CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 INTRODUCTION

Having obtained the general information about the crystal system to be studied (Chapter 1), it is equally necessary that a good knowledge of both the experimental techniques and the instruments used should be acquired prior to commencement of a fruitful research work. In the investigations carried out and described in this thesis, a number of experimental techniques such as silvering technique, optical microscopy, X-ray diffraction, microhardness testing, etc. have been employed. The present chapter embodies a brief account of them.

3.2 SILVERING TECHNIQUE

Crystal surfaces as well as optical flats have to be coated with highly reflecting layers of silver necessarily for microscopic as well as interferometric studies.

The method essentially consists of thermally evaporating pure metallic silver on the specimen surface at a low pressure. A commercial vacuum coating unit, "EDWARDS 12EA" used for this purpose is shown in Fig. 3.1. It consists of a cylindrical vacuum chamber in the form of large pyrex bell-jar resting in an angular recess upon gasket of neoprene rubber which rests on horizontal metal

plate. This vacuum chamber is evacuated by a three stage silicon oil diffusion pump backed by an oil rotary pump. A number of vacuum tight insulated electrodes pass through the base to which the evaporation filament and the electrodes for the high tension discharge are connected. A vacuum tight cone-shutter can be swung in and out of position over the filament. The vacuum at different stages is measured by a pirani gauge and Philips ionization gauge built in the unit. The experimental surfaces are thoroughly cleaned before the evaporation of silver. Of course, the cleaning process depends very much on the nature of the surfaces. Optical flats, for example were first cleaned with nitric acid, washed with water, applying soap, and then with H_2O_2. Thereafter they were cleaned by rubbing with dry cotton wool till no breath figures were formed on breathing over them. Freshly cleaved surfaces do not require any cleaning. The as-grown habit faces and the etched faces were normally cleaned by running water. Final cleaning was carried out by ionic bombardment in the "EDWARDS" unit by means of a high tension discharge.

The chamber is first evacuated by rotary pump and when a pressure of the order of 0.2 torr is reached the chamber is connected to the diffusion pump. When the pressure of about 10^{-5} torr is reached the

molybdenum boat is heated to red hot by passing a low tension high current. In order to prevent the surfaces to be coated from receiving vapours of burnt impurities, the boat while getting heated-up is covered with an adjustable shutter. Such impurities can have a serious influence in increasing film absorbtion. Deposition of silver is started half a minute after silver starts boiling, by keeping away the shutter from over the filament for the required direction.

3.3 OPTICAL MICROSCOPY

3.3.1 Incident light microscope "EPIGNOST"

Most of the preliminary examination of crystal surfaces and the photographic recording of the observations at lower magnifications was accomplished with the help of "Epignost", shown in Fig. 3.2. This microscope has been designed by Carl Zeiss, Jena, for rapid examination of ground, polished, etched and as-grown faces of the objects and hence it affords very convenience called for this kind of examination. Being an incident light type microscope, the objective has an infinite intersectional distance, i.e. the specimen lies in the front focal plane of objective and its image is formed at infinity. The instrument contains a permanently built-in

type lens, which together with eyepiece forms a telescope, thus resulting in a factor of 0.63 for calculating the total magnification. A 6 volt, 15 watt filament lamp serves as the source of light.

The "Epignost" can also be used for photomicrographic work for which it is provided with a specially suitable photomicrographic "MF" equipment in combination with a miniature 35 mm camera, shown fitted as in Fig. 3.2.

3.3.2 Vickers projection microscope

Vickers projection microscope, shown in Fig. 3.3, has been employed for the microtopographical studies. This is basically an inverted type metallurgical microscope in which the specimen to be studied is placed on a movable stage above the objective lens. The flexible illuminating system which can be used both for the transmission and the reflection photography consists of a powerful mercury lamp, pointolite or carbon arc lamp, a condenser and aperture-controlled iris diaphram. For visual observations, an eye piece with a reflector is pushed into the tube below the objective. For photomicrography, a projection eyepiece is used and the final image

is focussed on the projection screen after reflecting from the projection mirror. A slight refocussing is necessary when the visual system is required to be changed over to the projection system.

3.4 X-RAY DIFFRACTION TECHNIQUE

3.4.1 "Philips" Unit

The Philips 1000 W X-ray generator type PW 1009 unit (Fig. 3.4) provides a good quality recording of diffraction patterns with all types of cameras. This unit provides continuously adjustable high voltage 0-55 KV and tube current 0-40 mA. In the present investigation the Laue camera (Philips Holland) and the goniometer of type PW 1031/00 were employed to test the single crystallinity and to identify the habit and cleaved faces of the crystals grown.

3.4.2 "Carl Zeiss" powder diffractometer

Basically, a diffractometer in principle is designed somewhat like a Debye-Scherrer camera, except that a movable counter replaces the strip of film. In both instruments, essentially monochromatic radiation is used and the X-ray detector (film or counter) is placed on the circumference of a circle centred on the

powder specimen.

The diffracted radiation is detected by counter tubes which move through angular range of reflections. An important feature of diffractometer is its ability to focus into a sharp diffraction line, the radiation which is Bragg-reflected from an extended specimen area. This improves the sensitivity as well as the signal-to-noise ratio. The powder diffractometer, shown in Fig.3.5, consists of the X-ray generator TUR M 61 made by VEB Transformatoren und Rontgen werk Dresden, the horizontal counter goniometer HZG-3 and the linear momentum density recorder VAD 53-1 made by Freibeerger Prazisions Mechanik GDR. A selection of five different angular velocities of $1/12^{o}$ min^{-1} to 2^{o} min^{-1} and various recorder chart speeds are available.

Here the specimen is placed on a proper mount in the centre of the diffractometer and rotated by an angle θ around an axis in the mount plane. The counter is attached to an arm rotating around the same axis by angles twice as large as those of the specimen rotation. Only those (hkl) planes which are parallel to the mount plane contributed to the diffracted intensity. It is necessary to align the component parts so that the

following conditions are satisfied :

(1) Line source, specimen powder surface and receiving slit axis are all parallel.

(2) The specimen surface mount coincides with the diffractometer axis.

(3) The line source and the receiving slit both lie on the diffractometer circle.

The X-ray integrated intensity is the total energy reflected as crystal is rotated through the reflecting region (1). Essentially, it is the area lying under the diffractometer trace of a line. Its magnitude is proportional to the volume of the material giving rise to reflection. Thus the integrated intensity for the (hkl) reflection is proportional to the volume of all crystallites that have their (hkl) planes lying parallel to the surface of the mount. A synchronously advancing strip chart records the intensities. Determination with the diffractometer, in general, requires approximately 100 times more of the substance than the conventional Debye-Scherrer methods. Compared with the photographic methods, the diffractometry, in most cases, offers essential advantages due to the higher sensitivity, the higher resolving power, the better accuracy in the

intensity measurements and the elimination of the elaborate work in dark room. Above all, the diffractometric records can be outlined in a much shorter time than with photographic methods.

3.5 EDAX

The scanning transmission electron microscope (STEM), Philips EM 400, schematically depicted in Fig. 3.6, has an attachment EDAX (Energy Dispersive Analysis of X-rays) which is shown in Fig. 3.7. This helps the purpose of chemical analysis. The principle underlying EDAX is the same as that of electron probe microanalysis. When a beam of electrons strikes a specimen a fraction of the incident electrons excite the atoms of the specimen which then emit X-rays while they return to their ground states. The energy of these X-rays are strictly related to the atomic number of the elements excited and therefore their detection forms the basis of elemental analysis in the electron microscope. In this method, however X-ray diffraction is not involved.

The various wavelengths in the X-radiation emitted by the sample are separated on the basis of their energies by means of Si (Li) counter and a multi

channel analyser (MCA); this counter produces pulses proportional in height to the energies in the incident beam, and then the MCA sorts out the various pulse heights. The table or the chart of the energies of all K and L lines arranged consecutively may be stored in the memory of MCA, to be retrieved when needed. The qualitative analysis depends on the identification of the peaks on the video-display of the MCA, which shows the counts accumulated vs X-ray energy. Because there is no physical separation in space of the various wavelengths (energies), such a spectrometer is often simply called nondispersive (1).

The EDAX gives information about the chemical elements present in the sample, irrespective of their state of chemical combination or the phases in which they exist, unlike the X-ray diffraction which discloses the various compounds and the phases present in the sample. Hence the EDAX is much more rapid than the ordinary methods of chemical analysis and is non-destructive. This method can detect elements from sodium upwards in the periodic table. The quantitative detection limit for homogeneously distributed elements is often 0.1 - 0.01 atomic percentage (2).

3.6 MAGNETIC GOUY BALANCE

The magnetic permeability μ of a compound subjected to constant magnetic field is given by the relation

$$\mu = 1 + 4\pi k$$

here k is the volume susceptibility.
The quantity often calculated is the magnetic susceptibility per gram, χ_g, which is defined as $\chi_g = k/d$, where d is the mass density of the material used for study.

Diamagnetism arises from the electrons in closed shells tending to orient their planes of rotation so as to suffer minimum interaction with the imposed magnetic field. All the diamagnetic substances are characterized by negative value of k and χ_g. Paramagnetism arises from the angular momenta orbital and/or spin, associated with the unpaired electrons; for all paramagnetic substances k and χ_g are positive.

Ferromagnetism and anti-ferromagnetism are subdivisions of the paramagnetism and are known as

"co-operative phenomena", which means that they arise when the paramagnetic centres within a sample intersect magnetically with each other.

In order to detect and determine the magnetic susceptibility of a given sample, it is finely powdered first and then packed into a glass container whose weight is exactly measured on an electrically sensitive magnetic Gouy balance (Fig. 3.8) the pan of which is situated between the poles of a powerful electro-magnet whose field can be varied by changing the current passing through the coils.

The change in weight after applying the magnetic field is measured by the calculation of χ_g ;

$$\chi_g = \frac{KV + \beta\, dW}{W}$$

where K is volume susceptibility of air.

V is volume of water.

β is tube constant.

dW is the aparant change in weight of the sample.

W is weight of the sample.

3.7 INDENTATION TECHNIQUE

In order to study the micromechanical

hardness of the crystals and the propagation of dislocations in them, the indentation technique is usually employed. The equipment used for the purpose is required to be attached to the Vickers projection microscope (Fig. 3.3) and is shown separately in Fig. 3.9. The various components numbered in the figure are as follows :

1. Filar micrometer eyepiece in centering mount.
2. Tube length scale for magnification setting.
3. Base plate contact anvil.
4. Beam contact tip.
5. Collect chuck securing specimen.
6. Chemical balance weight to apply load.
7. Load centre indicator.
8. Red signal lamp.
9. Auxiliary counter weight.
10. Counter weight.
11. Diamond indenter objective.
12 Electricity supply terminals.

The specimen, under test, is mounted on a circular aluminium disc and inserted into the collect. The light beam is then balanced by the addition or removal of counter weights in such a way that the contact was just made which can be indicated by

the flickering of the red signal lamp. The required load is then applied. The region to be indented is scanned with the help of the reading objective and then the diamond indenter is properly placed. After lowering the stage to bring the indenter near the crystal test surface, the diamond indenter is lowered with the help of fine motion mechanism until it just makes a contact with the test surface. The contact is normally maintained for, say 30 seconds. By reversing the motion, the indenter is removed and the indented region is examined with the reading objective through the filar eyepiece.

The diagonal of such indentation marks are measured and the Vickers Hardness Number (VHN) is calculated using the formula (3)

$$VHN = \frac{2L \sin \theta/2}{d^2} \quad kg.\ mm^{-2}$$

where L is the load applied to the indenter in units of kilogram weight,

θ is the angle between the opposite faces of the indenter and

d is the average diagonal length in mm.

For $\theta = 136^{\circ}$, as is the case with Vickers pyramidal indenter, the formula simplifies to

$$VHN = \frac{1.854\ L}{d^2} \text{ kg. mm}^{-2}$$

It is generally believed that VHN is independent of load when measured by a standard Vickers hardness machine operating at loads greater than 2.5 kg. However, several investigators found the variation in VHN with decrease in load (for operating loads less than of 1 kg) and have tried to explain their results with suitable modified formulae. Specially, the formula suggested by Onitsch (4) is

$$VHN = 1.854\ ad^{n-2} \text{ kg.mm}^{-2}$$

where 'a' and 'n' are constants for a given material.

REFERENCES

1. B. D. Cullity. (1978)
Elements of X-ray diffraction; Addison-Wesley, Inc., California, 2nd edition.

2. P. J. Dean, A. G. Cullis and A. M. White. (1980)
Hand Book of Semiconductors; North-Holland, Amsterdam, Vol. 3, 115.

3. B. W. Mott. (1956)
Microindentation Hardness Testing; Butterworths Pub., London.

4. E. M. Onitsch. (1947)
Microscopie, 2, 131.

Fig. 3.1 'Edwards' vacuum coating unit, 12 EA.

Fig. 3.2 Incident light microscope, 'Epignost'.

Fig. 3.3 Vickers projection microscope.

Fig. 3.1

Fig. 3.2

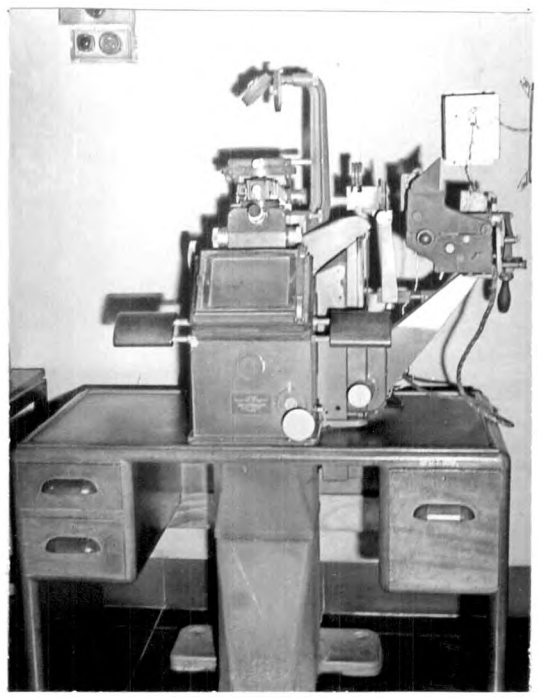

Fig. 3.3

Fig. 3.4 'Philips' X-ray unit, PW 1009.

Fig. 3.5 X-ray powder diffractometer.

Fig. 3.6 Cross-sectional view of the electron-optical unit of the Philips EM 400.

Fig.3.4

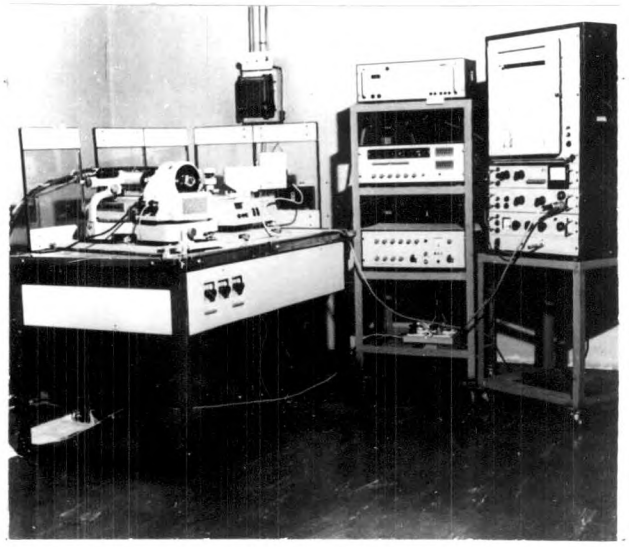

Fig. 3.5

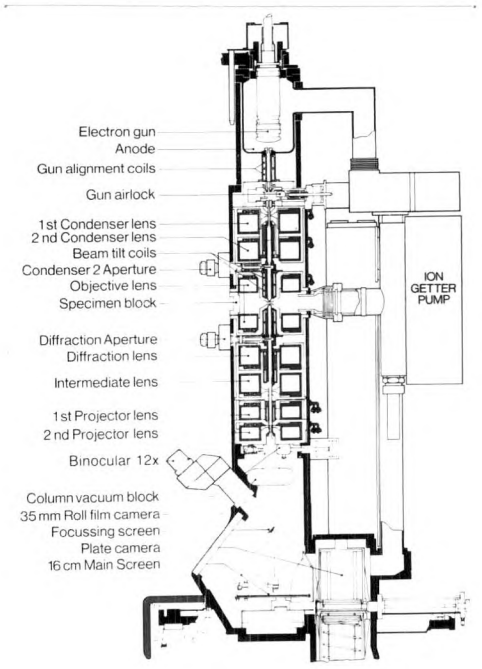

Fig. 3.6

Fig. 3.7 'Philips' EM 400 with EDAX attachment.

Fig. 3.8 Magnetic Gouy balance.

Fig. 3.9 Experimental set-up for indentation.

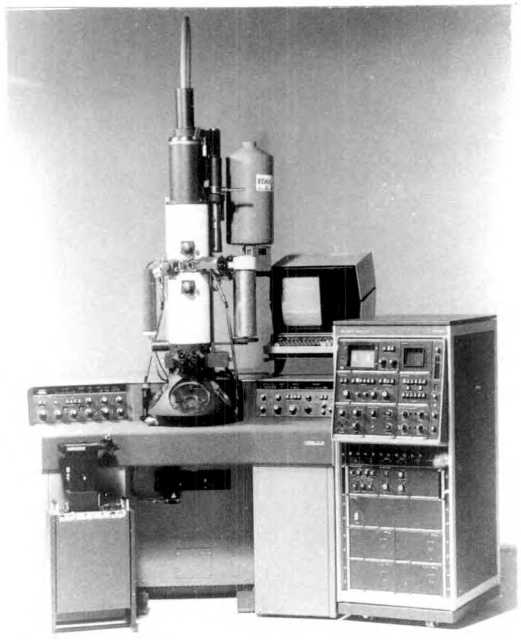

Fig. 3.7

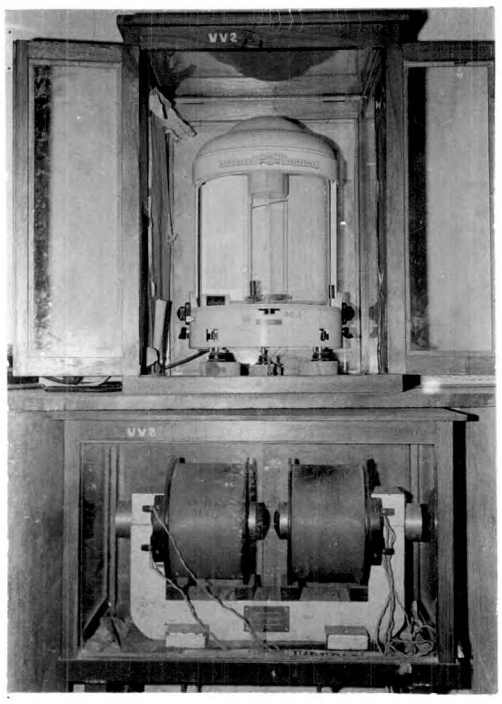

Fig. 3.8

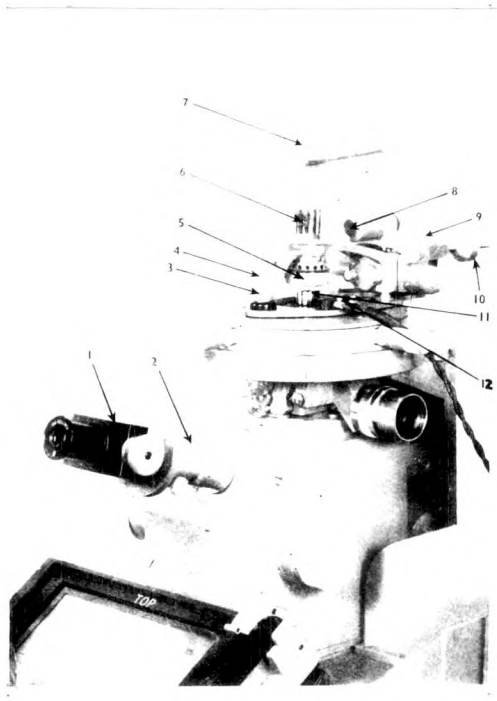

Fig. 3.9