$$\sigma_{xi}^2 = \Sigma(w\Delta F)^2/(n-s) \{\Sigma w\Delta F . w(\partial F/\partial x)/\Sigma(w.(\partial F/\partial x))^2\}$$

where

σ_{xi} is the s.d. of the x coordinate of the ith atom,
n = number of reflections,
s = number of variable parameters,
w = weight.

The values for the final coordinates are 0·005 Å, 0·010 Å and 0·006 Å for x, y and z respectively. The greater error in the y direction is explained by the comparative sparsity of data contributing to the determination of the y coordinates. From the standard deviations of the coordinates the standard deviations of the bond lengths are derived by the expression

$$\sigma(l)^2 = [(\sigma_{x_1}^2 + \sigma_{x_2}^2)\cos^2\alpha + (\sigma_{y_1}^2 + \sigma_{y_2}^2)\cos^2\beta + (\sigma_{z_1}^2 + \sigma_{z_2}^2)\cos^2\gamma]$$

where

$\sigma(l)$ is the s.d. of the bond length,
σ_{x_1}, σ_{x_2} the s.d. of the x coordinates of atom 1 and atom 2 *etc.*,
$\cos\alpha$, $\cos\beta$, $\cos\gamma$ the direction cosines of the bond with respect to a, b and c^*.

All values for $\sigma(l)$ come to less than $1{\cdot}5 \times 10^{-2}$ Å. The standard deviations of the B-coefficients are of the order of 10%.

Analysis of thermal vibrations

Finally, an attempt was made to interpret the anisotropic temperature factors in terms of translations and librations of the molecule and of intramolecular movements of the atoms resulting in distortion of the molecule (Lonsdale, 1960). The physical interpretation of the thermal factors so obtained is a large translatory motion in the plane of the molecule, normal to the chains of the molecules, which is in accordance with Lonsdale's results for diketopiperazine (1961); the librations are largest about the long axis of the molecule, which is usual for long-chain compounds.

The accuracy of the X-ray data is not sufficient to produce reliable values for the distortional vibrations as these are arrived at as residues.

The early stages of the work described in this paper were carried out at Birkbeck College, London, and it was completed at University College, London.

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Cascade: An Automatic Single-Crystal X-ray Diffractometer

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An automatic system is described for the measurement of intensities of X-ray reflections from single crystals. It is controlled by a programmable plugboard and punched paper tape output from an IBM 1620 computer. The goniometer used is the G.E. single crystal orienter. A circuit is provided which maximizes the counting rate before the intensity is measured.

1. Introduction

A few years ago the factor limiting the scope and precision of an X-ray crystal structure analysis was the lack of proper computing facilities. Now we have computers which can handle whatever calculations one wishes in an extremely short time and the factor limiting the scope of an X-ray analysis is frequently the collection of data. CASCADE (Colorado Automatic

Single Crystal Analysis Diffraction Equipment) was designed in an attempt to make the data collection time an insignificant part of the total required for the X-ray analysis. Other automatic X-ray diffractometers have been described (*e.g.* Drenk *et al.*, 1959; Arndt & Phillips, 1961; Abrahams, 1961). However CASCADE has a number of features not shared by these.

One important feature of the machine described here is that it is relatively inexpensive to build. This was achieved by using equipment already available, wherever possible. Thus it was decided to modify the G.E. single crystal orienter (Furnas, 1957) for automatic operation. The settings for the orienter are prepared on an 8-channel punched paper tape by an IBM 1620 computer and refined by CASCADE. The intensities and other relevant information are output on 8-channel punched paper tape for future processing by the 1620. The entire operation is controlled by a plugboard sequencer.

The IBM 1620 programs used to process the output tape were written here. These programs make the LP corrections, absorption corrections and place the data on an absolute scale using a combination of the Wilson and Kartha methods (Macintyre *et al.*, 1961).

2. General description

The G.E. single crystal orienter has three angular settings which define the relative orientation of the crystal, counter and X-ray beam. These are the polar angle φ, the azimuthal angle χ and the Bragg angle θ of the reflection being considered. When the single crystal orienter is automated servo-motors must be supplied to adjust each of these angles and these servos in turn must be informed of the magnitudes of the angles which have to be set for the measurement of the intensity of a reflection.

The servo-motors consist of a combination of a Bodine AC motor and a four decade Coleman Digitizer. One such combination is provided for the adjustment of each of the three angles, φ, χ, θ, as defined by Furnas (1957). The motor which adjusts the crystal to the appropriate Bragg angle also sets the scintillation counter to an angle 2θ relative to the X-ray beam, which is of course a standard procedure on the single crystal orienter. The servos are activated one at a time and continue to operate until the Digitizer setting matches the precalculated angle.

These settings are calculated on an IBM 1620 computer and punched out on 8-channel paper tape. They are read from the tape one at a time and stored in the memory of the control unit. Whenever a particular setting is read into memory the corresponding servo-motor is energized and continues in motion until the Digitizer setting matches memory.

Frequently the settings which are computed from measured unit cell dimensions are not exact. Such a situation commonly arises, even when the cell dimensions have been measured with high precision, and can be ascribed to imperfection of the crystal, gradual missetting of the crystal owing to flow of the adhesive, or to a variety of other causes. Therefore the pre-computed settings are regarded as a good first approximation only. The system control, having set the orienter to the pre-computed φ, χ and θ, then automatically adjusts any or all of these angles by 0·005° increments until the counting rate measured by a ratemeter is at a maximum. Only then does

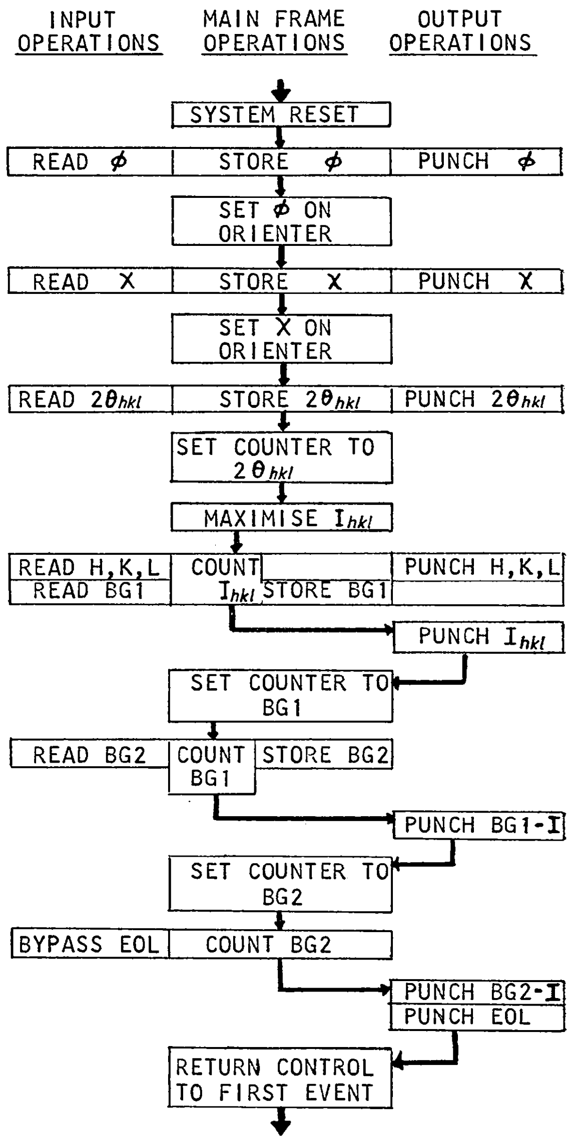

Fig. 1. Flow chart for a program of operations for CASCADE. $BG1$ is some angle ($=2\theta-$constant) to which the counter is moved to measure one background intensity ($BG1$–I). $BG2$ is some angle ($=2\theta+$constant) to which the counter is moved to measure the second background intensity ($BG2$–I). EOL is the end-of-line character code on 8-channel paper tape. This is a possible sequence of operations carried out for intensity measurements by the stationary crystal and counter technique.

CASCADE begin to measure the intensity of the reflection.

CASCADE is designed to measure the integrated intensity of the reflection and two background intensities and to punch these on 8-channel paper tape. In addition h, k, and l for the reflection are punched on the tape together witn φ, χ, and 2θ (which are required in the absorption correction program).

The entire operation is controlled through a plugboard control panel which gives the system considerable flexibility. For example, intensities may be measured either by the stationary crystal-stationary counter method or by the θ, 2θ scan. Further, the sequence of the various events involved in the operation may be changed at will simply by rewiring the plugboard.

A typical intensity measurement by the stationary crystal-stationary counter technique might be carried out as shown in Fig. 1.

3. Orienter and counter assembly

A photograph of the modified G.E. single crystal orienter is shown in Fig. 2.

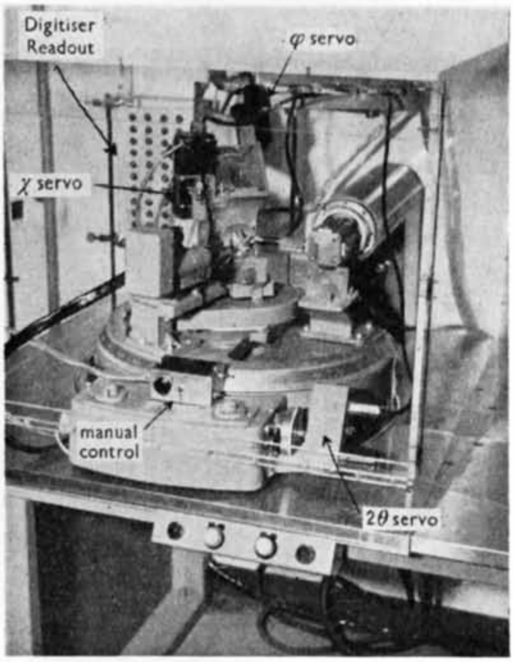

Fig. 2. The modified G.E. single crystal orienter and spectrogoniometer. The 2θ servo is seen at the front of the base tank and to the right. The χ servo is at the center of the photo and to the left. The φ servo is seen at the center and towards the top.

The Digitizer controlling the adjustment of the Bragg angle θ is seen at the front of the spectrogoniometer base tank and to the right. The drive shaft carrying the worm which drives the θ, 2θ adjustment has been extended to the right, through the vernier, and linked directly to the Digitizer drive shaft by a sleeve. Thus one revolution of the worm gear, corresponding to a change of 1° in 2θ, corresponds to a single revolution of the Digitizer drive shaft, corresponding to a change of setting of 100 units, giving a precision in the Digitizer setting of 0·01°. The Digitizer controlling the χ adjustment is seen at the center left; it is geared to provide a precision of 0·01 in the χ setting. The remaining Digitizer controls the φ adjustment, giving a precision of 0·02° in the φ setting.

The collimator and beam tunnel system used is that supplied by G.E. without change.

A 'Norelco' scintillation counter and scaler-ratemeter is used. This scaler has eleven stages of which the first is a 1 μsec. stage. These eleven binary stages are not capable of storing the counts accumulated in the measurement of many intensities. In manual operation, therefore, a scale factor is selected which keeps the number accumulated within the range of the eleven binary stages. In constructing an automatic machine this scale factor is an unpleasant complication. It has been eliminated by the addition of another twelve binary stages, making 23 in all. Thus an accumulated count of $2^{23}-1$ can be accommodated without scaling.

4. Input-output

The goniostat angles are calculated on the IBM 1620 computer using a program by Johnson (1961), modified to provide paper tape output. The angles so calculated are not in a form suitable for entry into the automatic system and so the paper tape produced is processed by another program (written by us). This program sorts the reflections in ascending order of φ. Those reflections with the same φ value are then sorted on χ and 2θ in order to minimize the adjustments to be made to the previous settings to bring the plane into reflecting position. When the reflections have been properly ordered in memory the angles are then converted to Digitizer settings and an output record accumulated ready for punching.

A flag on the low order digit of a Digitizer setting indicates that this setting is lower than the previous one and that the motor should move in a negative direction to reach it.

A flag on the high order digit indicates nothing to the control unit of CASCADE. It is transferred to the output tape of the system with the Digitizer setting. It is required by the programs processing this tape to resolve an ambiguity in the meaning of the number which arises as follows.

In controlling the θ, 2θ movement a four decade Digitizer is used, with each units digit representing 0·01°. Thus the entire range of the Digitizer 0000 to 9999 represents a range in angle of 0° to 99·99°. It is clear then that a 2θ setting of 100·00° would be achieved by the same Digitizer setting as for a 2θ setting of 0°. For 2θ Digitizer settings between 0000 and 8000 there is an ambiguity in the corresponding angle. There is a similar ambiguity associated with settings on the φ Digitizer on which the full scale of the Digitizer covers only 200°.

During processing of the system output tape the computer interprets a flag placed over the high order position as indicating that the true Digitizer reading should be 10000 plus the indicated setting.

5. Control system

CASCADE can measure integrated intensities in a variety of ways. Such versatility is achieved by investing control of the system in what we call 'the program'. This consists of a five-deck fifty-position stepping switch and four relays connected in such a way as to simulate a stepping switch of one deck with 250 positions. The main supply voltage (−70) is applied to these 250 positions one at a time, in sequence, by advancing the stepping switch. A two cycle per second signal is taken from the timer, amplified and used to drive the stepping switch. Three additional relays are used to stop, start and reset the stepping switch. These 250 positions are connected to 250 points on a plugboard. In addition, there are twenty-two terminals on the plugboard connected to the circuits which carry out the twenty-two operations that CASCADE can perform. These operations are listed in Table 1.

Table 1. *List of operations available to CASCADE with codes*

Code	Operation
A	Tape Punch
B	Tape Feed
C	Select *EOL*
D	Select 2θ Servo
E	Tape Read
F	*SR*1 Step
G	*SR*1 Reset
H	Motor Control Reset
I	Select χ Servo
J	Servo Start
K	Select φ Servo
L	Memory Erase
M	Hunt Circuit
N	Punch Scaler Contents
O	Timer and Scaler Reset
P	Timer Start
Q	Program Stop
R	Punch Select
S	Blank (for future use)
T	*SR*2 (program) Reset

Some of the operations are self-explanatory and some will be discussed more fully below.

Fig. 3 represents a small portion of the plugboard with some plug wires on it. Notice that operation '*P*' is programmed to be performed at times sixteen and fifty-eight by connecting terminal *P* with terminals 16 and 58. Some of the operations are repeated several times in the course of measuring one reflection and its two background counts. A typical reflection requires about 200 steps on the program after which operation '*T*' is performed which automatically resets

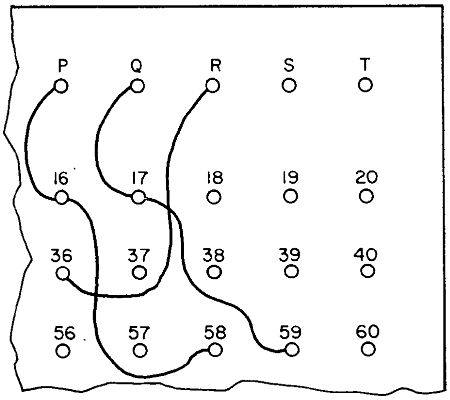

Fig. 3. The diagram represents a section of the plugboard control. The terminals labelled *P*, *Q*, *R*, *S*, *T* are connected to the circuits performing some of the operations CASCADE can carry out. The numbered terminals are connected to the corresponding positions of the 250 position stepping relay which controls the sequence of operations performed.

*SR*2 and the system proceeds to examine the next reflection.

The program provides approximately one-half second for each operation. For most operations this is sufficient. However, some require more time. This is taken care of by an operation called 'Program Stop' which stops the program for an indefinite length of time. The program is started again upon completion of the lengthy operation. For example, (see Fig. 3) operation '*P*' is timer start. Since the count time is longer than one-half second, we stop the program by energizing '*Q*' after '*P*' and the program rests here until the selected time has elapsed. When the selected time has elapsed the scaler stops counting and a signal starts the program, which then moves on to points 18, 19, *etc.*

Operation '*B*' (tape feed) refers to the tape reader. It advances the incoming tape by one character. A closely related operation is '*E*' (tape read) which energizes the relay circuits that convert a binary coded decimal number on the tape to a decimal coded number and stores this number in the memory circuit and/or the code magnets of the tape punch.

The four digit number on the input tape corresponding to the next position of a servo is read into memory one digit at a time, high order digit first. Memory consists of four banks of ten relays each. Each memory relay is provided with its own holding circuit which enables it to remain energized until memory erase (*L*) is performed. A ten deck four position stepping switch designated *SR*1 selects the memory bank into which each of the four digits of a given angle setting is channelled and subsequently stored. Thus the operation '*F*' (*SR*1 Step) selects the program memory bank. Operation '*R*' (punch select) is energized if the above mentioned digit is to be transferred to the output tape. When a number is to be read into memory only, the sequence goes as follows: *B*, *F*, *E* repeated once for each digit. When a number is transferred to the output tape only, the sequence goes as follows: B, R, E, A repeated once for each digit. If a number is to be read into memory and transferred to the output tape, then the sequence is B, F, R, E, A repeated once for each digit. We assume that $SR1$ was reset (G) and the memory erased (L) before starting to read in each 4 digit number and not between each digit of this number.

Operation 'M' (Hunt Circuit) is a circuit which when energized will cause the servo to move in such a way as to maximize the counting rate. This operation may require more than one-half second, so it will be followed by operation 'Q' (program stop). The hunt circuit senses the rate meter and charges a capacitor by an amount proportional to the counting rate. The servo is then allowed to advance in either a positive or negative direction approximately 0·005°. The counting rate will then either increase or decrease depending upon whether it advanced up or down the slope of the peak. If the count rate decreased, corresponding to a motion down the slope of the peak, the capacitor would discharge and cause the motor direction relay to operate and reverse direction. We step again (now going up the slope), sensing the charge in the capacitor at each step, until one step will cause another decrease in count rate which corresponds to starting down the other side of the peak. Again the direction of the steps is reversed. Each direction reversal is counted on a scaler which stops the procedure on the third reversal and restarts the program. For this purpose we use two stages of the existing scaler.

The operation 'N' (punch scaler reading) is used to transfer data (the number of counts) from the scaler to the output tape. This is done by scanning each of the binary stages one at a time with a 2-deck 25-position stepping switch ($SR3$) which is driven by a two cycle per second signal from the timer. $SR3$ advances one step which connects the punch to the last binary stage (2^{19}) and reads the zero or one stored there into the punch. $SR3$ then advances to binary stage 2^{18}, simultaneously punching information concerning stage 2^{19} and clearing its memory to accept data from stage 2^{18}. This is repeated twenty times after which the program is restarted. We have 23 stages in all, but punch on the output tape only the data stored in the last twenty. The first three stages of the scaler input are ignored.

The intensity measurement involves counting for a fixed length of time and so an accurate way of measuring time was needed. Upon checking with the local power company, we found that the line frequency was not too stable over the twenty-four hour day. It was therefore decided to use a crystal controlled 100 kcyc. oscillator as a base for time rather than a clock or scaler which depended on the AC frequency. Two time signals are required by CASCADE, a two cycle per second signal and one of six cycles per minute. These signals are obtained from the 100 kcyc. oscillator by means of binary dividers. The six cycle per minute signal is amplified and used to drive a fifty-position stepping switch ($SR4$). Several of the fifty terminals are connected to a time selector switch such that times of approximately 20, 50, 100, 200 or 300 seconds may be selected as desired. The word approximately is used because the absolute values are not exactly 20, 50, *etc.*, but are multiples of 2^{20} divided by 10^5, *i.e.* 10·486. The timer is consistent to within ± 25 milliseconds from count to count. The two cycles per second signal is used to drive the program, and the tape punch when it is punching out the data in the scalers.

6. Effects of modifications on the goniostat

Servo motors have been supplied to adjust the φ, χ and θ–2θ settings on the goniostat. The physical limitations of space around the single crystal orienter prevented installation of a servomechanism to adjust the angle ω. Therefore intensity measurement by an ω-scan is not available in CASCADE.

No clutch is provided on the φ adjustment servo and hence the φ angle of the crystal can be changed only by activating this servo. This servo changes φ at a rate of 7° per minute. Thus the procedures involved in centering a crystal may be quite time consuming. This problem has been largely overcome by careful calibration of the viewing telescope and replacing its crosshair eyepiece with a vernier eyepiece.

CASCADE can be switched into manual mode and in this mode the goniostat may be operated as intended by its designers, except for the restrictions mentioned above. Each servo motor can be selected manually and it can be controlled by start-stop buttons on the manual control. A neon light digital readout shows the setting of the Digitizer of the selected servo so long as that servo remains selected.

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