An Automatic System for X-ray Studies of Phase Transitions at Low Temperatures

BY R. CLARKE AND R. E. MORLEY

Wolfson Unit for the Study of Phase Transitions in Dielectrics, Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, England

(Received 28 May 1976; accepted 18 July 1976)

A low-temperature system is described for the automatic recording of lattice-parameter variations in crystals down to $-185^\circ$C. The design is based on a continuous gas-flow method with 'three-term' control of the local gas temperature to within $\pm 0.5^\circ$C. The temperature can be programmed up or down over a range of 200°C. Consumption of coolant (~1 l h$^{-1}$) is minimized by automatically decreasing the rate of gas flow as the temperature is increased. Results obtained for the structural phase transition in $\text{Sn}_{0.65}\text{Ge}_{0.35}\text{Te}$ are presented.

1. Introduction

Multiple-exposure X-ray techniques, which allow the variation of single-crystal lattice parameters to be measured precisely from ambient to high temperatures, have been developed by Glazer (1972). These techniques have proved particularly useful in the study of structural behaviour in the vicinity of solid-state phase transitions, for example in $\text{NaNbO}_3$ (Glazer & Megaw, 1973) and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (Clarke & Glazer, 1974; Clarke & Whatmore, 1976). This paper describes a system which enables the 'continuous' recording of single-crystal lattice parameters to be extended to temperatures below ambient.

2. Design requirements

There are several existing designs for cryogenic attachments to X-ray goniometers (see the review by Post, 1964) and many, for ease of manufacture and flexibility of use, employ a continuous flow of gas to cool the crystal. However, none are immediately compatible with the special requirements of the continuous-recording technique. These requirements may be stated as follows: (i) The measurement of the lattice parameters on a single film over a temperature interval of 200°C can take up to 24 h in a typical continuous-recording run. For this, efficient use of cryogenic fluid and a long-term temperature stability of at least $\pm 1^\circ$C are required. (ii) It must be possible to programme the temperature up or down over an interval of about 200°C, and at rates as low as 1°C h$^{-1}$. Furthermore, the design should allow this to be done automatically so that the equipment does not require constant attention. (iii) It is necessary to displace the film cassette through small steps (of around 1 mm) parallel to the camera axis during the course of a run, with a total displacement (~18 cm) sufficient to permit a complete run to be photographed on a single film. (iv) It must be possible for the film cassette to be loaded and unloaded while the crystal is held at any temperature; this enables a run to be carried out both on heating and on cooling.

Added to these requirements are several others which would apply to any X-ray cryostat, such as the ability to oscillate the crystal freely, minimal loss of incident and scattered X-ray intensity, small thermal gradients and instabilities, and no icing up of the crystal, the body of the cooling device or the film cassette.

3. Design of system

The system described in this section was designed to attach to a Weissenberg camera (Stoe & Cie). This camera can be used with a double-radius (57.3 mm) cassette giving the advantages of a large amount of space inside the cassette and of higher resolution on the film.

To achieve the low temperatures required, gas is boiled off from a 25 l Dewar containing liquid nitrogen by means of a small immersion heater; the gas is fed through a short vacuum-jacketed ($10^{-6}$ mm Hg) transfer tube to the low-temperature attachment. The general arrangement of the gas-flow system can be seen in Fig. 1. A thermistor is placed near the bottom...
of the liquid nitrogen and set to switch off the system if the Dewar boils dry. After passing through a small coiled nichrome wire heater (Fig. 2) the cooled nitrogen gas is directed through a nozzle on to the crystal, which is mounted on the tip of a copper-constantan thermocouple (36 S.W.G.) with Durafix glue. This heater controls the temperature of the gas passing over the crystal and is driven by a three-term temperature controller. The design of the controller, together with that of the temperature programmer, has already been described by Bett & Glazer (1972). For low-temperature operation the thermocouple has a reference junction at \(-196{\degree}C\).

An important feature of the design is the way that the gas is made to pass over and around the crystal area three times by means of mylar baffles [see Fig. 3(a)]. This has the effect of reducing thermal gradients and increasing the efficiency of cooling at the crystal (Sugino, Hidaka & Okazaki, 1973). A close-up photograph of the low-temperature attachment is shown in Fig. 4. Icing up of the crystal is prevented by totally enclosing the attachment with a brass cylinder covered inside and out with a thin layer of expanded polystyrene. The cylinder has a slot cut in it so that it can also act as a screen for isolating the zero layer on an oscillation photograph; this slot is covered on the inside and outside with mylar film to form a double-walled window [see Fig. 3(b)]. The outside of the window tends to ice up at the lowest temperatures, but this can be prevented by blowing a gentle stream of air between the attachment and the film cassette.

The need for temperature programming over a wide range, as mentioned in § 2, and for low consumption of liquid nitrogen, means that the rate of gas flow has to be decreased as the temperature is programmed up towards ambient. This is achieved by subtracting automatically the set-point voltage from a preset reference,
V₀ (see Fig. 5). The difference signal is then fed to an output stage supplying power to the heater inside the Dewar. In this way the rate of flow automatically rises from a preset minimum value at ambient to a maximum at -196°C. To the authors' knowledge this feature is unique among continuous-flow designs. It should be emphasized here that temperature control is achieved solely by the three-term controller supplying power to the heating coils in the nozzle (Fig. 2), and not by varying the gas flow. This is only adjusted to the minimum required for precise control at any given temperature in order to economize on liquid nitrogen.

4. Performance

The system described above is capable of being programmed automatically at rates between 1 and 1000°C h⁻¹, from the lowest temperature obtainable (about -185°C) to about 45°C, and vice versa, with a stability of ±0.5°C at ambient and ±0.25°C at -185°C. The radial temperature gradient, measured at -150°C using a differential thermocouple, was less than 0.25°C mm⁻¹ at the crystal increasing to about 3°C mm⁻¹ at the surface of the inner mylar baffle [Fig. 3(a)]. In the direction of the gas flow the temperature gradient was negligible on the camera axis rising to about 6°C mm⁻¹ at the surface of the inner mylar baffle. We can safely say, therefore, that by careful positioning of this baffle with respect to the crystal, the temperature difference over the length of the crystal (~0.1 mm) will be less than 0.1°C. The minimum time required to attain -185°C is about 30 min and the consumption of coolant at this temperature is approximately 1.5 l h⁻¹, averaging about 1.0 l h⁻¹ over a typical run. Using a 25 l Dewar the apparatus can therefore be left for about 24 h without attention.

The results of a typical low-temperature run are shown in Fig. 6. The photograph shows the related 444 and 444 reflections of a twinned crystal of Sn₀.₆₅Ge₀.₃₅Te recorded sequentially on the same film at 4°C intervals as the crystal undergoes a transition from a low-temperature rhombohedral phase to a cubic phase possessing the NaCl structure (Briere, Muldawer & Beckman, 1963). The temperature in the experiment was increased at a rate of 6°C h⁻¹, each exposure taking 45 min, and the whole run took about 20 h to complete. The thermocouple EMF was monitored using a DVM having a 10 µV sensitivity and the corresponding temperature was read from calibration tables (National Bureau of Standards, 1974). The details of the continuous-recording technique are discussed fully by Glazer (1972) and will not be described here. The rhombohedral angle, which is measured by the splitting in Fig. 6 of the 444 and 4444 reflexions, is plotted in Fig. 7 in order to show the precision with which lattice parameters can be obtained with this method. The transition temperature is seen to be -21.5°C and agrees well with previous estimates (-21.0°C by ultrasonic measurements; W. Rehwald, private communication), showing that the absolute measure of temperature is correct to within ±0.5°C.

The system has also been used successfully to in-
investigate the low-temperature phase transitions of BaTiO$_3$ (Clarke, 1976). In addition to the continuous-recording capabilities of this system it can also be used for standard low-temperature crystallographic studies requiring, for example, oscillation, or zero and limited upper-layer Weissenberg photographs.

One of us (R.C.) wishes to thank the Wolfson Foundation and the Science Research Council for financial support. We are grateful to A. M. Glazer for useful advice and to G. K. Lang (RCA, Zürich) for supplying crystals of (Sn, Ge)Te.

References


