AN EFFICIENT METHOD FOR RECORDING LOW TEMPERATURE X-RAY DIFFRACTION PHOTOGRAPH

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A new experimental technique has been developed for taking X-ray photograph within the range of gaseous nitrogen temperature. The special Nonius integrated Weissenberg camera was used to record the full range of intensity data. A metal dewar of special design was constructed and a steady temperature anywhere from room temperature down to −185°C or so was obtained.

Introduction

Low temperature X-ray diffraction technique not only makes possible the study of single crystals of interesting substances which are liquids or gases at room temperature and the phase change of certain compounds, e.g. methyl ammonium alum[1] at 170°K, but also makes available a convenient means of increasing the quantity and improving the quality of intensity data obtainable from many crystalline solids. Further, the thermal vibrations of the atoms are greatly reduced at low temperature and hence the anisotropy due to thermal vibrations is reduced to a great extent.

The standard errors in structure analysis are decreased both by a reduction in the ΔF's and increase in the curvatures of electron density at peak centres. At low temperature the intensities of reflexions, especially at higher angles, are enhanced and can be measured with a good deal of accuracy. Moreover, the peak curvatures are increased as a consequence of reduced thermal vibrations, and it is possible that the standard errors in many complex structures can be reduced by a factor of two by recording X-ray diffraction data at low temperature.

The technique discussed in this paper was developed by the author at the Crystallographic Laboratory of the University of Manchester Institute of Science and Technology, England, in 1966. The photograph was recorded on a special Weissenberg camera built on the technique as developed by Krueger,[2] and Fletcher.[3] But there were certain obvious disadvantages in these methods. The most important of them is that the glass dewar which is used as a delivery tube becomes soft after being exposed to a low temperature for a considerable time. Since tubes with sufficiently high vacua cannot be obtained easily from commercial suppliers, it causes great difficulty in replacing them during exposure. Loss of temperature also occurs when the delivery component is connected to the exit component of the nitrogen container. The minimum temperature obtained by these methods is about −160°C. The method of obtaining a cold stream of nitrogen is quite unsatisfactory for the special Weissenberg goniometer.

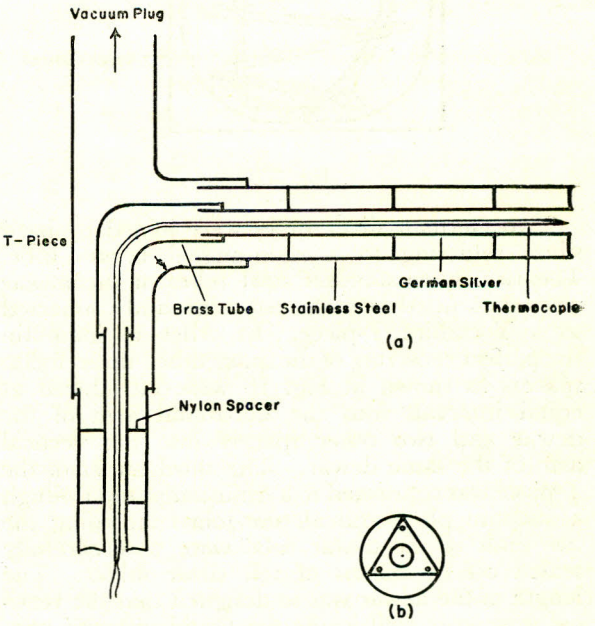

Fig. 1

In view of this, a metal dewar of new design was constructed and it was fitted to the specially constructed liquid-nitrogen container and connected to the Weissenberg goniometer.

The High-Vacuum Delivery Tube

Because of differential expansion and contraction, the outer tube of the metallic dewar was of stainless steel having the dimensions external diameter $\frac{1}{2}''$ and thickness $1/8''$, and the inner tube was of German silver having the external diameter of $3/16''$ and thickness of $\sim 1/100''$. The dewar which was made right angled was constructed as follows (Fig. 1a).

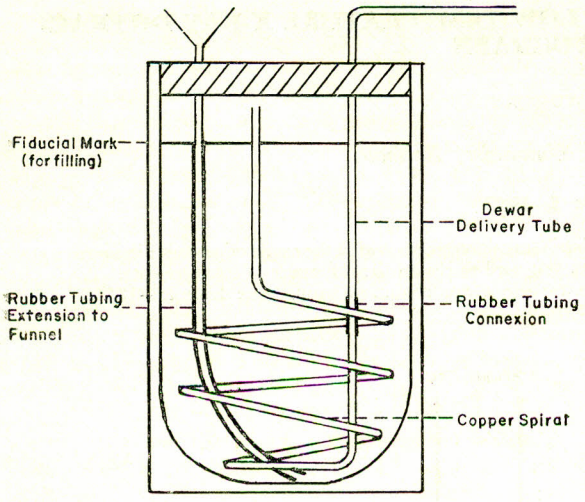

Fig. 2.

Two German silver tubes were joined by hard silver soldering to a right-angled brass tube. The two outer stainless steel tubes of the dewar were then fitted over the two arms and connected to a Yorkshire T-piece. In order to maintain the perfect centering of the inner tube, three nylon spacers as shown in Fig. 1b were introduced at equal intervals into the horizontal arm of the dewar and two other spacers into the vertical arm of the same dewar. The third outlet of the T-piece was connected to a diffusion pump through a vacuum plug, and all the joints including the two ends of the dewar tube were very carefully sealed off by means of soft silver solder. The length of the dewar was so designed that the vertical arm went well inside the liquid nitrogen container (Fig. 2) and was connected to a hollow copper spiral placed in it. The horizontal arm of the dewar reached conveniently into the vicinity of the crystal. The annular space was constantly evacuated by a diffusion pump throughout the exposure period so as to maintain a vacuum of the order of 10^{-6} mm of Hg.

Liquid-Nitrogen Container

The cold nitrogen reservoir which was fitted with a lid having two holes was a 5-litre flask. A funnel was fitted in one of the holes for pouring in liquid nitrogen. In order to avoid surface disturbances when the liquid-nitrogen supply in the flask was replenished, a piece of rubber tubing, long enough to ensure that the inflowing liquid entered at the bottom, was attached to the funnel. The vertical arm of the metal dewar was introduced through the other hole of the lid. A hollow copper spiral tube of internal diameter about 1 cm, the other end of the spiral being well above the liquid level, was connected to the metal dewar by means of a short piece of rubber tubing. A mark was put on the outside of the container and this indicated the height of the entrance end of the spiral. Care was always taken to ensure that the level of the liquid nitrogen in the container did not rise above that of the open upright end of the spiral. The level of the liquid nitrogen in the stem of the funnel was checked with a gauge on which the difference in height between the fiducial mark and the top of the funnel was clearly shown. The gauge was simply a piece of plastic covered copper wire (insulated electrical conducting wire), one end of which was made to touch the surface of the liquid nitrogen. The level of the liquid in the stem of the funnel was at any time above that of the rest of the liquid in the container because of the small pressure acting on the surface of the liquid. In order to boil the liquid nitrogen, a heating coil was introduced into the reservoir and was connected through a variable resistance to a battery.

Measurement of Temperature

In order to measure the temperature of the outflowing nitrogen stream bathing the crystal, a precalibrated copper–constantan thermocouple of very fine wire was introduced into the metal dewar so that the hot junction of the thermocouple went near the end pointing towards the crystal and the cold junction of the same was put into the liquid-nitrogen container. The thermocouple was then joined to a galvanometer through a variable resistance.

The thermocouple was calibrated with its cold junction in liquid nitrogen and the hot junction at the following thermometric fixed points: (1) the boiling point of liquid nitrogen (−196°C), (2) the boiling point of liquid oxygen (−181°C), (3) the melting point of pure ethyl alcohol (−114.5°C), (4) the sublimation point of carbon dioxide (−76°C), (5) the melting point of ice (0°C) and (6) the room temperature. The current through the thermocouple was indicated by the deflection scalamp galvanometer.

Mounting and Setting the Crystal

The crystal was mounted in the following way. The closed end of a tube was broken and the inside wall of the capillary tube was smeared with glue by means of a small glass rod and finally sealed with a very small flame. The specimen (the crystal) was then made to roll down the tube until it reached the adhesive. It was then held with a glass rod having some glue at the end of it so that it could not touch the wall of the tube.

When the adhesive set, the segment of the tube was broken off and sealed in a flame. This was then attached to the goniometer head with plasticine, the shape of which was adjusted for any vertical zone axis of the crystal. The plasticine was then coated with dental cement (fast drying acrylic cement) which was allowed to set, and the orientation of the crystal was completed by adjusting the goniometer arcs. As the acrylic cement has a negligible thermal coefficient of expansion, orientational disturbances due to the thermal expansions were found to be negligible.

Exposure at Low Temperature

The liquid-nitrogen container wa splaced in an adjustable platform just near the shield tube of the Weissenberg camera and the delivery component of the dewar was made in line with the shield tube. Prior to exposure at a low temperature, the crystal was set at room temperature and the camera with loaded films was kept in position. The camera was then covered with a polythene enclosure made for the purpose. The enclosure was provided with two windows—one for introducing the delivery end of the dewar and the other was used for adjusting the camera, if necessary. The metal dewar was then evacuated by means of a diffusion pump permanently connected. When a sufficiently high vacuum (10^{-6}mm of Hg) was obtained, the container was gradually filled with liquid nitrogen and the temperature and the flow of the outgoing gas were adjusted by the heating coil. When a perfectly steady flow of nitrogen was obtained, the window of the enclosure was quickly opened and the liquid container was slowly pushed forward so that the metal dewar with its level frame provided in the special Weissenberg goniometer, just slid through the shield tube of the goniometer. The window was then immediately closed. By adjusting the flow and the temperature of the gas stream, the crystal was gradually cooled to the required temperature. The exposure was then started. A heating coil was also introduced into the metal dewar in order to maintain a steady temperature anywhere between room temperature and–185°C or less.

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References

1. R.O.W. Fletcher and H. Steeple, Acta Cryst., **17,** 290 (1964).
2. A. Krueger, Acta Cryst., **6,** 348 (1955).
3. R.O.W. Fletcher, Ph.D. Thesis, University of Manchester (1962).