CHAPTER IV

EXPERIMENTAL PROCEDURE

4.1 X-ray counter diffractometer:

The X-ray equipment used in the present experiment is manufactured by Philips Inc., Holland-type PW 1009 with extra stabilizer unit. A 360-watt water cooled Philips tube having a copper target is used as the X-ray tube. The X-ray beam was passed through a nickel filter to cut off the β component. It emerged at an angle of 6° to the normal to the tube window. The specimen was put at the centre of the horizontal diffractometer disc. The disc was calibrated in degrees (θ, each degree divided into four parts) and had a diameter of 500 mm. The Geiger counter was enclosed in a cylindrical enclosure with a slit in front of it. The counter could be rotated on the graduated scale about the specimen. The specimen was flat having an area of about 2 sq. cm. and rotated at half the speed at which the Geiger counter rotated so that its surface remained tangential to the focusing circle (refer fig. 7). The counter could either be rotated by means of a spherometer (whose disc...
had a diameter of about 70 mm.) or by a synchronous motor. The disc of the spherometer carried graduations so that readings of counter positions could be read up to 1 minute of arc and by estimation up to \( \frac{1}{2} \) minute. The synchronous motor could rotate the counter at any of the six speeds, viz., \( \frac{1}{2} \) min./\( ^{\circ} \), 1 min./\( ^{\circ} \), 3 min./\( ^{\circ} \), 5 min./\( ^{\circ} \), 10 min./\( ^{\circ} \), 30 min./\( ^{\circ} \). The widths of the entrance slit (placed near the X-ray window) and of the receiving slit placed in front of the Geiger counter were variable from 0 to 2 mm. A screening plate with a slit of about 3 mm. was placed in front of the counter to cut off stray radiation.

The pulses from the Geiger counter were fed to a ratemeter through an amplifying circuit. A microammeter put in the ratemeter showed a deflection whenever the Geiger counter passed across an X-ray line. Thus the position of the X-ray line could be located and read on the diffractometer scale. The scale of the microammeter was directly calibrated in counts per second and could read up to a maximum of 30,000 counts/sec. in six ranges.

In figures (8) and (9) are shown the photographs of the whole X-ray unit and of the diffractometer with the small furnace (with outer cover removed) in the centre.

The output of the ratemeter could also be fed to an automatic chart recorder. The chart recorder could
be run by a synchronous motor. The Geiger counter and the chart recorder were simultaneously run by their respective motors to obtain the X-ray diffraction pattern on the chart of the recorder. The recorder could be run at any of the three speeds, viz., 1200 mm./min., 600 mm./min. or 300 mm./min.

4.2 **High temperature attachment:**

In order to heat the specimen a furnace is required. As described earlier, a number of high temperature cameras are described in literature but hardly a few furnaces are described which can be used with a recording diffractometer. Those which are described are either meant for special purposes, e.g. for determining phase transformations in metals and hence have to be used with the Geiger counter in a fixed position, or in others, materials like zirconium, tantalum etc. are used in their construction. Such materials are not easily available in ordinary laboratories. Moreover, most of the furnaces described in the literature are designed for the vertical circle (e.g. Philips) diffractometers. There are hardly any furnaces which are designed for horizontal diffractometers. Also large temperature gradients are likely to exist in the powder sample e.g. when it rests on a hot metallic surface. Williamson and Moore (1956)
have shown that in a hot-plate-type heater, gradients as large as 600°C/cm through the sample and 6°C/cm along the surface at 500°C exist. Probably this is one of the principal causes of the wide discrepancies in the values of the thermal expansion at high temperatures, especially in X-ray determinations with a diffractometer. Hence it was decided to construct a small furnace from materials available in our own laboratory and which is free from the above drawbacks. A number of different designs were tried, but either the furnace became unduly large in size and heated the whole diffractometer or in small designs the coil would burn off during the experiment. The final design shown in fig. 10 and detailed below was found to work satisfactorily and has given very reliable service throughout the course of the present investigation.

The heater of the furnace assembly is shown in fig. 11. A porous pot used in Danial cells was cut from both sides so as to obtain a cylinder of about 3.5 cm. in length and 5 cm. in diameter. A slot of 1.6 cm. width was cut along its length, as shown in the figure, for X-rays to enter and leave. The heating element consists of nickel wire of S.W.G. 26. The element is in the coiled coil form inside the furnace and straight outside. The distance between two consecutive coils and the pitch of the coil
were so adjusted, especially near the slot, that a region of as uniform a temperature inside the furnace as possible was obtained.

The heater is placed on an asbestos cement disc E (fig. 10) of about 15 cm. diameter. Four pegs A B C D (C D not shown) are screwed on the disc to fix the position of the heater (shown dotted). The asbestos disc is placed on a hollow metal disc M of the same diameter and height about 1 cm. During the experiment, cold water is continually circulated through this disc in order to prevent the heat of the furnace from reaching the main body of the diffractometer. Two pillars P_1 P_2 carry the specimen holder as shown. The fused silica rods R_1 R_2 rest in the specially designed grooves in the pillars.

The specimen holder F consists of a slice of size about 3.5 cm. x 3 cm. x 0.3 cm. cut from an insulation brick of a burnt out muffle furnace. A hole S of size 1.0 cm. x 1.3 cm. was cut through it. On its back-side grooves are made to carry the fused silica rods R_1 and R_2. The back side is then covered by a thin sheet of platinum. The specimen in the form of powder is filled in the groove S. The thermocouple consisting of Pt/Pt-10%Rh is placed in contact with the front surface of the specimen. The pillar P_2 can be moved perpendicular to the plane of the paper by about 0.5 cm. by a screw adjustment in order to
bring the front surface of the specimen along the central vertical axis of the diffractometer.

The whole furnace assembly was covered with a copper cylinder. A slot about 2 cm. wide and 180° in circumference was cut in the cylinder and covered with aluminium foil. The advantage of this furnace assembly is that the sample holder can be detached at will. The heater can also be removed with the sample holder in position. The furnace (with nichrome wire) was used up to about 930°C but with Pt-10%Rh winding the range can be extended to 1200°C. The furnace assembly was designed to fit the horizontal diffractometer made by Rich. Seifert, Germany.

The inside region of the furnace was investigated with a Pt/-10%Rh thermocouple at different temperatures. Typical results of such one investigation are shown in figs. 12 and 13. It is seen from fig. 12 that between 3.5 cm. and 4.9 cm. a region of fairly uniform temperature is obtained along the furnace axis. The variation of temperature between these extreme points is about 3°C. Similarly, in fig. 13 the region between 2.1 cm. and 2.7 cm. (depth of 0.6 cm.) is again of fairly uniform temperature, the difference of temperature being only 4°C. In view of the fact that the specimen thicknesses
FIG. 12

DISTANCE FROM ONE END ALONG THE AXIS IN CM.

FIG. 13

DISTANCE FROM THE SLOT \perp TO AXIS IN CM.
is about 0.3 cm. and X-rays normally penetrate only about 0.01 cm. of the specimen, the design of the furnace was considered quite satisfactory.

4.3 Measurement of line positions:

The advantages of using high angle lines in the measurement of lattice constant are well known. But the intensity of the high angle lines was found to decrease at about 400°C to such an extent that no meaningful measurements could be made. Hence above 400°C, lower angle lines in the range 60° to 30° were also used. The accuracy of the observations was estimated to be about 4% below 600°C and about 1% at higher temperatures.