A Microprocessor-Controlled Continuous-Flow Cryostat for Single-Crystal X-ray Diffraction in the Range 10–300 K

BY S. ALLEN, J. COSIER, A. M. GLAZER, T. J. HASTINGS, D. T. SMITH AND I. G. WOOD
Clarendon Laboratory, Parks Road, Oxford OX1 3PU, England

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Abstract
A low-temperature attachment for Weissenberg cameras operating in the range 10–300 K is described. It consists of an Oxford Instruments continuous-flow helium cryostat and a laboratory-built microprocessor-based temperature controller. The temperature stability and accuracy of the controller are both better than ±0.1 K over the entire range of operation. Helium consumption is 0.2 l h⁻¹ at 200 K, 0.3 l h⁻¹ at 100 K, 0.65 l h⁻¹ at 30 K and 1.5 l h⁻¹ at 10 K. Slight modifications to the Weissenberg camera enable it to be operated in a continuous-recording mode, in which a series of oscillation photographs may be taken at different temperatures. The very sophisticated temperature programming system allows complex experiments of this type to be carried out automatically, requiring no intervention by the operator.

Introduction
The examination of materials under non-ambient conditions of temperature and pressure is becoming an increasingly desirable feature of modern crystallographic research. In particular, experiments carried out at low temperatures are of interest to a wide variety of workers, since as well as their obvious applications in the fields of structural phase transitions and structure-property relations, they are also necessary when very accurate determinations of electron density are made. Unfortunately, the nature of most X-ray crystallographic apparatus, involving restricted working spaces combined with fine mechanical tolerances, is such that the incorporation of cryogenic attachments often presents severe problems. These difficulties have led to the development of a large number of instruments [Rudman (1976) lists over 400] which are often very similar in nature; indeed, for temperatures accessible using liquid nitrogen as a refrigerant it must now be considered that further basic development of new instruments is probably not required. For temperatures below about 80 K, however, the position is less satisfactory, since the cryogenic problems, usually involving the use of liquid helium as a refrigerant, are far more severe. The approach adopted in previous designs of apparatus for use in this region varies considerably. In one extreme case (Chieh, Stokhuyzen & Beck, 1977) the entire X-ray camera is immersed in liquid helium, whilst other apparatus (Woodard & Straumanis, 1971; Samson, Goldish & Dick, 1980) involves the use of pressurized-helium closed-style refrigerators requiring no supplies of liquid cryogens. The majority of recent designs, however, use helium cryostats, which may be either of fairly conventional design requiring vertical operation (see e.g. Thomas, 1972; Odou & More, 1975; Maeta, Kato & Okuda, 1976; Hohlwein & Wright, 1981), or may operate using remote reservoirs, with continuous transfer of liquid helium via flexible linkages (Coppens, Ross, Blessing, Cooper, Larsen, Leipoldt, Rees & Leonard, 1974; Albertsson, Oskarsson and Stahl, 1979). An alternative method of cooling, which has particular advantages over reservoir cryostats when the available working space is limited, is the continuous-flow cryostat, in which the sample chamber is cooled by drawing past it a flow of helium vapour. When carefully designed, such cryostats can be extremely economical in consumption of helium (see e.g. Edmonds & Mailer, 1977), and they may readily be adapted for use in diffraction experiments [a system suitable for neutron diffraction has been described by Herbert & Campbell (1977)].

The particular application for the low-temperature system described in the present work was the study of solid-state phase transitions below 80 K, using the continuous-recording method (Glazer, 1972). This method requires the taking of a number of oscillation photographs at different temperatures, with the film cassette translated by a small distance between each exposure. The temperature dependence of the lattice parameters, intensities of particular Bragg reflections and also the thermal hysteresis and domain behaviour of the specimen may be readily determined in this way. The apparatus used is a slightly modified Weissenberg camera and some experience had already been gained in adapting this system for low-temperature work down to liquid-nitrogen temperatures (Clarke & Morley, 1976). The principal requirements of the proposed new apparatus were that:
(a) it should operate down to at least 10 K;

(b) it should be able to make scans over a wide range of temperature and be able to operate continuously for about 48 h;
(c) a large region of reciprocal space should be available for examination;
(d) the cooling device should be adaptable, with as few modifications as possible, to modern, horizontally operated Weissenberg cameras;
(e) the system should be amenable to use with a computer-based control system (Cosier, Glazer, Hastings, Smith & Wood, 1981), allowing complex experiments to be carried out without operator intervention.

Points (d) and (e) above are, perhaps, worthy of further comment. Weissenberg cameras currently manufactured are designed to operate in a horizontal position and, whilst it may be possible to modify them to operate vertically their mechanical system is not usually suitable for supporting the weight of a cryostat. Thus if systems such as that of Thomas (1972) are to be employed they will now require the construction of an entire Weissenberg camera in addition to the cryogenic equipment. For this reason it was felt that the present apparatus, requiring the minimum of camera modification, would offer considerable advantages. The use of the equipment in conjunction with a microprocessor-based control system is essential in the present application where the experiments are often of long duration and require very sophisticated temperature programming. Cryogenic systems requiring manual intervention by the operator (for example to refill reservoirs or reset flow rates) were therefore considered to be unsuitable. We believe that the apparatus described below successfully meets all these design criteria and thus provides a useful facility for general crystallographic research as well as phase-transition studies. The temperature controller/programmer is probably the best and certainly the most flexible currently available. It is potentially applicable to a wide variety of crystallographic problems in addition to its present use.

Cryogenic hardware

(a) Camera modifications

The only modifications necessary to the X-ray camera involve the introduction of a low-conductivity heat path between the cold goniometer head and the camera headstock (which remains at room temperature) and the provision of O-ring vacuum seals on the oscillation shaft and headstock (see Fig. 1, Fig. 2). These seals, which remain at room temperature, prevent loss of helium gas to the atmosphere and air leaks into the helium space: the helium system operates at a pressure of approximately 40 kPa (300 torr) and so only gross leaks need be eliminated. In the case of our camera (a Research Engineers Ltd Leeds Weissenberg camera), these modifications necessitated the removal of approximately 4 cm from the camera headstock, so as to give a headstock-to-crystal distance of about 12.5 cm. The oscillation shaft was replaced by a hollow stainless-steel spindle (8 mm outer diameter, 0.5 mm wall thickness) to which copper baffles were attached, an arrangement which provided adequate mechanical strength combined with low thermal conductivity. The crystal is mounted on a commercially manufactured miniature goniometer head (Stoe & Cie Ltd). We found it desirable to reduce further the size of this goniometer head in our workshops, though this is not essential. The film holders used for Weissenberg photographs and accurate lattice-parameter studies are of 57.3 mm radius. The construction of the cryostat does, however, allow Laue and oscillation photographs to be taken using a standard 28.65 mm radius film cassette.

Although built for use with the very versatile Leeds Weissenberg camera, which may operate either horizontally or vertically, the cryostat may also be used in conjunction with the modern, horizontally operated...
Weissenberg cameras which are commercially available at present. A similar system, for use with a Stoe Weissenberg camera (Stoe & Cie Ltd) is currently in use at the University of Cambridge – only minor modifications to this camera were required.

(b) The cryostat

After discussions with the Oxford Instrument Co. Ltd we purchased a specially designed version of their continuous-flow cryostat. This is shown schematically in Fig. 1. The cryostat is attached to the camera headstock by a clamp incorporating an O-ring seal. Apart from a support (remote from the camera) for the helium transfer-line coupling, no further clamps are required. This means that the left-hand side of the Weissenberg camera is completely unrestricted, allowing collimators, layer-line screens, film holders, etc. to be exchanged at will. The inclination angle of the camera may also be altered, even with the specimen at low temperature, in the usual way. The design of the cryostat allows inclination angles of at least 25° to be used. During operation liquid helium is drawn from a large storage vessel (50 or 100 l) through a flexible vacuum-insulated transfer line (see Fig. 3). The refrigerant passes directly to the heat-exchanger block (Fig. 1), which incorporates a labyrinth, 30 W electrical heater and a temperature sensor. A continuous jet of helium issues from the nozzle and passes over the crystal (and thermometer if present), goniometer head and baffles before entering a second heat exchanger mounted on the radiation shield (Fig. 1). The refrigerant flow is produced by a low pressure on the return side of the circuit, which is maintained by means of a diaphragm pump (Fig. 3). The flow rate is determined by a motorized needle valve (Fig. 1). Temperature sensing is currently carried out using ultra-miniature diodes (Lake Shore DT-500P/GR-U; 1 mm diameter x 4 mm length), one of which is permanently mounted in the heat-exchanger block. For routine work this is an adequate thermometer; when higher precision is required a second diode mounted on the goniometer head and in direct thermal contact with the specimen may also be employed.

The three cryostat windows (inner case, outer case and radiation shield) are of Melinex and have a total thickness of 0.2 mm. They allow examination of a 20° range of 20 (symmetrically positioned about 20 = 90°), covering an angular range of greater than ± 25° from the equatorial plane of a normal-beam photograph. The X-ray transmission of these windows, which produce a reduction in beam intensity of approximately 30% with Cu Kα and 4% with Mo Kα radiations, is quite satisfactory with no regions of unacceptably high background. Since the windows are uncoated, the specimen may be examined optically using the microscope attached to the Weissenberg camera, although reflection of light from the inner windows does reduce the image quality. Provided that a low-power (approximately 50 mm focal length) objective is used, however, this is not a serious problem. The large window size (40 mm diameter, 20 mm width) inevitably leads to some ‘crinkling’ of the outer window, produced by the atmospheric pressure. This is undesirable since, as well as affecting the optical clarity of the window, it can also produce regions of rapidly varying background in the diffraction pattern. Alternative window materials have been considered, but the recent article by Ewen, Wirth & Hallock (1981) suggests that, with the exception of beryllium, no material significantly superior to Melinex is available. Melinex windows do have some advantages over beryllium as they are optically transparent and are much easier to fabricate.

The thermal insulation of the cryostat is produced by a vacuum space between the inner and outer cases (Fig. 1). We have found it advisable to evacuate this space continuously using a 1 inch (25 mm) oil diffusion pump, which maintains a vacuum of approximately 1 mPa (10⁻⁵ torr). The crystal and goniometer head are thermally isolated from the camera headstock, which always remains at room temperature, by the poor thermal conductivity of the stainless-steel oscillation shaft, which is able to maintain the required temperature gradient (25 K cm⁻¹) without excessive heat transfer to the crystal. Even when operating for long periods at the lowest temperatures the headstock and associated moving parts of the camera remain warm; we have thus encountered no mechanical problems when operating the system.

Control system hardware

In addition to the cryogenic requirements, i.e. control of helium flow rate and of electrical power to the heat exchanger, the system, as used for the study of phase transitions, also required facilities for temperature programming and for control of an X-ray beam...
shutter and film incrementing motor. In particular, it was necessary that the temperature-controller/programmer should be able to carry out long and relatively sophisticated experiments, consuming as little helium as possible, without supervision by the operator. Previously we had developed just such a control system, based on an Intersil IM6100 microprocessor which is software compatible with PDP8 computers, for use with a high-temperature X-ray camera (Cosier, Glazer, Hastings, Smith & Wood, 1981). The present system is an extended version of our original microprocessor-based controller, but with a larger memory to allow high-level language operations during the course of an experiment.

A block-diagram of the system is shown in Fig. 4. It consists of a series of modules which plug into a 12-bit address/data bus. The control panel is used primarily for system development and program debugging, working programs being stored on audio-cassette (Smith, 1978). 16K words (12-bit) of random access memory (RAM) are included. Progress of the experiment may be monitored continuously by a five-digit display module. This will display one of 12 software-controlled channels, selected by a switch. A digital clock and printer enable information to be output during the course of an experiment; the clock gives an interrupt signal every 20 ms, which is used in control timing.

The temperature-sensing diode is fed with a bias current of 10 μA. The diode forward-bias voltage varies from about 0.4 V at room temperature to 2.7 V at 4 K. This voltage is amplified (×3.3) and then fed into a 16-bit analogue-to-digital convertor (ADC) with a 10 V input range, thus producing a change of 1 bit for about every 50 μV change in diode voltage. The temperature resolution is then 0.018 K bit⁻¹ above 35 K, rising to 0.007 K bit⁻¹ below 20 K.

The main temperature control output is from a 12-bit digital-to-analogue convertor (DAC) to a 30 W linear amplifier and heater. Coarse temperature control is achieved by a motorized needle valve, activated by a relay, which regulates the flow of helium gas. Other relay outputs are used to control the X-ray beam shutter and film incrementing motor.

Control-system software

Two distinct programs are used, which operate by time-sharing the central processor unit (CPU) on an approximately equal basis.

The first of these programs is a high-speed machine-coded program [similar to that used by Cosier et al. (1981) for high-temperature work] which controls the experiment and therefore has ultimate priority in the CPU. This program updates (every 40 ms) the crystal-temperature measurement, the three-term temperature control, the set-point temperature, the refrigerant flow, the X-ray shutter and film increment, the printer, the digital display and the system diagnostics. The temperature control loop requires the conversion of the digitized diode voltage to true temperature readings. This is carried out using a series of 28 segmented straight-line fits, producing maximum errors in the derived temperature of ±0.1 K. The three-term (proportional, integral and differential) control routine holds the required set-point temperature to a stability of ±0.05 K or better, the control constants being automatically compensated for the reduction, by a factor of 100, in the heat capacity of the cryostat as it cools. In addition to this fine temperature control via the power output to the heater in the heat-exchanger, the refrigerant flow rate is also varied (via the motorized needle valve) so as to give just sufficient excess cooling to allow stable temperature control to be achieved by the three-term controller. This ensures that the system operates at all temperatures with the minimum consumption of helium.

The program also incorporates diagnostic checks on the experiment. For example, if a large temperature error, due to lack of refrigerant flow or a broken electrical connection, is found, then the system will automatically shut down safely.

The second program used by the controller is in a high-level language (Focal). This is an interactive program, proceeding by questions and answers, which enables the operator to input the necessary parameters via a visual display unit (VDU).

The following program options are currently available to the user.

1. Input of data

The data are loaded as a series of PHASES each consisting of one of the MODES shown in Table 1. A MODE is defined by up to six variables (starting temperature, finishing temperature, rate of change of temperature, number of X-ray exposures, exposure time, film increment). This method of programming the experiment, described in more detail by Cosier et al. (1981), has the great advantage that an effectively
Table 1. Temperature/camera programming modes

<table>
<thead>
<tr>
<th>MODE 00 - OFF</th>
<th>This causes the shutter to close, any film increment to cease, the helium flow and heater power to be switched off and the controller program to stop. A system shutdown.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MODE 01 - HOLD</td>
<td>The crystal is held at temperature T1 indefinitely. No film exposure occurs.</td>
</tr>
<tr>
<td>MODE 02 - UNPLAT</td>
<td>The crystal is kept at temperature T1 for the required time. No film exposure occurs.</td>
</tr>
<tr>
<td>MODE 03 - EXPLAT</td>
<td>As above but including an X-ray exposure for the duration of the plateau. The film is incremented at the end of the exposure time.</td>
</tr>
<tr>
<td>MODE 04 - UNRAMP</td>
<td>The crystal temperature is changed from T1 to T2 at the required rate. No X-ray exposure occurs.</td>
</tr>
<tr>
<td>MODE 05 - EXRAMP</td>
<td>The crystal temperature is changed from T1 to T2 during which time one or more exposures of equal temperature span occur. The film is incremented at the end of each exposure.</td>
</tr>
<tr>
<td>MODE 06 - RAMPLAT</td>
<td>The crystal temperature is changed from T1 to T2 in one or more ramps of equal temperature span. After each ramp the film is exposed at constant temperature for the required period and the film is then incremented.</td>
</tr>
</tbody>
</table>

Each mode is specified by the operator in terms of a maximum of eight numbers, and can be performed with temperature either increasing or decreasing.

An infinite number of sequential operations (e.g., a sequence of the form 'alter temperature, expose film, increment film, alter temperature, ...') may be specified by a single MODE. Software control of temperature programming is a facility which does not seem to be currently available on commercial temperature controllers, even when microprocessors are used in their construction. The present system has advantages over that previously described (Cosier et al., 1981) as the data input is in decimal rather than octal formal and also as the data input program automatically detects and rejects errors in the parameters supplied (temperature jumps between phases, etc.). The RUN DATA may be amended or further commands may be supplied by the operator from the VDU even during the course of an experiment.

2. Check temperatures
Checks the RUN DATA for errors such as temperature jumps, excessive heating rates, etc. and then lists the initial and final temperatures of each PHASE.

3. Warm start
Initiates the flow of refrigerant and establishes a stable starting temperature prior to commencing the first PHASE of the experiment.

4. Shut down
Produces immediately a safe termination of the experiment, stopping the helium flow and closing the X-ray beam-shutter.

5. Jump to next phase
Allows the operator to initiate the next PHASE of the experiment before the completion of the current one. This is a useful facility if, for example, it is desired to hold the temperature for an indefinite period to allow Weissenberg photographs to be taken.

6. Program check
Produces a full listing of the RUN DATA on the VDU.

7. Memory change
Allows data to be loaded from the VDU into a previously specified machine address.

In addition to the high-level language options described above, it is envisaged that several further facilities will be incorporated into the system in the future. The microprocessor has a sufficiently large memory to enable quite sophisticated analysis of experimental data to be undertaken. One example of such a computation would be to sample repeatedly the temperature during each X-ray exposure and to compute its mean value, standard deviation and maximum recorded error from the set point.

Performance
The final specification of the instrument [described using the suggestions of Rudman (1977)], which has now operated successfully for over one year, is as follows.

(a) Sample type: designed for use with single crystals but powder photographs may also be taken.
(b) Type of cooling: cold gas stream (N₂ or He).
(c) Frost prevention: sample enclosed within cryostat.
(d) Temperature range: 10–300 K (He), 75–300 K (N₂). Thermometric sensitivity 0.018 K (above 35 K), 0.007 K (below 20 K). Absolute thermometric accuracy ±0.1 K at sensor. Temperature stability better than ±0.05 K (at sensor) over whole range for an indefinite period.

A temperature difference of up to about 15 K (for temperatures greater than 35 K) exists between the sensor in the heat exchanger and the crystal. The magnitude of this temperature difference, which depends primarily on the helium flow rate, has been measured, under normal operating conditions, as a function of temperature. The results were reproducible from run to run to better than ±0.5 K.

There are therefore two possible modes of operation. For experiments where the absolute temperature does not need to be very accurately known (e.g. for Weissenberg photographs), temperature control is most conveniently obtained via the diode thermometer in the heat-exchanger block. The crystal temperature is then known to within ±0.5 K and is stable to
better than ±0.1 K. For experiments where accurate crystal temperatures are required (e.g. lattice-parameter measurements), a second diode thermometer is used, mounted in a small copper block attached to the end of the goniometer head. The crystal is in direct thermal contact with this copper block and so the thermometric accuracy and stability at the crystal will then closely approach those at the sensor.

The temperature gradients in the helium gas at the specimen position have been measured in both the radial and axial directions using a gold/iron–chromel differential thermocouple. Both gradients show maxima (under normal operating conditions) at about 150 K. Typical values are:

- 50 K: 0.2 K mm⁻¹ axially; 1 K mm⁻¹ radially;
- 150 K: 1 K mm⁻¹ axially; 4 K mm⁻¹ radially;
- 250 K: 0.15 K mm⁻¹ axially; 1.5 K mm⁻¹ radially.

However, the temperature gradients within the specimen are expected to be considerably smaller because of its thermal conductivity.

(e) X-ray instrument: Weissenberg camera, horizontal operation (may also operate vertically if required).

(f) Special characteristics: designed for accurate lattice-parameter studies using very high Bragg angles (θ = 80–85°) but covers a complete range of θ.

(g) Rate of consumption of cryogen: He 0.2 l h⁻¹ at 200 K, 0.3 l h⁻¹ at 100 K, 0.65 l h⁻¹ at 30 K, 1.5 l h⁻¹ at 10 K. N₂ less than 0.25 l h⁻¹ at all temperatures.

Particular advantages of this apparatus over existing equipment include the following:

(a) It may be used with horizontally-operated Weissenberg cameras.

(b) Ease of operation.

(c) Very sophisticated facilities for control of the experiment.

(d) Specimen contained within an atmosphere of He or N₂ gas – there is no possibility of condensation or frost formation on either specimen or cryostat windows.

(e) The refrigerant is drawn past the specimen by a pump on the outlet line. This produces a much more regular flow of refrigerant than may, for example, be obtained by the use of an evaporator. Furthermore, since the storage dewar is not pressurized it may be refilled at will, giving an effectively infinite period of operation (at present, in our laboratory, this operation is only possible when using nitrogen as a refrigerant).

(f) The continuous-flow cryostat may be used independently of the X-ray camera as a small general-purpose variable-temperature cryostat.

Disadvantages of the equipment are:

(a) there is no means of resetting or recentering the specimen when cold. We have, however, not encountered serious problems with this effect, provided that care is taken not to disturb the specimen when fitting the cryostat to the camera.

(b) The Melinex windows inevitably produce an undesirable background on the film. This is not a serious handicap to lattice-parameter studies, but may hamper the collection of accurate intensity data, especially at low Bragg angles. When working with helium as a refrigerant the use of some form of window is unavoidable and the scope for improvement of the present system is therefore very limited, being confined to possible reductions in the thickness of the outer window on the cryostat (0.125 mm thick at present) or replacement of the existing Melinex by beryllium.

For intensity measurements, as opposed to lattice-parameter studies, in the temperature range accessible with liquid nitrogen, windowless nitrogen gas-flow systems may therefore be more suitable.

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