Flat-Cone Diffractometer Utilizing a Linear Position-Sensitive Detector

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The recent development of linear position-sensitive detectors for neutrons and X-rays leads to the possibility of large improvements in the efficiency of data collection in single-crystal diffractometers. In order to take advantage of the properties of a linear position-sensitive detector it is desirable to use a diffraction geometry which causes the diffracted beams from many different reflecting planes to lie in a common plane. A design for a diffractometer utilizing the flat-cone geometry is described, and the relevant mathematical formulas are summarized. An instrument using this design has been constructed as a modification to an existing four-circle diffractometer and is now operating. Practical details of its construction, of the collection and handling of data, and of data rates are discussed.

Introduction

In recent years many attempts have been made to increase the efficiency of data collection in single-crystal diffractometers, particularly in the study of crystals with complex structures and correspondingly large unit cells such as those of proteins. Some of the fast methods proposed for measuring the diffracted intensities comprise screenless oscillation or precession photographs (Arndt, Champness, Phizackerley & Wonacott, 1973; Xuong & Freer, 1971) and multi-counter diffractometers in which two or more conventional quantum counters are used in connection with a variety of diffraction geometries designed so that two or more reflections develop simultaneously or quasi-simultaneously (Phillips, 1964; Hamilton, 1970; Banner, Evans, Marsh & Phillips, 1977).

Recently, quantum counters have been developed for X-rays and neutrons which produce pulses whose amplitude is a function of the position along the center wire at which the quantum is absorbed (Kjems, 1970; Kuhlmann, Lauterjung, Schimmer & Sistemich, 1966; Borkowski & Kopp, 1968). Diffractometers utilizing position-sensitive detectors (PSD's) do not require the mechanical complexity usually necessary with multi-counter diffractometers, and are not limited to X-ray diffraction, as the photographic methods are. Although two-dimensional PSD's have been constructed and shown to work satisfactorily in at least one X-ray diffractometer (Cork, Hamlin, Vernon, Xuong & Perez-Mendez, 1975; Matthews, Alden, Bolin, Freer, Hamlin, Xuong, Kraut, Poe, Williams & Hoogsteen, 1977), they are still in an early stage of development, particularly for neutrons (Alberi, 1975), and are not easily available. Those that do exist (Hendricks, 1976) have been used primarily for small-angle scattering, where the requirements of resolution and angular range are different. In addition, the very highly specialized and efficient computing hardware necessary for the processing of the data, as well as the high cost of area detectors, make them at this time unsuitable for updating existing four-circle diffractometers. The construction of linear PSD's, on the other hand, is a well established art and these detectors are available commercially for both X-rays and neutrons. For X-ray powder diffractometry detectors with cylindrical geometry have been developed recently (Byram, Han, Rothbart, Samdahl & Sparks, 1976).

This paper describes the design of a single-crystal diffractometer utilizing a linear PSD in the flat-cone geometry (Buerger, 1942). Such an instrument has been constructed at the National Bureau of Standards Reactor as a modification of an existing four-circle neutron diffractometer. Preliminary test data for this new 'flat-cone diffractometer' are presented.

Flat-cone geometry

In order to utilize the properties of the linear PSD it is necessary to use a diffraction geometry which causes the diffracted beams for a large number of reflections to appear in a common plane. The most straightforward and efficient way to accomplish this objective is to use the flat-cone geometry, one of the Weissenberg methods first studied and applied by Buerger (1942) with the photographic technique and later implemented with a single counter by Clifton, Filler & McLachlan (1951). With this method the crystal is mounted so that it may be rotated around an axis normal to a set of layers of the reciprocal lattice (see Fig. 1), the c axis for example. If this axis makes an angle 90° + μ with the incident beam, where sin μ = λl/c, the center of the sphere of reflection will lie in one of the reciprocal layers, and, as the crystal is rotated about the c axis, the lattice points in that layer will intersect the reflection sphere on a great circle. If the detector lies in the plane parallel to the great circle passing through the center of the sample it will intercept all the diffracted beams from that layer.

The flat-cone geometry, however, has two main
disadvantages: (i) for upper levels ($\mu \neq 0^\circ$) there is a circular region of reciprocal space of radius $1 - \cos \mu^*$ which is not accessible to the diffractometer and, (ii) if, because of crystal symmetry, the chosen zone axis is also a reciprocal-lattice row, the flat-cone geometry, like the equi-inclination and normal-beam geometries, has the undesirable property of intrinsic simultaneous diffraction (Burbank, 1965; Santoro & Zocchi, 1966).

It has been shown (Zachariasen, 1965) that for certain crystals simultaneous diffraction causes significant systematic errors in intensity measurements. On the other hand, in studies of complex crystals such as proteins, in which the PSD can be most efficiently used, the errors due to this effect usually seem to be small enough to be neglected (Phillips, 1964).

If the rotation around the zone axis is performed by a single circle (this axis is designated $\omega$ in the Weissenberg camera; it will be termed $\omega$ here to avoid confusion with the $\omega$ axis of a four-circle diffractometer) a remounting of the crystal will be necessary to measure reflections in the blind region of the reciprocal lattice, or to measure reflections particularly affected by simultaneous diffraction. If, however, the crystal rotation is performed by using the three independent angles of a four-circle diffractometer, measurements may be made about more than one axis with a single mounting of the crystal and the disadvantages mentioned above may be circumvented. Of course, all such rotation axes must lie within a cone around the $\psi$ axis with a semiangle of no more than about 45°.

For these reasons, in what follows use is made of a four-circle diffractometer to produce the geometrical conditions required by the flat-cone method.

**Diffractometer settings**

A PSD may be mounted on the detector arm of a four-circle diffractometer in a vertical plane which includes the diffractometer axis. The arm then determines the $\mu$ angle, and the $\phi$, $\chi$ and $\omega$ axes of the diffractometer can be used to rotate the crystal around an axis perpendicular to the plane defined by the detector and the crystal. In order to calculate the diffractometer settings necessary to perform this rotation, it is convenient to define several right-handed Cartesian reference systems. The systems attached to the reciprocal lattice, to the $\phi$, $\chi$ and $\omega$ shafts and to the laboratory are defined as described by Busing & Levy (1967) for four-circle diffractometers, and in what follows we will use the same symbols and conventions unless explicitly indicated. For describing the operation of a flat-cone diffractometer of the type described here it is useful to introduce an additional system attached to the counter $\mu$ shaft. The rotations $\mu$ and $\omega$ take place about the vertical axis of the instrument and, for simplicity, they are taken with the same positive sense. The rotation matrix $M$ therefore is

$$M = (\cos \mu, \sin \mu, 0; -\sin \mu, \cos \mu, 0; 0, 0, 1).$$

The coordinates of a reciprocal point*

$$x = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

are transformed into the Cartesian crystal system and, successively, into the $\phi$, $\chi$, $\omega$, $\mu$ and laboratory systems by the transformation matrices $B$, $U$, $\Phi$, $X$, $\Omega$, and $M$, respectively. The coordinates $x_i$ of the point in the laboratory system are therefore related to the coordinates $x$ in the reciprocal-lattice system by the equation

$$x_i = M\Omega X \Phi U B x$$

in which all matrices except $B$ are orthogonal.

The reciprocal point $x$ lies on the reflecting sphere when

$$x_i = \begin{pmatrix} \cos Y \sin \mu \\ \cos Y \cos \mu - 1 \\ \sin Y \end{pmatrix},$$

where $Y$ is the angle between the diffracted beam and the equatorial plane, as shown in Fig. 2. The angle $Y$ is related to the position on the counter at which the reflection is detected. From Fig. 3 we have

$$\tan Y = d \sin \alpha / (D - d \cos \alpha).$$

The orientation matrix $U$ can be obtained from the observation of two reflections of known indices $h_1$ and $h_2$, provided that the lattice parameters are also known, following the procedure of Busing & Levy (1967). (With PSD's the observation of the two orienting reflections is not limited to the equatorial plane.)

Let

$$u = \begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

* If the point is a reciprocal-lattice point, the symbol $h = \begin{pmatrix} h \\ k \\ l \end{pmatrix}$ instead of $x$ will be used.
be the symbol of the zone axis selected as rotation axis. The coordinates \( \mathbf{u} \), which are expressed in the direct-lattice system, are transformed to the \( \varphi \)-axis system by means of the equation

\[
\mathbf{u}_\varphi = \mathbf{UBS}^{-1} \mathbf{u}
\]  

(6)

where \( S_{ij} = a_i^* a_j^* \) and where \( a_i^* \) are the reciprocal-lattice vectors. The zone axis is brought into the horizontal plane of the instrument by the rotations

\[
\varphi_0 = \tan^{-1} \left( \frac{u_{\varphi 2}}{u_{\varphi 1}} \right)
\]

\[
\chi_0 = \tan^{-1} \left[ \frac{u_{\varphi 3}}{(u_{\varphi 1}^2 + u_{\varphi 2}^2)^{1/2}} \right].
\]

(7)

We consider this configuration of the diffractometer as the origin of the rotation \( \psi \). [Note that this definition of origin is different from that adopted by Busing & Levy (1967).] The rotation \( \psi \) about \([uvw]\) is accomplished by appropriate combinations of the rotations \( \varphi, \chi \) and \( \omega \). These rotations are the same as those used for setting a reciprocal-lattice vector in a conventional four-circle diffractometer and can be evaluated by means of the same equations [equations (48) of Busing & Levy (1967); note that the last of equations (48) should be \( \omega = \tan^{-1} \left( -\frac{R_{23}}{R_{13}} \right) \)].

Design of the prototype instrument and preliminary results

The flat-cone neutron diffractometer has been constructed as a modification of an existing four-circle instrument. A single counter was replaced on the \( 2\theta \) arm by a vertically mounted, 1 m long \( ^3\)He PSD (2.5 cm diameter). The counter shield (35 × 35 cm in cross-section) and its support were the only items specially manufactured for this project. The detector can be pivoted around its center to provide the range of angle \( \alpha \) between 60 and 90° (Fig. 4). With \( \alpha \) set to 90°, distance \( D \) can be varied from 70 to 200 cm. Thus for an incident wavelength of 1.6 Å, \( D \) set to 100 cm at \( \alpha = 90° \) and then \( \alpha \) moved to 60°, data can be collected up to 2 Å resolution for the zero level (higher for upper levels). If needed, the maximum resolution can be increased by using neutrons with shorter wavelength, but this may lead to problems with resolving the reflections. The detector may also be raised in such a way that it will no longer intersect the horizontal plane (although some low-order reflections will become inaccessible in this configuration).

The effective aperture of the detector can be changed by adjusting the two parallel cadmium masks on the front face of the shield. The width of the opening can be experimentally adjusted to minimize the background, while leaving it wide enough to include all of the reflections (see the following section).

The electronic circuits have been described by Alberi, Fisher, Radeka, Rogers & Schoenborn (1975). The output from each end of the detector wire is fed into a delay-line-clipped linear amplifier through a charge-sensitive preamplifier. The output of one amplifier (the 'numerator signal') is fed directly to a linear gate and stretch (LGAS) circuit which produces a flat-topped output signal with a height equal to the highest point of the amplifier output and a width of 9 \( \mu s \). The outputs of both amplifiers are fed to a summing circuit whose output (the 'denominator signal') is fed to another LGAS circuit. The outputs of the two LGAS circuits are then fed into an analog divider circuit which produces an output proportional to the quotient of the inputs. The output of the divider is then fed to an analog-to-digital converter (ADC).
which stores a digital representation of the amplitude in the computer's memory. The uncertainty due to electronic circuits is ±2 channels out of the total of 1024. The computer used for instrumental control is a PDP 11/40 with 128 K of core, which, in addition to the flat-cone diffractometer, controls eight other spectrometers, is used for program development, and also functions as a remote job-entry terminal to a large computer.

The 9 μs output pulse width of the LGAS circuit accurately defines the dead time of the counting system. Counting-loss corrections, which amount to 1% of a PDP 11/40 with 128 K of core, which, in addition to the computer's memory. The uncertainty due to also functions as a remote job-entry terminal to a spectrometers, is used for program development, and also functions as a remote job-entry terminal to a large computer.

The performance of the flat-cone diffractometer has been tested by measuring a number of reflections diffracted by a single crystal of Ta2O5. This compound is orthorhombic with cell parameters a=6.198, b=40.29, c=3.888 Å. While the unit-cell volume is too small to allow optimum efficiency in the data collection, the reciprocal layers perpendicular to c are sufficiently dense to check instrumental resolution, peak shapes, peak positions on the counter, etc. Fig. 5 shows the output of the detector for three values of ψ 1° apart. Two weak reflections can be separated without difficulty from the neighboring strong one (along b*). As indicated by (2), (3) and (4) the position of the reflection 1,1,1,0 varies along the counter length with varying ψ angle.

Measurement of intensities and data processing

The evaluation of the structure amplitude of a reflection hkl of a crystal requires a measurement of the integrated intensity in the vicinity of a reciprocal-lattice point. The use of PSD's for that purpose is associated with two important features not present in the conventional counter methods. First, the peak and the background intensities of several reflections may be measured simultaneously, and, second, the detector's vertical width needed for the measurement of integrated intensities is not fixed by slits, but can be determined by computer for each reflection. This is particularly important since the peak shapes are variable in the flat-cone geometry, as in other Weissenberg techniques. The maximum horizontal width is fixed by the lateral extent of the sensitive area of the linear detector, but can be adjusted to lower values for smaller crystals of low mosaic spread to minimize the background. Both of these widths can be estimated by known procedures (Burbank, 1964; Alexander & Smith, 1962, 1964a, 1964b).

In a typical data-collection procedure the crystal is rotated in small steps around the ψ axis. In each step position the quanta are counted for a specified length of time or until the preset monitor count has been reached (the latter method is more common in neutron diffractometry). At the end of the counting interval the buffer is examined, and for all detected counts a determination is made whether they come from a region near a reciprocal-lattice point or from a background region. This is accomplished with the following procedure.

As stated in the previous section, the amplitude of a pulse produced by a PSD is a function of the linear position at which a quantum is absorbed and is converted electronically to a digital signal, thereby dividing the detector into a number of segments of length p each. The center of the nth segment is located at a distance d_n along the counter and receives radiation diffracted by a point, located on the diffraction sphere, whose coordinates x_i in the laboratory system are given by (3) in which the angle γ is that corresponding to the distance d_n. The coordinates of this point, expressed in the reciprocal-lattice reference system are given by

\[
x = B^{-1} \hat{U} \Phi \mathbf{x}_i = \hat{U} \mathbf{x}_i,
\]

where \(\hat{U}\) denotes the transpose of \(\mathbf{U}\), etc. The coordinates \(\mathbf{x}\) define the region of the reciprocal space contributing to the intensity received by a counter element. If \(x_1, x_2\) and \(x_3\) differ from integral numbers by not more than specified intervals ±Δx_1, ±Δx_2 and ±Δx_3, the region of the counter under examination is receiving radiation diffracted by a reciprocal-lattice point. For a perfectly aligned crystal, all quanta scattered by points located outside this region could be considered background radiation. In practice, however, only counts corresponding to points located within specified regions of the reciprocal lattice are retained as backgrounds of neighboring reflections.

![Fig. 5. Output of the PSD for three values of ψ. The crystal under study was Ta2O5 and the rotation was around c, \(\lambda = 2.4\) Å, \(D = 100\) cm, \(\alpha = 65°\), counting time 60 s per frame, reactor power 10 MW.](image-url)
With the procedure currently in use, a list of reflections is stored on a disk together with the $\psi_h$ settings corresponding to the peak positions of each reflection. The value of $\psi_h$ of a given $hkl$ can be determined by solving for $\tan(\psi_h/2)$ the equation

$$2(-h_{o1} \sin \mu + h_{o2} \cos \mu \cos \psi_h + h_{o3} \cos \mu \sin \psi_h) + h_{o1}^2 + h_{o2}^2 + h_{o3}^2 = 0 \quad (9)$$

in which $h_{o1}$, $h_{o2}$ and $h_{o3}$ are the coordinates of the reciprocal-lattice point, expressed in the system attached to the $\omega$ shaft, for $\psi = 0$. \textit{i.e.}

$$B_{\phi} = X_0 \Phi_0 U \Phi_0 . \quad (10)$$

[In (10) matrices $X_0$ and $\Phi_0$ correspond to the values of $\chi_0$ and $\phi_0$ given by (7).] During the actual data collection, this list is updated and the counts pertaining to each reflection properly stored. Counts corresponding to reflections not on the master list, as well as those outside of the peak or background regions, are not retained. This procedure is repeated for each step position. A complete reciprocal-lattice layer is examined by one revolution around $\psi$, but for crystals of high symmetry all unique data can be recorded in a fraction of the $\psi$ rotation.

In order to evaluate the absorption corrections it is necessary to evaluate for each reflection the direction cosines of incident and diffracted beams in the reference system in which the shape of the sample is described. A unit vector along the primary beam is a vector directed from the center of the reflection sphere to the point at which the reciprocal node touches the sphere. The direction cosines of the primary and diffracted beams in the laboratory system are, therefore

$$P_i = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad d_i = \begin{pmatrix} \cos \gamma \sin \mu \\ \cos \gamma \cos \mu \\ \sin \gamma \end{pmatrix} \quad (11)$$

respectively.

Finally, the correction for the Lorentz factor in the flat-cone geometry can be evaluated with one of the expressions derived by Buerger (1960). A particularly simple expression for the correction is

$$L^{-1} = \cos \mu \sin \gamma \quad (12)$$

where $\mu$ and $\gamma$ are the angles previously defined.

Discussion

Two diffractometers based on Weissenberg geometry have been built recently. In one case (Hamilton, 1970) the equi-inclination method is used with a ring of solid-state detectors surrounding the crystal in a one-dimensional array. In another (Cain, Norvell & Schoenborn, 1976) the normal-beam method is used with three linear detectors positioned so that each of them is tangent to the diffraction cone of the layer being measured. In both these techniques the diffracted beams do not lie in the plane of the counters and thus it is necessary to vary the width of the sensitive area for each layer. In addition, these instruments require a translational motion of the detectors along the rotation axis of the crystal. This additional motion increases the complexity of the diffractometers, especially in the neutron diffraction case.

A five-circle diffractometer using the flat-cone geometry has been proposed by Phillips (1964) and built by Banner, Evans, Marsh & Phillips (1977). In this arrangement, however, the flat-cone setting is used exclusively as a device to bring into reflecting position and measure quasi-simultaneously a number of reflections which belong to different layers. (With our diffractometer reflections are measured layer by layer as is done with a traditional Weissenberg camera.) Such a diffractometer, with five axes of rotation, is mechanically more complex than a four-circle instrument.

The advantages of two-dimensional data collection have been pointed out by Arndt (1968). For a cubic crystal with lattice parameter of 50 Å, rotated about one of the axial directions, the number of reflections developing from the zero layer during a 1° rotation is about ten at 1.5 Å resolution. Of these reflections five have $\gamma>0$ and hit the linear detector, and five, with $\gamma<0$ are out of the range of the detector. Since, with our conditions, reflections develop within an angular interval $\delta\psi$ of about 2°, including background points, this means that, on the average, at each value of $\psi$ the diffractometer is measuring either the backgrounds or the diffracted intensities of about ten reflections. As the angle $\mu$ increases this number decreases somewhat because of the existence of the blind region mentioned previously. We may therefore conclude that the diffractometer described in this paper is about ten times faster than a conventional four-circle instrument in analyzing crystals of the type considered in the example. The number of reflections being measured at each value of $\psi$ varies, of course, with the size of the unit cell and with the zone axis chosen as the rotation axis. The efficiency of the flat-cone instrument decreases when the unit-cell volume decreases. On the other hand, when studying crystals with very large unit cells, the choice of the rotation axis may be dictated by the need to avoid overlapping of the reflections.

By analyzing the cubic crystal of our example with a two-dimensional detector, the number of reflections measured at each position of the crystal would be about 400 (Arndt, 1968). These results show dramatically the increase of efficiency one can aim for by the use of two-dimensional PSD's. At the present, however, for the reasons previously mentioned the use of linear PSD's seems to represent the best compromise for neutron intensity measurements from large structures. These detectors do not have the dead spaces...
which make single-detector arrays difficult to use and, usually, have uniform efficiency along the wire, except near the ends. As shown in this study, PSD’s, in connection with flat-cone geometry, allow modification of four-circle X-ray and neutron diffractometers at relatively low cost, without adding extra motions to the instruments or extensive reprogramming to the existing software.

References


