CHAPTER II

THE EXPERIMENTAL TECHNIQUE

1. Spectral region

The wavelengths of the K absorption edges\(^{17}\) of selenium and germanium, \(\lambda = 977.80\) and \(\lambda = 1114.27\) X.U. respectively, can very well be studied with crystals. Also in this region the radiation being fairly penetrating, the spectra can be recorded in air. The most suitable instrument for this study is evidently the Cauchois type bent crystal X-ray spectrograph.

Fig. 2 gives a general view of the experimental setup used in this investigation. It mainly consists of an X-ray generator and a spectrographic unit which are described in Sections 2 and 3.

2. X-ray generator

For excitation of X-rays a Philips Metalix X-ray generator was employed. Its principal components are --

(a) the high tension transformer.
(b) the low tension transformer
(c) the control unit
and (d) the X-ray tube.

The L.T. transformer provides voltage to heat the filament of the X-ray tube. The high voltage to the X-ray tube is supplied by the H.T. transformer at the cathode, the anode being earthed. The generator does not contain any device, such as, a kenotron for rectification of the high voltage. The high tension on the tube could be regulated with the control unit in the range 20 to 60 kV. Similarly the tube current could be regulated in the range 0 to 40 mA.

A sealed X-ray tube with tungsten target (type Philips 25294) was used as a source of white radiation, for as is well known a tungsten target gives an intense continuous radiation. It was observed that the tube did not emit any impurity lines which could interfere in the region of our study. A spectrum of the background radiation is shown in Fig. 3 along with the K absorption spectra of metallic selenium and germanium.

The X-ray tube gives four beams from four windows provided on the tube. Out of these four windows, two give beams from a sharp focus on the anode and the other two from a wide focus on account of the linear geometry of the filament. We have utilised a beam of the latter type in this work as is required for work with bent crystal spectro-
graphs. Because all these X-ray beams make an angle of $8^\circ$ with the horizontal plane, the spectrograph had to be inclined accordingly.

Continuous cooling of the anticathode and the metallic body of the tube was achieved by a current of water obtained from a water pump connected to a reservoir. A safety device in the generator could switch off the apparatus when the cooling was insufficient.

3. The spectrograph

The spectrograph used in this investigation was a Cauchois type X-ray spectrograph of 40 cm. diameter constructed in the Poona University Central Workshop. A line diagram of the spectrograph is shown in Fig. 4.

Essentially the spectrograph consists of the following components:

(a) Base plates: The base plate $P_1$ is supported by three levelling screws $L$. Another plate $P_2$ rests on $P_1$ and can rotate about the vertical axis passing through the point $O$. A circular scale $S_1$, whose centre is at $O$, reads the angular setting of the plate $P_2$ with respect to $P_1$. The scale is graduated to read up to a degree. The knob $K$ clamps the plate $P_2$ on $P_1$ at any desired setting.

(b) Crystal holder: This is a very vital part of the
spectrograph. It is fixed vertically on the upper plate $P_2$ in a groove in such a way that the centre of the useful aperture of the crystal is located on the vertical axis passing through $O$. The crystal holder (H) is made of a stainless steel block having one surface plane and the other convex cylindrical with a radius of curvature of 40 cm. Its convex surface was very carefully machined to an accuracy of one thousandth of an inch. There is an opening of 1 cm. x 1 cm. at the centre of the crystal holder. However, the effective aperture of the crystal can be controlled by adjusting two lead shutters. The crystal is fixed to the cylindrical surface of the crystal holder by means of several rubber bands. This method is found to be very effective in giving the crystal the required uniform cylindrical shape.

(c) Photographic plate holder: The plate holder $P$ is rectangular in shape in which quarter sized (4 1/4" x 3 1/4") plate or film can be loaded. Clips are provided at the back of the plate holder to keep the film or plate tightly pressed. The construction of the plate holder is such as to protect the films or plates from external light. However, they were always wrapped in black paper as an additional precaution.
(d) **Arm and plate holder carriage**: The arm $R$ carrying the plate holder carriage $T$ is vertically pivoted at the point $C$ upon the plate $P_2$. The point $C$ is exactly located at a distance of 20 cm. from $O$, the line $OC$ being normal to the crystal surface. The plate holder is mounted on the carriage $T$ along two grooves in such a way that the photographic plate is always tangential to the focussing circle whose centre is at $C$. An arrangement is provided on the arm for varying the distance between the plate and the point $C$ by means of the screw $W$. This adjustment, which sets the plate on the Rowland circle, is facilitated by the scale $S_2$ graduated to read up to 1 mm. Movement of the arm $R$ gives the required angle to the plate, which is read by the pointer $G$ on the scale $S_3$ having graduations up to $\frac{10}{2}$.

Provision of two stainless steel strips on the plate holder carriage which could be slided on a groove enables one to obtain two different spectra on the same plate.

(e) **Lead screens**: Two lead screens $F_1$ and $F_2$ (not shown in Fig. 4) are provided on the spectrograph in order to avoid scattered radiation on the photographic plate. $F_1$ is attached to the base plate $P_2$ and lies between the X-ray tube window
and the crystal. \( F_2 \), a separate piece, is placed between the crystal holder and the photographic plate. The centres of the openings of the lead screens and the crystal were carefully aligned with the centre of the plate.

4. **Mounting of crystal**

The spectroscopic results are known to depend to a large extent upon the quality and the nature of the crystal analyser. Although, Brogren\(^{18}\) has claimed that the best crystals suited for spectroscopic work are quartz and then calcite, equally good results have been obtained in many laboratories with muscovite mica also. Moreover, mica has the additional advantage of being bent easily. We have therefore employed it throughout this work.

The orientation of the mica crystals was determined from their Laue photographs taken on a Laue camera specially built for this purpose in the University Workshop. It can be seen in Fig. 2 mounted on one of the X-ray tube windows. Only those crystals were selected for mounting on the crystal holder which gave sharp and symmetric Laue patterns.

Surface uniformity was used as the next criterion for a further selection of crystals. It was tested by reflection method employing an optical bench which essentially consists of a source of light (100 watts bulb), a screen with a slit at its centre and a stand for a crystal holder. Keeping the
crystal at a distance of 40 cm. from the illuminated slit, reflected image of the slit was observed on the screen. Sometimes just an adjustment of the position and number of rubber bands used to fix the crystal was found to improve the image. However, optical focussing cannot be overemphasized as it is only a preliminary test. The real quality of the crystal is judged by its performance on the X-ray spectrograph. After a large number of trials a crystal giving sharp, intense and undistorted spectral lines was finally selected.

5. Spectrograph setting

The Bragg angles for the K absorption discontinuities of selenium and germanium in the first order can be calculated from the equation

$$\lambda = 2d(h,k,l) \sin \theta$$

For the (100) and (201) reflection planes of mica, which have been used in this work, $d_{(100)} = 2.61\text{A}$ and $d_{(201)} = 2.65\text{A}$. The Bragg angles thus calculated are shown in Table 1.

The (100) and (201) planes make angles $\alpha = 10^\circ 10'$, $\alpha = 4^\circ 56'$ respectively with the normal to the cleavage plane. Therefore to set the crystal for Bragg angle the crystal has to be rotated through the angle $(\theta + \alpha)$ around the vertical axis $O$. In practice we rotate the plate $P_2$ which carries the crystal over it through the angle $(\theta + \alpha)$. 
In order to receive the diffracted X-rays the photographic plate is kept at the angle $2(\varphi - \alpha)$. This is achieved by rotating the arm $H$ through the angle $2(\varphi - \alpha)$. The values of $(\varphi + \alpha)$ and $2(\varphi - \alpha)$ are given in Table 1.

Table 1

<table>
<thead>
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<th></th>
<th>$(100)$ planes</th>
<th>$(\overline{2}01)$ planes</th>
</tr>
</thead>
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<tr>
<td>$0$</td>
<td>$10^\circ 10'$</td>
<td>$4^\circ 56'$</td>
</tr>
<tr>
<td>$0 + \alpha$</td>
<td>$20^\circ 58'$</td>
<td>$10^\circ 38'$</td>
</tr>
<tr>
<td>$0 - \alpha$</td>
<td>$10^\circ 16'$</td>
<td>$15^\circ 34'$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$10^\circ 16'$</td>
<td>$11^\circ 24'$</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>$12^\circ 18'$</td>
<td>$12^\circ 8'$</td>
</tr>
<tr>
<td>$\varphi + \alpha$</td>
<td>$22^\circ 28'$</td>
<td>$17^\circ 4'$</td>
</tr>
<tr>
<td>$\varphi - \alpha$</td>
<td>$4^\circ 16'$</td>
<td>$14^\circ 24'$</td>
</tr>
</tbody>
</table>

For recording Se K absorption spectra of pure selenium and some selenides ($\text{Ag}_2\text{Se}$, $\text{CuSe}$, $\text{Cu}_2\text{Se}_2$, $\text{ZnSe}$, $\text{CdSe}$ and $\text{HgSe}$) the settings were made as given in Table 1. However, the Se K and Ge K absorption discontinuities in germanium selenides were recorded on approximate mean settings of the values given in Table 1, in order to obtain both the discontinuities on the same plate.

6. **Principle of the spectrograph**

Fig. 5 explains the principle of the spectrograph. The X-ray beam from the wide focussing spot $\text{EF}$ of the anticathode is made incident on the convex side of the crystal and the different rays in the beam are reflected by the
atomic planes of the crystal as shown in Fig. 5. The atomic planes follow the directions $O\delta$, $O\alpha$, $OC$ etc., because of the curvature acquired by the crystal due to bending. The rays of a particular wavelength $\lambda_1$ after reflection at the Bragg angle $\theta$ are brought to focus on the Rowland circle at the point $L_1$. Similarly other wavelengths $\lambda_2$, $\lambda_3$ etc. in the beam are focussed at the points $L_2$, $L_3$ etc.

The crystal aperture can be regulated by using the two shutters $N_1$ and $N_2$ as mentioned earlier in Section 3. The crystal edges, which sometimes give rise to noticeable distortion in the spectral lines due to non-uniform bending, can be covered by properly adjusting the shutters $N_1$ and $N_2$.

In this spectrograph the different wavelengths contained in the wide incident beam are focussed on the Rowland circle after reflection from a large number of planes in the crystal. Thus the spectrograph has a high luminosity and has also a good resolving power. Besides these advantages, there is no need of oscillating the crystal during exposure, e.g. as in the Bragg method, and a wide energy region can be studied on a single plate.

7. **Optimum conditions for obtaining the spectra**

In order to obtain good absorption spectra from the points of view of both contrast and microphotometric work it is necessary to work under certain optimum conditions. They are discussed below.
(a) **High tension**: It is well known that details of the absorption spectra are often obscured due to an unnecessary high value of the tension applied to the X-ray tube. Sandström has shown that good spectra can be obtained provided the value of the high tension applied to the X-ray tube does not exceed 1.5 times the excitation potential of the energy level from which the electron is ejected. The energies of the K levels of selenium and germanium according to Hulubei and Cauchois are 12625.3 and 11079.0 eV. Thus in our investigation the values of the high tension on the X-ray tube should be about 1.5 x 12625.3 ≈ 18.9 kV and 1.5 x 11079 ≈ 16.6 kV for studying the absorption spectra of selenium and germanium respectively. The minimum high voltage available from our generator, 20 kV, was applied to the tube in this work. The tube currents ranged from 10 to 15 mA.

(b) **Thickness of the absorber**: Sandström has given the following formula for the optimum thickness of the absorbing screen

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

where \(x\) is the mass of the absorbing element in grams per square cm. and \(\mu_1, \mu_2\) are the mass absorption coefficients on the short and long wave-
length sides of the absorption edge respectively. The coefficients \( \mu_1 \) and \( \mu_2 \) can be calculated from the curves of Jönsson given by Cauchois. In the case of selenium \( \mu_1 = 179.5 \) and \( \mu_2 = 22.36 \) \( \text{cm}^2\text{gm}^{-1} \), while for germanium \( \mu_1 = 221.0 \) and \( \mu_2 = 28.27 \) \( \text{cm}^2\text{gm}^{-1} \). Thus \( x \) for selenium comes to be about 13 milligrams per square cm. and for germanium about 11 milligrams per square cm. However, in practice one has to try several thicknesses for preparing the most suitable absorbing screen. The thickness which gave best spectra for these samples were found to be generally of the same order as obtained from Sandström’s formula.

(c) Preparation of absorbers: Absorbing screens of the samples were prepared by uniformly spreading their very fine powders on cellophane adhesive tape. This tape was fixed to a specially designed stainless steel sheet. A front view of this sheet is shown in Fig. 6a, while in Fig. 6b is shown its end view. In this figure D is the stainless steel sheet and C the adhesive tape. The area on which the sample is spread is indicated by cross lines. The stainless steel sheet was mounted on the shield of the X-ray tube by means of two screws H and H’ (not shown in Fig. 6) through the holes B and B’.
(d) Exposures and development: Trial spectra of each sample were first obtained on Ilford double coated X-ray films in order to determine the conditions of exposure. These preliminary studies were also helpful in judging the suitability of the absorbing screens. Since plates are much more suitable for microphotometric work, several spectra of each sample were finally photographed on Agfa Ultraviolet plates (type Nr 3649). It was observed that exposure times on plates increased nearly four-fold as compared to those on films. Exposure times on plates varied between 4 and 14 hours and were always given in such a way that the densities of blackening on both sides of the absorption edge remained on the linear part of the calibration curve of the emulsion.

It is of utmost importance to develop films and plates very carefully in such type of work. The plates and films in this work were always developed in freshly prepared ice-cooled Agfa 30 X-ray rapid high contrast developer.

3. Microphotometry and measurements

Microphotometric records of the plates were obtained with magnifications of 4 and 50 on a Moll microphotometer. Great care was taken to wrap the drum of the microphotometer
as tightly as possible with photographic paper. At least 4 to 6 records of each plate at different positions of the spectrum were taken.

Measurements were made on microphotometric records with magnification 50 only. Care was taken to measure at right angles to the reference lines. Attempts were made to judge the maxima of the reference lines and the inflexion points of the absorption edges as accurately as possible.

In work with bent crystal X-ray spectrographs reference lines are used for relative measurements of wavelengths. It is desirable as far as possible to have reference lines on both sides of the spectral line or the edge to be measured. The wavelength of the Se K discontinuity was measured using $\text{Ly}_2$, $\text{Ly}_3$ and $\text{Ly}_4$ lines of tungsten as reference lines. In case of Ge K discontinuity the reference lines were $\text{Ly}_1$, $\text{Ly}_2$, $\text{Ly}_3$ and $\text{Ly}_5$ lines of tungsten. The wavelengths of these reference lines were taken from the wavelength tables of Cauchois and Hulubei. Reference lines used for the measurement on the Ge K discontinuity lie on both sides of the Ge K edge, while reference lines for the Se K discontinuity lie only on the low energy side. Therefore the measurements on the Se K edge had to be done by extrapolation method. +

As is well known in this region of X-ray spectroscopy dis-

+ In the laboratory where the author has carried out this work there was no possibility of giving exposures for the reference lines on both sides of the Se K edge.
persian is quite linear and therefore extrapolation will not cause appreciable errors in measurements. Moreover, in the present study we are primarily interested in $\Delta \lambda$ values rather than the wavelengths themselves. The $\Delta \lambda$ values should not be affected by the choice of the reference lines.

As a rule a very large number of measurements were made, but in the final calculations only those measurements (on the average about 50) were included which appeared to be consistent with each other. The average error in measurements was estimated by the well known formula,

$$\frac{V_1 - V_2}{\sqrt{n}}$$

where $V_1$ and $V_2$ are the maximum and minimum values in a given set and $n$ is the number of readings.

9. Dispersion

The linear dispersion obtained on a bent crystal spectrograph is given by

$$\frac{\delta \lambda}{\delta L} = \frac{\lambda}{R \tan \theta}$$

where $R$ is the radius of curvature of the crystal and $\theta$ is the Bragg angle. The dispersion calculated with this formula, 12.79 A.U. per mm, agrees fairly well with the dis-
perspective actually obtained on the plates (12.45 X.U. per mm.). The dispersion in energy on microphotometer records with magnification 50 is found to be about 2.6 eV per mm.

10. Preparation of samples

A vacuum unit shown in Fig. 7 was set up for vacuum sealing of the samples. It essentially consists of a rotary pump R, a three-way cock C and drying tubes D1 and D2 filled with KOH and P2O5 respectively. A polythene tubing P connects the vacuum system with the silica tube T containing the sample. Vacuum of the order of 10⁻⁹ mms of Hg could be obtained by the pump in the system.

For heating of the vacuum sealed samples two different furnaces were used. One of these, designed and constructed in the laboratory, could give temperatures up to 1000°C. The other furnace used was a commercial unit (Weckfield type) with which temperatures up to 1350°C could be obtained.

The methods of preparing the samples used in this investigation are briefly described below.

(a) Amorphous selenium: Vacuum sealed samples of pure selenium (A.R. grade) were heated for 15 minutes at a temperature of 270°C, which is well above the melting point of selenium (220°C). These melts of selenium were then quenched at different temperatures between 0°C and 30°C. The amorphous selenium thus prepared was ground to a fine powder form.
(b) Selenides: Pure powders (A.R. grade) of the components were mixed in stoichiometric proportion as indicated by the chemical formula of the compound. The vacuum sealed mixture (in silica tube) was first slowly heated to a temperature ranging between 230°C - 300°C. The sample was kept at that temperature for some time and the temperature was again raised to a certain maximum temperature. For some compounds this final temperature was of the order of the melting point of the component other than selenium. However, for compounds in which the melting point of the other component was higher than what could be attained in the furnace, the final temperature was maintained at a sufficiently high degree for diffusion to take place easily. While preparing the latter type of compounds the maximum temperature was maintained for a much longer time. Annealing of the samples was then done by slow cooling. Only in some cases a particular annealing temperature was maintained for some time. Table 2 gives the data about preliminary temperatures of heating, maximum temperatures maintained, temperatures of annealing and durations of their maintenance for the different compounds.

Special care had to be taken while preparing
HgSe. Both selenium and mercury build up high vapour pressures at high temperatures and hence there is a possibility of explosion in this preparation. Therefore small quantities of selenium and mercury were used for preparing this compound.

The crystallinity and the quality of the samples prepared were controlled by X-ray diffraction method. The diffraction patterns of the samples will be given in Chapters IV and V.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Stoichiometric proportion</th>
<th>Preliminary heating temperature in °C and time of its maintenance in hours</th>
<th>Maximum temperature maintained in °C and time of its maintenance in hours</th>
<th>Temperature of annealing in °C and time of its maintenance in hours</th>
<th>Period of slow cooling to room temperature in hours</th>
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<td>1000 – 2</td>
<td>500 – 2</td>
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<td>725 – 1</td>
<td>575 – 15</td>
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<td>850 – 12</td>
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