AN APPARATUS FOR LOW AND HIGH TEMPERATURE OPTICAL GONIOMETRY OF HYGROSCOPIC CRYSTALS

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1. INTRODUCTION

MORPHOLOGICAL study is often helpful in the identification of crystalline solids existing in phase systems. For example, recently optical goniometric studies definitely disproved the existence of $LiNO_3.\frac{1}{2}H_2O$. (Aravamudan and Ramaseshan, 1961). In the study of heterogeneous equilibria, it is essential that the crystal be examined on the goniometer under conditions in which no transformation in the solid phase can occur. It was desirable to extend the utility of goniometry to crystals which are highly hygroscopic or reactive towards moisture or air or which can exist only at low temperatures. With the arrangement for low temperature goniometry described in this paper and that for low temperature X-ray crystallography developed in the authors' laboratory (Singh and Ramaseshan, 1963, 1964), it is hoped to launch upon a systematic programme of phase equilibrium studies at low temperatures. The instrument described in this paper is based on the simple technique of blowing dehydrated air (or any gas) at the requisite temperature on the crystal enclosed in a suitable chamber (*see* for example Kaufman and Fankuchen, 1949).

2. DESCRIPTION OF THE DEVICE

Figure 1 shows the sketch of the arrangement used to obtain dehydrated air (or gas) at different temperatures. Compressed air from a cylinder (200 kg./cm.^{2}, 4 metre^3) is dehydrated as it passes through a steel cylinder (10 cm. diameter and 25 cm. long) containing activated silica gel. The dehydrated air flows through a coil immersed if necessary in a suitable liquid or mixture in an insulated vessel. For room temperature work with hygroscopic crystals, the vessel may be empty. For moderately low temperatures the insulated vessel is filled with a freezing mixture of ice and calcium chloride. If the rate of flow of air is between 0·2 and 0·5 litres per second —which is more than adequate—the air that emerges may have a temperature as low as − 20° C. For lower temperatures the insulated vessel is replaced by a three-litre Dewar flask containing liquid air. For experimentation at elevated temperatures, the chamber is filled with glycerine or oil and heated by an immersion electric heater. One charge of silica gel can be used for about 30 to 40 metre^3 of air or for 24 hours of continuous operation. For continuous operation a battery of compressed air (or gas) cylinders has to be used. After use the silica gel can be rejuvenated by heating it to 110° C.

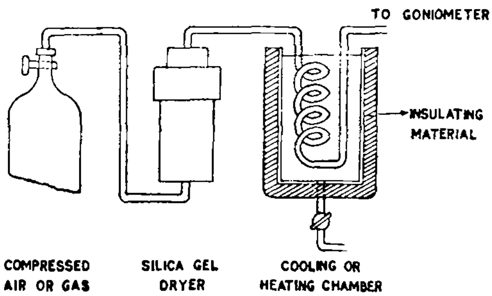

Fig. 1. Device for obtaining dehydrated air (or gas) at different temperatures.

The attachment made for the goniometer is shown in Fig. 2. It consists of a circular " hylam " base plate (3/8″ thickness and 3″ diameter) with three holes in it. The stem of the goniometer head is inserted into the central hole and the other two are used for the inlet and outlet of the dry air. The goniometer carrying the crystal under investigation is enclosed in a rectangular glass cell whose edges fit in the deep grooves machined in the base plate. Silicone grease is used at the joints and grooves to prevent humid air leaking into the system. The stem of the goniometer is fixed to the spindle of a conventional one-circle or two-circle goniometer. A screw fixes the enclosure to the base of the instrument so that when the spindle with goniometer head rotates the enclosing chamber is stationary. Insulated rubber tubes with screw pinch-cocks are used as the connecting leads. A thermocouple is used to measure the temperature.

A rubber stopper plugged into a circular hole on one of the sides of the glass vessel holds a " spanner " by which angular and translational movements of the goniometer head could be made. In actual practice the attachment is moved in or out or rotated till the " spanner " comes exactly opposite the one required of the four adjusting screws of the goniometer head. The enclosure is so set that none of the plane glass sides reflect the incident light into the observation telescope. During a measurement any parasitic re - tion could easily be suppressed by slightly rotating the chamber. It is also found from experience that the preliminary adjustments (Dana, 1945) could be most conveniently made if the top glass surface makes a small angle (3° or 4°) with the axis of rotation.

When the incoming air was cold, it was found that there was deposition of dew on the outside of the glass enclosure. To eliminate this, the arrangement shown in Fig. 2 was made. The relatively wider mouth of the exit tube helped to collect cold air and lead out efficiently the incoming cold air so that the glass walls did not get unduly cold. With this arrangement a better temperature control could be obtained and the current of cold air necessary for maintaining the same temperature was very much smaller. In fact, this arrangement was so efficient that for many hygroscopic crystals, the outer optical glass covering was not all necessary.

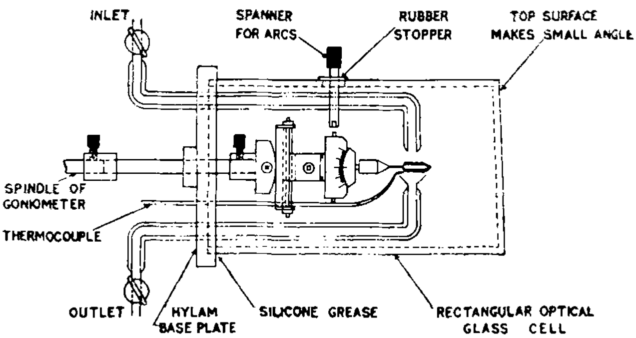

FIG. 2. Low and high temperature attachment to the optical goniometer.

3. Procedure for Mounting

The goniometer head was taken into a cold glove box which contained the crystal under investigation. The crystal was mounted on to the goniometer head with " durofix " or solution of sealing wax in benzene or an alcoholic shallac solution. For studies at elevated temperatures, silicophosphate was used.

When the crystal is mounted, the goniometer stem is slipped through the central hole of the base plate and the rectangular optical glass cover pushed into the groove. Silicone grease is applied to the grooves and outlet tubes. Air is then allowed to flow. All these operations are made in the glove box. The whole arrangement is taken out of the glove box by a special opening in the side.

The stem of the goniometer head is fixed on the spindle of a one-circle or two-circle goniometer. The enclosing optical glass chamber is set at the proper angle and screwed firmly to the stationary base. The preliminary adjustments and the angle measurements are made by the conventional methods.

It must be added that this arrangement was extremely efficient. A crystal of $LiNO_3 . 3H_2O$ remained in its pristine beauty, its faces giving perfect splendent reflections for more than four hours. However, when the flow of the dehydrated air was stopped and the crystal exposed to the atmosphere, it dissolved away within 100 seconds.

4. SOME APPLICATIONS

(*a*) *Variation of interfacial angles with temperature.*—To test the performance of the instrument, the variation of interfacial angles with temperature was measured. A crystal of calcite was fixed to the goniometer head by dental cement and it was subjected to a series of cycles of heating and cooling. Table I gives the interfacial angles for two prominent faces at different temperatures. The interfacial angles at temperatures other than the room temperature were calculated from the shift and direction of the reflected signal as the temperature of the crystal was changed.

TABLE I

Temperature	−70° C.	22° C.	91° C.	172° C.
$10\bar{1}1 \wedge 10\bar{1}0$	45° 32′	45° 26′	45° 22½′	45° 17′
c/a	0·8505	0·8530	0·8548	0·8575
$10\bar{1}1 \wedge \bar{1}101$	74° 45½′	74° 53′	75° 0′	75° 7′
c/a	0·8513	0·8537	0·8559	0·8581
c/a (from thermal expansion data)	0·8520	0·8543	0·8561	0·8585

There is a fair agreement between the values of c/a at different temperatures deduced from the experiment and those computed from thermal expansion data of Srinivasan (1955).

(*b*) *Studies on lithium nitrate crystals.*—The work of Campbell (1942) definitely disproved the existence of lithium nitrate hemihydrate ($LiNO_3 \cdot \frac{1}{2} H_2O$) which Donnan and Burt (1903) had reported. According to these authors, the anhydrous salt separating at higher temperatures (70° to 90° C.) had a different crystal form from the "hemihydrate" crystals which they claimed were formed at about 40° C. This suggested that the morphological study of crystals grown from concentrated aqueous solution by evaporation or by cooling at various temperatures from 0° to 90° C. would be of interest. Using this attachment, these hygroscopic crystals were examined on the optical goniometer. There is no doubt from the stereographic projection (Fig. 3) that all crystals obtained were definitely the anhydrous rhombohedral $LiNO_3$. When the temperature was raised to 120° C., the interfacial angles remained practically the same showing thereby that no phase transformation took place. Our *c*/*a* value at room temperature (0·8111) is well in agreement with that (0·8131) computed from X-ray data (Zachariasen).

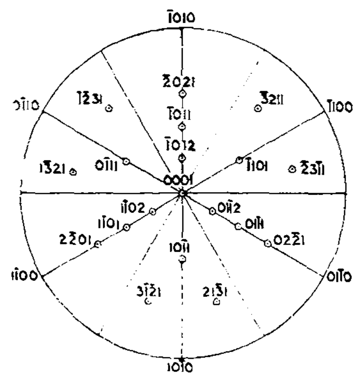

FIG. 3. Stereographic projection of anhydrous lithium nitrate.

5. SUMMARY

Crystals which are hygroscopic or which exist only at low temperatures can be conveniently studied on an optical goniometer with the attachment and method described. The apparatus is simple in design and uses a current of air (or gas) at suitable temperature blowing on the crystal mounted on a goniometer head inside a glass chamber.

6. ACKNOWLEDGEMENT

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