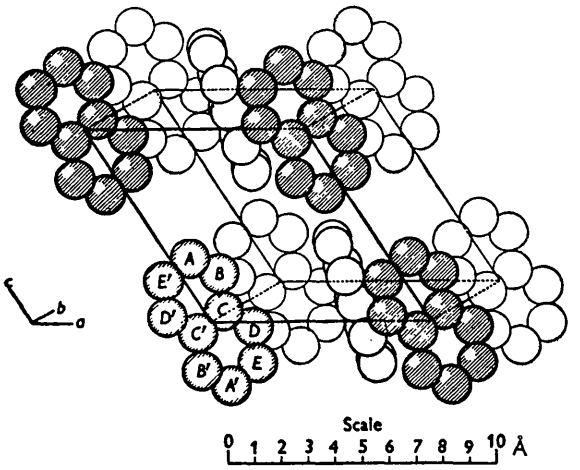

Fig. 3. Positions of the naphthalene molecules in the unit cell.

Table 9. *Close intermolecular approaches*

(Distances in Å)

Atom in reference molecule	Atom in neighbouring molecule
H–E'	2·66, H–A'(0, 0, 1); 2·86, H–A($\frac{1}{2}$, $-\frac{1}{2}$, 1); 3·07, H–B($\frac{1}{2}$, $-\frac{1}{2}$, 1)
H–A	2·66, H–E(0, 0, 1); 2·86, H–E'($\frac{1}{2}$, $\frac{1}{2}$, 1); 2·40, H–B($\frac{1}{2}$, $-\frac{1}{2}$, 1)
H–B	2·95, H–D'(0, 1, 0); 2·40, H–A($\frac{1}{2}$, $\frac{1}{2}$, 1), 3·07, H–E'($\frac{1}{2}$, $\frac{1}{2}$, 1)
C	2·82, H–D($\frac{1}{2}$, $-\frac{1}{2}$, 0)
D	2·82, H–D($\frac{1}{2}$, $-\frac{1}{2}$, 0)
H–D	2·95, H–B'(0, 1, 0); 2·82, C($\frac{1}{2}$, $\frac{1}{2}$, 0); 2·82, D($\frac{1}{2}$, $\frac{1}{2}$, 0)

approached directly are C and D, and C' and D'. C and D are both 2·82 Å from the hydrogen D of the molecule at ($\frac{1}{2}$, $-\frac{1}{2}$, 0), which lies almost immediately above C and D, so causing the negative deviations of these atoms from the mean molecular plane.

The shortest H–H distance which is presumed in naphthalene is 2·40 Å, as compared with 2·50 Å in anthracene. The explanation of this extra shortness seems to be that the next shortest in naphthalene, 2·66 Å, is considerably larger than the next shortest in anthracene, 2·54 Å, so that the total energies of molecular interaction are roughly comparable.

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On the Determination of Crystal and Counter Settings for a Single-Crystal X-ray Diffractometer

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A simple analogue computer is described with which crystal and counter settings for a three-circle single-crystal diffractometer can be determined. It is shown that the accuracy attainable is quite adequate for the measurement of integrated intensities by a rocking-crystal technique.

Introduction

Furnas & Harker (1955) have described two schemes of data-collection for use with three-circle single-crystal diffractometers in which the motion of the counter is restricted to a plane. The one referred to in this note is the so-called 'cone diffractometer' method,

which permits the survey of an entire hemisphere of the reciprocal lattice with a single mounting of the crystal. It is illustrated in Fig. 1.

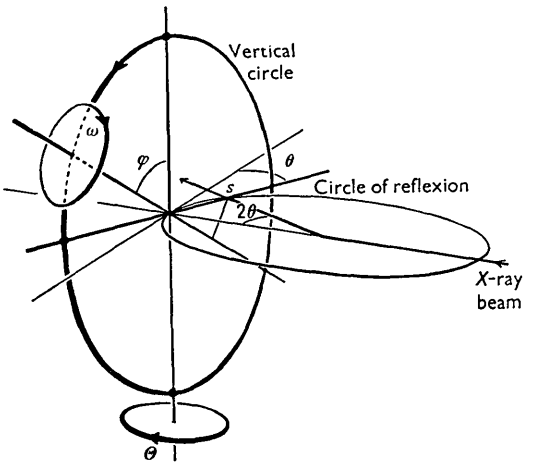

Fig. 1. Diagram showing crystal and counter settings for three-circle X-ray diffractometer.

The crystal is mounted with its unique axis, if it has one, coincident with the axis of the goniometer head, i.e. with the axis of the ω-circle. Any reciprocal-lattice point S may then be brought into the equatorial circle of reflexion in the horizontal plane, the plane in which the counter moves, by the adjustment of three angles. The ω-circle is used to bring the reciprocal-lattice vector into the plane of the vertical circle, the φ-circle. φ is adjusted to bring the vector into the horizontal plane and the whole vertical circle is turned about its vertical axis through the angle θ, the Bragg angle, in order to bring S into the equatorial circle of reflexion. The counter is of course set at 2θ. In order to set the instrument to measure any reflexion, therefore, it is necessary to know the angles ω, φ and θ.

An analogue computer

For crystals of monoclinic or higher symmetry, these angles may be determined quite conveniently by the use of a simple analogue computer. Such a computer, made out of two 360° protractors and a celluloid sheet, is shown in Fig. 2. It will be described with reference to the method used in determining the settings for a monoclinic crystal mounted with the unique b axis coincident with the axis of rotation of the ω-circle. The orientation of the crystal with respect to the ω-circle, which must be determined, is assumed to be such that the reciprocal lattice vector **a*** lies in the plane of the vertical circle when $\omega = 0$.

RPQ denote the celluloid sheet, which is constrained to move along the diameter A_0OA_3 of the protractor A. This protractor, with zero at A_0, is pivoted about its centre at O, the origin of the diagram of the $h0l$ reciprocal-lattice net upon which the device

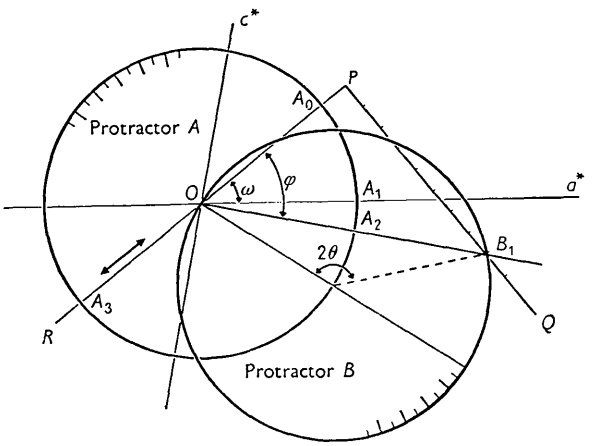

Fig. 2. Analogue computer for determination of crystal and counter settings.

is superimposed. Protractor A thus represents the ω-circle. The reciprocal-lattice diagram is drawn on such a scale that protractor B, pivoted about its *zero* at O, represents the circle of reflexion, i.e. 1 r.l.u. equals the radius of this protractor.

This device is sufficient to determine the settings for $h0l$ reflexions. φ, the vertical-circle angle, is set at zero so that the $h0l$ reciprocal-lattice net lies in the horizontal plane. In order to determine $\omega(h0l)$ the point P is made to coincide with the point $h0l$ in the reciprocal-lattice diagram: $\omega(h0l)$ is then read directly from protractor A at A_1, the intersection with the a^* axis. The angle $2\theta(h0l)$ is read from protractor B at the point in its circumference which can be made to lie over the point $h0l$ in the reciprocal-lattice diagram.

The settings for a reflexion hkl are determined by a simple elaboration of this method. $\omega(hkl)$ is the same as $\omega(h0l)$ since at this setting all reciprocal-lattice points in the row hkl with h and l constant lie in the plane of the vertical circle. In order to determine φ and 2θ the point P is again set at the point $h0l$ in the reciprocal-lattice diagram and the line PQ, at right angles to RP, is marked out in intervals of b^*. A radial line OB_1, conveniently the diameter of protractor B, is set to lie over the point corresponding to the appropriate value of k on the line PQ, and $\varphi(hkl) = \angle POB_1$ is read at A_2 on protractor A. The angle $2\theta(hkl)$ is again read on protractor B at B_1, the point on its circumference which can be made to lie over the point hkl.

If 10 in.-diameter protractors are used with a reciprocal-lattice diagram drawn on the scale 1 r.l.u. = 5 in. the angles can easily be read to an accuracy of $\pm 0{\cdot}2°$. For crystals with large unit cells (e.g. proteins) and when Mo $K\alpha$ or other radiation of short wavelength is used it is convenient to adopt a larger scale, say 1 r.l.u. = 100 cm. The diameter of the circle of reflexion is then inconveniently large, but it is not necessary to use the full circle since reflexions in such

circumstances are not generally measurable at higher angles than $2\theta = 40°$. The protractor B may then be replaced by a rectangular piece of 'perspex' on which an arc of the reflexion circle graduated from 0 to 40° is engraved. With such a scale it is easily possible to determine 2θ to within $\pm 0{\cdot}02°$.

Accuracy of setting

The accuracy with which the angles need to be set depends on the dimensions of the diffractometer and its various slit systems and also on the technique adopted for measuring the integrated intensities.

Thus when the crystal is oscillated or turned through the reflecting position the setting of θ may be less critical than it is when the crystal is set at the reflecting position. The present discussion applies in particular to the use of a method in which the crystal, mounted in a parallel beam of X-rays, is rotated through the reflecting position over the angular range $\theta-\varepsilon$ to $\theta+\varepsilon$. The counter, with a wide entrance slit, is set at 2θ and kept stationary. The accuracy with which θ and 2θ need be set is determined by the amplitude of scan (2ε) and the size of the counter slit, and these may be chosen to give reasonable latitude in setting so long as they provide adequate resolution of the reflexions and good peak-to-background ratios in the intensity measurements. The instrument in use in this laboratory gives adequate resolution of the reflexions of Cu $K\alpha$ radiation from all crystals with linear cell dimensions less than about 65 Å when the amplitude of scan is 2°. Most of the intensity in any given reflexion is recorded within $\pm 0{\cdot}3°$ of the peak so that a 2° scan includes measurements nearly at background level over some 0·7° on either side of the reflexion. Good integration of the reflexion intensity is obtained when the total effective error in θ does not exceed 0·5°. The size of the square counter entrance slit is such that the maximum allowable deviation of the reflected ray from its correctly set direction is about 0·3°.

It is clear that the conditions for a reflexion to take place are upset by mis-setting of ω or φ. The reflexion conditions may, however, be satisfied for such a mis-set crystal (i.e. the appropriate reciprocal-lattice point may be brought into the sphere of reflexion) by turning the vertical circle so that it no longer exactly bisects the angle between the incident and reflected beams. The angle between the normal to this circle and the incident beam is then no longer θ, the Bragg angle, so to avoid confusion it is referred to henceforth as Θ, where $\Theta = \theta$ for a correctly set crystal and $\Theta = \theta+\Delta\Theta$ for a mis-set crystal brought into the reflecting position by an adjustment $\Delta\Theta$. The direction of the reflected beam from such a mis-set crystal deviates from the direction for a correctly-set crystal by some angle δ.

$\Delta\Theta_\varphi$ and δ_φ, $\Delta\Theta_\omega$ and δ_ω, due to small setting errors $\Delta\varphi$ and $\Delta\omega$ respectively, may readily be shown to have the following values:

$$\Delta\Theta_\varphi = -\tan\theta.\Delta\varphi^2/2\,, \quad (1)$$

$$\delta_\varphi = 2\sin\theta.\Delta\varphi\,, \quad (2)$$

$$\Delta\Theta_\omega = \cos\varphi.\Delta\omega\,, \quad (3)$$

$$\delta_\omega = \sin\theta.\sin 2\varphi.\Delta\omega^2/2\,. \quad (4)$$

The maximum θ obtainable with the present instrument is 45°.

$\Delta\Theta_\varphi$ and δ_ω are negligibly small for all reasonable errors, so that the maximum errors which can be tolerated in setting φ and ω are determined by (2) and (3) and may be considered independently.

δ_φ, the deviation in reflected-beam direction due to a small error $\Delta\varphi$, lies very nearly in the vertical plane determined by the reflected-beam direction for a correctly set crystal and the vertical axis about which the counter moves. The component deviation in the horizontal plane is negligibly small. It is possible, therefore, to treat the errors due to mis-setting 2θ (the counter angle) and φ independently. Clearly 2θ must be known to within $\pm 0{\cdot}3°$, stated above to be the maximum allowable deviation of the reflected beam from the correctly-set direction. Similarly δ_φ should not exceed 0·3°. Equation (2) shows that, for reflexions observed at the instrument limit ($\theta = 45°$), φ must be determined, therefore, to within about $\pm 0{\cdot}2°$, while for reflexions at lower angles, including all those observed from protein crystals, greater latitude in setting may be tolerated.

A reasonable maximum value for $\Delta\Theta_\omega$ to allow for the possibility of small errors in setting θ is again 0·3°. (The instrumental error in the circles is negligible by comparison.) Equation (3) then shows that when $\varphi = 0$ the maximum allowable error in setting ω is $\Delta\omega = \pm 0{\cdot}3°$, and that greater errors may be tolerated at other values of φ.

These considerations show that the angles determined by means of this analogue computer are quite accurate enough for use with the rocking-crystal technique, even when no hunting for the reflexion maximum is allowed.

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