Acta Cryst. (1955). 8, 741

A Single-Crystal Automatic Diffractometer. I

By W. L. Bond

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

(*Received* 10 *November* 1954 *and in revised form* 9 *May* 1955)

An instrument has been built for recording simultaneously the integrated intensities of X-ray reflections and the corresponding crystal orientation angles and Bragg angles. The intensities are determined by a counter and integrating circuit. A two-pen recorder makes a record of each level. Transcription of the data on to the plotter gives an undistorted reciprocal-lattice plot. All levels may be plotted to the same scale.

1. Introduction

The methods most often used in single crystal analysis for determining intensity involve visual estimation of the density of spots on photographic films. This method is arduous and time consuming. Existing equipments either do not give enough information to enable one to index the reflection, or else such equipment must be hand-set to the position in which calculation shows a reflection should be found, and the h, k and l values written in as each peak is recorded. Since a great number of intensities are ordinarily measured for each crystal, it seemed worthwhile to set up for automatic reading.

To index completely a set of X-ray intensity readings, it is necessary to know for each reflection the corresponding crystal position and the Bragg angle. For purposes of discussion we will consider first the zero level, i.e. reflections ($hk0$). The extension to other levels follows simply.

In Fig. 1(a) we show an orthorhombic crystal in what we define as initial conditions. Here the X-ray beam direction defines the y axis and the crystal b direction is made to coincide with y. The crystal will later be caused to rotate around the z axis, which coincides with the c axis of the crystal. Initially the a axis coincides with x; the fixed axes, x, y, z serve to define the rotations of the crystal axes a, b and c.

At an angle ε from a is the vector N_{hk0}, the normal to the ($hk0$) plane. For an orthorhombic crystal ε is given by:

$$\tan \varepsilon = \frac{k/b}{h/a}\,, \tag{1}$$

where a and b refer to relative axial lengths along the a- and b-directions. If the crystal be rotated clockwise through an angle ε, N_{hk0} would coincide with x and the X-ray beam would be parallel to the lattice plane ($hk0$). In order to have an X-ray reflection upward from this plane, the crystal will need to be rotated further by amount θ, where θ is the Bragg angle. Hence the total crystal rotation necessary to have a reflection ($hk0$) is

$$\omega = \varepsilon + \theta\,. \tag{2}$$

If we record for each reflection the value of ω and θ we can find by (2) the direction ε of each plane normal. A polar plot of $1/d$ values (or their equivalent, $(2/\lambda)\sin\theta$) against ε gives the reciprocal lattice of the zero level, which enables one to index all ($hk0$) reflections.

Fig. 1(b) shows a crystal that has turned through

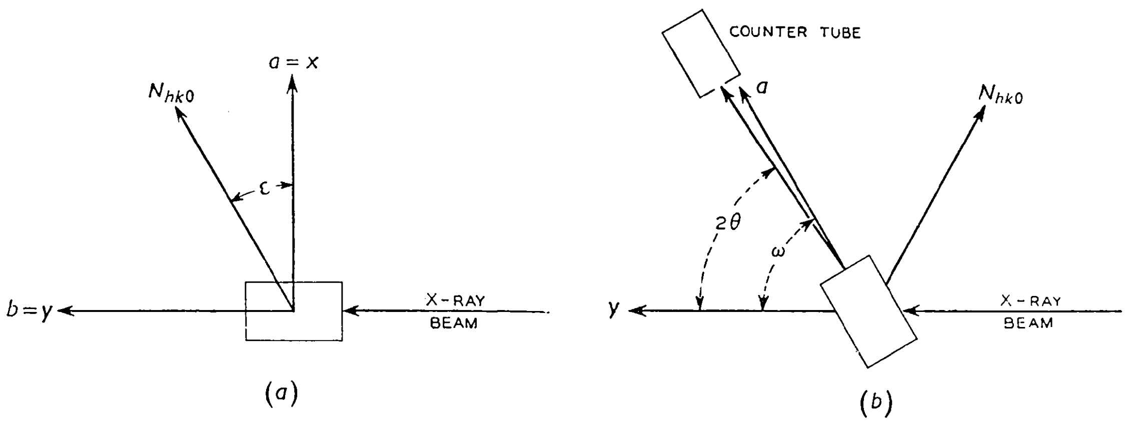

Fig. 1. (a) Initial position of a crystal. (b) A crystal turned through angle ω.

an angle ω and is reflecting a ray into a counter tube placed at an angle 2θ from the y axis. In order to find all the combinations of ω and θ that correspond to Bragg reflections the counter tube could be set initially at zero angle, i.e. on the y axis, the crystal turned through 360°, the counter tube raised a little, the crystal turned through 360°, the counter tube raised again and the process continued until all combinations of ω and θ are covered, i.e. all Bragg reflections in the level obtained. The opening of the counter tube must subtend an angle at the crystal equal to or greater than the increments by which the counter tube is raised per revolution of the crystal. Instead of using a step system as described above it is better to gear the counter to the crystal so that the motion is continuous. A record of ω gives both ω and θ. A second pen records the counter-tube activity.

In our diffractometer the counter is geared to the crystal in a mechanical ratio of 1:180, i.e. the counter tube moves 2° ($= 2\Delta\theta$) for every complete revolution of the crystal. We can hence consider 'crystal turns' on the record as also 'degrees θ'. We record ω by connecting to a recorder the contact arm of a continuous potentiometer attached to the crystal axis. The arm picks up a potential that rises and falls uniformly, making a saw tooth trace on the record. One tooth is one turn, 360° of ω or 1° of θ. If no intensity above background is recorded, for example, until the 21st turn, then there is no reflection of observable intensity at a Bragg angle less than $\theta = 21°$. The crystal position at the time of the reflection is given by the position on the tooth at which the reflection occurred. It might seem difficult to read this position on the steep slope of a tooth, but subsequent developments simplify this reading.

A recorder pen needs time in which to work. A fast pen stabilizes in a new position in about 1 sec. Consequently the crystal must rotate slowly enough so that a reflection does not pass through the sphere of reflection in less than a second. If a peak is $\frac{1}{2}°$ wide, the crystal must turn more slowly than $\frac{1}{2}°$ in 2 sec. or one crystal turn in 24 min. At this rate it would take 36 hr. to cover one level, which is too slow for practical purposes. Consequently, we consider two speeds of drive, fast between reflections and slow while recording a reflection. We use a fast drive slightly slower than one turn of the crystal per minute, a slow drive 1/100 this speed. To record a complete level on the fast drive would take a little over $1\frac{1}{2}$ hr. and on the slow drive a little over 150 hr. On the fast drive a sharp peak is nearly covered in the reaction time of the relays that control the ω speed. To ensure a complete record the crystal is 'back set' a few degrees when the fast speed clutch is disengaged. The reflection is scanned at slow speed, and the crystal advanced (the same amount as the back set) when the high-speed clutch re-engages. This back-setting device serves as a reflection anticipator which slows the motion in time to get a complete record of each Bragg reflection. When the back setter turns the crystal back, the signal drops back to background. Another relay (ratchet type) prevents the fast clutch from re-engaging and the back setter from returning to its scanning position. The contacts of this relay are opened by one electric impulse through its winding, closed by the next such impulse. Hence it operates as an 'alternator' and prevents the premonitory impulse fall (caused by the back setter) from being treated as the drop of the signal upon completing a reflection.

2. Goniometer details

Fig. 2 shows the general scheme of the apparatus. The geared motor 1 drives fast clutch 2 and worm 3. Worm 3 turns worm gear 4 and worm 5, which turns worm gear 6 and the slow clutch, 7. Slow clutch 7 is a one-direction clutch, i.e. it slips in one direction but holds in the other direction (see Fig. 6(b)). Consequently, when fast clutch 2 receives no current, shaft 8 is driven slowly by the slow clutch, but when the fast clutch (see Fig. 6(a)) does receive current shaft 8 is turned at 'high' speed, and the slow clutch slips.

Shaft 8 drives worms 11 and 12. Worm 11 turns worm gear 13 and worm 14. Worm 14 turns worm gear 15, which drives the sleeve that supports the counter tube. Worm 12 turns worm gear 16, which is fastened to the crystal shaft 17. This drives the crystal 180 times as fast as the counter tube is being driven. Worm 12 is keyed to shaft 8 so that it can be slid along the shaft by the solenoid 18. This constitutes the back setter. A spring (not shown) returns worm 12 to its rest position when no current is flowing in the solenoid.

For each X-ray quantum received in counter tube 19 an impulse is sent to circuit 20 (ignoring dead time of the tube). In circuit 20 these pulses are clipped to a standard height and trimmed to a standard duration. A part of this standardized output goes through a scaling circuit to the integrating circuit 38 and part is fed into a rate-meter circuit in the discriminator. As long as the rate of pulse reception is below a predetermined threshold, relay T of the discriminator keeps conductor 23 connected to conductor 24. In this situation current from the power supply 29 can flow through contact 26 to 24–23, then to the grounded motor and shaft of worm 3 then to the clutch 2 through the winding of relay G and thence back to the power supply. Consequently, if the X-ray reflection is below threshold, clutch 2 drives the diffractometer at high speed and relay G keeps contact 30 open so that the back setter is in its forward position.

When the X-ray intensity rises above threshold, relay T loses its current and contact 23–24 is broken and 23–25 is made. The breaking of 23–24 stops the current through the fast clutch and relay G, causing a shift to slow drive and, because circuit 30 closes, power goes to the solenoid 18, the crystal is set back and the signal falls rapidly. When 23 is connected to 25, power goes to relay R, which steps up one step;

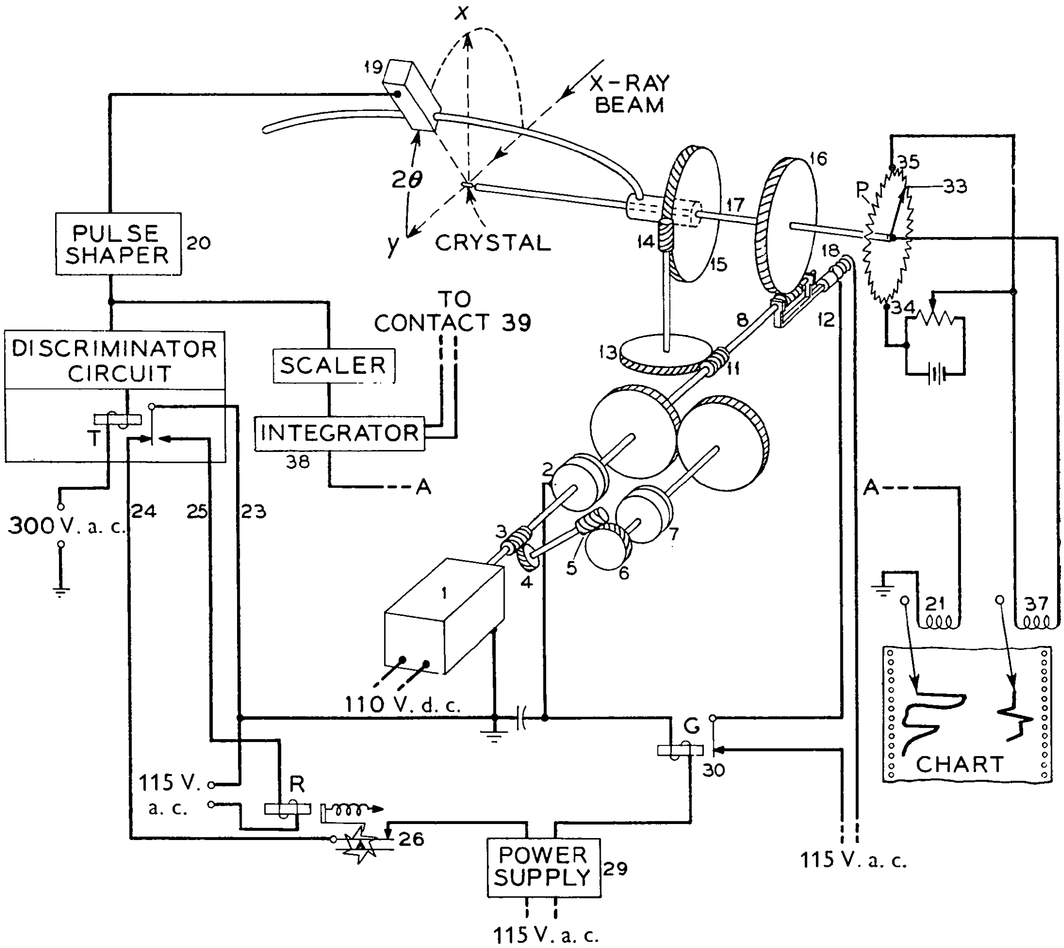

Fig. 2. Schematic diagram of the diffractometer.

this opens 26 so that when 23 is re-connected to 24 the clutch circuit is open and high speed cannot be re-established until the signal has risen and fallen once again—i.e. the reflection intensity is properly recorded at slow speed. This second rise of the signal causes another impulse to go to the winding of relay R so that it steps up another step and contact 26 closes again. When the signal falls now, the circuit is again in the condition shown in Fig. 2.

It has been stated that part of the standardized output of circuit 20 goes to the integrator 38. Here the impulses are stored in a high-quality condenser. Since each impulse brings in the same quantity of electricity, the voltage across the condenser is a measure of the number of impulses. This voltage controls the grid of an electrometer tube, the plate current of which goes to the recorder. The condenser is kept shorted by contact 39, when there is no signal, but when the signal rises to threshold the back setter operates and opens a microswitch, and impulses start to charge the condenser. The recorder pen climbs continuously making a record of the accumulating voltage across the condenser, climbing more slowly as the rate falls. When the rate falls below threshold, contact 39 again shorts the condenser. The highest point of the curve, the point just before the fall, represents the integrated intensity. The calibration is intentionally non-linear. So that the percentage accuracy will be the same throughout the range a logarithmic representation is desired. This is approximated by the constants of the integrating circuit, but a linear integrator can be used with a logarithmic potentiometer in the recorder. For further details see the accompanying paper by Benedict (1955).

The crystal-position-indicating potentiometer P has a small voltage difference between opposite points 34 and 35. The potential difference between points 33 and 35 varies from zero to maximum then back to zero in a linear way as the arm turns. This potential difference is fed to pen 37. When the crystal is turning fast, the pen makes a series of saw teeth, each complete tooth representing a complete turn of the crystal and an increase in θ of 1°. Whenever a reflection is being recorded, the diffractometer is in slow drive, and pen 37 moves so slowly that its trace is almost parallel to the time axis. One is interested in the fraction of a turn ω only when an intensity is being recorded, at which time this value is read simply from the chart.

The record of a few reflections from a sodium chloride crystal is shown in Fig. 3. The diffractometer

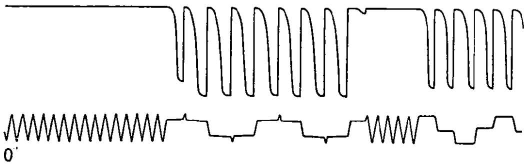

Fig. 3. A part of the record of a level made by the diffractometer.

was set at $\theta = 0$, $\omega = 0$, the starting point was marked, and the apparatus set in motion. There is no reflection until $\theta = 15°$, when the saw teeth stop and the 'parallel' line starts. Eight reflections are recorded (200, 020, $\bar{2}00$ and $0\bar{2}0$, each recorded twice (see § 5)) after which the saw teeth continue uninterruptedly for some distance until the next form 220 enters the picture.

3. The plotter

The plotter does the arithmetic in equation (2), rewritten as $\varepsilon = \omega - \theta$. Here, however,

$$\theta = \omega/360 \,, \tag{3}$$

so that

$$\varepsilon = \omega(1-1/360) = \omega(359/360) \,. \tag{4}$$

A drive shaft in the plotter (1 in Fig. 4) is turned once for each turn of the crystal. A gear system causes a turntable to turn 360 times for each 361 turns of the drive shaft. The drive ratio should be 359 to 360, but 359 is not factorable. Gears with such a great number of teeth as 359 are not practical here. The drive ratio 360 to 361 is factorable into 18×20 to 19×19 and hence can be compounded with small gears. Since $360/359 = 1{\cdot}002785$ while $361/360 = 1{\cdot}002778$ we see that the difference is negligible.

The turntable carries a paper disk on which the

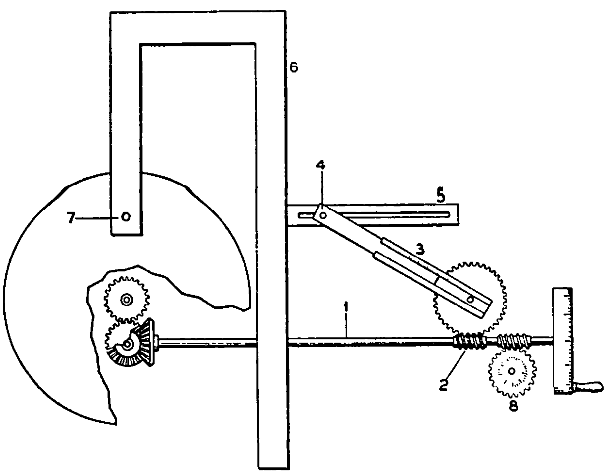

Fig. 4. Schematic diagram of the plotting device.

transcription is made by marking the paper through hole 7 at plotter settings that correspond to reflections. The drive shaft carries a drum graduated to 5° intervals for obtaining fractions of a turn of ω.

A polar plot of $(2/\lambda) \sin \theta$ against ε constitutes a plane reciprocal lattice, which can be immediately indexed. Consequently, if we supply a reference point that moves away from the center of the turntable by an amount proportional to $\sin \theta = \sin (\omega/360)$ we will have a machine that converts crystal turns into a reciprocal lattice. In Fig. 4, worm 2 turns arm 3 a quarter turn for ninety turns of the drum. Hence pin 4 moves from its starting position (arm 3 horizontal) with a vertical motion equal to arm length L times $\sin \theta$. The scotch yoke 5 transmits this motion to the finger, 6. On starting, hole 7 in finger 6 is at the center of the turntable. When the drum is turned through angle ω, the hole is moved upwards by amount $L \sin (\omega/360)$. For the zero level we use $L = 10$ cm. Other levels are recorded similarly to the equi-inclination Weissenberg method (Buerger, 1942). Arm length L is shortened in proportion to $\cos \mu$, where μ is the level setting angle (see below). With this precaution all levels are plotted to the same scale.

Worm gear 8 serves as a turn counter. It is graduated from 0 to 90 turns so that one can tell the number of crystal turns at a glance.

Fig. 5 is a plot of the data for sodium chloride

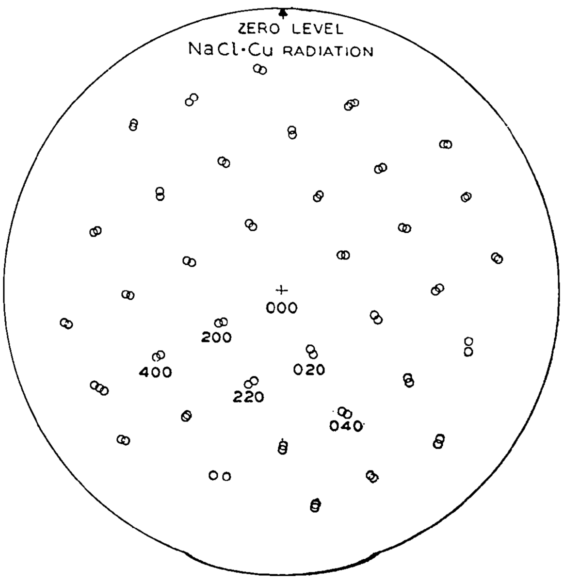

Fig. 5. The zero level of NaCl as plotted from data recorded by the diffractometer.

transcribed from the record of which Fig. 3 is a part. The fractions of a turn of the crystal are read from the chart by means of a hand scale. When starting, the top of the chart was marked by a short radial line, as seen in Fig. 5. The crystal position at starting did not correspond to 'an axis perpendicular to the X-ray beam'. This was a convenience for description but unnecessary in actual operation. When the first few points of the zero level are plotted, the orientation of the reciprocal lattice becomes obvious.

The eight reflections of the {200} form actually reflect at the same θ value; their apparent dispersion in θ here is due to the size of the window of the counter tube and the link between the drive of crystal rotation and the counter tube motion.

If we had plotted $\sin\theta$ against ω instead of against ε, the lines of h constant and of k constant would be curves instead of straight lines. These lines would start radially from the origin, but curve around so as to advance 90° by the time they reach the edge of the chart.

4. Upper levels

While the zero level of a crystal is being run, a hemicylinder of film in a light-tight black paper envelope is secured below the crystal and exposed to downward reflected X-rays. This produces an ordinary rotation photograph and is used as in Weissenberg photography to determine the layer-line settings for subsequent levels. By the time the zero level is completed we will have developed this film and determined the settings for level 1 ($l = 1$) level 2 ($l = 2$), etc. A layer line deviated from the direct beam by an amount y on the film (which is bent to radius r) requires, for equi-inclination recording

$$\sin\mu = y/2\sqrt{(r^2+y^2)}\,. \tag{5}$$

To set for this level we turn the diffractometer through an angle μ about axis x provided for this purpose (see Figs. 2 and 7). We then turn the counter tube on

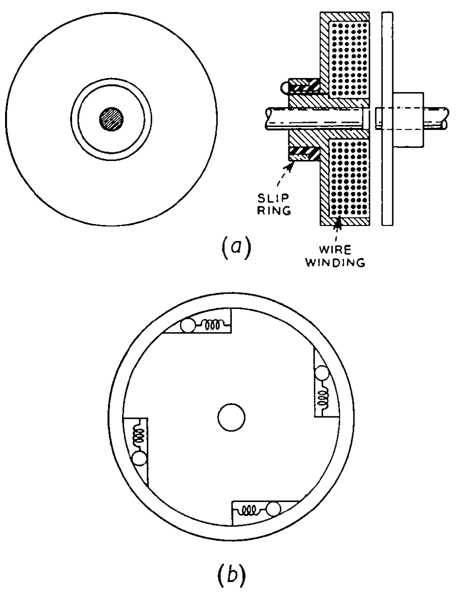

Fig. 6. (a) The fast clutch.
(b) The slow clutch (schematic). The 'swastika' shaped piece can drive the outer ring clockwise because the spring loaded rollers will then bind. The ring, however, cannot drive the swastika clockwise.

its arm through an additional angle μ, close the tube port to an opening smaller in the ratio $\cos\mu$, and are then ready to record this level. When we plot this level, arm length L is reduced to $\cos\mu$ times the length for the zero level. The new level is then plotted to the same scale as the zero level was plotted.

5. Aperture size

If the counter tube aperture is of a size that we scan with no overlap, we will split reflections and have to determine intensities by adding together two parts. If the gears are not perfect, this addition will not be safe. In order to avoid this risk we use a 100% overlap. Each reflection is covered twice, and is hence fully covered in a single pass at least once. We use only full reflections, disregarding parts. This double recording requires a counter tube aperture four times the θ equivalent of one turn of the crystal; in our case the aperture is then 4°. The counter tube was found to have uniform sensitivity over this region. In Fig. 5 this 100% overlap causes most $hk0$ points to be double; a split reflection is triple. One of the points, however, was made in one pass and is a reliable measure of intensity.

6. Limitations on cell size

The larger the unit cell of the crystal the smaller the angle between successive reflections. If this angle is not greater than $\frac{1}{2}\delta$ (where δ is the angular aperture of the counter tube) the corresponding lines are not resolved. (The factor $\frac{1}{2}$ is caused by angle-doubling in reflection.) Consider a plotter chart of zero level. The largest radius represents $2/\lambda$. If T is the smallest distance on the chart between points representing successive reflections, the angle between these is never smaller than $\Delta\omega$, where

$$\sin\tfrac{1}{2}\Delta\omega = \frac{T/2}{2/\lambda} \quad\text{or}\quad \Delta\omega = 2\sin^{-1}\frac{T/2}{2/\lambda}\,.$$

But $\Delta\omega$ must be larger than $\frac{1}{2}\delta$, hence $T > (4/\lambda)\sin\frac{1}{4}\delta$. But $T = 1/d_m$, where d_m is the maximum interplanar spacing in the level. Hence

$$d_m < \frac{\lambda}{4\sin\frac{1}{4}\delta}\,. \tag{6}$$

For the apparatus described, used with copper radiation, $\delta = 4°$, $\lambda = 1{\cdot}54$ Å, hence $d_m < 22$ Å. For a face-centered crystal this means a cell of maximum edge of 44 Å while for a body-centered cell the maximum cell edge is $22\sqrt{2}$ Å $= 31$ Å. For larger cells we may use longer wavelengths or other gear ratios of the diffractometer. If we go to higher drive ratios, say 360 to 1 so that a turn of the crystal means an increase in θ of $\frac{1}{2}$°, we must also change gears in the plotter. The plotter ratio instead of 359:360 should be 719:720. However, 719 has no factors, so again we use an approximation $720:721 = 36\times20:7\times103$.

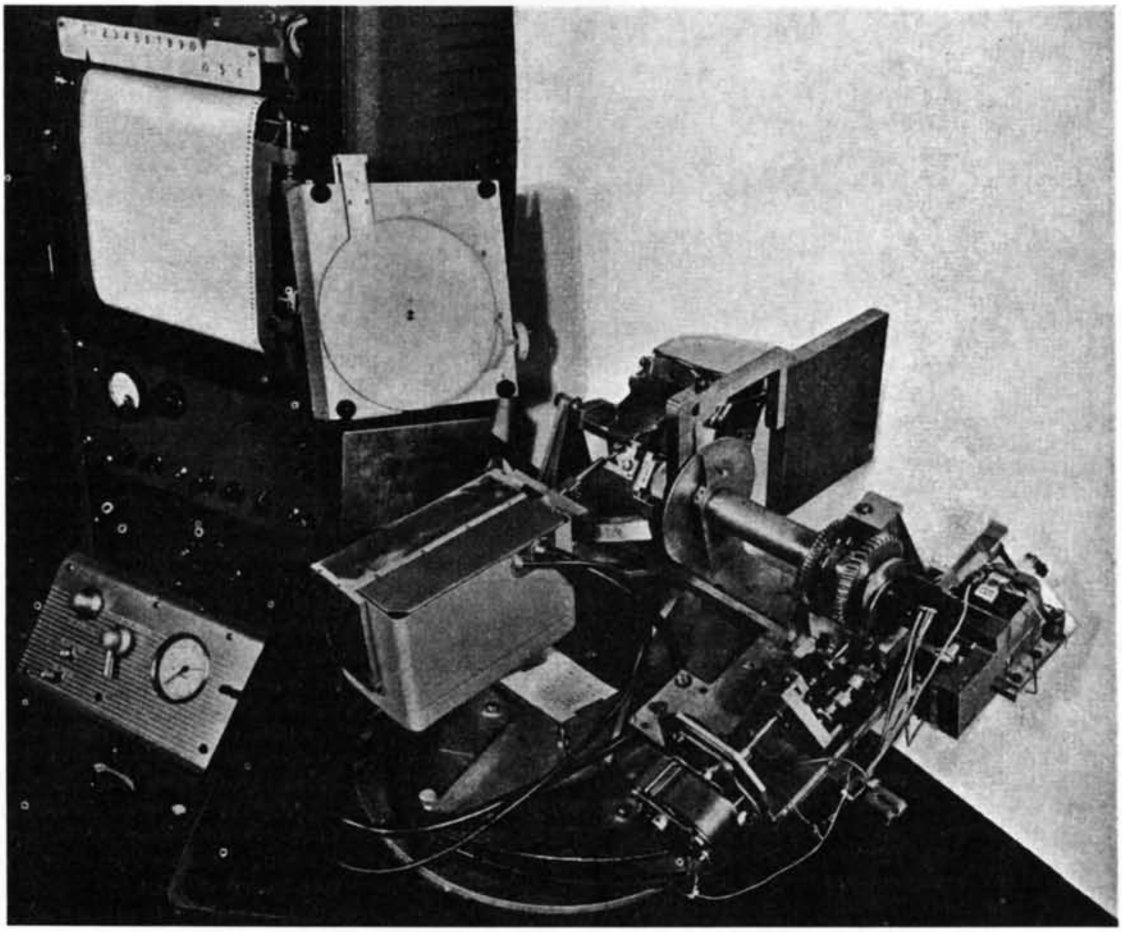

Fig. 7. The diffractometer and plotter with associated equipment.

The drive ratio 540:1, for which one crystal turn means $\frac{1}{2}°$ increase in θ, requires a plotter drive 1079:1080. This is factorable as $13 \times 83 : 27 \times 40$. Changing the diffractometer from 180:1 drive to 360:1 drive merely requires exchanging one set of commercially available gears for another.

7. The use of a monochromator

A monochromator was built into the unit because of the presence of white radiation, which would have made it impossible to record strong reflections accurately since white radiation near the characteristic radiation reflects strongly enough to operate the discriminator. Hence the instrument would waste time recording wrong intensities. The monochromator also bends the ray path in such a way that a wider θ range is achieved.

8. Discussion

Since this technique does not involve setting the crystal and counter for particular reflections, obtaining the intensity data is not dependent on the knowledge of highly accurate lattice constants, which does appear to be a requirement for some of the counter techniques in current use.

The design and operation of a pilot model single-crystal automatic diffractometer which obtains highly accurate intensity data has been presented above. Needless to say, we feel that improvements can and will be made. For example, a proportional counter is to be substituted for the Geiger counter and it is hoped eventually to use a print-out scheme for recording intensities. We have presented the essentials of the equipment so as to give crystallographers who are interested the opportunity to see what has been done and to go ahead with building similar equipment if they so desire.

The writer wishes to express his appreciation to Dr S. Geller for valuable suggestions made during the development of this apparatus and the writing of this paper.

References

Benedict, T. S. (1955). *Acta Cryst.* **8**, 747.
Buerger, M. J. (1942). *X-ray Crystallography*, chap. **14**. New York: Wiley.