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Operation of a Computer-Controlled Equi-Inclination X-ray Diffractometer

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(*Received* 24 *December* 1968 *and in revised form* 14 *April* 1969)

The control program for a Buerger–Supper equi-inclination diffractometer on-line to a PDP–8/S computer is described. The computer calculates the angular settings, scan-range and optimum scan-speed for each reflexion, pulses stepping motors to provide the crystal and counter motions, inserts attenuators or balanced filters, and activates and interrogates the scaler which is part of the standard counting circuitry. A careful choice of counter apertures, and the re-measurement of reflexions whose precision or background imbalance fails to meet pre-set criteria, appear to overcome the major systematic errors to which diffractometer data recorded in the equi-inclination ω-scan mode are subject.

The Buerger single-crystal equi-inclination diffractometer (Buerger, 1960*a*) has been commercially available for some years in the form of the Supper–Pace Automatic Diffractometer,§ incorporating standard counting circuits and a small fixed-logic computer. The replacement of this fixed-logic computer by a PDP–8/S digital computer with appropriate low-level interfaces‖ produces a relatively low-cost installation of surprising versatility (Fig. 1).¶

Instrumentation

The variables μ and ν (equi-inclination angles), Υ (counter setting) and φ (crystal setting) for this type of diffractometer have been defined by Buerger (1960*b*,*c*). The values of μ and ν are adjusted manually for each reciprocal-lattice layer. Within a layer, the counter and crystal are moved to their respective settings, Υ and φ, for each reflexion by two Digitork stepping motors** operating under computer control.

The counting chain consists of standard Philips electronic components (scintillation counter, pulse-height analyser, scaler, rate-meter, printer- and punch-control units). Counts are initiated by impulses from the computer to the scaler and are timed by an electronic clock in the computer.

Some physical constants of the equipment are as follows: X-ray source-to-crystal distance, 14·5 cm; crystal-to-counter distance, 7·5 cm; $0 \le \mu, \nu \le 55°$; the lower limit of Υ is $-10°$ and the upper limit is given empirically by $\Upsilon \le 73 + 65[1 - (\mu/55)^2]^{1/2}$. The motors are geared to give a resolution of 0·01 degree per step on the Υ and φ scales. The maximum slewing speed of both motors, operating singly or simultaneously under computer control, is 3 deg.sec^{-1}. The PDP–8/S computer has a memory of 4K twelve-bit words, a cycle time of 8 μsec and an addition-time of 36 μsec.

Input to the system is from the keyboard or tape-reader of an ASR–33 Teletype unit, and output is *via* the same unit both in printed and punched-tape form. There are provisions for the programmed insertion of balanced filters, attenuators or a fast-acting shutter, for the manual operation of one or both motors, and for the mechanical interruption of power to the Υ-motor in the event of the counter colliding with any part of the equipment.

The control program

The program (which was written almost entirely by J. M. G. and C. E. N.) consists of a number of routines which perform the following functions: Input (cell parameters, constants for scan-range calculation and control parameters); calculation and listing of crystal and counter settings for a single reflexion or for a

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‖ Digital Equipment Corp., 146 Main Street, Maynard, Mass. 01754, U.S.A.
¶ A detailed User Manual and an expanded version of this paper are available.
** Model No. M218TW, Motion Control Systems Division, Warner Electric Brake & Clutch Co., Beloit, Wis. 53511, U.S.A.

group of reflexions; movement of the crystal and counter motors; measurement cycle for a single reflexion; and data collection for all the reflexions in a given range of indices or diffraction angles. Programmed stops are provided so that the operator can call for a particular routine at any time by setting one of the switches of the Switch Register on the computer console. Instructions or data are inserted by calling the appropriate routine in this way. The user may select a reflexion which is remeasured at regular intervals during automatic data collection. Excessive changes or drifts in the value of the standard reflexion cause the program to halt.

Description of one measurement cycle

In the automatic data collection mode the program goes through the following sequence:

(1) The indices *hkl* are generated.

(2) The counter and crystal settings Y and φ are calculated.

(3) The scan-range $\Delta\varphi$ is calculated.

(4) The scan-speed is set equal to a selected value φ'_{max}.

(5) The counter and crystal are moved to the settings Y and $(\varphi-\frac{1}{2}\Delta\varphi)$, respectively.

(6) A fast measurement of the reflexion is then made and the results are stored in the computer memory:

(i) First background count B_1 for a time $t/2$.

(ii) Integrated peak count P with the crystal moving through the angle $\Delta\varphi$ at a constant scan-speed during a time $t=\Delta\varphi/$(scan-speed).

(iii) Second background count B_2 for a time $t/2$.

(7) If the peak count in 6(ii) exceeds a value specified by the experimenter, an attenuator is inserted in the X-ray beam and steps (5) and (6) are repeated.

(8) If the difference between the two background counts exceeds a pre-set limit, the scan-range is incremented and steps (5)–(7) are repeated.

(9) The program uses the stored peak and background counts to compute the integrated intensity I and its statistical standard deviation $\sigma(I)$. If $\sigma(I)/I$ lies within pre-set limits, the program proceeds with step (11). Otherwise a new scan-speed φ' is computed, such that remeasurement of the reflexion at this speed will lead to the desired precision. Obviously $\varphi' \leq \varphi'_{max}$. If φ' is less than a pre-set minimum φ'_{min} then φ' is set equal to φ'_{min}.

(10) Steps (5) and (6) are repeated with a new scan-speed φ'.

(11) The counts from the slowest measuring cycle (or from the fast cycle if the slow cycle was not carried out) are punched on paper-tape and listed.

Some details of the expressions used in the calculations are presented below.

Calculation of the scan range

In diffractometry by the ω-scan (stationary-counter rotating-crystal) method, errors in the integrated intensities can arise from a failure to include the contribution of Laue streaks to the background measurements. Burbank (1964) and Alexander & Smith (1964) have shown that these errors can be reduced, if not eliminated, by the combination of a correctly calculated scan-range and a correct choice of counter aperture. We can confirm this from our experience with more than a dozen complete sets of data, recorded in each case about two different axes for two different crystals of a single compound. A relative scale-factor can be calculated for each layer by the least-squares method of Rae (1965). Data recorded with a single counter aperture or a constant scan-range, or both, show systematic variations of the relative layer scale factors with the equi-inclination angle μ. Such trends are absent from data recorded with a carefully chosen counter aperture for each layer and with a calculated scan-range for each reflexion. These two experimental variables therefore seem to be major sources of the types of systematic errors to which data recorded on equi-inclination instruments are prone (see, *e.g.* Mathieson, 1969).

In the Buerger–Supper instrument, the counter aperture can be controlled by inserting metal slides with circular holes of various diameters in a series of slots in a block mounted on the counter arm. The usual working range of apertures subtend angles from 3° to 5° at the crystal, the correct choice being the smallest aperture which allows the most extended reflexion in a layer to be recorded without being truncated.

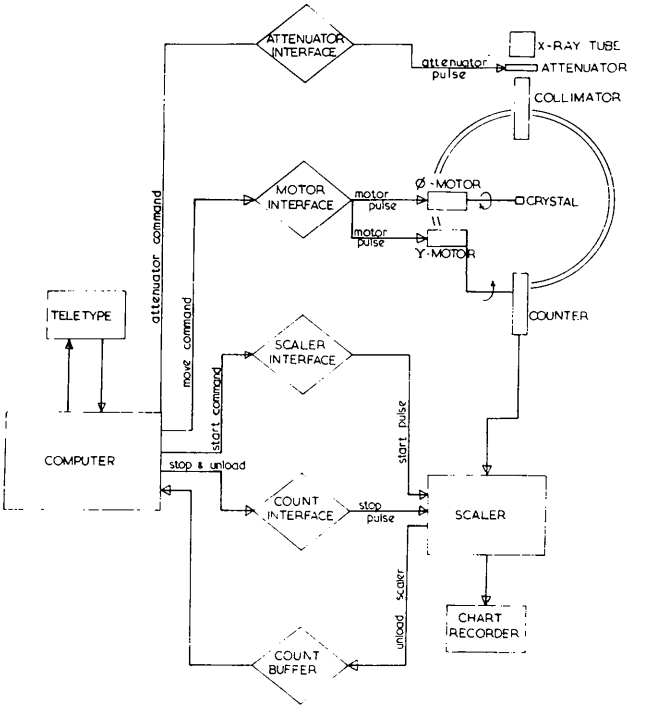

Fig. 1. Diagrammatic representation of the Supper–Buerger diffractometer, PDP-8/S computer and counting circuits.

The scan-range is calculated from the expression

$$\Delta\varphi = \varphi_\lambda + \varphi_D + \varphi_M + \varphi_E$$

where φ_λ is due to wave-length dispersion, φ_D is due to the divergence of the X-ray beam, φ_M is due to the mosaicity of the crystal, and φ_E is a term to allow for possible errors in the crystal settings. The contributions to $\Delta\varphi$ are given by equations (1) to (4), in which

λ_m is the mean wave-length of the incident radiation,
μ is the equi-inclination angle (Buerger, 1960*b*,*c*),
$\Delta\lambda$ is the wave-length dispersion,
S is the angle subtended at the crystal by the source,
C is the angle subtended at the source by the crystal,
X is the effective angular X-ray beam divergence, $X=S+C$,
p is the estimated fractional error in the reciprocal parameters ζ and ξ, which are defined by Buerger (1960*c*),
$(\delta\mu)$ is the estimated error in μ, in degrees.

$$\varphi_\lambda = \left(\frac{180}{\pi}\right)\frac{\Delta\lambda}{\lambda_m}\tan\frac{\Upsilon}{2}(1+\tan^2\mu) \quad (1)$$

$$\varphi_D = \frac{X}{\cos\mu} + X\sin\mu\cot\frac{\Upsilon}{2} \quad (2)$$

$$\varphi_M = \text{constant (assumed)}, \quad (3)$$

$$\varphi_E = 2\left(\frac{180}{\pi}\right)p\tan\frac{\Upsilon}{2}(1+\tan^2\mu) + 2(\delta\mu)\frac{\zeta}{\xi}\,. \quad (4)$$

For $\Delta\lambda$ in equation (1), values equal to the separation of the $K\alpha_1$–$K\alpha_2$ doublet, plus from 3 to 10 times the sum of the widths of $K\alpha_1$ and $K\alpha_2$ lines at half peak intensity, have been proposed (Burbank, 1964; Alexander & Smith, 1964). The second term in (2) is derived from an expression given by Phillips (1954) for the angular range over which a crystal reflects in an upper-level equi-inclination setting. The first term in equation (4) is derived with some approximation by differentiating the expression for φ in the equi-inclination case (*International Tables for X-ray Crystallography*, 1959). The fractional errors, p, in ζ and ξ are assumed to be equal and independent of μ. The second term in (4) is due to Sayre (1954).

For a zero-level reflexion,

$$\Delta\varphi = \frac{\Delta\lambda}{\lambda_m}\tan\theta + S + C + \varphi_M + \varphi_E$$

which differs from the expression derived by Burbank (1964) only by the addition of φ_E.

The constants X and φ_M can be determined approximately by measuring the widths of low-angle reflexions on zero and upper layers, respectively. (Typical values for the constants used in data collection are: $\Delta\lambda$= 0·005–0·009 Å, $X=0{\cdot}6°$, $\varphi_M=0{\cdot}3°$, $p=0{\cdot}001$, $(\delta\mu)$= 0·05°.)

Background imbalance test

After the fast measurement cycle, the program tests whether

$$|B_1-B_2| < c_B(B_1+B_2)^{1/2} + c_I(P-B_1-B_2)\,.$$

The constants c_B and c_I are supplied by the user. In our experience, $c_B=6$ and $c_I=0{\cdot}01$ have been used successfully. If the inequality is satisfied, the measurement cycle is continued; if not, the scan-range is incremented. Where a crystal has been accurately aligned, the unit-cell dimensions have been precisely determined and appropriate scan-range parameters have been chosen, the failure of the imbalance test will generally imply that some instrumental malfunction has occurred.

Calculation of the scan speed

Having stored the integrated peak count, P, and the sum of the two background counts, B, measured at the fast scan-rate $\varphi'_{\max}$, the program computes a new scan-rate φ' where

$$\varphi' = \varphi'_{\max}\left\{\frac{R_e}{50}\right\}^2\left\{\frac{P-B}{P+B}\right\}^2\,. \quad (5)$$

In this equation R_e is the expectation value of the conventional percentage residual R. The above expression for φ' is based on the design for a 'constant agreement analysis' diffractometer experiment (Killean, 1967). The value of R_e is specified by the user. The upper and lower limits of φ' are $\varphi'_{\max}$ and $\varphi'_{\min}$ respectively. If $\varphi' < \varphi'_{\min}$, it is reset to the value $\varphi'_{\min}$. On the other hand, a sufficiently large value of R_e causes the calculated value of φ' to be always greater than $\varphi'_{\max}$. In this case φ' is ignored, and all reflexions are measured only once at the constant scan-speed $\varphi'_{\max}$.

For a given crystal, the proportion of reflexions which will be recorded as 'unobservably weak' depends mainly on the value which is chosen for $\varphi'_{\min}$. The value of $\varphi'_{\min}$ also affects the rate of data-collection more than do the values of $\varphi'_{\max}$ and R_e. (Typical values which have been used in this laboratory are: $\varphi'_{\max}$= 0·25–0·33 deg.sec^{-1}; $\varphi'_{\min}=0{\cdot}02$–$0{\cdot}05$ deg.sec^{-1}; R_e= 2–5%.)

Averaged over full three-dimensional sets of data, the rate of measurement has been found to vary from a minimum of 15 to a maximum of 50 reflexions per hour.

Programming details

The control program is written in the symbolic language PAL III (Digital Equipment Corp., 1967), punched on cards, and assembled on a CDC 3600 computer using a modified version of the program *PALFTN* (Busing, 1965). The resulting 8-channel binary paper tapes are read directly into the PDP-8/S computer. For arithmetic and input-output we have used PDP-8/S library subroutines with modifications similar to those made by Busing, Ellison, Levy, King & Roseberry (1968). The program occupies almost all of the 4K 12-bit word store.

This work was supported by the National Institute of General Medical Sciences, U.S. Public Health Ser-

vice (Grant GM-10867) and by the Australian Research Grants Committee (Grant 65-15552).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about* 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

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Comments on the BJR theory of electron diffraction.

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(*Received* 25 *November* 1968 *and in revised form* 20 *May* 1969)

In the BJR theory of electron diffraction an absorption effect due to weak beams is introduced into the two-beam approximation for the dynamical diffraction of electrons by thick crystals. This is shown to be unjustified for diffraction from perfect crystals. The use of the theory to derive the temperature dependence of diffraction intensities must therefore be modified.

The BJR theory of electron diffraction (Boersch, Jeschke & Raith, 1964) has been used successfully as the basis for interpretation of intensity measurements in electron diffraction, particularly in relation to the temperature variation of relative intensities of rings from thick polycrystalline specimens (Glaeser & Niedrig, 1966; Albrecht & Niedrig, 1967, 1968). However, the basic assumptions of the theory have been brought into question (for example by Fukuhara, 1965) chiefly because of the introduction of an absorption effect due to weak beams in the two-beam approximation to the dynamical theory of electron diffraction. Starting from a slice-type formulation of scattering theory, the scattering from an individual layer of atoms is regarded as the scattering by a phase grating which can be expressed in terms of complex atomic scattering factors. This is somewhat similar in principle to the assumptions of the theory of Cowley & Moodie (1957) which has been quoted in this connexion. Hence we feel it is appropriate to discuss the differences between the Cowley–Moodie and the BJR theories and to point out the nature of the deficiency in the latter.

In the approach of Cowley & Moodie (1957) the transmission of an electron wave through a thin slice of crystal is treated in terms of a modification of the phase of an electron wave by a two-dimensional projected potential distribution, acting as a planar phase-grating, plus the modification of the phase due to Fresnel diffraction between slices. It has been shown (Moodie, 1968) that, in the limiting case of the slice thickness tending to zero, this gives a solution to the scattering problem which is exactly equivalent to a solution of the Schrödinger wave equation. In the absence of absorption due to inelastic scattering or elastic diffuse scattering by crystal imperfections, the periodic potential distribution inserted into the Cowley–Moodie formulation and into the wave equation is a real one.

For purposes of the calculation of intensities, the Cowley–Moodie formulation has been used with finite slices. In the case of a slice thickness corresponding to a single layer of atoms, which gives no appreciable error in calculated intensities, the scattering by the slice could be written approximately in terms of the complex atomic scattering amplitudes deduced by partial wave scattering theory by Ibers & Hoerni (1954) or Raith (1968), but this constitutes only a convenient mathematical device for representing the scattering from a real potential. In such scattering by a pure phase grating, energy is conserved and no absorption is involved.

In the BJR approach however, when the scattering by a single layer of atoms is expressed in terms of complex scattering amplitudes, manipulation of the expressions appears to lead to the introduction of an absorption effect which is mathematically equivalent to the use of a complex potential in the wave equation. This complex potential is formed by summing over complex atomic scattering amplitudes in the same way as the real potential is obtained by summing over the real, first Born approximation, scattering amplitudes which are used because they are proportional to the structure amplitudes obtained by Fourier inversion of the real atomic potential distributions. The origin of the absorption is said to be the effect of weak beams on the two strong beams considered in a two-beam approximation, since for each single-atom layer some intensity will be scattered into the weak beams. The error in this treatment arises from the fact that, while scattering from strong beams into weak beams is taken into account, the scattering from weak beams into strong beams is not.

Complete n-beam calculations, such as those of Goodman (1968), have clearly demonstrated that, for thickness greater than about one or two 'extinction distances' of the