A Mechanically Refrigerated Gas Stream (to \(-120^\circ C\)) and Some Useful Accessories

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A system for cooling a stream of dry air to \(-120^\circ C\) is described. Mechanically refrigerated cooling units are used to maintain the cold baths in which heat exchangers are immersed. Adapters for converting a precession camera to a flat-plate oscillation–rotation camera and for mounting crossed polaroids on the precession camera are described. These devices are particularly useful for examining and aligning crystals grown \textit{in situ} at low temperatures. They can also be used for aligning crystals on the precession camera even when monochromatized radiation is used.

Introduction

A uniform stream of cold gas is an efficient means of cooling samples during low-temperature X-ray diffraction studies (Cioffi & Taylor, 1922; Post, Schwartz & Fankuchen, 1951). The basic gas-stream system consists of a reservoir containing the cryogen, a gas generator with provision for cooling the gas, and an insulated delivery tube for conducting the cold gas to the sample. Provision is also made for measurement of the temperature and for prevention of condensation of atmospheric vapors on the sample.

Some advantages of using this method include minimal absorption by the cooling apparatus, reasonably constant temperatures and, if necessary, means for easily growing single crystals from materials that are liquids or gases at room temperature. A major disadvantage of most of the systems described in the literature is that they require the use of consumable cryogens which must be purchased and fed to the system on a regular basis.

It has recently been shown that a heat exchanger immersed in a bath cooled by a mechanical refrigerator can be used for cooling a gas stream (Rudman, 1972; Marsh & Petsko, 1973). Temperatures as low as \(-70^\circ C\) were reported. However, for many investigations lower temperatures are needed.

In this paper, a system utilizing a refrigerated Dewar operating at a temperature of \(-135^\circ C\) is described. An efficient heat exchanger and a vacuum-insulated gas transfer line result in a sample temperature of \(-120^\circ C\). The measures used to dry compressed air for use at this temperature and several accessories designed for our low-temperature precession camera studies are also described.

As Coppens & Vos (1971) have shown for cyanuric acid, the major reduction in thermal motion takes place between room temperature and \(-115^\circ C\). Although many systems utilizing liquid nitrogen are designed to operate at \(-150^\circ C\), it is clear that the slight increase in thermal motion that would be present at \(-120^\circ C\) is more than compensated for, in most cases, by the convenience of not using consumable cryogens.

Low-temperature system

A schematic diagram of the system, which is an improved version of a previously described system (Rudman, 1972), is shown in Fig. 1. Cooling is accomplished through the use of commercially available refrigeration units (see Appendix).

Compressed air is obtained from a large compressor with standard drying tanks. The air is delivered to the laboratory at 7 kg/cm$^2$ pressure with a flow rate up to 40 l/min. The air is further dried by passing it through two coarse filters and two self-regenerating molecular sieve air dryers. It is then divided into three air streams (to be cooled in the heat exchanger; to furnish a warm outer stream; and to mix with the cold air for temperature control). The cooling gas stream then passes through a precooler consisting of 6 m of copper tubing immersed in a cold bath \((-85^\circ C)\) of methanol which is cooled by a refrigerated flexible probe. A chamber (4 cm diameter and 20 cm long) is located inside this cold bath on the inlet side of the copper tubing heat exchanger. This serves to allow the condensation of any residual moisture or oil without restricting the passage of air through the narrow copper tubing (Owen & Williams, 1954; Harding, 1956; Olovssen, 1960).

The precooled air (at \(-70^\circ C\)) now passes through a 15 m copper coil heat exchanger inside a 4 l refrigerated Dewar containing freon-12 at \(-135^\circ C\). This refrigerated Dewar is furnished with a magnetic stirrer and a temperature programmer for maintaining a desired rate of cooling or a preset temperature.

A plastic cover, which prevents moisture from entering the refrigerated Dewar, is sealed in place with silicone sealant. All connections through the cover are also sealed in place. One of the tubes passing through the cover contains two thermocouples which are used to check the level of freon in the Dewar. One of the thermocouples is fixed as a reference point at the
bottom of the tube (and Dewar), while the other can be lifted within the tube. If the movable thermocouple registers a higher temperature than the reference thermocouple, then the amount of freon to be added can be ascertained by referring to a previously calibrated scale attached to the tube. In practice it has not been necessary to add any freon over a three month period.

The temperature of the air as it leaves the refrigerated Dewar is \(-128^\circ\)C. The air passes through a specially designed evacuated glass transfer line. This transfer line is attached to the heat exchanger within the Dewar by means of a modified compression fitting. A standard outer stream is located at the end of the transfer line, which also has an inlet for a warm gas-stream (for controlling the temperature of the cooling gas-stream). The temperature of the crystal can be adjusted to any temperature between ambient and \(-120^\circ\)C if a constant air flow of 8 l/min is used.

The stability of the crystal temperature, under constant operating conditions, is 0.5\(^\circ\) over several months duration. (It has been noticed that if the temperature of the room changes drastically for some reason, e.g. if the air conditioning is shut off, then a 7\(^\circ\) change in room temperature results in a 1\(^\circ\) change at the crystal.)

**Crystal growth**

Crystals of materials which are liquids at room temperature can be grown in the usual manner (Rudman, 1976). In addition, it is possible to use the built-in temperature programmer to control the temperature of the refrigerated Dewar. Cooling rates between 0.5\(^\circ\)/h and 1\(^\circ\)/min can be selected.

This apparatus has been used on a precession camera. The transfer line is located in the plane of the collimator in such a manner that the axis of the goniometer head (and sample tube) is collinear with the cold gas stream when the precession camera arc is turned to a horizontal position and set at \(\mu = 30^\circ\). This configuration ensures a uniform temperature gradient along the sample tube and facilitates crystal growth. Once the crystal is grown, precession photographs (both Polaroid and regular film) can be obtained in a normal manner.

**Crossed-polaroid adapter for precession camera**

The precession camera employed uses a side-mounted telescope for observing, centering and aligning the crystal. This arrangement does not permit the construction of a simple crossed-polaroid device for use in studying and aligning single crystals grown \textit{in situ} (Post \textit{et al.}, 1951). The mirror support that comes with the precession camera was modified by replacing the mirror with a crossed-polaroid holder and a second telescope was mounted above the crystal, parallel to the axis of the precession camera (Fig. 2). The telescope can be swung out of the way during data collection.

**Adapter to convert precession camera to oscillation-rotation camera**

A reversible, high-torque (100 in oz), low speed (\(\frac{1}{2}\) r.p.m.) motor with adjustable limit switches attached to a mounting bracket was designed and built. The shaft of the motor is mounted collinearly with the spindle axis of the precession camera (when \(\mu = 0^\circ\)) without requiring any modification of the precession camera (Fig. 3). This device can be mounted and removed without disturbing the camera or crystal alignment.

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**Fig. 1.** Schematic diagram of the low-temperature system. Dry air is passed through a pre-cooler which is cooled by a mechanically refrigerated probe and through a refrigerated Dewar. Minimum temperature at the sample is \(-120^\circ\)C.

**Fig. 2.** Photograph of crossed-polaroid adapter mounted on precession camera. A second telescope, mounted parallel to the camera axis, is used for observing the crystal between the crossed polaroids.
It can be used to obtain flat-plate rotation or oscillation photographs with regular or Polaroid film. The oscillation range is completely adjustable from 5 to 300°.

This adapter has several applications, especially for single crystals grown in situ, including the following.

(a) Simplified single-crystal alignment, even with monochromatic radiation (Rudman, 1968).

(b) Detection of twinning in crystals (Rudman, 1968).

(c) Alignment of highly disordered single crystals (with few observable reflections).

(d) Rapid survey of the diffraction pattern at high or low temperatures.

(e) Conversion of precession camera to flat-plate powder camera.

(f) By locking the spindle and loosening the screw controlling the goniometer head translation, it is possible to translate the sample during crystal growth, using the zone refining and/or temperature gradient methods (Rudman, 1976).

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APPENDIX

Refrigerated Dewar: Model MC-4-128-MS, F.T.S. Systems, Inc., P.O. Box 158, Stone Ridge, N.Y. 12484, U.S.A.

Refrigerated probe: Model CC-100F, Neslab Instruments, Inc., 891 Islington St., Portsmouth, N.H. 03801, U.S.A.

Air dryer: Self Regenerating Dry-Pak, Model 4103-3, Wilkerson Corp., Englewood, Colorado 80110, U.S.A.

References


