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X-Ray Camera for Continous Recording of Diffraction Pattern-Temperature Diagrams

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In the course of work on the structure of phthiocerane [1] it became necessary to study crystal structure changes with temperature in a series of methylsubstituted long chain hydrocarbons. This was done by taking X-ray photographs at a series of different temperatures, but this procedure proved very tedious and time-consuming, and the need was felt for an X-ray camera capable of automatically recording diffraction pattern-temperature diagrams. A simple form of such an apparatus can be obtained by allowing the diffraction pattern from the specimen to fall through a horizontal slit on to a cylindrical photographic film with the axis parallel to the slit. If the film cylinder moves in such a way that a certain angular position always corresponds to a certain temperature of the specimen, heating or cooling the latter at a constant rate will give a continous recording of the diffraction pattern as a function of the temperature. Thermal expansion of the lattice is thus easily followed, and the occurrence of a transition to a new crystal form will be evident as a displacement of the lines in the diagram. The diffraction pattern disappears on melting, and the melting point is therefore also recorded. The synchronism between temperature changes and the rotation of the film cylinder can be accomplished in different ways. In the first instrument constructed the EMF of a thermocouple in the goniometer thermostat was counteracted by the potential of a slide-wire potentiometer whose movable contact was turned with the film cylinder. Any difference in potential caused a deflexion of the mirror of a sensitive galvanometer placed in series with the thermo-couple and the slide-wire, light thereby falling on one of the cathodes of a double photocell, which in turn via an electronic amplifier and relays caused a small motor geared to the film cylinder to turn the latter with the attached slide-wire arm until the potential of the slide-wire and the thermo-couple balanced each other.

The photocell-relay system was sensitive to changes in temperature of 0.15 °, and the device worked satisfactorily for a long period, but the camera was not fully automatic as the temperature calibration had to be performed by hand. This was done by removing the stop for the primary beam for about one second, thus causing a mark on the film.

It has recently been possible to use the recording camera in conjunction with a Speedomax G type temperature recorder.* With the aid of the latter instrument the temperature calibration has been made fully automatic and it has also been possible to obtain the temperature synchronization in a more simple manner. In the Speedomax recorder the angular position of the shaft carrying the arm of the main potentiometer depends on the temperature at the measured point, and the desired movement of the film cylinder can therefore be obtained by linking the movement of the film drum in the camera to that of the potentiometer shaft of the recorder, provided that the balancing motor of the latter is able to cope with the extra load. As this appeared to be the case, the camera was redesigned and the movement of the film is now obtained from the potentiometer of the recorder via a synchronous link system employing two "Magslip" motors **. Direct mechanical coupling would have been very awkward in the present case.

DESCRIPTION OF THE APPARATUS

Goniometer thermostat

Fig. 1 shows two sections through the thermostat, which is machined from a piece of copper rod 5 cm in diameter and 5 cm long. The upper part of the thermostat has a hollow mantle through which oil from a separate bath is circulated. When specimens deposited on glass plates are investigated the plate is clamped in a slot in the threaded copper rod *r* which is then screwed into the threaded central hole of the thermostat. The slot is made in such a way that the side of the glass plate carrying the specimen comes along a diameter of the rod. The rod *r* is provided with a knurled bakelite head *b* and is locked in position by the knurled nut *c*. By means of the handle *d*, which engages into a longitudal slot on rod *r*, the latter can be prevented from turning when nut *c* is tightened. Rod *r* is provided with a central hole *a* into which a small Anschütz type thermometer can be inserted. Specimens

* Made by Leeds and Northrup Co., Philadelphia, U.S.A.; obtainable from AB Max Sievert, Ulvsunda.

** Made by Muirhead and Co., Ltd., Beckenham, Kent, England, obtainable from Ingeniörsfirma Hugo Tillquist, Stockholm.

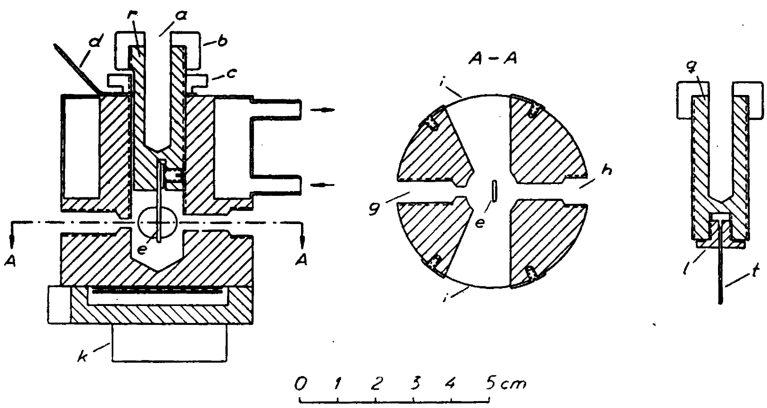

Fig. 1. Goniometer thermostat. For explanation of letters see text.

contained in Keesom-capillaries or extruded cylindrical specimens are mounted on the rod shown in Fig. 1 *q*. The small tube or rod holding the specimen is inserted into a small inset *l* as shown and attached by means of a trace of shellack.

The X-rays pass through two sector-shaped slots *s* whose outer openings are covered by thin cellophan films *i*. A threaded hole *g* is provided for a miniature lamp which throws light on the specimen while the initial adjustments are being made. On the opposite side is another threaded hole *h* which takes an iron-constantan thermo-couple. The thermo-couple, which measures the temperature at a point close to the specimen, is connected to the Speedomax recorder.

The thermostat is mounted on a goniometer head of fairly sturdy construction (cf Fig. 2) which makes it possible to set the specimen in the correct position with respect to the primary X-ray beam.

Arrangements for heating (or cooling) the specimen at a controllable rate

Over the temperature range 10—100 ° the heating or cooling of the specimen at a controlled rate is accomplished by circulating oil (transformer oil), through the goniometer thermostat from a separate bath. The oil is pumped by a small gear-wheel pump immersed in the oil to the goniometer thermostat via flexible oil-resistant tubing. Fairly flexible tubing is necessary in order not to interfere with the rocking motion of thermostat. The oil bath is provided

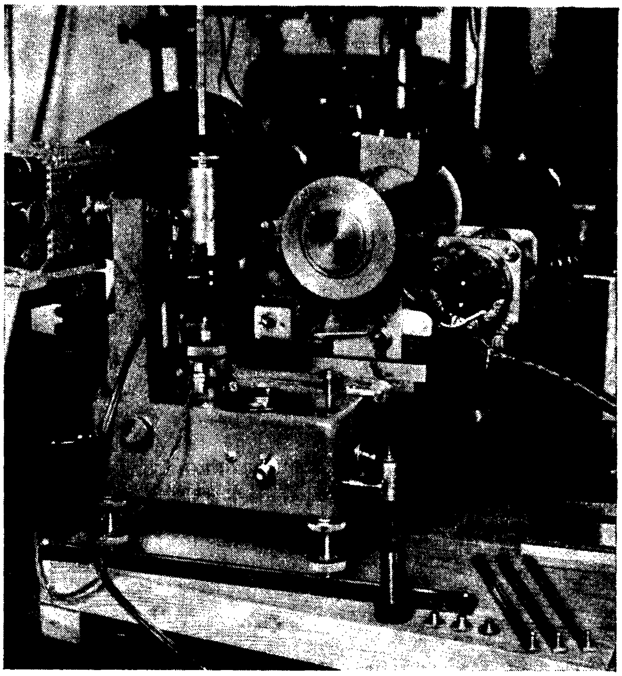

Fig. 2. Goniometer with thermostat and camera for continous recording of diffraction pattern-temperature diagrams. In the lower front part of the photograph are shown copper rod with insets for cylindrical specimens and three slits of different width.

with an electric heater controlled by a contact thermometer driven by a small synchronous motor. The latter is fed from an RC-generator whose frequency can be varied from 8 to 64 cycles/second, thus allowing the motor speed to be varied in the ratio 1 : 8. The motor (Bodine type KYC *) requires an input power of 8 watts at 115 volts (at 50 cycles). The oil is vigorously stirred by a separate motor, and when the thermometer motor runs with 50 cycles current the temperature of the bath is changed by one degree every five minutes. The motor driving the contact thermometer is of the reversible type, and when it is desired to record the diffraction pattern on cooling the specimen from an elevated temperature the motor is reversed, and the heating system used to balance the cooling provided from a coil of copper tubing immersed in the bath. The circulation rate of the coolant (usually tap water) is manually adjusted to a suitable value.

* Made by Bodine Electric Company, Chicago, U.S.A., obtainable through Ingeniörsfirman Sandblom and Stohne, Stockholm.

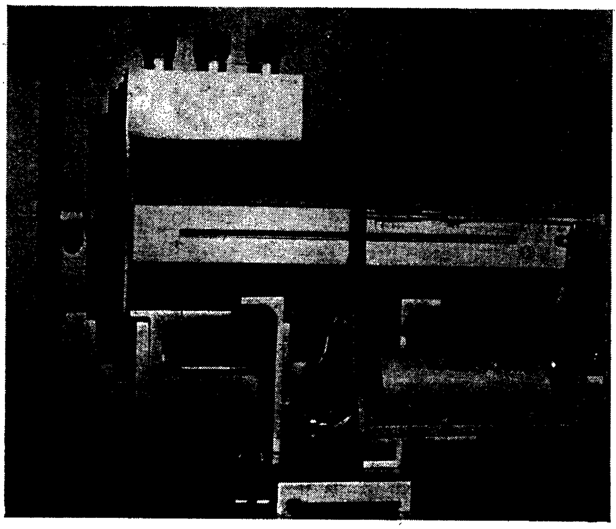

Fig. 3.

For temperatures above 100 ° (up to 150 °) direct electric heating of the goniometer thermostat is used. The small heater *f* (Fig. 1) interposed between the thermostat and the insulating (bakelite) support *k* is fed from a variac type transformer driven by a synchronous motor. The device has proved quite satisfactory although the heating curves deviate more or less from straight lines. It would appear that the oil bath could be used also at temperatures above 100 ° by substituting a silicone oil for the transformer oil. Silicone oil also has the advantage of a smaller change in viscosity with temperature, but the high cost has so far prevented its use.

Camera and synchronous link system

A removable film drum 5.9 cm in diameter and 13.5 cm long (for 13 × 18 cm films) rotates behind a horizontal slit in the housing shown in Figs. 2 and 3. A series of exchangeable slits 0.5, 1, 1.5 and 2 mm wide respectively is provided (some of these are shown in the lower right hand part of Fig. 2). The drum shaft is supported by ball bearings at both ends (one bearing is mounted in the removable lid) and is driven by a 2'' Magslip motor through gears having the ratio 7.5 : 1. An identical motor serving as transmitter in the synchronous link is connected to the main potentiometer shaft of the Speedomax recorder through a system of gears having the ratio 1 :11.25. The method

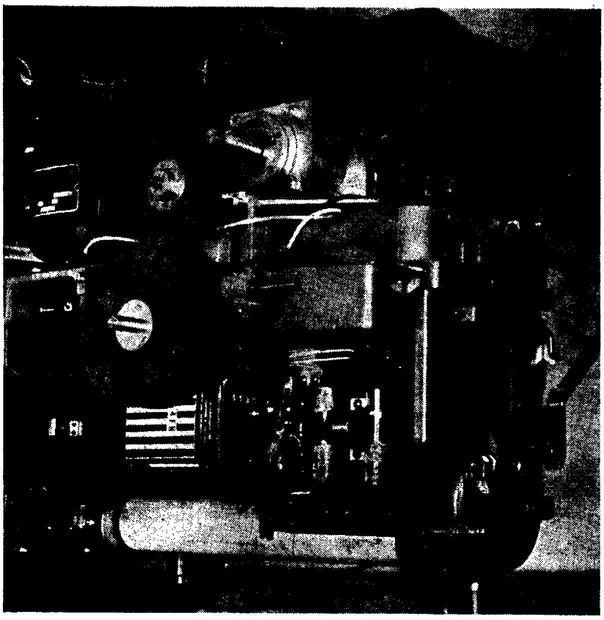

Fig. 4. Method of mounting Magslip transmitter motor in the Speedomax recorder. The contact disc for the temperature marking device is visible behind the large gear wheel on the main potentiometer shaft.

of mounting the transmitter motor is shown in the photograph of Fig. 4. In order to minimize backlash it might be preferable to use spirally cut gears instead of the straight ones shown.

With the gear ratios used a temperature interval of 1 ° corresponds to 1.6 mm on the film. The alignment error of the Magslip motors is less than one angular degree. With the gear ratio of 1 : 11.25 this will correspond to an error in the temperature measurement on the film of less than 0.05 °, and is hence negligible. Gear backlash, if present, will of course increase the alignment error.

Temperature marking device

A mark on the film at a certain temperature can be made by removing the stop for the primary beam for about one second. This can be done manually at any time by means of the small handle shown to the right in Fig. 3, and is done automatically at every 10 ° by means of the magnet shown in the lower part of Fig. 3 and the associated electrical circuit shown in Fig. 5. The magnet consists of a telephone type relay whose moving part has been provided with

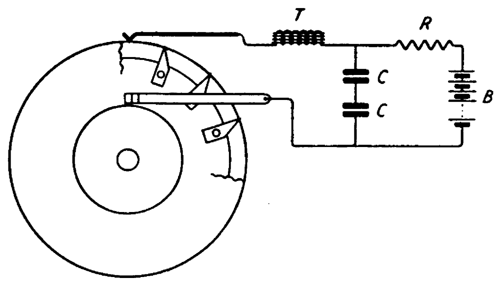

Fig. 5. Circuit used for the automatic temperature marking. T = telephone type relay, 2 000 ohms resistance, normal working current 8 mA, B = 40 volts dry cell battery, R = 0.4 megohm, C = electrolytic condenser 500 mF, 12 volts D.C. working.

an extension resting on the stop for the primary beam. When the magnet is energized, the stop is moved towards the side. A small spring returns it to the original position as soon as the magnet is deenergized. In order to limit the marking time to about one second and to prevent chattering, the current for the magnet is obtained from the discharge of a condenser. The circuit is closed by a series of adjustable contacts on a disc mounted on the main potentiometer shaft of the recorder (cf Fig. 4). The contacts are empirically adjusted to the correct position. After one temperature marking has been made the marking device is inoperative until the condenser has been recharged to about 20 volts. In order to prevent a possible jerky motion of the recorder potentiometer arm from causing more than one marking at one temperature, the condenser is charged at a slow rate from a battery in series with a large resistance. With the arrangement of Fig. 5 it was found that the leakage current of the electrolytic condensers was about 40 μA. The two series-connected condensers therefore become charged to a maximum of 24 volts. The low current drain allows the battery to be permanently connected in the circuit.

As an example of the use of the apparatus*, Fig. 6 shows the automatically recorded diffraction pattern-temperature diagram for *n*-heptacosane ($C_{27}H_{56}$)**. This hydrocarbon is orthorhombic at room temperature, but as shown by Müller [2], long chain hydrocarbons undergo a reversible transition to a hexagonal crystal structure a few degrees below the melting point. According to Piper, Chibnall *et al.* [3] *n*-heptacosane melts at 59.0—59.1 °, and the

* Further examples will be given in forthcoming communications from this laboratory.

** The author is indebted to Professor A. C. Chibnall, Cambridge, England, for a specimen of this hydrocarbon.

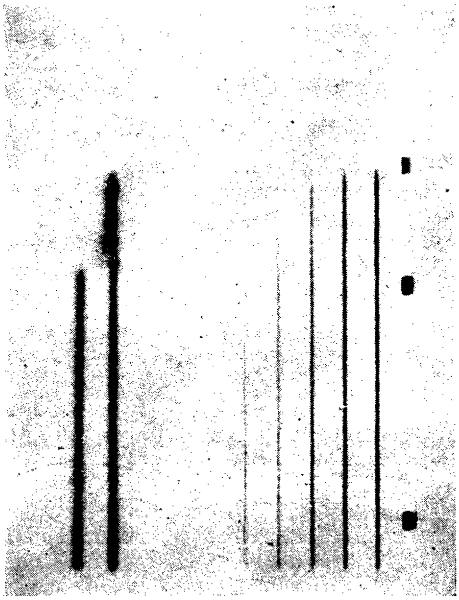

Fig. 6. Diffraction pattern-temperature diagram for n-*heptacosane* ($C_{27}H_{56}$).

transition occurs at 52.8—53 °. The corresponding temperatures read from the recorded diagram of Fig. 6 are 59.2 ° and 51.5 ° respectively. As usual for powder and oriented powder photographs of long chain compounds, the diffraction pattern consists of a series of 00*l* reflexions (corresponding to the long crystal spacing) and a series of *hk*0 reflexions, the latter making up the so-called side spacing pattern. In Fig. 6 the strong *110* and *200* reflexions of the orthorhombic form are very prominent. The *200* reflexion disappears at the transition and at the place of the previous *110* reflexion there appears two reflexions situated close together [2]. As the temperature is increased and the full hexagonal symmetry is attained these two reflexions unite to a single strong reflexion. A feature not previously noticed is that there is a slight shortening in the long spacing just around the transition point.

Apart from the recording of transition temperatures and melting points, the diagrams also give continous records of the thermal expansion of the lattice. On the whole, the continously recorded diagram gives a much clearer picture of the changes taking place within the crystal than a series of separate photographs taken at different temperatures, and no transitions are missed.

The temperature markings in Fig. 6 are of different strength (that for 40 ° is missing). This is caused by the rocking motion of the goniometer thermostat, which screens off the primary X-ray beam near one of the end positions of the movement. The diagram in Fig. 6 was obtained with a rate of heating of 1 ° per 5 minutes. The slit width was 2 mm. This combination gives sufficient exposure in most cases when nickel-filtered copper radiation from a Philips-Müller tube is used, and the tube run at 30 kV and 20—30 mA. Smaller slits of course decrease the exposure and as a rule necessitate a lower rate of change of the temperature of the specimen*. As the melting and transition points can be read off with sufficient accuracy when using the larger (1.5 and 2 mm) slits, the latter are almost always used. The diffraction pattern-temperature diagrams for many long chain compounds with sharp and accurately known melting points have been recorded, and it has been found that the melting point can be determined from the diagrams with an accuracy of about 0.3 °.

An apparatus of the type described should prove useful also for phase analysis of organic as well as inorganic mixtures, including alloys. The temperature range of the camera can of course be considerably extended. As described, the apparatus is capable of recording reflexions over Bragg angles up to 15 ° only. For larger angles a different goniometer thermostat must be used. It would appear to be a comparatively easy matter to change a Weissenberg camera such as the Buerger type made by LKB-Produkter, Stockholm, into a temperature recording camera. A slit is already provided by the layer line slit supplied, and the film motion could be obtained by a Magslip motor linked to the potentiometer of the temperature recorder. The friction of the film carriage, which is considerable in the instrument mentioned, could be overcome either by a slight redesign or by interposing a capstan type torque amplifier [4] between the Magslip motor and the film carriage.

The recording speed of the camera is essentially that of the temperature recorder which in the case of the Speedomax G recorder employed is 4 seconds across the scale of 150 °. Provided that a sufficiently powerful source of X-rays is available, it might thus be possible to study crystal structure changes under processes involving very high heating or cooling rates.

The author is indebted to Mr. S. Liliedahl, former instrument maker of the Institute of Physiology, Uppsala, for the construction of the goniometer and the goniometer thermostat, to Mr. P. Olsson of this Institute for the construction of the recording camera and accessories, and to Diplomingenjör J. Björkman for the design and construction of the variable frequency generator. The purchase of the Speedomax recorder and the redesign of the apparatus was made possible by a grant from *Statens naturvetenskapliga forskningsråd.*

* In the first instrument the exposure could if necessary be increased by compressing the temperature scale by sending more current through the potentiometer slide-wire. In the present form of the apparatus the temperature scale can only be altered by changing the gear ratio between the film drum and the Magslip motor.

SUMMARY

An X-ray diffraction camera for the continous recording of diffraction pattern-temperature diagrams is described. The apparatus has been designed mainly for the study of polymorphism in long chain compounds, but should prove useful also for other purposes, *e.g.* for the study of thermal expansion of crystals and for phase analysis of mixtures.

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