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Determination of the Inherent Reflecting Range of a Single Crystal in Diffractometry

By Leroy E. Alexander, Gordon S. Smith and Patricia E. Brown

Mellon Institute, Pittsburgh 13, *Pennsylvania, U.S.A.*

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A combination photographic and counter technique is described for measuring the inherent angular reflecting range of a crystal without affecting its alignment or the geometry of the diffractometer for subsequent intensity measurements. The method reveals mechanically induced flaws in the crystal as well as native mosaicity, and it provides sufficiently accurate values of the overall reflecting range for the calculation of minimum receiving aperture dimensions.

Previously formulas were derived for calculating minimum receiving aperture dimensions to be employed in measuring single-crystal reflections with the three-circle counter diffractometer (Alexander & Smith, 1962). It was shown that the minimum dimension in the goniometer plane, or width (γ_R), is a linear function of the inherent angular reflecting range, γ_m,* when the 2θ scan technique is used. However, the aperture width is independent of γ_m for the ω-scan technique, which commends the use of this method for highly imperfect crystals (Furnas, 1957, pp. 90 ff.; Alexander & Smith, 1962). In the same study it was shown by means of convolutional synthesis of reflection profiles that the magnitude of γ_m strongly influences the shape of the calibration curve for reducing peak to integrated intensities. Furthermore, very large values of γ_m render the stationary-crystal technique inapplicable to the measurement of meaningful intensities, as has been pointed out by Furnas (1957, p. 73). These considerations focus attention on the need for a suitable method of measuring the mosaic spread of a given crystal prior to undertaking extensive intensity measurements.

The dimensions of present-day counter windows impose a limit on γ_R of the order of 1 or 2 degrees; hence, we need values of γ_m which are highly reliable but not necessarily of high precision. For example, a precision of $\pm 0{\cdot}05°$ would suffice. The methods for measuring mosaic spread described in the literature are generally unsuitable because of the specialized character of the apparatus or the extremely painstaking techniques required (for example, Compton & Allison, 1935; Guinier & Tennevin, 1949; Reis, Slade & Weissmann, 1952; Weissmann & Evans, 1954). The present authors have used a photographic method which in no way interferes with the alignment of the crystal or alters the geometry of the apparatus as

* In the preceding paper (Alexander & Smith, 1962) the quantity γ_m, or $2\delta\omega_m$, was designated as the *angular mosaic range* of the crystal, although it was meant to include the effects of both native mosaicity and abnormalities such as cracking of the crystal into misaligned components.

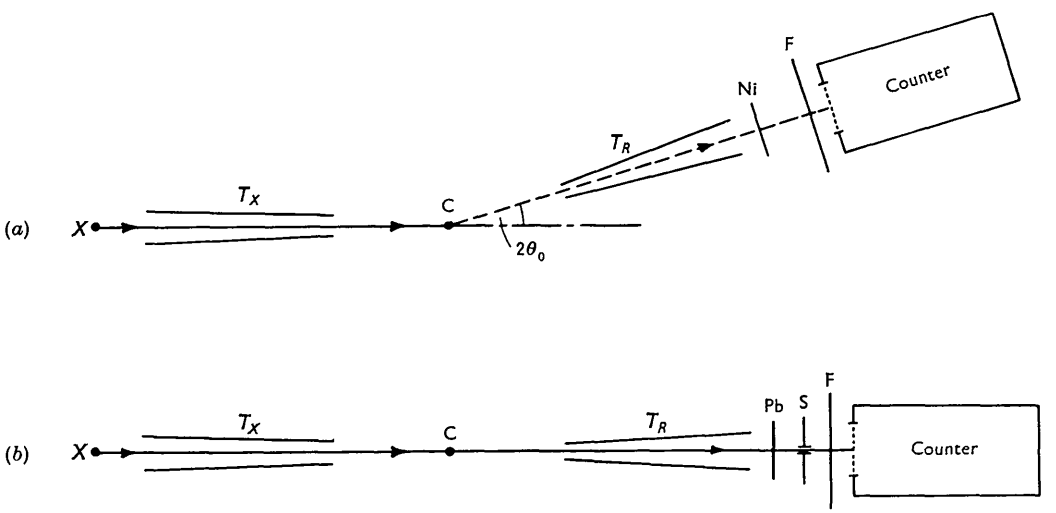

Fig. 1. Experimental arrangement for measuring mosaicity.

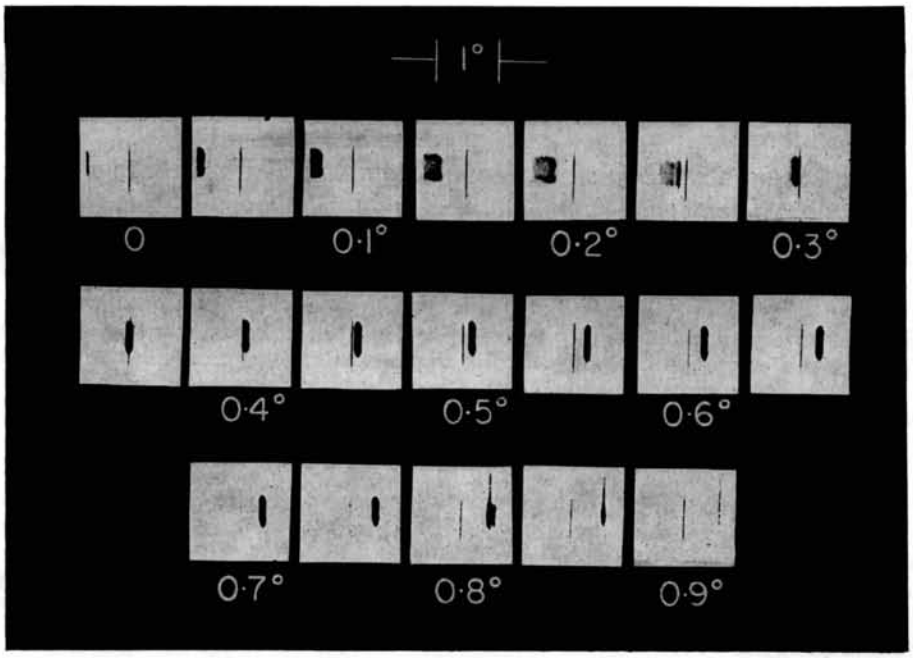

Fig. 2. The (100) reflection of a small α-quartz crystal sampled at angular increments of 0·05°. Cu $K\alpha$ radiation, $2\theta_0 = 20{\cdot}88°$.

required for subsequent intensity measurements. Moreover, the method portrays qualitatively as well as quantitatively the overall inherent reflecting range of the crystal, revealing any unsuspected contributions which might render the crystal unsuitable for diffractometry, such as cracking of the crystal into misaligned components as a result of cutting, grinding, *etc.* By way of comparison, the diffractometric technique described by Furnas (1957) necessitates a change in the target 'take-of' angle of the X-ray beam and realignment of the crystal for the subsequent ntensity measurements.

With the direct and diffracted beam tunnels in place (T_X and T_R of Fig. 1(*a*)), the crystal C is set at an angle β near the midpoint of its diffracting range for some reflection of good intensity at a small Bragg angle (if possible $\theta < 10°$), and the receiver is set at the calculated angle $2\theta_0$. Ni represents an absorbing foil of sufficient thickness to restrict the counting rate to the linear response range of the counter, and F is a strip of X-ray film contained in a light-tight envelope suitably shielded from scattered X-rays. With the crystal and receiver stationary, a few test exposures are made with the counter simultaneously counting in order to ascertain the number of counts N corresponding to a photographic image of suitable blackness.

Once this has been done, a full series of mosaic exposures is carried out as follows: (1) With the crystal stationary at an angle β at one end of its reflecting range and the counter fixed at the angle $2\theta_0$, a reflection is recorded until approximately N counts have been received, and the counting time t_N is noted (a knowledge of t_N is useful in selecting suitable exposure times since $1/t_N$ is a measure of the total diffracted energy entering the receiver with the crystal set at the angle β). (2) The counter arm is set at 0° 2θ using the standard $2\theta - \theta$ motion of the counter and crystal, and a very narrow receiving slit S such as used in powder diffractometry and a thin sheet of lead Pb are inserted in the positions shown in Fig. 1(*b*). (3) The film is now exposed long enough to the direct beam, strongly attenuated by Pb, to produce a calibrating line on the film. (4) The film pack is translated a distance of, say, 1 cm, the counter is returned to the original position $2\theta_0$, and the crystal is turned to the angle $\beta + 0{\cdot}05°$. (5) Steps (1), (2), and (3) are now repeated to give a reflection and calibration line corresponding to the crystal orientation $\beta + 0{\cdot}05°$, and so on. In this way a series of reflections is prepared, each with its own calibration line, by steps of 0·05° over the entire range of diffraction for this reflection. If preferred, exposures for constant time rather than constant counts may be used in order to save time, but this tends to reduce visibility of the reflection near the limits of the reflecting range.

Fig. 2 shows the reflection images obtained in this way from a quartz crystal 0·10 mm in diameter using Cu $K\alpha$ X-rays taken at an angle of 4° from the anode surface. The equivalent angular parameters are: angle subtended by crystal diameter at X-ray source, $\gamma_c = 0{\cdot}04°$; angle subtended by full width of X-ray source at crystal, $\gamma_x = 0{\cdot}70°$. The (100) reflection at $2\theta_0 = 20{\cdot}88°$ has been recorded photographically at

0·05° intervals over a range of 0·90°. The first five pictures show only portions of the 'white' radiation spectrum, which are rather dark due to long exposures. The characteristic Cu $K\alpha$ reflection appears at $\beta=$ 0·25° and vanishes beyond 0·90°. The exposure times varied from 1262 seconds at 0° to 15 seconds in the range 0·40 to 0·65°.

The experimental situation most commonly encountered is that in which $\gamma_m<(\gamma_x+\gamma_c)$, as in the example just given. If the positions of the leading (L') and trailing (T') edges of the crystal reflection are measured to $\pm 0{\cdot}1$ mm on a suitable measuring

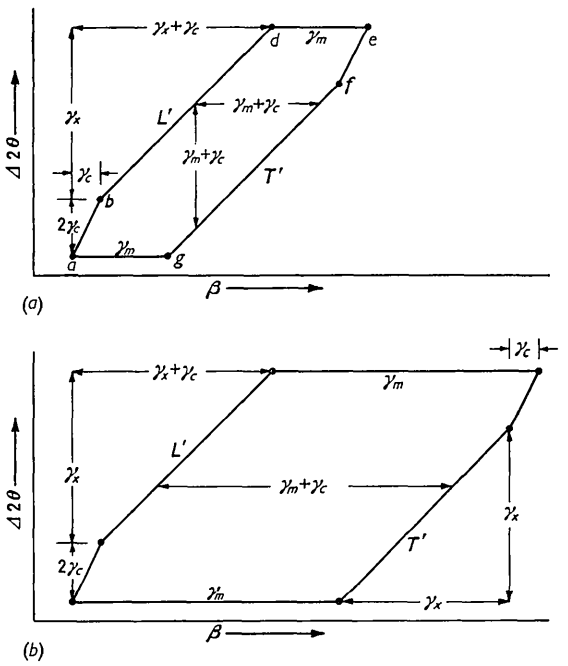

Fig. 3. Idealized reflection hexagons for (a) $\gamma_m<(\gamma_x+\gamma_c)$, (b) $\gamma_m>(\gamma_x+\gamma_c)$. $R_x/R_z=1$, $2\theta_0$ small.

instrument and plotted on a scale of $\Delta 2\theta$ (referred to the calibrating line as 0°) *versus* the crystal rotation angle β, a diagram resembling the centrosymmetric but irregular hexagon of Fig. 3(*a*) is obtained. From the equations developed earlier (Alexander & Smith, 1962, equations (D·5) and (D·8)) expressing the angular locations of L' and T' on the $\Delta 2\theta$ scale as a function of β, the lengths and slopes of the six sides of the hexagon can be derived. We assume that 2θ is small and that the X-ray source-to-crystal distance (R_x) equals the crystal-to-receiving aperture distance (R_z). As the crystal is turned in the $+\beta$ direction, diffraction commences at β_a and the leading edge of the beam moves through the angle $2\gamma_c$ to point *b* when the crystal turns through the angle γ_c, the slope of side *ab* being 2. Then when the crystal turns through the angle γ_x, the leading edge of the beam moves through the angle γ_x to the point *d* with unitary slope; and, finally, when the crystal turns through the angle γ_m, the leading edge stays fixed at $\Delta 2\theta_d=\Delta 2\theta_e$ (zero slope). During this sequence of events the trailing edge executes an identical path of three component sides but in reverse order, *ag, gf, fe*. In this construction we have chosen to neglect the angular effect of wavelength dispersion, γ_λ, which is very small at low Bragg angles.

Thus it can be seen that the dimensions of the figure give the parameters γ_c, γ_x, and γ_m as indicated. The points defining the upper right-hand and lower left-hand portions of this hexagon cannot be established very precisely because of the feebleness of these reflections, which are generated by X-rays emanating from the marginal areas of the focal spot, but the sides L' and T' can be located accurately and the vertical interval $\gamma_m+\gamma_c$ determined with a precision of $+2'$ or better. It then remains only to measure the crystal diameter microscopically using a calibrated eyepiece and subtract γ_c from the sum $\gamma_m+\gamma_c$.* Actually the span $\gamma_m+\gamma_c$ is simply the overall width of the reflection on the film as observed near the midpoint of the reflecting range, and in some cases a sufficiently accurate value of $\gamma_m+\gamma_c$ can be obtained by directly measuring a single good-quality reflection. However, this procedure is only to be trusted when it is very certain that γ_m is considerably smaller than $\gamma_x+\gamma_c$, and this can most readily be proved by constructing the $\beta-2\theta$ hexagon and verifying the presence of the vertical span $\gamma_m+\gamma_c$.

When $\gamma_m>(\gamma_x+\gamma_c)$ the hexagon assumes proportions such as shown in Fig. 3(*b*), which is characteristic

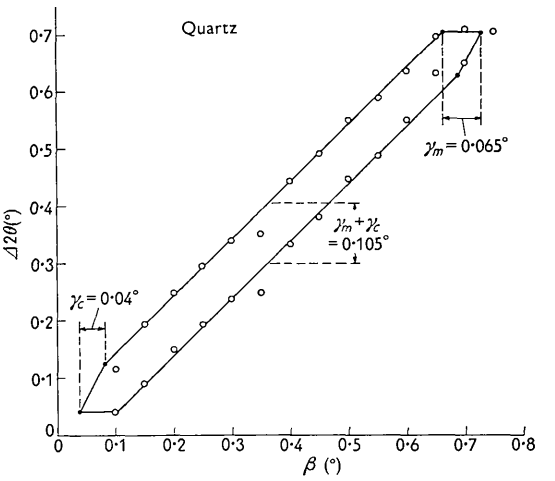

Fig. 4. Experimental reflection hexagon for the α-quartz data of Fig. 2.

* Strictly, γ_c is the effective angular diameter of the crystal measured in the plane of diffraction and at right angles to the diffracted beam. However, since γ_c is small with respect to the sum of the other terms governing the receiving aperture dimension (Alexander & Smith, 1962, equation (D·9)), it suffices in practice to define γ_c as the mean diameter in the plane of diffraction.

Table 1. *Experimental values of mosaicity* (γ_m)

Crystal	*hkl*	2θ	Crystal diameter *d*	γ_c	$\gamma_m+\gamma_c$	γ_m
Quartz No. 1	100	20·8°	0·10 mm	0·040°	0·105°	$0{\cdot}06_5°$
Quartz No. 2*	100	20·8	0·17	0·065	(1) 0·060	(1) $-0{\cdot}00_5°$
					(2) 0·180	(2) $0{\cdot}11_5°$
$(C_6H_5)_4Si$†	200	15·4	0·11	0·045	0·320	$0{\cdot}27_5°$
$[(CH_3)_2SiNH]_4$	200	15·2	0·30	0·120	0·430	$0{\cdot}31_0°$

* Two 'perfect' components misoriented by $0{\cdot}11_5°$. (1) refers to either component separately and (2) to both components taken together.

† Two components slightly misoriented.

of very highly mosaic crystals. It is clear that the vertical span $\gamma_m+\gamma_c$ can no longer be measured directly on the film, although it can be obtained graphically by extrapolating the L' or T' edge or by directly measuring the horizontal span of L' and T', which is likewise of magnitude $\gamma_m+\gamma_c$.

Fig. 4 shows the experimental hexagon plotted from the quartz reflections of Fig. 2. The vertical span L'–T' is 0·105°, from which by subtracting the crystal diameter (0·040°) the mosaic range is found to be 0·065°. Fig. 5 gives the diagram obtained from the (200) reflection of tetraphenyl silicon. The greater scatter of the experimental points observed in this case results from the use of an earlier, less precise method of imprinting the calibrating marks. The overall $\gamma_m+\gamma_c$ is 0·32°, which with the optically measured crystal diameter of 0·045° leads to $\gamma_m=0{\cdot}27_5°$.

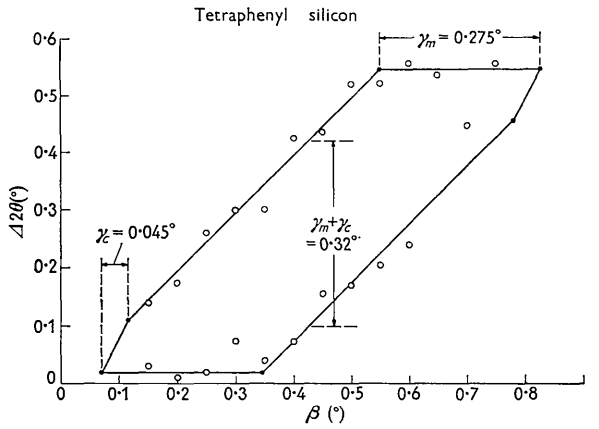

Fig. 5. Experimental reflection hexagon for a crystal of tetraphenyl silicon, $(C_6H_5)_4Si$.

Table 1 summarizes the results obtained for four crystals including the two just described. The apparent negative value of γ_m found for either component of quartz crystal No. 2 is, of course, meaningless, being well within the experimental error of the method. Thus the two components are individually nearly perfect but misoriented with respect to each other by $0{\cdot}11_5°$ as indicated in part (2).

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