CHAPTER III:

X-RAY SPECTROSCOPIC TECHNIQUE
3.1 INTRODUCTION

The wavelength range of X-rays is from one tenth of an Angstrom to a few hundreds of Angstroms. Since X-rays could be dispersed by a single crystal, the same can be used to study the emission and absorption spectra. Therefore, different types of spectrometers were designed of different ranges of wavelengths to study the X-ray spectra.

A number of plane crystal spectrometers were designed by Siegbahn\(^1\), Siegbahn and Larsson\(^2\), Seeman\(^3\) etc. In these spectrometers the collimation was achieved by using the slits. These spectrometers have low resolving power and poor intensity. The use of plane crystal in double spectrometers\(^4,5\), has improved the resolving power of the instrument to a great extent. Dumond\(^6\) extended the principle of curved optical grating to work out the geometry of the bent crystal spectrograph. Dumond and Watson\(^7\) and Johann\(^8\) constructed instruments using the reflection geometry, whereas the instrument of transmission type was constructed by Mme. Cauchois\(^9\). Since photographic recording is made possible, bent crystal spectrographs have found extensive use.

In the present chapter details of the experimental technique of X-ray spectroscopy including those of X-ray generator, optimum conditions and microphotometry are described.
3.2 X-RAY SPECTROSCOPIC TECHNIQUE :

3.2 a) X-ray generator and relevant details :

X-ray unit used in the present work was supplied by M/s Radon House Company, Calcutta, India. As the excitation potentials of different elements are different and as the details of the spectra depend upon the potentials applied across the X-ray tube, one must be able to vary the potential across the X-ray tube at will. Therefore, unit was modified by one of the workers of this laboratory to suit this type of work.

3.2 b) Power Supply Unit :

The electrical circuit diagram of the power supply unit is shown in Fig. 3.1. It consists of,

i) Input transformer
ii) Variac
iii) High tension transformer and rectifiers
iv) L.T. transformer.

3.2 c) Input Transformer :

This is heavy duty multitapped autotransformer. The different tappings provided with the transformer are used to give different voltages, 0-6 volts for indicator bulb and 0-220 volts for L.T. transformer and variac etc. Since it is essential that the potential across and the current through the X-ray tube is to be kept constant, the output of the single phase stabilized power supply unit was fed to the input transformer.
3.2.d) Variac:

This is a continuous variable auto-transformer, the maximum current rating of which is 15 Amps. at 260 volts. Input to this is given from input transformer and the continuous variable output is fed to H.T. transformer, through the appropriate circuitary.

3.2 e) H.T. transformer:

Input supply to primary winding is given from variac. The circuit is so designed that the input can be given in steps or in a continuous variable manner; and hence the H.T. available is in steps or the same can be varied as per requirement from 0 to 48 kV at 0-30 mA. The H.T. (a.c.) made so available is rectified by rectifier circuit and is applied to the x-ray tube at cathode, the anode being earthed. The H.T. transformer along with the rectifiers is immersed in an oil tank.

Since there are drastic variations in supply voltages occasionally, in order to avoid the damage to the x-ray unit, a miniature type circuit breaker is used in series with the stabilizer.

3.2 f) L.T. transformer:

L.T. transformer is used for heating the filament of the x-ray tube. The voltage and current specifications for the filament of x-ray tube used for the present work were 7 volts and 4 amps., as specified by the manufacturer. Since the transformer has a potentiometric arrangement, the filament current can be varied to control the intensity of x rays.
3.2 g) X-ray tube:

X-ray tube used for the present work is a sealed type Chirana X-ray tube with tungsten (W) target. It is designed to give two wide focussed beams through the two side windows. This tungsten tube is used to furnish intense white radiation along with the emission lines of tungsten. Also it is found to give some impurity lines of copper, nickel and iron.

3.2 h) Cooling system:

During the production of x-rays tremendous amount of heat energy is generated due to which the anode gets heated. Therefore, it is necessary to cool the anode and metallic body, continuous and effective cooling of both being achieved by circulating demineralised water with the help of a water pump connected to a pressure tank. Water is circulated at a specific pressure by adjusting relay in the water pump circuit. The thermal and over loading relays are put in the circuit to protect x-ray machine from damage.

3.3) The spectral region:

Since x-ray radiations used for present studies of edge shifts, and EXAFS of the samples are fairly penetrating, the spectra can be recorded in air, in the range 1.3 Å to 1.7 Å. The most suitable instrument for this type of study is Cauchois type bent crystal spectrograph. A Cauchois type bent crystal spectrograph having radius 400 mm is fabricated in the departmental workshop. The details of the same are described in
following sections. The general view of the experimental set up is shown in Plats 3.1.

3.4 The spectrograph:

The metal plate \( P_1 \) which forms the base for the whole spectrograph is supported by four levelling screws \( L_1 - L_4 \). The plate is cut such that it forms a sector of a circle with centre at \( O \) and radius equal to 400 mm. The plate \( P_2 \), which rests on \( P_1 \), can be rotated about a vertical axis passing through \( O \). This plate acts as a Rowland circle of radius 200 mm with centre at \( C \). A circular scale \( S_1 \) graduated on \( P_1 \) whose centre is at \( O \) reads the angular position of \( P_2 \) with respect to \( P_1 \). The knob \( K \) can be used to clamp the plates \( P_1 \) and \( P_2 \) for any desired setting. Schematic diagram is given in Fig. 3.2.

3.4.1) Crystal holder:

This is the most important part of the spectrograph consisting of two matching metal pieces \( A \) and \( B \) (Fig. 3.3), one of the being concave cylindrical and the other being convex cylindrical which can be fixed together with the help of four spring loaded screws in the corners, machined accurately such that radius of both is the same and is equal to 400 mm. The crystal (mica sheet) is sandwiched between 'A' and 'B'. The required uniform distribution of pressure and the associated tension for the mica crystal are achieved by adjusting the four spring loaded screws. A rectangular window having dimensions 2 cm x 1 cm at the entrance and 4 cm x 1 cm towards the spectrograph is provided at the centre. The effective size of the window could be adjusted by sliding the lead shutters from the side grooves.
Fig. 3.2: Spectrograph
Fig. 33: Crystal holder
3.42) **Film holder**

The geometry of the spectrograph gives exact focussing on the focal circle and the film should be exactly on the Rowland circle. The photograph of $WL_{41}$ and $WL_{42}$ emission lines of the tungsten as well as the corresponding photograph of original microphotometer trace of the same is shown in Plate 3.2. The plate holder $P$ is rectangular in which a quarter size plate or film can be loaded. The dispersion in the focussed region is almost linear (12 X.U./mm) on the film and the experimental accuracy comes out to be quite reasonable. The film used in the present work is ORWO XR-11 dental x-ray film of 3 cm x 4 cm size. The film was held in place in the plate holder with the help of lead strips carefully and the spectra were recorded. Since this film does not require any dark room loading, it was not necessary to take any special precautions for safety as regards external or stray light.

3.4.3) **Arm and film holder carriage**

The arm $R$ carrying plate holder carriage $T$ is vertically pivoted at point $C$ upon the plate $P_2$, the distance $OC = 200$ mm, $OC$ being normal to the crystal holder surface. The plate holder can be slid in the grooves provided with carriage $T$ in such way that the photographic film is always tangential to the focussing circle. The arm is designed in such a way that the setting of the film holder exactly on the circumference of the Rowland circle can be done accurately by using a spring and screw $W$. The movement of the arm $R$ gives required angle to the
3.4.4) Selection and mounting of the crystal:

In x-ray spectroscopic studies, crystals of different types such as quartz, gypsum, calcite, mica, rock salt are in use, although according to Brogren the quartz is the best suitable crystal. Good results have been obtained in many laboratories using mica as a dispersing medium and focusing agency with additional advantages of easy cleavage and ease of bending. We also selected mica for our x-ray spectroscopic studies.

The results of x-ray spectroscopic studies are found to get influenced to a great extent by the quality of the crystal used as well as the accuracy with which it is mounted.

A number of clean mica sheets were cleaved to get thin pieces and Laue patterns for these were obtained. One of those giving symmetrical and sharp Laue pattern was selected for the spectroscopic work and was sandwiched between two metal pieces A and B. The pre-final selection of the crystal so chosen was made by testing the crystal on an optical bench. The concave part of the crystal was made to give an image of luminous slit placed at a distance of 400 mm. Well defined and sharp image of the slit, on a screen was obtained by adjusting the radius of curvature of the crystal and adjusting the size of the window. The crystal thus tested was then, mounted on the spectrograph in its position. After levelling the spectrograph, and aligning it
with the x-ray beam target, emission spectrum was obtained at the predetermined position of the film holder. (Refer to section 3.5)

The crystal which could give sharp, intense, undisturbed emission line spectrum was finally selected.

3.5 Principle and setting of the spectrograph:

Fig. 3.4 illustrates the principle of the spectrograph. The divergent x-ray beam is allowed to fall on the convex side of the crystal, and different rays that are reflected by atomic planes follow the directions OA, OB, OC, etc. The rays of a particular wavelength $\lambda_1$ after reflection at the angle $\phi$ are brought to focus on the circumference of the Rowland circle, where the photographic film $P$ is held in the film holder.

Similarly other wavelengths $\lambda_2$, $\lambda_3$, etc., in the beam are focussed at the points $P_2$ and $P_3$. The rays reflected from different atomic planes contribute to the increased intensity. The instrument has good resolving power and therefore, can be used in the wide range of energy region. Bragg angles for the K-absorption discontinuities of Fe, Cu, Zn in first order can be found using the equation

$$\lambda = 2d_{(hkl)} \cdot \sin \phi$$

For (1 0 0) and (2 0 1) reflection planes of mica which have been used in this work $d_{(1 \ 0 \ 0)} = 2.61 \ A^0$ and $d_{(2\ 0\ 1)} = 2.65 \ A^0$. 
Fig. 3.2: Principle of Cauchois type spectrograph.
The Bragg angles thus calculated are presented in table 2.1. The (1 0 0) and (2 0 1) planes make angles $\alpha = 10^\circ 10'$ and $\alpha = 40^\circ 56'$ respectively with the normal to the cleavage plane. Therefore, to set the crystal for Bragg angle the crystal has to be rotated through $(\phi + \alpha)$ around the vertical axis passing through $O$. In practice, the plate $P_2$ is rotated, which carries the crystal through $(\phi + \alpha)$. In order to receive the diffracted rays the photographic plate is kept at an angle $2(\phi + \alpha)$. This is achieved by rotating the arm $R$ through angle $2 (\phi - \alpha)$. The values of $(\phi + \alpha)$ and $2 (\phi - \alpha)$ are given in Table 3.1.

Though the Table 3.1 gives the exact angles of setting, the actual setting of the film holder was carried out by taking the mean value in order to record two different absorption spectra.

3.6 Optimum conditions to obtain good spectra:

In order to obtain good absorption spectra from the viewpoint of the 'contrast' obtained on the photographic film and microphotometric work, it is most essential to avoid undesired scattering on the film and to work under optimum conditions of high tension and absorber thickness.

Lead screens were deployed around the crystal holder and the spectrograph to prevent most of the scattered radiation from reaching the film.
Table 3.1: Data for Setting of the Spectrograph

<table>
<thead>
<tr>
<th>K absorption disco. of</th>
<th>Wavelength inÅ°</th>
<th>$\phi$</th>
<th>$\phi + \infty$</th>
<th>2 ($\phi + \infty$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane (1 0 0), $= 10^\circ 10'$, $d_{100} = 2.61$ Å°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe metal</td>
<td>1.74346</td>
<td>15°30'</td>
<td>29°40'</td>
<td>18°40'</td>
</tr>
<tr>
<td>Cu metal</td>
<td>1.38058</td>
<td>15°20'</td>
<td>25°20'</td>
<td>10°20'</td>
</tr>
<tr>
<td>Plane (2 0 1), $= 4^\circ 56'$, $d_{201} = 2.65$ Å°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe metal</td>
<td>1.74346</td>
<td>19°12'</td>
<td>24°8'</td>
<td>24°23'</td>
</tr>
<tr>
<td>Cu metal</td>
<td>1.38058</td>
<td>15°5'</td>
<td>20°1'</td>
<td>20°18'</td>
</tr>
</tbody>
</table>
3.6.1) **High tension** :

It has been observed that the details of the absorption spectrum are usually obscured due to unnecessary high values of potential difference applied across the x-ray tube most probably because of higher weightage to characteristic emission spectrum of the target as compared to the continuous spectrum.

Sandstrom\(^{12}\) has shown that good spectrum can be obtained if the voltage applied across x-ray tube does not exceed 1.5 times the minimum voltage required to excite x-rays of corresponding wavelength. The energies of K levels of Cu, Fe, according to Bearden\(^{13}\) are 7.112 Kev and 8.903 Kev respectively. Hence in our studies the high tension should be about 1.5 times of the energy of the K level for these elements to photograph the K\(^{-}\) absorption discontinuities. We could apply the calculated optimum voltage as we have a continuously variable power supply unit in our laboratory.

3.6.2) **Thickness of the absorber** :

To obtain good absorption spectrum, the absorption screen should have optimum thickness. Two different criteria exist depending on whether the structure at the edge itself or the extended fine structure is to be studied.\(^{14,15}\) Sandstrom\(^{16}\) has given the following formula for optimum thickness of the absorption screen.

\[
x = 2.3 \log \left( \frac{\mu_2}{\mu_1} \right) / \mu_2 - \mu_1 \quad \ldots \quad (3.1)
\]

where \(x\) is the mass of the absorbing element in grams per
square centimeter and $\mu_1$ and $\mu_2$ are linear absorption coefficients on low and high energy side of the absorption edge.

Kurylenkov\textsuperscript{17} has suggested the following formula for the optimum thickness of the absorber for fine structure studies.

$$x = \frac{1}{\mu_2}$$ \hspace{1cm} (3.2)

It is seen that the absorption screen should be thinner to record extended fine structure. Studies of the effect of thickness variation on the recording of fine structure have been also carried out by Krishnan and Nigam\textsuperscript{18,19} and K. Tsutsumi et al.\textsuperscript{19}

In addition to thickness the uniformity of the absorber and the grain size of the material under investigation also play an important role in recording the absorption edge and EXAFS on a photographic film. The grain size should be less than 5 times of the thickness of the absorber.\textsuperscript{20} We have prepared uniform absorber films with a few milligrams of very fine powder without any obvious pores in it, by trial and error, the result of recording a number of spectra for different absorbers taking the prerogative of the judgement. In order to obtain good EXAFS the absorber was made as thin as possible maintaining its thickness uniformity. The screens were prepared by spreading fine powder on cellulose tapes and sandwiching between them.

3.7 Exposure and Photographic Processing:

The trial spectra of each sample were obtained on ORWO XR-11 dental X-ray film, in order to determine the exposure times. This was useful in judging the suitability of the absorbing screens
also. It is a fine grain high contrast film and requires comparatively low exposure times. It was observed that slow development (about 7 minutes) at lowered temperature gives a better contrast and transparency of the film. The deterioration of the film due to back reflection from the film holder was avoided by placing a lead screen behind the film. Since developing is very important process in this type of work, the films were always developed in fresh developer.

3.8 Microphotometry and Measurements:

Carl-Zeiss Jena rapid photometer GII connected with the potentiometric recorder GI BI (Plate 3.3) was used to obtain microphotometric records of film. The height and the width of the slit of the instrument was adjusted to get good line profile. For the same film at different positions several records were obtained. The magnification used was 120 mm/min. The film was placed on the scanning platform in such a way that the line was exactly parallel to the slit and the spectrum was scanned such that the lines always remained parallel to the slit.

The said chart speed reveals the minute details of the x-ray spectrum without disturbing the synchronization of wrapping and unwrapping of the chart paper. A comparator was used for the measurement. The exact location of the inflexion point on the edge and maxima of the EFS was done very carefully by inspecting a number of similar records for the same film.
In the present work for the measurements of wavelengths of the Cu K-edges in all ferrite samples, Cu K_{13} emission line was used as a reference line while for Fe K-edge wavelength measurements FeK_{13} line was used as a reference line. The dispersion being linear, extrapolation is justified without any loss of accuracy as discussed in 3.9.

Sufficiently large number of measurements were made; but in the final estimation of wavelength and average error those measurements were included which appeared consistent with each other. However, number of discarded readings did not exceed 10% of the total number in a set.

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

$$\frac{dx}{xL} = \frac{\lambda}{R \tan \theta}$$

where R is the radius of curvature and $\theta$ is the Bragg angle for particular value of $\lambda$. The linear dispersion calculated by this formula for WL_{11} - WL_{22} lines is 12.60 X U/mm, which agrees fairly well with the dispersion accurately obtained on the film which is 12.50 X U/mm.

3.10 Errors and Accuracy of Measurements :

There are many sources of errors involved in the determination of the wavelength of the edge. Errors may be introduced due to either non-uniform photographic processing and contraction of the film, or backlash in motion of the rotors involved in micro-
photometric work. In addition the personal error, further complicates the situation.

Necessary precautions were taken to minimize these errors. Each film was processed for predetermined fixed time and every time freshly prepared developer of the same strength was used. To minimize the additional error due to line fluctuations, doubly stabilized power supply was employed. The average error in wavelength determination is estimated from a number of readings taken by using well known formula,

\[ \sigma = \frac{\sum_{i=1}^{n} | R_i - R |}{n} \]

with usual notations.

The average errors in the measurements are indicated along with the results.
REFERENCES


5. Dumond, J.W.M., Phys. Rev. 36, 1702 (1930) and Hoyt, A.


