CHAPTER II

EXPERIMENTAL TECHNIQUE

2.1. ELECTRON DIFFRACTION CAMERA

The electron diffraction camera was constructed at the Institute of Science, Bombay by the author. It is of a conventional Thomson-Fraser design placed on a horizontal wooden support with its axis along the magnetic field of the earth. All parts of the camera are sealed by 0 rings and are demountable. The camera consists of five main parts: (1) Electron gun, (2) Anode assembly, (3) Collimating tube, (4) Specimen chamber, and (5) Plate chamber. The essential features of each are briefly described below.

2.1 A. The electron gun:

The electron gun is of a novel design in which all the necessary controls are incorporated with the simplicity of demountability. The design is shown in Fig. 1a. A pyrex glass tube G of 6 cm. dia. and 15 cm. length is sealed by 0 rings to brass blocks A and L machined to the shape and size shown in the figure. Another glass tube M of 8 mm. bore and 35 cm. length is sealed by Wilson type 0 ring seal in the central hole of the brass block L. The electrical connections for the filament F are taken in through this tube M and sealing is effected by pinching the glass. At the other end of the tube M, a porcelain holder B for insulating and supporting the filament F is attached. The filament ends are fixed up friction tight in the slots of two nickel rods which are...
Fig. 1 - The diagram of electron diffraction camera

(a) electron gun

(b) anode assembly

(c) focus sing ccil.

(d) specimen chamber

(e) plate chamber

high vacuum metal valve

to diffusion pump.
screwed tight in the porcelain holder N. An aluminium tube Q with a cap having a smooth spherical surface on the inside is screwed in the brass block L and it serves as the sheath for the filament. On the other side of the brass block L is fixed an ebonite tube N carrying four screws S which can rest on the glass tube M. At the open end of the ebonite tube N slides the collar of the nut P which is engaged on the screw tightly fixed to the glass tube M.

2.1 B. **Anode assembly:**

The anode assembly consists of a brass block machined to the shape shown in Fig. 1b. In its central hole of 18 mm. dia. slides friction tight the tube carrying the anode. The anode is made of aluminium with a circular groove on its face in which an aluminium disc with an aperture of about 40 micron can be fitted. The four screws D engaged in the threaded holes of the anode assembly rest on the brass block A of the electron gun.

**Adjustment for aligning the gun:**

In order to get the electron beam on the screen it is essential that the tip of the filament, the aperture of the sheath and the aperture of the anode must be in a line. This alignment can be effected by the following adjustments:

1) By means of the nut P, the tube M can be moved along the axis of the gun so as to suitably adjust the distance between the filament tip and the aperture of the sheath.
2) The four screws S enable the centering of the filament with respect to the aperture of the sheath.
3) The electron gun sealed on the anode assembly by an O ring can be made to move as a whole with respect to the anode by means of the four screws D in any lateral direction until the gun is centred with respect to the aperture of the anode. This completes the centering adjustments of the gun.

A hair pin filament of tungsten wire of 0.2 mm. diameter is found suitable for the efficient working of the gun.

2.1 C. Collimating tube:

It is constructed from a drawn tube of brass of 2.5 cm. bore and 40 cm. length. It is sealed by O rings on one side to the anode assembly and on the other to the main body of the camera as shown in Fig. 1c. Close by the anode assembly, the tube is fitted with a vacuum flap valve which on closing can keep the electron gun under vacuum, whenever the camera is opened to atmosphere. At the other end of the tube is centred the focussing coil. A diaphragm of 1 mm. bore is fitted at this end to limit the electron beam and also to shut off the light from the filament.

2.1 D. Specimen chamber:

It is made of a fine grain bronze casting of 16 cm. inside diameter. There are two ports each of 7 cm. diameter for carrying the specimen holder (Fig. 1d). The specimen to plate distances with respect to these ports are 42 cm. and
21 cm. Symmetrically situated with respect to each specimen port, there are three small ports of 2 cm. diameter, which can be used for various purposes, such as (1) Viewing glass windows, (2) Air admittance valve, (3) Evaporation chamber (4) Discharge tube.

2.1 E. Specimen holder:

The specimen holder is of Thomson Frazer design as modified by Kehoe and others (1956). The specimen holder is useful exclusively in reflection technique. The azimuthal rotation of the specimen is obtained by connecting the rotor to the external control knob through a pair of crown gears in the ratio of 1:3 so that the rotation of the specimen is slowed down to one third of that of the external control knob. This facilitates an accurate adjustment of the specimen for a given azimuthal setting. The other external control knob moves the specimen in or out of the electron beam through a rack and pinion mechanism. The third motion required to vary the glancing angle is achieved by rotation of the whole specimen holder in its port.

2.1 F. Plate Chamber:

The plate chamber is a fine grain bronze casting of the same diameter as the specimen chamber. It is threaded to the specimen chamber and vacuum sealed by picien wax. At the other end of the chamber there are four arms which are at right angles to each other and tangential to the wall of the chamber as shown in Fig. 1e. Through the holes of these arms,
four brass rods are sealed by O rings, three of them carry photographic plate carriers and the fourth rod carries a fluorescent screen. By suitably rotating these rods, the plate carriers and the screen can be placed normal or parallel to the wall of this chamber.

The fluorescent screen is made of fine willemite powder evenly spread on a circular glass plate from a solution of canada balsam in xylol.

With an O ring in the groove of its flange, the plate chamber can be closed by a thick brass plate. The central hole in this brass plate is covered with a glass window of 7 cm. diameter enabling one to view the patterns on the fluorescent screen. The glass window is made vacuum tight by an O ring.

2.1 G. Vacuum system:

A three stage metal diffusion pump of Edwards type F 203 running on silicon oil D.C. 703 at pumping speed of 50 litres per sec. is connected to the main body of the camera through a metal vacuum cock of 2.5 cm. bore designed and constructed by the author. A Cenco Megavac with a pumping speed of 60 litres per min. is used for the forevacuum. A phosphorous pentoxide trap is used between the diffusion pump and the Megavac to avoid the contamination of the Megavac oil by water vapour. The final pressure reached in the camera as measured by a Pirani gauge was less than $10^{-4}$ mm. of Hg. A vacuum glass cock of 15 mm. bore between the diffusion pump and rotary pump and another between the camera and the rotary pump
are introduced to facilitate the rapid change-over of the specimen for examination without allowing the diffusion pump to be exposed to atmosphere.

2.1 H. **Electrical supplies:**

The filaments of the gun and the single wave rectifier (Machlett ML15, air cooled) are run from the secondaries of two oil-cooled step down transformers with high insulation between the primary and the secondary of each. The variacs in the primary circuit of each transformer allow suitable voltages to be applied to the filaments.

The filament of the electron gun draws a current of about 4 A. at 5 V. and the filament of the rectifier draws a current of about 10 A. at 10 V.

The focussing coil draws a current of about 1 A. from an accumulator of 12.6 V.

**H.T. Circuit:**

The mains A.C. supply is fed through a variac to the primary of the high tension transformer. The high tension from the secondary after rectification is smoothened by a condenser (Philips 0.004 μF.) across the rectified H.T. and a high glycerine resistance 10 megohm in series. The cathode is kept at the negative H.T. and the anode along with the camera at zero potential by earthing.

2.2. **GROWING COPPER CRYSTALS**

The slow cooling method by Thomson (1931) is adapted for growing copper crystals. This method far surpasses any
other method of growing single crystals in its simplicity, suitability and adaptability for the present type of work. In one run, a number separate crystals of various orientations can be obtained.

The furnace consists of a porcelain tube (5 cm. bore and 35 cm. long) with close equidistant winding of Nichrome wire A (S.W.G.No.18) lagged by a thick roll of asbestos sheet. The resistance of the winding is about 26 ohms. About 900 w. are required to maintain the temperature at 1150°C which is measured by a Pt - Pt, Rh. thermocouple connected to a Foster's 'Resilia' millivoltmeter calibrated for the measurement of temperature. The current in the furnace is regulated by a variac of 8 A. capacity.

Carbon rods of high purity are adapted for making the crucibles. About ten holes of 8 mm. dia. and 15 mm. depth are drilled along the length of the carbon rod (18 mm. dia. and 30 cm. length). The carbon rod is fired in the silica tube at 1150°C for six hours at a pressure of 10⁻² mm. of Hg to remove the vapours of volatile impurities in carbon.

The holes in the carbon rod are filled with copper of A.R. quality (99.9 %) and the rod is inserted in the silica tube so that the carbon rod, the silica tube and the furnace are symmetrically placed one inside the other. Over a length of about 10 cm. in the central part of the furnace, the temperature is found to be uniform. The silica tube is evacuated by a rotary pump (10⁻² mm. of Hg). The furnace is heated to 1150°C and maintained at this temperature for two
hours to ensure that all copper in each crucible is melted. The furnace is next slowly cooled down to 1060°C over a period of 12 hours by slowly decreasing the voltage from the variac. An annealing treatment at 1000°C is given for the next 48 hours and afterwards the temperature is slowly brought down to the room temperature.

About 3/4 of the copper pieces are found to be single crystals of various orientations with respect to their geometrical axes.

2.3. CUTTING OF CRYSTAL TO DESIRED PLANE

The copper crystals are etched in a 30% solution of nitric acid for about five minutes so that large facets are developed all over the crystal surface. A preliminary visual examination immediately reveals the crystalline nature of the copper pieces. If it is formed of crystallites of various orientations, it is indicated by different light intensities on either side of their grain boundaries. A well grown single crystal exhibits reflections all over the illuminated surface for its various orientations without any indication of the grain boundary.

For cutting the crystals to the desired plane, the optical method indicated by Bridgman (1928) is developed further so that the crystal can be cut to a plane within an accuracy of 2°. An optical goniometer was constructed particularly suitable for cutting the crystal in addition to being suitable for the measurement of the interfacial angles.
2.3 A. Goniometer:

The optical goniometer is diagrammatically shown in Fig. 2. It consists of two separate parts: 1) A disc graduated in angles with its attachment for holding a crystal, 2) An optical equipment to obtain a parallel beam of light.

1) At the centre of the graduated disc, an ebonite tube is held erect by a spring and a nut screwed from the lower side of the disc. The ebonite tube rotates freely about its axis and a pointer attached to its lower part indicates its angular displacement. The ebonite tube carries in its bore a brass rod which can be adjusted to any desired height by means of a clamping screw on the ebonite rod. On the flat head of the brass rod, a crystal can be fixed in a pallet of plasticine.

It was found necessary to construct another crystal holder to cut the crystal to a plane of higher indices. This holder includes one more axis of rotation (B) perpendicular to the first one (A) (Fig. 2). The solid rod P freely rotates in the tube Q without any lateral play. The rod P carries a head which is used to support the crystal. At one end of P can be attached a pointer which measures the angular displacement of P on a graduated disc fixed to Q. The pointer and the graduated disc can be demounted when not required. A screw in the tube Q at the other end of P allows the rod P to be fixed. A slot in the central portion of the tube Q allows the rod P with its head to swing through 120° from one end to the other.
Fig. 2: The diagram of the goniometer.

Fig. 3: The electrolytic cell.

Fig. 4: The potentiometric circuit used for polishing.
2) The optical equipment is similar to that used in a metallurgical microscope. Fig. 2 shows the diagram which is self-explanatory. No lenses are used in the viewing tube. The two sets of cross wires one at the middle and the other at the farthest end of the viewing tube are useful for alignment of the eye with the parallel beam of light reflected from the crystal.

With the help of a small triangular prism placed on the head of the crystal holder of the goniometer, the parallel beam of light is adjusted perpendicular to the axis of rotation A of the goniometer.

A freshly etched copper crystal is mounted on the head of the crystal holder by means of a pallet of plasticine. The crystal is manipulated in plasticine until a bright reflection is received from the crystal facets. The crystal holder is, then, rotated through $90^\circ$ about the axis A and again the crystal is manipulated in plasticine about an axis perpendicular to both A and the parallel beam of light until a reflection from another set of facets is received. This procedure is repeated until each set of facets shows maximum intensity of its reflected light. An important zone, in the present case $\langle 001 \rangle$ or $\langle 110 \rangle$ zone is adjusted parallel to the axis A of rotation of the goniometer.

By choosing various crystallographic zones parallel to axis A and determining the angles between the reflections, it was possible to ascertain the indices of a set of facets from the nature of the intensity of reflected light from them. In the case of copper crystals etched in nitric acid, the
(001) facets show maximum intensity, (110) facets much less and (111) facets, the least. No other facets could be detected from the reflected light.

After determining from the reflections the interfacial angles on the crystal adjusted on goniometer, and the nature of the intensity of the reflected light, the zone of the crystal parallel to the axis A of the goniometer can be immediately found. The $\{001\}$, $\{110\}$ and $\{111\}$ zones are the easiest to determine.

When the crystal is to be cut to any other plane different from the above, the other crystal holder has to be used. An example will make the method easier to follow. Suppose the crystal is to be cut to (112) face. In the cubic lattice, (112) plane along with the (001) and (110) planes is contained in $\{110\}$ zone and the angular separation of (112) plane from (001) plane is $35.27^\circ$. From the nature of the intensity of the reflected light, the indices of zone of the facets can be readily found as described earlier. The crystal should be adjusted on the crystal holder as follows. The $\{001\}$ zone should be parallel to A; $\{110\}$ zone should be parallel to B. On rotating rod P through $35.27^\circ$ by means of the auxiliary pointer and graduated disc, $\{112\}$ zone becomes parallel to A.

The rod P is fixed by the screw, the auxiliary pointer and disc are removed and the crystal with its holder is ready for further operation.
The final operation is to grind the crystal to the desired plane. The holder carrying the crystal is gently removed from the goniometer and transferred to an ebonite cup. The cup is machined on a lathe. A hole of the same size as the rod of crystal holder is drilled along its axis and a screw along its diameter can fix the crystal holder rigidly. The crystal holder is lowered in the cup such that a small portion of the crystal projects above the rim of the ebonite cup. The crystal is set in the cup by means of plaster of paris.

The grinding is carried on a small grain emery stone with ample supply of paraffin until the projection is ground away. With careful and systematic grinding, uneven grinding of the rim of the ebonite cup can be avoided. The crystal face is next ground on emery papers graded from 0 to 0000. The surface is thus ground to (112) plane within an error of 2°. The crystal face is etched in nitric acid and transferred to the camera for examination.

Much of the manual labour can be saved if the crystal from the lot is so chosen that its geometrical axis is nearly parallel to the desired zone.

On examination by electron diffraction, the inaccuracy of grinding the crystal faces following this method was found to be less than 1° in most of the cases.

2.3 B. Accurate cutting of crystal to a plane using electron diffraction:

The method followed is due to Thomson (1931). In
electron diffraction patterns, the reflections of various orders from a family of planes are in the normal direction to those planes. In reflection patterns, the crystal face casts a shadow on the screen. If the crystal is correctly cut to the crystallographic plane so that the plane and the face are parallel, the reflections due to these planes will be in a direction normal to the plane and also to the shadow edge and hence will be exactly in the plane of incidence. In the case of a crystal face deviating from the crystallographic plane by a few degrees, the reflections from this plane will not be in the plane of incidence. The angle between the plane of incidence and the direction in which the reflections due to this plane occur, is the inaccuracy of the face from the plane. Another pattern after an azimuthal rotation of 90°, will show the inaccuracy of the face from the plane in a direction perpendicular to the first. From the knowledge of the inaccuracy in two directions on the face, the crystal is again cut in a jig similar to that used by Thomson (1931).

2.4. ELECTROLYTIC POLISHING AND ETCHING

After cutting a crystal to a plane accurately, it is next electrolytically polished. A small electrolytic cell was fabricated from polyethylene tubing and sheet. Polyethylene is not attacked by strong acids or alkalies or organic solvents.
2.4 **Electrolytic cell**

The assembly of the cell (Fig. 3) rests on an ebonite disc, which has a central hole of 2 cm. dia. and two upright screws at diametrically opposite ends. The cell consists of a polyethylene disc over which is placed a polyethylene tube of 4 cm. dia. and one cm. length. The cell is covered by a thick copper disc, which serves the purpose of the cathode. A small glass window pasted on the central hole of the copper disc is used to view the polishing process. The crystal face is inserted in the cell through a hole in the polyethylene disc. Two polyethylene tubes of two millimeter bore are connected to the central polyethylene tube and help circulating the electrolyte in the cell. The whole assembly is clamped tightly by means of the uppermost plate and nuts.

The cell can be placed on the stage of an incident light type microscope which allows the examination of the polishing process at a magnification of X 60. A slight tilt of the microscope stage helps the rapid removal of the gas bubbles formed on the cathode.

2.4 B. **Electrolytic polishing**

The surface of the copper crystal, after grinding on 0000 emery paper and washing in benzene and alcohol, is ready for electrolytic polishing.

Orthophosphoric acid of A.R. quality is used as the electrolyte for polishing (Tegart 1959). The acid is diluted with water in the proportion of 2 : 1. A potentiometric circuit is used as shown in Fig. 4. The current is drawn from
an accumulator of 6 V. The crystal is connected to the
anode and the upper copper disc to the cathode.

The electrolyte is allowed to circulate through the
cell. A pressure head of 100 cm. was found suitable for the
circulation of the electrolyte. The current is started at
a pre-determined voltage, so that the potential difference
across the electrolytic cell is about 1.1 V. A microscopic
examination of copper surface shows that it is covered by a
gray film. Within 2 to 5 minutes, the film is let loose
from the surface and starts moving with the flow of the
electrolyte. At this stage, the voltage across the cell
suddenly rises to about 1.5 V., which is accompanied by a
sudden fall of the current. At this stage polishing starts
and the voltage across the cell gradually rises to 2 V. Within
about 15 minutes the polishing is completed. The microscopic
projections on the copper surface are thus removed and the
copper surface now appears black in the field of view of the
microscope. Precaution is always taken to see that the
voltage does not rise above 2 V., beyond which the gas
evolution from the copper surface starts resulting into its
spotty appearance.

After polishing is over the copper crystal is quickly
removed from the cell and washed in distilled water.

2.4 C. Electrolytic etching:

Fifteen minutes after the commencement of polishing,
the voltage across the cell may be lowered for etching. Etching
can be carried over the range of 0 to 1 V. However, at 1 V.
etching is very rapid and uncontrollable. Hence etching is carried at about 0.2 V. for various time intervals. After etching is over, the copper face is washed in distilled water.

2.5. OXIDATION ETCH

In a preliminary study of the oxide growth on copper by electron diffraction, it was observed that etching the copper faces by repeated oxidation is a far better method of etching than electrolytic etching. The electrolytically polished surface is oxidised so as to form an oxide layer of thickness of about 380 Å or less. The estimation of the thickness is quite rough. On dissolving the oxide, the copper face is very lightly etched. By repeating this procedure, various stages of roughness can be imparted to the copper face and at each oxidation, the oxide growth on the etched copper face can be simultaneously studied by electron diffraction. This method of oxidation etch, being easier and more controllable than the electrolytic etching, was very frequently followed. Both methods of etching were observed to give similar patterns due to oxide grown on copper faces.