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The Linear Diffractometer

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A fully automatic single-crystal X-ray diffractometer is described, which uses a mechanical analogue of the reciprocal lattice for setting crystal and counter. Its use and performance are discussed.

1. Introduction

There is an increasing demand among crystallographers engaged in the determination of complex crystal structures, especially those of proteins and of alloys, for a simple, rapid, and accurate method of measuring the integrated intensities of large numbers of reflexions from single crystals. To meet this demand, automatic counter diffractometers are being developed in many laboratories. Most of these developments are based on standard X-ray counter diffractometers (e.g. Wooster & Martin, 1936; Cochran, 1950; Furnas & Harker, 1955) which were themselves derived from the original ionization spectrometer (Bragg & Bragg, 1913) and from the two- and three-circle goniometers of classical crystallography. In the most versatile of these instruments the crystal, set in the X-ray beam, can be rotated about three axes, so that any set of crystal planes can be brought into position to reflect in a convenient orientation. The counter position is similarly controlled by means of one or two circles. Several systems have been described for making the operation of these instruments automatic (e.g. Prince & Abrahams, 1959; Brown, Calder & Forsyth, 1958), usually making use of methods similar to those developed for the automatic control of machine tools for the setting of the various shafts to values previously calculated on an electronic computer. A punched tape or card input is used.

The automatic diffractometer described here is of a different and completely novel type. In effect it incorporates an analogue computer by means of which the settings of the crystal and counter are generated by the instrument itself, given only the reciprocal-lattice dimensions of the crystal under investigation. This computer comprises a mechanical model of the reciprocal lattice composed of three slides representing the reciprocal-lattice axes to which the motions of the crystal and counter are linked. Once the crystal has been correctly oriented with respect to the slide system, any reflexion *hkl* can be found by setting the coordinates ha^*, kb^*, lc^* of the corresponding reciprocal-lattice point on the three slides. The crystal and the counter take up their correct positions automatically. This facility in setting makes the automatic operation of the diffractometer for measurement of the complete diffraction pattern a relatively simple problem. Various schemes of automatic operation are possible, some of which are described and discussed in detail below; none of them requires the preliminary calculation of angular settings. In particular it is possible to measure the X-ray intensity distribution along lines in reciprocal space—hence the name 'Linear Diffractometer'—either continuously or, most economically in structure analysis, in sequence at the points of the most densely populated reciprocal-lattice rows. In this mode of operation, as described below, the Linear Diffractometer can measure automatically the integrated intensities of all the reflexions with $2\theta < 60°$ corresponding to points in one reciprocal-lattice level, and record them, together with their indices *hkl* and appropriate background measurements, both in plain language and on punched tape ready for immediate transfer to a computer. Resetting for the next level involves only one adjustment.

Preliminary accounts of the instrument and its automatic operation have already been given (Arndt & Phillips, 1958, 1959†) and the prototype was exhibited at the 42nd Physical Society Exhibition in 1958. Since then similar developments have been reported from other laboratories (Mathieson, 1958; Ladell & Lowitzsch, 1960), although these do not appear to have led as yet to an instrument capable of routine use for automatic three-dimensional data collection.

2. Description of the diffractometer

The design of the instrument is based directly on the reciprocal-lattice representation of the genesis of X-ray reflexions. The principle is illustrated in Figs. 1(*a*), 1(*b*) and 1(*c*) which show the familiar construction in such a way that the instrument (Figs. 2(*a*), 2(*b*), 2(*c*)) can be compared directly with it. *YXO* represents the direction of the incident X-ray beam with *X* the centre of the Ewald sphere and *O* the origin of the reciprocal lattice. *A'OA*, *B'OB* and *C'OC* are the principal axes of the reciprocal lattice, here assumed

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Fig. 1. Reciprocal-space diagrams showing the direction of the incident X-ray beam, the Ewald sphere and the genesis of reflexions (*a*) in an equatorial plane; (*b*) in an upper-level in the normal beam setting; and (*c*) in an upper-level in the equi-inclination setting. Principal reciprocal-lattice directions are shown in thick line for comparison with the slides in the apparatus shown in Fig. 2. The lettering is explained in the text.

Fig. 2. The linear diffractometer set for (*a*) zero-level reflexions; (*b*) upper-level reflexions in the normal-beam setting; and (*c*) upper-level reflexions in the equi-inclination setting. The principal components are described in the text.

to be orthogonal. XP is the direction of the reflected X-ray beam corresponding to the reciprocal-lattice point P which lies in the surface of the sphere of reflexion. The reciprocal lattice can be rotated about the axis $C'OC$ and this axis can be inclined to the direction of the incident X-ray beam by rotation about the axis $D'OD$ which is perpendicular to the incident beam.

The linear diffractometer is simply a mechanical version of this diagram. The reciprocal lattice is represented by the three slides A, B and C, which are parallel respectively to $A'OA$, $B'OB$ and $C'OC$. They are mounted to rotate about the axis $C'O$ and arranged so that the saddle P can be set at any position in space within the coordinate system which they define. This saddle P is connected to the point X by means of a link of fixed length $XP=XO$, corresponding to the radius of the sphere of reflexion. The link XP, which in effect can pivot freely at X and P, lies always along the direction of the reflected X-ray beam and thus becomes the counter arm of the diffractometer. The crystal is mounted at X for rotation about the axis $R'XR$ (independent of the link XP which pivots about an independent coaxial bearing at X) and the rotation of the crystal about this axis is coupled by means of gears, steel tapes and pulleys to the rotation of the slide system about the axis $C'OC$. The axes $R'XR$ and $C'OC$, held parallel by means of parallel linkages, can be tilted with respect to the incident X-ray beam by rotation about the axes $D'OD$, $E'XE$, as shown in Fig. 2(*c*).

The main features of the design can be seen in Fig. 2. Only a few details require comment. It will be clear that the scale of the instrument depends only on the length chosen for $XO=XP$. In the present instrument this length, which is equivalent to 1 reciprocal-lattice unit, is 5 inches. The position of the saddle P on the three slides is controlled by means of lead screws, all of which are cut with 20 turns/inch. The counters which indicate revolutions and fractions of a revolution of the lead screws thus read directly in decimal divisions of reciprocal-lattice units. The screws in slides A and B are driven by means of synchro receivers M forming a synchro-link with corresponding transmitters driven by a synchronous motor mounted in the control panel. The oscillation mechanism T and the various electrical fittings and connections are described below.

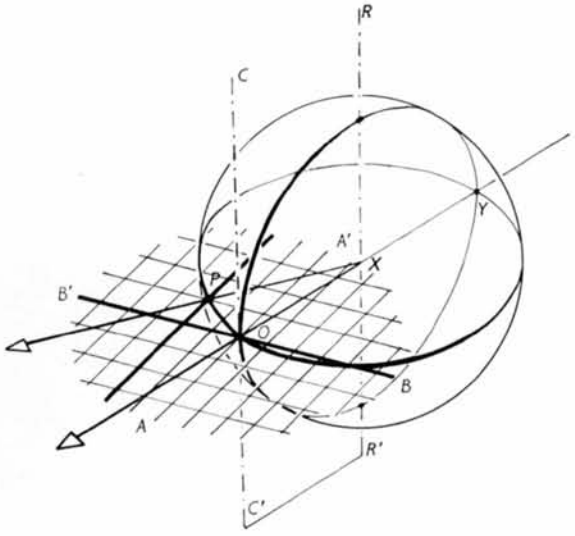

Fig. 1(*a*).

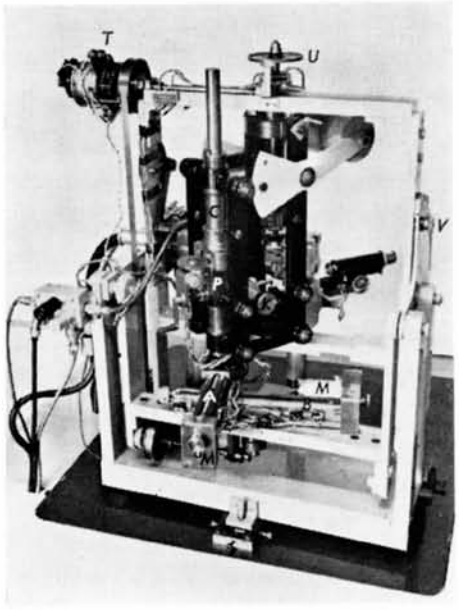

Fig. 2(*a*).

The slides A and B extend only to ± 1 reciprocal lattice unit while slide C extends only from zero to $+1$ r.l.u. and the instrument in its present form is capable of measuring only those reflexions for which $\Upsilon(2\theta$ for zero levels$) \leq 60°$. This limitation is not an essential feature of the linear diffractometer which could be re-designed to cover a wider range of angles, but this was felt to be unnecessary for most applications. The chosen angular limits are closely the same as the angular limits of the Buerger precession camera. In fact more reflexions can be observed with Mo $K\alpha$ radiation within the range $2\theta < 60°$ than are accessible with Cu $K\alpha$ radiation. The reduction in reflected

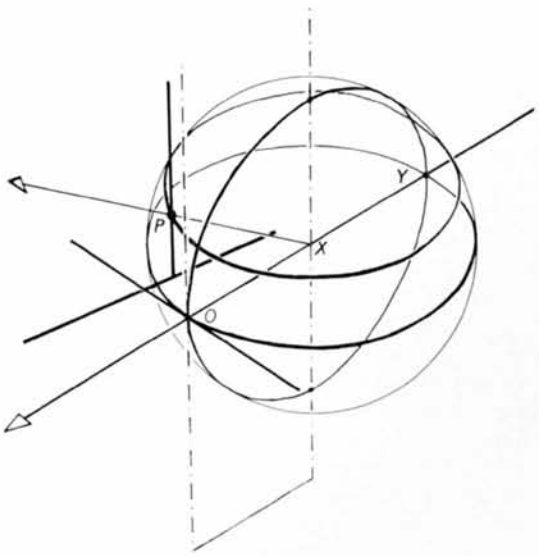

Fig. 1(*b*).

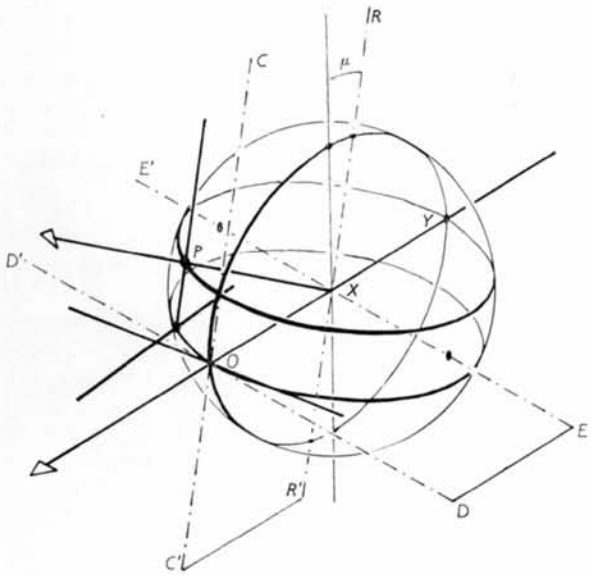

Fig. 1(*c*).

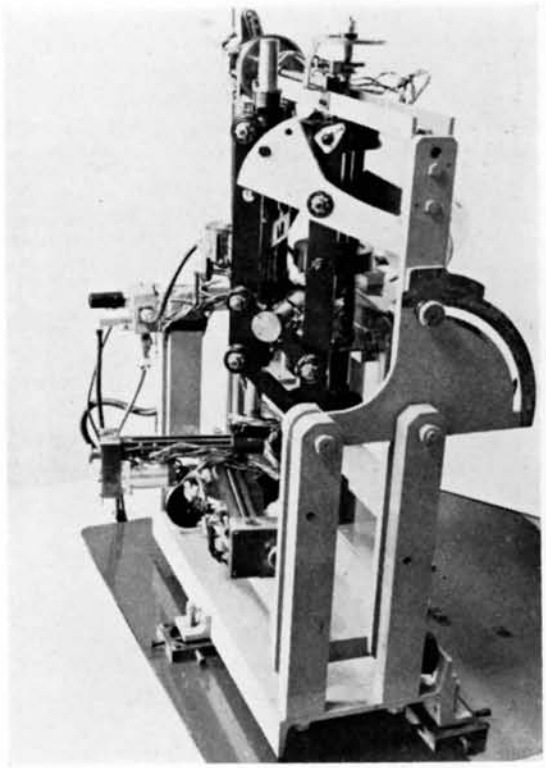

Fig. 2(*b*).

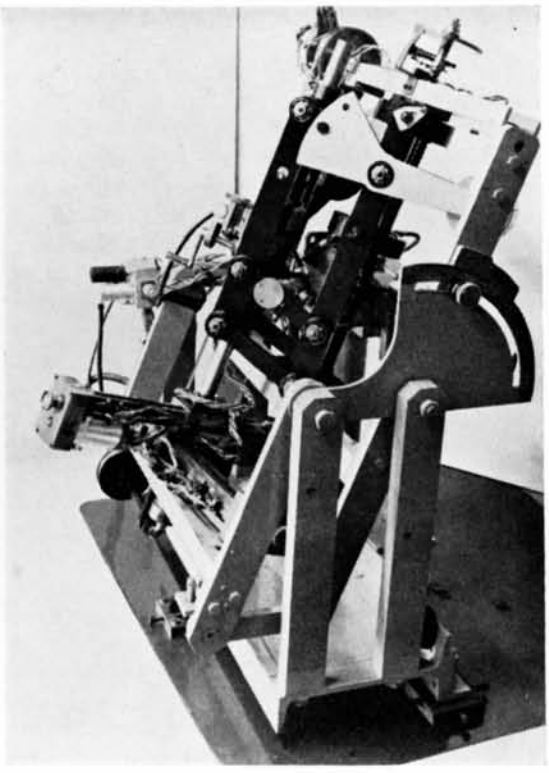

Fig. 2(*c*).

intensity which attends decrease in wavelength often can be compensated by the use of larger crystals, since absorption often decreases also. A scintillation counter is used with Mo $K\alpha$ or Ag $K\alpha$ radiation and a proportional counter with Cu $K\alpha$ radiation; these detectors are much more efficient than is photographic film in the detection of short wavelength radiation (cf. Arndt, 1955).

3. Crystal setting

The diffractometer has been designed primarily for measurement of the integrated intensities of reflexions

from single crystals. It can also be used very conveniently for other measurements, such as diffuse scattering, but its operation is described here with particular reference to the measurement of Bragg reflexions.

The requirements of any automatic diffractometer are:

(*a*) that it should be capable of setting crystal and counter in position for each Bragg reflexion in turn;

(*b*) that it should measure the integrated intensities of these reflexions and record them in a convenient form for direct use in subsequent calculations.

These requirements can sometimes be met in a single operation, as will be seen, but it is convenient to describe the operation of the diffractometer separately under the two headings.

Orthogonal crystal systems

The crystal is first set with one of its axes, say c, and hence c^*, as the axis of rotation. It is then oriented by rotation about this axis so that the a^* and b^* axes are parallel to the slides A and B of the reciprocal-lattice model. To set a^* parallel to the slide A it is necessary only to set the saddle P a distance ha^* along A corresponding to a particular $h00$ reflexion and to rotate the crystal with respect to the slide system by means of the dial U and its screw control until that reflexion is found. Since the slides A and B are at right angles to one another, it follows that the $0k0$ reflexions can be found simply by returning the saddle to zero on slide A and setting it to the kb^* values on B. Similarly any $hk0$ reflexion in the central reciprocal-lattice level can be found by setting the saddle P to the position ha^*, kb^* on the two slides. These coordinates are set directly in reciprocal-lattice units as read on the revolution counters and the crystal and counter take up their correct orientations as the position of the saddle is adjusted (Figs. 1(*a*) and 2(*a*)).

A general hkl reflexion is found equally simply. If the settings of slides A and B are made zero and the saddle P is moved along the third (vertical) slide C through a distance lc^*, the axes $C'O$ and hence XR' are constrained to tilt towards the incident X-ray beam, since XP is a fixed length. The instrument in fact takes up automatically the equi-inclination setting for the lth upper-level. This angle of tilt can be fixed by means of the locking screw V and the reflexions in the upper level hkl can then be found systematically by operation of the slides A and B in exactly the same way as those in the zero-level Figs. 1(*c*) and 2(*c*)).

The equi-inclination setting is not, of course, the only one in which reflexions can be found. All reflexions other than the $00l$ can be found at various angles of inclination but only the equi-inclination setting is free from blind regions. Thus for example in the normal-beam setting, in which the axes $C'O$ and XR' are not allowed to tilt with respect to the incident X-ray beam for the setting of upper-levels, the instrument cannot be set for all those reflexions which correspond to lattice points near the axis $C'O$. The possible settings and the blind regions are the same as the settings and blind regions of a Weissenberg Camera and the actual mechanism of the present instrument illustrates clearly how the blind regions arise (Figs. 1(*b*) and 2(*b*)).

When the tilt is not fixed, any hkl reflexion within the range of the instrument can still be found by setting the coordinates ha^*, kb^*, lc^* of the corresponding reciprocal-lattice point on the three slides A, B and C, but the instrument may then take up one of a range of possible angles of inclination. The equi-inclination angle setting, which is most convenient for routine operation, is taken up automatically (see Section 7 for accuracy of setting) only when slide C is set first and the inclination angle is locked while slides A and B are still at zero.

Crystals with non-orthogonal axes

The three slides which correspond to reciprocal-lattice axes are set permanently at right angles to one another in the present form of the instrument so that the method of locating reflexions outlined above cannot be used without modification for crystals having non-orthogonal axes. It is, however, always possible to determine the coordinates of reciprocal lattice points for such crystals in an orthogonal axial system and this need not involve much calculation. Thus in the examination of a monoclinic crystal, with its unique b axis set parallel to the vertical slide, reflexions in the non-orthogonal $h0l$ and parallel levels can easily be found. If the a^* axis is again set parallel to slide A the rows $h00$, $h01$, ... etc. with constant l are located at intervals $c^* \sin\beta$ along slide B and in these rows reflexions again are found at intervals of a^* when the origin is shifted by $lc^* \cos\beta$. The location of reflexions from triclinic crystals is only slightly more complicated.

The setting of crystals with non-orthogonal axes would, however, be simpler if the angle between the horizontal slides were adjustable and this modification is being incorporated in a new version of the instrument. In the meantime without this facility it has been found convenient, particularly for automatic operation, to use the diffractometer with orthogonal crystal axes parallel to slides A and B. With monoclinic crystals this is easily arranged, by mounting them to rotate about their c (or a) axis. The vertical repeat distance between parallel levels with orthogonal axes is then $\lambda/c = c^* \sin\beta$ and the origin of the lth upper level has to be offset by an amount $lc^* \cos\beta$ along the a^* axis.

Finding any given reflexion once a crystal has been set on the diffractometer is thus seen to be a simple matter; furthermore re-adjustment to any other re-

flexion is readily accomplished since it involves at most three translations which, for an orthogonal lattice at least, are integral multiples of the reciprocal-lattice unit-cell dimensions, the change of one index only, of course, corresponding to one single such translation. A logical, systematic survey of the reciprocal lattice thus suggests itself in which a reciprocal lattice line is traversed from one end to the other, to be followed by a return along the next parallel line until one plane of the lattice is covered. After an adjustment of the third translation the next plane can be surveyed in the same way.

This type of survey can be made automatic in a variety of ways and several methods of measuring the reflexion intensities have been tested, of which two are described in some detail below.

4. Intensity measurement

In the simplest way of scanning the reflexions and recording their intensities, the saddle P is made to carry out the zig-zag movement described above in such a way that it is driven at constant speed along the whole length of one slide, hereafter referred to as the scanning slide; it is then moved by one unit translation along the other slide, known as the stepping slide, and returns along the next line at constant speed on the scanning slide. Meanwhile the radiation entering the detector is recorded with the aid of a linear or logarithmic counting ratemeter and a chart recorder. Alternatively a scaler accumulates the counts received as the saddle P moves from a position half-way between two reflexion points, through a reflexion, to the next half-way point, this accumulated total being printed out and the scaler being cleared automatically at each half-way point. Many refinements of the digital recording are possible. Thus, for example, the range of movement on the slide during which the reflexion count is accumulated may be restricted more closely to the vicinity of the reflexion itself and a part of the motion between the points can then be used for measurement of the background intensity.

The continuous scanning method has the merit that the setting and measuring functions of the diffractometer are combined in a single motion. However, owing to a geometrical effect, discussed in the Appendix, the breadth of the reflexions varies over a given level: in certain regions, if the unit cell of the crystal is large enough, individual reflexions may be broadened to such an extent that they are not resolved. Fig. 3(*a*) shows a chart record in which resolution is incomplete on the right hand side of the trace. It is shown in the Appendix that each reflexion can be measured without excessive broadening if two scans are made, one on each side of the direct beam. Rather than double the number of measurements it seems better to retain the continuous scan only for a rapid semi-quantitative survey, and for more accurate work to resort to a point-by-point method described in the next paragraph.

Point-by-point measurements

In this method of measuring the intensities the motorized slide system is used merely to set the crystal and counter at the appropriate positions for each reflexion in turn to be observed. At each reciprocal-lattice point the integrated intensity of the reflexion is measured. Two well-known possible methods of measurement (Cochran, 1950) are:

(*a*) to use a convergent incident beam from a uniform-focus X-ray tube such that each part of a stationary crystal sees an equivalent source and to measure only the peak intensity of the reflexion; or

(*b*) to rotate or oscillate the crystal through the reflexion position while the total energy reflected by it in that reflexion is measured.

In the use of both these methods it is necessary also to measure the background intensity scattered incoherently from the crystal and from its support, the slits and the air in the instrument.

The former method has a considerable advantage over the latter in speed for given statistical accuracy; unfortunately no X-ray tube is yet available with a sufficiently uniform focus for it to be used with confidence. We have therefore adopted the second method though it will be seen that the mechanism used to oscillate the crystal could be adapted very conveniently to the convergent beam technique if a suitable X-ray tube were to become available.

The method employed is to interrupt the connection between the slide system and the crystal by means of a mechanism, T in Fig. 2(*a*), capable of oscillating the crystal independently. This oscillation mechanism, which has been described in detail elsewhere (Arndt, Faulkner & Phillips, 1960), rotates with the crystal as the diffractometer is being set to a reflexion position and then controls the independent motion of the crystal in such a way that the latter remains stationary at a given angular setting for a time t, rotates at uniform rate over a predetermined angular range for a time $2t$, remains stationary at the final angular setting for a further time t, and then returns quickly to its original setting. The correct setting for the reflexion peak is at the mid-point of the rotation which may be through any angle from 1° to 5° according to the setting of a lever in the oscillation mechanism. For initial adjustments the motor can be arrested at this mid-point by means of a micro-switch operated by a switching disc rotating with the cam. This disc in normal use actuates contacts which start and stop the count of the scaler. Three counts are made: the first is a background count n_1, made while the crystal is stationary on one side of the reflexion position, the second is an integrated intensity count N accumulated as the crystal rotates through the reflexion and the third is a further background count n_2

The background-corrected integrated intensity of the reflexion is taken to be

$$N_0 = N - (n_1 + n_2) . \quad (1)$$

Furnas (1957) has given a thorough account of conditions which have to be fulfilled in ensuring that proper measurements of the integrated intensities are made, for example in determining what slit sizes and oscillation ranges must be used; these are not discussed in detail here. Some additional factors, however, arise from the geometrical arrangement adopted in this diffractometer. In the measurement of upper-level reflexions the crystal is not oscillated about an axis perpendicular to the plane of the reflexion (i.e. the plane containing the incident and reflected beams) and thus the effective angular range of reflexion is generally greater for upper-level reflexions than for those in the zero-level and it may be necessary to adjust the oscillation range accordingly (cf. Cox & Shaw, 1930; Tunnell, 1939). It is not possible to measure the $00l$ reflexions in the setting of the crystal which has been discussed so far, since for them the axis of oscillation coincides with the normal to the reflecting planes, and the oscillation range required may be intolerably large also for some other reflexions with reciprocal-lattice points near the oscillation axis. The angular range of reflexion in upper levels depends also on the vertical divergence of the X-ray beam (Phillips, 1954) as a result of which it is further increased, particularly for low values of ξ at high values of ζ.

The most satisfactory procedure in practice is to determine the appropriate range of oscillation experimentally for each set of measurements. The oscillation range can be altered by means of a simple control which leaves the period of one complete oscillation unchanged. The measured value of an integrated intensity N_0 (equation (1)) is proportional to the angular velocity of crystal rotation and it varies inversely therefore with the oscillation range. The measurements must be scaled appropriately to produce a consistent set. These intensities are subject to the same Lorentz-polarization factors as for Weissenberg photographs.

5. Measuring and recording equipment

The X-ray counter at present in use with Cu radiation is a xenon-filled proportional counter which fits into the horizontal tube K in the counter arm (Fig. 2). An adequate degree of monochromatization is achieved by the employment of the usual pulse-height-discrimination technique (see, for example, Arndt, 1955).

The associated circuits are quite conventional in design. Their general arrangement is shown in the block diagram, Fig. 4. Only the recording circuits require special mention.

Two recording systems are available for use, corresponding to the two methods of measurement discussed above. The first of these, comprising two ratemeters (linear and logarithmic) either of which can be used in conjunction with the chart-recorder, has already been mentioned. Typical records of continuous scans are shown in Fig. 3. The second system consists of a 6-decade printing scaler which is used to record actual counts both in plain numbers for immediate inspection, by means of a solenoid-operated listing/adding machine, and in 5-hole code on punched tape, by means of a tape punch. The particular 5-hole code used can be changed at will to suit the particular computer employed for data processing by plugging in the appropriate diode translating matrix. The counts are recorded together with their signs, according to whether they represent background or reflexion measurements, and the background counts are subtracted automatically in the adding machine record. Typical results are shown in Fig. 7.

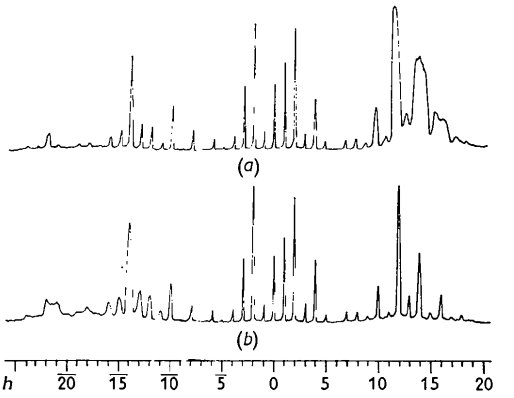

Fig. 3. The counting rate measured by a linear rate meter during scans of the $h23$ reflexions from a sperm-whale myoglobin crystal. Rate of scan 0·096 r.l.u./minute. (*a*) with 2θ positive and (*b*) with 2θ negative (cf. Fig. 8).

The print-out control unit is an integral part of the scaler and is arranged to operate automatically at the end of each count. The duration of these counts and their sequence in the different modes of operation are controlled through the central control unit.

6. Automatic operation

Either of two automatic sequences, corresponding to continuous scanning with chart recording or digital recording reflexion-by-reflexion with crystal oscillation, can be set up on the control unit by appropriate switches. The two sequences are outlined below. The various components of the automatic control system and their main interconnections are shown in Fig. 4.

Sequence of operations

(*a*) *Continuous scan.*—The sequence in this mode of operation is summarized by the flow diagram of Fig. 5.

(*b*) *Point-by-point scan.*—In this mode the scanning point P moves in a series of equal steps, corresponding to unit reciprocal-lattice translations, on the scanning

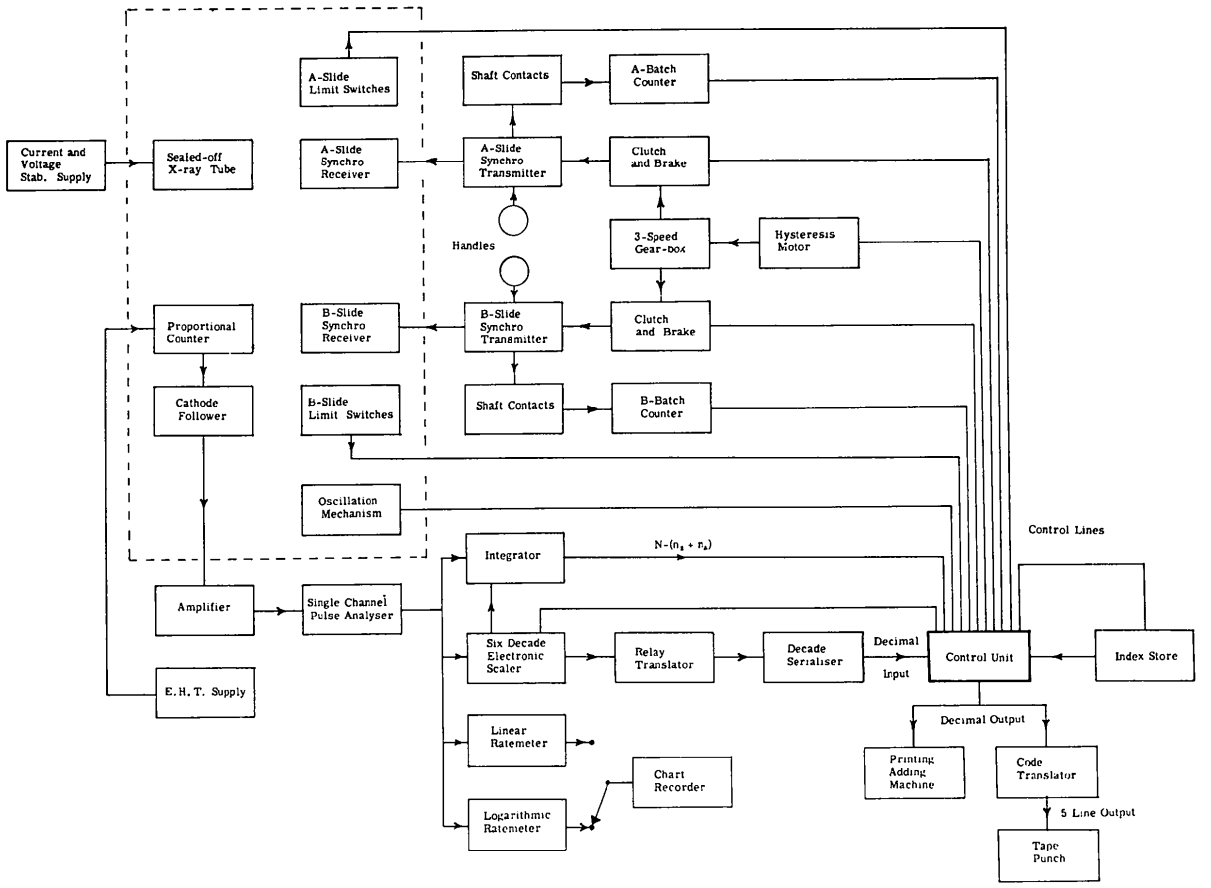

Fig. 4. Principal components and interconnections in the measuring and control system. Components enclosed in the broken line are mounted on the diffractometer.

slide also. At the end of each step the oscillation mechanism takes control for the measurement of the reflexion intensity which is recorded as the three numbers n_1, N and n_2, corresponding to the background, reflexion and background counts. The measurement is followed by a step on the slide to the next reflexion position and so on until a limit switch is reached. When this switch is made the current translation on the slide is completed, otherwise the instrument would be mis-set for the next row, the intensity of the last reflexion in the row is measured and recorded, and the saddle P is then moved one step on the stepping slide to the next parallel row. Again this row is scanned in the same way, though in the opposite direction, and the sequence is repeated until the whole level has been scanned when the limit switch on the stepping slide is reached.

Two limit switches are fitted at each end of the slides A and B. The inner switches are moveable and control the range of movement on the slides in the automatic operation. The outer switches are merely safety devices which interrupt the motor supply at the end of the slide in case of failure of the reversing sequence. In addition to those on the slides, switches are also fitted on the counter arm. The inner ones again are moveable and can be set so that all reflexions

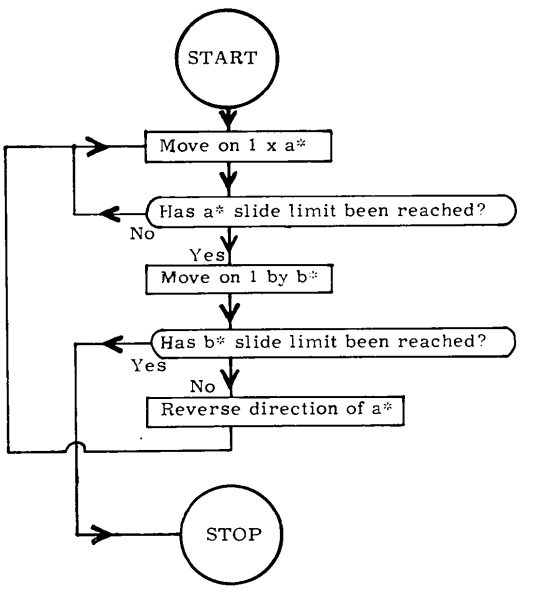

Fig. 5. Sequence of operations in the continuous-scan mode.

within a particular value of $\Upsilon(2\theta$ in a zero level) are measured. The outer switches are additional safety cut-outs. An additional protective switch fitted on the microscope interrupts the motor supply if the microscope has not been racked back sufficiently to be cleared by the counter arm.

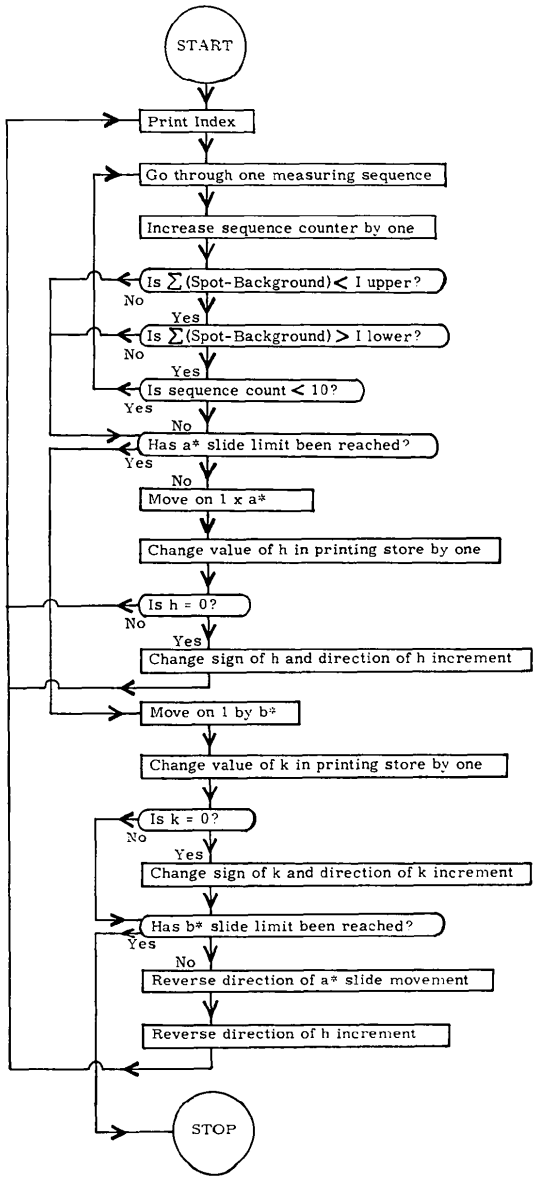

Fig. 6. Sequence of operations in the point-by-point mode with integrating circuit.

The sequence of operations in this mode is summarized in Fig. 6, from which it will be seen that two facilities not yet described have been included. Arrangements have been made

(i) to keep count of the indices of the reflexions and to record them along with the corresponding intensity measurements; and

(ii) to measure each reflexion more than once if that is desirable.

Indexing

It is clear that the reflexions are measured in a systematic order. For example with the scanning slide and stepping slide parallel respectively to a^* and b^* and the vertical slide parallel to c^* the index l is the slowest-moving index, changing only when the level is changed by hand, and the index h is the fastest moving, changing by one for each step on the scanning slide. The index k changes by one for each step on the stepping slide.

The control system includes three switches corresponding to the three indices, one of which is set by hand to the appropriate value for any particular level while the other two are bi-directional electro-mechanical stepping switches *USA* and *USB* operated by the setting control system. Their settings are read and printed out at the beginning of each cycle of intensity measurements in the point-by-point mode of operation. The order in which the three indices are printed can be selected by means of three key switches to suit the particular crystal under investigation. The choice of scanning slide (A or B), i.e. fastest moving index, is also made by means of a key switch.

Number of oscillation cycles

The number of times any particular reflexion is measured, and hence the statistical accuracy achieved in the measurements, is controlled in two ways. Each reflexion may be measured up to ten times according to the setting of a switch on the control panel. By this system each reflexion is measured the same number of times, that is effectively for the same total time, and as Cochran (1950) has shown the absolute standard deviation of F values derived from the measurements is very nearly constant. Alternatively, an integrating circuit is provided which tests the background-corrected count, N_0, at the end of each measuring cycle and causes measurements to be repeated until this quantity exceeds a pre-set limit or until the number of cycles is ten or some other pre-set number whichever occurs first. Measurements made in this way give rise to an approximately constant $\sigma(F)/F$, for all but the weakest reflexions which are measured once only if N_0 fails ro reach a pre-set minimum after the first cycle.

Control system

(*a*) *Setting control.*—The saddle P must be moved along either of the two slides A or B at constant speed or through predetermined distances. Synchro-transmitters, which drive the receivers on the slides, are mounted in a gearbox in the control panel. They can be turned by handles, for manual setting, or by a synchronous motor to which they are connected by electrically operated clutches through a three-speed

gearbox, providing a scanning speed of 0·384, 0·096 or 0·024 r.l.u./min.

Distances moved along a slide are measured by counting electrical pulses generated by contacts on the synchro-transmitter shafts. One pulse corresponds to a motion along a slide of 0·0001 reciprocal-lattice units. These pulses are fed to the appropriate one of the two batch counters. The latter can be set by means of four decade switches to any four-digit number which thus represents ten-thousandths of r.l.u. When this number of pulses has been received, the counters automatically reset themselves ready to accept another batch of the same size, and at the same time produce a signal which is used to disengage the clutches, to operate brakes and to initiate the next operation in the sequence.

The switching system governing the motion on the slides has to allow for 8 different situations during automatic operation. These 8 states are listed in Table 1 which also shows the origin of the signal which changes the state to the next one following. The various circuits corresponding to these eight states are

Table 1. *States of setting control*

State	Move-on signal
1. Negative motion on scanning slide, index + decreasing	Index register zero
2. Negative motion on scanning slide, index − increasing	Limit switch
3. Making last step on scanning slide	Scanning-slide batch counter
4. Moving on stepping slide	Stepping-slide batch counter
5. Positive motion on scanning slide, index − decreasing	Index register zero
6. Positive motion on scanning slide, index + increasing	Limit switch
7. Making last step on scanning slide	Scanning-slide batch counter
8. Moving on stepping slide	Stepping-slide batch counter

controlled by a telephone-type stepping switch (uniselector), *USC*, which is wired to produce six identical sequences of eight per revolution.

(*b*) *Sequence control.*—In the point-by-point scan the sequence of events in the measurement of one reflexion is controlled by another 25-station uniselector, *USD*. This uniselector controls the index-printing cycle, the measuring cycles and the operation of the setting-control system. It is moved on from station to station by a low-frequency relay oscillator and by completion signals from the subsidiary control units as shown in Table 2 which lists the functions of this uniselector station-by-station.

In the continuous scan mode of operation the crystal oscillation cam is arrested at the mid-point, the uniselector *USD* rests permanently in station 23 and

Table 2. *Sequence of operations in the measurement of one reflexion*

Stations	Function	Move-on Signal
1	Punch line-feed (L.F.)	Relay oscillator (R.O.)
2–9	Print and punch indices $h_1h_2 \pm k_1k_2 \pm l_1l_2 \pm$	R.O.
10	Punch code symbol *	R.O.
11	Punch carriage return (C.R.)	R.O.
13–22	Measurement cycles (punch out includes initial (L.F.) and terminal (C.R.))	R.O. or oscillation mechanism
23	Setting motor switched on	Batch counter
24	Optional rest position	R.O.
25	Punch (L.F.)	R.O.

the sequence of events is controlled by *USC* as indicated in Table 1.

7. Accuracy of setting

The foregoing description of the way in which the diffractometer sets itself is of course idealized to some extent and there are some practical limitations. The system for setting crystal and counter in position for any particular reflexion has been found to work quite satisfactorily over most of the range of operation of slides *A* and *B*. It is clear that the crystal can rotate freely with the slide system when these slides are set at zero but the crystal orientation is quickly defined as the saddle is moved away from the zero position. Table 3 shows the range of angular positions which the crystal can be constrained to adopt at various values of ξ. The values of $\Delta\varphi$ listed show the differences between the positions in which the crystal settled after the slide system had been pushed by hand first in a clockwise and then in an anti-clockwise direction. The positions to which the crystal is set in normal operation have also been compared with calculated values and the r.m.s. error has been found to be less than 10 min. for all values of $\xi > 0{\cdot}1$. Reflexions with $\xi < 0{\cdot}1$ are best set and measured individually.

Automatic setting of the inclination angle does not yet work so well. The inclination angle is not set automatically with sufficient accuracy (i.e. with $\Delta\mu < 10'$) with $\zeta < 0{\cdot}4$. This is not, however, a serious limitation to the use of the instrument since the inclination angle can be worked out with little trouble, from the relation $\sin\mu = \zeta/2$, and set at the same time as the vertical slide. In fact this is often a more convenient procedure since it obviates the necessity of returning to the zero position on slides *A* and *B* before making the manual *C*-slide adjustment.

The errors in setting are due to spring and backlash in the mechanism, and to machining errors. Backlash has been reduced as much as possible by spring loading of the nuts on the lead-screws of the slide system and the idler pulleys for the steel-tapes. The differences

in the lengths of nominally equal links of the parallel linkages are less than 0·002 inches in 5 inches. The most serious remaining imperfections in operation at very low angles are due to spring and it is expected that in future versions of the instrument they will be made even smaller by the use of more rigid members.

Table 3. *Latitude in setting crystal rotation at various* ξ

ξ (r.l.u.)	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08
$\Delta\varphi$ (degrees)	±12·18	3·55	1·72	0·99	0·66	0·40	0·28	0·18
ξ (r.l.u.)	0·10	0·15	0·20	0·50	1·0			
$\Delta\varphi$ (degrees)	0·12	0·06	0·05	<0·03	<0·03			

8. Speed of operation

The diffractometer is being used at present in the measurement of reflexions from crystals of sperm-whale myoglobin (e.g. Kendrew *et al.*, 1960) and a short account of these measurements will perhaps best indicate the potentialities of the method. A sealed-off X-ray tube with a Cu target and foreshortened focus 0·4 × 0·4 mm. is being used. It is operated at 800 watts and both current and voltages are stabilized. The oscillation mechanism of the diffractometer is driven by a 1 r.p.m. motor so that one oscillation cycle takes 60 seconds; the move on from one reflexion position to the next ($a^*=0{\cdot}025$; $b^*=0{\cdot}050$ r.l.u.) and the index printing take about 12 seconds. In the point-by-point mode of operation, therefore, the 800 non-

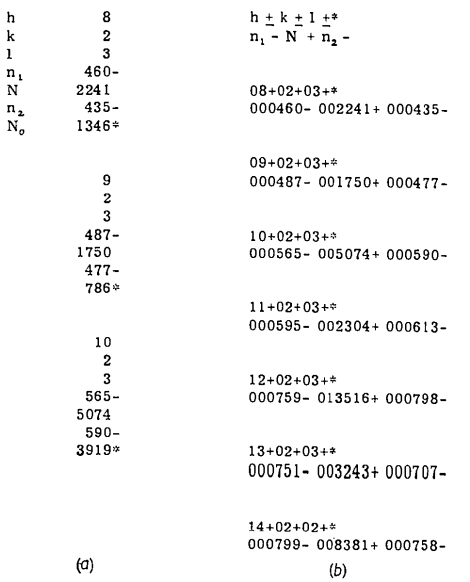

Fig. 7. Typical results (*a*) in the plain language, listing-adding machine output, (*b*) from the punched-tape output. Key to the layout indicated by conventional symbols.

equivalent reflexions that comprise (for example) the *hk*3 level out to 2 Å spacing can be measured once each in 16 hours or twice each in less than 30 hours. The presence of an operator is required only at infrequent intervals during such periods of automatic operation, chiefly to guard against movement of the crystal in its mounting, to assess the extent of radiation damage, and to check the stability of the measuring and recording systems. These objects are best satisfied by the routine measurement of a number of reference reflexions at intervals during the run. The settings for these reference reflexions have to be made by hand. In addition some 14 reflexions near the middle of the level are located manually.

Intensities measured in this way agree well with those measured with much more trouble and in a longer time by the densitometry of Buerger precession photographs. Such photographs have to be exposed for up to 20 hours (including the necessary short exposures) at a 3 kW. rotating anode tube. Densitometry, the measurement of densitometer traces and scaling then takes two skilled assistants about two days at the end of which the data are in the state produced automatically by the diffractometer. Fig. 7 shows the plain language output of the diffractometer and the printed lay-out obtained when a typical output tape is passed through a reproducer unit. Representative diffractometer and photographic measurements have been compared and the difference between these sets of measurements has been found to be less than 12%, which includes contributions from uncorrected absorption errors and radiation damage. The absolute accuracy of the diffractometer measurements will be discussed in detail elsewhere. The measurement of protein crystals provides a stringent test of diffractometer technique (and of the photographic method) and considerably higher speeds can be achieved with the linear diffractometer in the measurement of more strongly diffracting crystals. The duration of an oscillation cycle could then be reduced to 15 seconds by fitting a synchronous motor with a different gear-box to the oscillation mechanism.

For semi-quantitative work, for example the examination of possible heavy-atom derivatives of protein crystals, the continuous-scan mode of operation is also useful. A record of the same *hk*3 reflexions from myoglobin can be obtained by this method in about 4 hours, using the medium speed of scan.

9. Processing of results

Normally the output tapes are fed directly to a computer and programmes have been developed, in collaboration with Dr A. C. T. North, which check the tapes for errors, evaluate the background corrected intensities, apply Lorentz-polarization and absorption corrections and list the structure factors in a form suitable for immediate use in Fourier calculations. These programmes and the completely automatic processing of the data will be described in a further paper.

APPENDIX

Variation of reflexion breadth in continuous scan

The variation in reflexion breadth is readily understood from consideration of the way in which the crystal rotates as the points of a non-central reciprocal-lattice-line are scanned. Fig. 8(*a*) shows the extreme situation in which the scanning slide, on which the point P is moved from end to end at constant rate, is tangential to the sphere of reflexion. In this situation the crystal is momentarily stationary as the direction of crystal rotation changes and it is clear that a point P may then lie in the sphere of reflexion for a relatively long time. Furthermore a second point on a densely populated row may come into the sphere before the first reflexion is completed. Reflexions which are ill-resolved in one continuous scan, however, may be well resolved in another. This is illustrated in Fig. 8(*b*) in which the counter is moved to the other side of the incident beam. For the same point P as that shown in Fig. 8(*a*) the scanning slide then is more steeply inclined to the surface of the Ewald sphere so that a relatively small motion along the slide gives rise to a large rotation of the crystal. The reflexion corresponding to the point P is then sharp and may be well resolved—while reflexions corresponding to points at the other end of the row are broad in their turn. The two chart records shown in Fig. 3 show the same row of reflexions measured in these two situations.

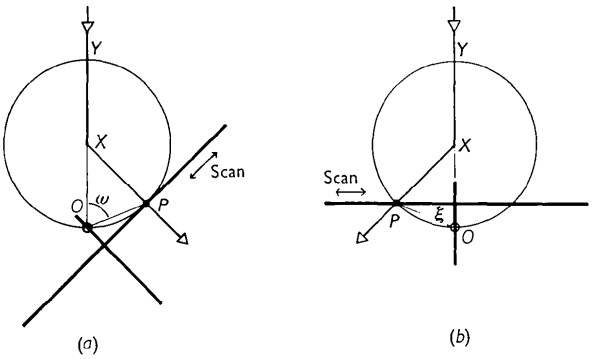

Fig. 8. Orientation of slide system (*a*) for maximum broadening of reflexions at $+2\theta$ in the continuous scan mode of operation, (*b*) in the alternative setting for the same reflexion at -2θ.

The way in which the crystal rotates during a uniform scan along a slide is readily derived. If x, y and z are the coordinates of any point P in the system defined by the three orthogonal slides A, B and C, it is easily shown that for uniform variation of x on the scanning slide A while y and z are held constant in the equi-inclination setting of the instrument, the angular velocity of the crystal is

$$d\omega/dt=[(x/(x^2+y^2)^{\frac{1}{2}}\{4-(x^2+y^2+z^2)\}^{\frac{1}{2}}) +(y/(x^2+y^2))]dx/dt\,. \quad (2)$$

The angular velocity of the counter arm, rotating about the same axis, which must be taken into account in determination of the slit sizes, is

$$d\Upsilon/dt=2x[(x^2+y^2)\{4-(x^2+y^2+z^2)\}]^{-\frac{1}{2}}dx/dt\,, \quad (3)$$

and we note in passing that when

$$y=z=0,\ d\Upsilon/dt=2d\omega/dt\,,$$

that is in scanning central rows the mechanism acts as a simple 2:1 coupling between counter and crystal rotation.

The reciprocal Lorentz factor appropriate to this continuous scan mode of intensity measurement is inversely proportional to the time spent by the crystal in a reflecting position and is given by

$$\alpha=\tfrac{1}{2}[x+y\{4-(x^2+y^2+z^2)\}^{\frac{1}{2}}/(x^2+y^2)^{\frac{1}{2}}]\,. \quad (4)$$

Fig. 9 shows the loci of points with constant α in the zero-level $z=0$. The broken circle shows the limiting value of $\xi=(x^2+y^2)^{\frac{1}{2}}$ for the present instrument but the variation of α over the whole reciprocal lattice level is included to emphasize its simple form. The lines of constant α are all circles given by the equations

$$\xi=2\alpha\cos\varphi\pm 2\sin\varphi\{(1-z^2/4)-\alpha^2\}^{\frac{1}{2}}, \quad (5)$$

where ξ, φ are polar coordinates such that $x=\xi\cos\varphi$, $y=\xi\sin\varphi$. These circles have radii $(1-z^2/4)^{\frac{1}{2}}$ and their centres lie on the circle $\xi=(1-z^2/4)^{\frac{1}{2}}$ at the points $x=\alpha$. The form of the variation of α is the same in all levels in the equi-inclination setting; only the radii of the circles vary.

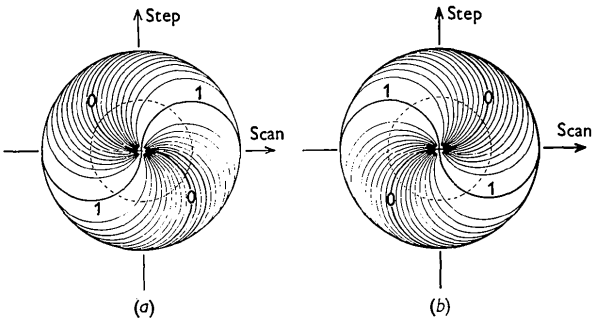

Fig. 9. Lines of constant inverse-Lorentz-factor plotted in reciprocal space for zero-level reflexions measured in the continuous scan mode (*a*) at $+2\theta$; (*b*) at -2θ. The two diagrams are related by a mirror plane in the stepping slide.

The two diagrams in Fig. 9 correspond to the two different settings of the instrument, with counter to the right or to the left of the incident beam, which are illustrated in Fig. 8. In these diagrams the lines for which $\alpha=0$ correspond to settings of x and y for which the scanning slide is tangential to the sphere of reflexion and the reflexion broadening is greatest. Lines with $\alpha=1$ on the other hand correspond to settings in which the scanning slide lies along a radius of the appropriate circle of reflexion. These figures

show that it is always possible to scan a reflexion in a situation in which it is not subject to maximum broadening.

The construction of the linear diffractometer has depended on the patience and skill of Mr T. H. Faulkner, who made the entire instrument in the Royal Institution workshop and is responsible for much of the detailed design. Our thanks are also due to Mr W. A. Coates for his help in the earliest stages of the development and to Messrs F. B. Jones and A. Long for building many of the final circuits. Without the continued encouragement of Sir Lawrence Bragg and Prof. R. King none of this work would have been possible. We are indebted to the National Institutes of Health (U.S.A.) for financial assistance.

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Silicate Transformations: Rhodonite-Wollastonite

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Details of the oriented transformation rhodonite → wollastonite have been studied. The results show conclusively that the cation–oxygen skeleton is preserved during the change, at the expense of silicon–oxygen bonds. This provides direct evidence of the migration of silicon during thermal transformations of silicates.

Introduction

In most silicate structures the Si–O bond is the strongest bond and the SiO_4 tetrahedron the most regular part of the structure. There is therefore a tendency to think of silicate structures in terms of the disposition of the tetrahedra, whether isolated or linked as endless chains, sheets, frameworks, etc., and to consider the other cations as occupying interstitial sites. This convenient simplification is not always justifiable, especially since it tends to imply that the Si–O framework is the most stable part of the structure as well as the most obvious.

Donnay, Wyart & Sabatier (1959) have pointed out that the tetrahedral units, which they refer to as building blocks, may be deformed from their idealized state by substitution of Al for Si or by variation of the cations. They emphasize that too little attention has been paid to the role of the cations in silicate structures, and also assemble convincing experimental evidence of the mobility of Si^{4+} and tetrahedral Al^{3+} under hydrothermal conditions. They postulate a mechanism to explain this, involving water as an essential catalyst.

Dent & Taylor (1956) had earlier studied the dehydration of xonotlite, $(Ca_6Si_6O_{17}(OH)_2)$ to β-$CaSiO_3$, and had concluded from the orientation relationships that the most probable reaction mechanism involved a disruption of the Si–O units of the structure and a