the calculated thickness for pure germanium and selenium are given in Table 3.4.

**TABLE - 3.4**

The optimum thickness of the absorbing screens of pure crystalline germanium and selenium.

<table>
<thead>
<tr>
<th>Absorber</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gm cm$^{-2}$</td>
<td>gm cm$^{-2}$</td>
<td>mgm cm$^{-2}$</td>
</tr>
<tr>
<td>Germanium</td>
<td>220.95</td>
<td>28.07</td>
<td>11</td>
</tr>
<tr>
<td>Selenium</td>
<td>171.42</td>
<td>22.27</td>
<td>14</td>
</tr>
</tbody>
</table>

However, in practice one has to try several thickness in every case and then arrive at the suitable thickness. The screens which gave the best spectra for the pure elements were found to have thickness of the order of 15 mgm cm$^{-2}$. For compounds the screen thickness used were of the order of 20 mgm cm$^{-2}$.

**3.2.13 Absorption Screens**

Uniformity of a absorption screens play an important role to get a good edge (15). All the alloys studied
in the present work were in solid form. Preparation of the absorption screen is indicated in Fig. 3.27 (a,b,c,d). First a cellophane sheet of desired thickness was taken and a square or rectangular hole of appropriate size is cut in it with a blade. After that a cellophane adhesive tape is pasted on the bottom face and then sample (alloys) in powdered form is uniformly spread on it. The upper face is then covered with the tape and a cylindrical roller is moved on the powder to compress it and spread it uniformly.

Also the thin films of glassy alloys were made at room temperature by vacuum evaporation technique at a base pressure $\sim 10^{-5}$ Torr. The substrate used was a thin mylar paper 10 cm x 30 cm kept fixed on the inner wall of the bell jar for covering the evaporation system of the unit. A single film is not suitable for recording the absorption edges. Therefore, the small pieces of the substrate were made and kept one behind the other. The total number of such pieces ranged from 800-1000 and the film thickness ranged from 5000-6000 Å.

If we put the absorbing screens after the diffracting crystal, then it causes the following practical problems.

1. The absorbing area must be sufficiently large to cover the diverged cross-section of the beam near the photographic plate.
2. The non-uniformity of the thickness of the screen produces a patchy impression on the general background of the spectrum.

But if we put the screens at the window of the x-ray tube, this suffers following drawbacks:

i) The total scattering (Compton, Rayleigh and Photo-absorption) is high. The contrast in the desired photo-absorption spectrum is enhanced when the sample is placed after the diffracting crystal.

Since the effect of Rayleigh and Compton scattering is very small, it is more practical to put the screen at the window of the x-ray tube.

3.2.14 Exposure and Development

The choice of photographic film and the time of exposure are important for obtaining good spectra. In this work we have used ILLford FP4 single coated x-ray photographic films. Several spectra of each samples were recorded with absorbing screens of different thicknesses. In general the exposure of the order of 6-10 hours were found to be necessary in this work. The films were then developed in freshly prepared fine grain Kodak IPC-76 developer. It is better to develop the film at about 16°C temperature. The developer solution should be diluted so that the development time is about 15 minutes or more. Slower is the development, better are the results. The films are then fixed in
Fig. 3.28 Intensity vs energy curve for K-edge
3.5 PREPARATION OF THE SAMPLE

The chalcogenide glasses $\text{Ge}_{10}\text{Se}_{90}$, $\text{Ge}_{15}\text{Se}_{85}$, $\text{Ge}_{22}\text{Se}_{78}$, $\text{Ge}_{30}\text{Se}_{70}$, $\text{Ge}_{22}\text{Se}_{76}\text{Bi}_{2}$, $\text{Ge}_{22}\text{Se}_{68}\text{Bi}_{10}$, $\text{Ge}_{22}\text{Se}_{68}\text{Sb}_{10}$, $\text{Ge}_{22}\text{Se}_{68}\text{Te}_{10}$ have been prepared by quenching method. Materials (99.999 % pure) were weighed in proportion to their atomic percentages and sealed in a quartz ampoules evacuated to $\sim 10^{-5}$ Torr and kept in a furnace where temperature was raised to 950°C at rate of 3-4°C/min. The ampoules were rocked frequently for 10 hours in order to make homogeneous melt. After that ampoules were taken out and quenched by blowing air at room temperature. The similar method has been followed in preparing the Se, $\text{Se}_{80}\text{Te}_{20}$, $\text{Se}_{80}\text{Te}_{10}\text{Sb}_{10}$ glasses except that the temperature of furnace was 700°C and ice quenching was used in place of air quenching.
REFERENCE