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A LOW TEMPERATURE ATTACHMENT TO THE WEISSENBERG GONIOMETER

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1. Introduction

The experimental work in low temperature crystallography can be classified in two groups: (*a*) the study of substances which are crystalline at room temperature and (*b*) the study of substances which are liquid at room temperature but crystallise at lower temperatures. For the study of latter type the present authors have described an integrating Weissenberg goniometer (1963). Recently, for some studies at low temperature, the authors designed an attachment to " Unicam S-35 ". The arrangement used was simple and it overcame many difficulties encountered in low temperature crystallography. A detailed account was, therefore, considered worth while.

2. Cooling Method

The method of cooling employed in the present arrangement is simple gas cooling which was developed and improved by Fankuchen (1951) and Lipscomb (1950). In this method liquid air contained in a metal dewar flask is evaporated by an electric heater. The stream of cold air thus obtained is used for cooling the specimen. The deposition of moisture on the crystal is avoided by blowing a sheath of dehydrated air at room temperature around the cold air stream. The gas cooling is quite simple and satisfactory, but has following disadvantages:

(*a*) The conventional film cassette cannot be removed without interrupting the cooling arrangement. This is a serious drawback if one is investigating a substance which is liquid at room temperature, because any interruption in cooling will melt the crystal. To overcome this difficulty, it is customary to use a split cassette so that the top half can be removed and film enclosed in an envelope slipped in.

(*b*) To grow single crystal *in situ* in the X-ray goniometer is sometimes tedious as the temperature gradient is obtained by adjusting the rate of flow of cold and warm air.

In the present arrangement, the problem of removing the camera has been solved in a simple way. To grow single crystal the temperature gradient is produced by a small heater.

3. The Cooling Attachment

The geometry of "Unicam S-35" goniometer does not permit the removal of the camera without detaching the layer-line screen holder. The present attachment essentially consists in suitably redesigning the layer-line screen holder. Unlike the conventional screen holder the new one has been made hollow so that the cold-air leads can be fitted inside. Moreover the part of the layer-line screen holder that clamps on to the goniometer is made bracket-like. As seen in Fig. 1, the camera can be removed without detaching the layer-line screen holder if the collimator-slot is wider than the cold-air lead. For this purpose a camera with ½" collimator-slot has been made. In this camera reflexions with Bragg angle $\theta > 85°$ are cut off.

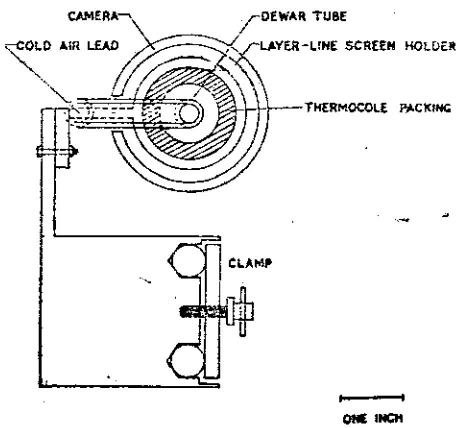

Fig. 1

The conventional layer-line screens on the right-hand side has to be removed for the adjustment of goniometer arcs. However, it is not possible to remove this screen when the cooling arrangement is in position. A screen tube 3 inches long with ½ inch slot was used in the present arrangement. The screen tube of this size, when pushed to the right end, exposes the goniometer head for adjustment.

4. Experimental Arrangement

The liquid air contained in a 25 litre metal dewar flask (supplied by Indian Oxygen Ltd.) is evaporated by a 25 W heater. The stream of cold air thus obtained is led to the goniometer by a vacuum-jacketed glass tube. Just before entering the goniometer the stream of cold air passes through a copper spiral tube immersed in liquid air. The stream of cold air exchanges heat with liquid air and finally cools the crystal on the goniometer head.

The temperature of the crystal is measured by a copper-constantan thermocouple and a calibrated mili-voltmeter, to an accuracy of $\pm 1°$ C. The temperature can be controlled by varying the current in the heater immersed in liquid air. The temperature can be maintained constant to within $\pm 1°$ C.

As the crystal is cooled, atmospheric moisture settles on it in the form of ice. Icing is not serious down to $-20°$ C. but below this it becomes necessary to blow a sheath of dehydrated air surrounding the cold-air stream. Even with this arrangement, below $-100°$ C., the goniometer as a whole gets cooled. Due to large volume of cold air coming in contact with the layer-line screen and the camera moisture deposits on them. This problem can be overcome if the cold air does not diffuse over the instrument but is drawn by a vacuum pump through a hollow circular plastic cup as shown in Fig. 2.

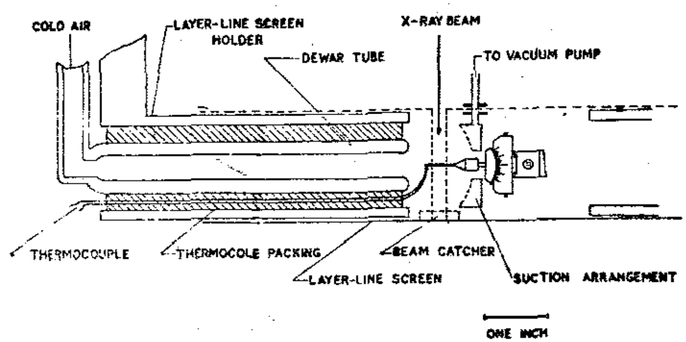

FIG. 2

5. CRYSTAL GROWTH

The specimen which is liquid at room temperature is sealed in a thin-walled capillary. In most cases it is found that mere cooling does not produce a single crystal. On cooling, the liquid usually turns into a poly-crystalline mass or amorphous solid and sometimes remains a super-cooled liquid. It has been suggested that by carefully manipulating the streams of cold and warm dehydrated air, it is possible to grow single crystals. However, the authors found the following arrangement more convenient.

A small nichrome heater in the form of a helical spring (Fig. 3) (4 to 6 turns of 30 gauge nichrome wire, 5 mm. dia. of the spring) is mounted on a perspex plate P. The two dovetail plates A and B which support P permit the removal of the heater without disturbing the cooling arrangement. The axis of the heater coincides with the axis of rotation of the goniometer. The ends of the heater are connected to a two-volt battery.

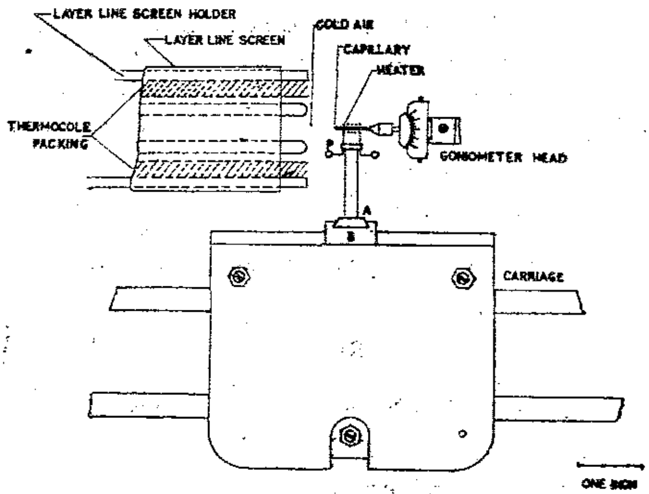

FIG. 3

First the carriage is attached to the leading worm screw (as is done while taking Weissenberg photographs). By turning the worm screw, the heater is brought to a position where it completely covers the specimen in the capillary. If the cold air is turned on, the liquid solidifies. The heater current is now switched on. The specimen melts. The heater is moved slowly towards the tip of the capillary, by switching on the motor or by turning the worm screw manually if slower motion is needed. As the heater is withdrawn the molten part cools slowly and grows into a single crystal.

6. VISUAL OBSERVATION OF THE CRYSTAL

If the crystal does not belong to cubic system, it is possible to observe the crystal between two polaroids. The lamp and the telemicroscope of the Weissenberg goniometer may be conveniently used for observing the crystal. The collimator is replaced by a brass tube similar in shape but having a bore of $\frac{1}{8}''$. A small piece of polaroid is stuck at the end facing the lamp. A second piece of polaroid is placed in front of the objective in crossed position. The formation of single crystal can be recognised by observing the extinction when the spindle of goniometer is rotated.

This arrangement has been used to crystallise a series of organic and inorganic liquids and to collect three-dimensional X-ray data. The results of these investigations will be reported later.

7. SUMMARY

A simple cooling attachment to " Unicam S-35 " goniometer has been described. The attachment permits the removal of the camera without disturbing the cooling arrangement. A simple method of growing single crystals *in situ* in the goniometer has also been discussed.

8. ACKNOWLEDGEMENT

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9. REFERENCES

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