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Seemann–Bohlin X-Ray Diffractometry. I. Instrumentation*

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The principles of using a counter tube diffractometer in the Seemann–Bohlin focusing arrangement are described. Simultaneous focusing of all reflections makes it possible to employ several detectors, and the stationary specimen simplifies the design of chambers to modify environmental conditions. Changing the specimen position to achieve a different angular range requires rotating the X-ray tube or goniometer around the X-ray tube focus. The diffracted intensity varies along the specimen length owing to the varying angle-of-view of the anode and the varying mean angle of incidence but does not affect the quality of the focusing. The resolution and intensity are dependent on the source and receiving apertures. The receiving slit may be pointed toward the middle of the curved specimen surface so that the aperture decreases with increasing θ, or toward the center of the goniometer to achieve a constant aperture.

Introduction

The principle of X-ray focusing, in which the incident divergent beam is reflected from a stationary curved specimen and all reflections occur simultaneously focused on the circumference of a focusing circle containing the source, specimen surface and cylindrical film, was first applied to X-ray powder cameras by Seemann (1919) and Bohlin (1920). In practice the advantage of the high intensities inherent in this focusing geometry was usually outweighed by the inaccessible low-angle region, the limited angular range that could be photographed with one setting and the broadening caused by inclination of the reflected beam to the film. Aside from occasional uses in metallurgical laboratories and the application to symmetrical back-reflection focusing cameras, the method was never as widely used as the Debye–Scherrer–Hull method. However, the use of a focusing crystal monochromator in conjunction with the Seemann–Bohlin (S–B) geometry has been used in a number of cameras, as for example, Guinier (1939), de Wolff (1948), Hofmann & Jagodzinski (1955).

The use of a counter tube detector in conjunction with the S–B geometry makes it possible to eliminate some of the difficulties of the S–B film methods and also offers some attractive new possibilities. The major potential advantages over the conventional diffractometer which prompted this study are: (*a*) simultaneous

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focusing of all reflections makes it possible to use several detectors to scan the pattern simultaneously thereby reducing the recording time, or to follow a solid state reaction by recording reflections at the same time from each phase while changing the specimen temperature; (*b*) the stationary specimen simplifies the instrumentation for subjecting the specimen to extreme environmental conditions.

Wassermann & Wiewiorowsky (1953) appear to have been the first to publish a description of a counter tube S–B diffractometer. The method is shown schematically in Fig. 1. The instrumentation used in this study was a mechanical linkage designed as an attachment to a conventional diffractometer (Parrish, Mack & Vajda, 1967). The linkage moves the receiving slit assembly and detector around the focusing circle while continuously pointing them to the middle of the specimen surface. Alternatively the receiving slit may be detached from the linkage and pointed to the center of the focusing circle to achieve a constant receiving aperture as described below. The slit system, detector and circuitry are the same as in the conventional diffractometer.

Geometry

The principal differences between the S–B and the conventional diffractometer geometry are that in the former the focusing circle *FC* has a constant radius *R* equal to the goniometer radius, the specimen remains stationary and the distance between the specimen and detector varies continually; in the latter, the focusing circle has a radius r_c which varies continually, the specimen rotates at one-half the angular speed of the detector to obtain focusing and the specimen to detector distance is constant at all diffraction angles. The aberrations and intensity of the S–B are compared with those of the conventional diffractometer in an accompanying paper (Mack & Parrish, 1967).

The geometrical source *F* is the line focus of the X-ray tube viewed at an angle ψ. Alternatively a slit or the focal line of a curved crystal monochromator may be used but the intensities would be lower. The angular aperture of the divergent beam striking the specimen in the focusing plane is

$$\alpha = 2 \text{ arc } \tan(W_{DS}/2a) \quad (1)$$

where W_{DS} is the width of the divergence slit and *a* the distance from *F* to *DS*. The extreme divergent rays view the target at angles of $\psi \pm (\alpha/2)$.

Fig. 2 shows the principal elements of the S–B geometry. The mean angle γ of the incident beam is defined by the central ray passing through the middle of the specimen surface at *O* and the tangent *t* to *FC* at *O*, and is given by

$$\gamma = \text{arc } \sin(b/2R) , \quad (2)$$

where *b* is the distance from *F* to *O*. The angle γ and the irradiated specimen length $l = 2\alpha R$ are constant at all diffraction angles. The flat specimen aberration is eliminated by the use of a specimen whose surface curvature is equal to the curvature of the focusing circle.

Let *H* be a set of planes which in the reflecting position makes an angle θ_H with the central incident ray and is observed on the counter tube scale at $4\theta_H$. The angle β_H is defined by *H* and *t*; $\theta_H = \gamma + \beta_H$. For a particular reflection diffraction occurs over an angular range determined by $\alpha/2$ and the rocking angle of the powdered crystallites. Each set of planes has a different inclination β_H to the specimen surface whereas in the conventional diffractometer diffraction occurs only from planes within $\alpha/2$ of parallelism to the specimen surface.

A serious limitation of the S–B geometry is that the zero-angle position is located at the source and a direct determination of this important calibration angle is not possible. The angle calibration thus requires measurements of standard substances whose lattice parameters have been determined accurately using another method. The accuracy that could be attained using the $180°4\theta$ angle for calibration (Pike, 1962) when the diffractometer is in the symmetric position (see below) has not been determined; it would require mounting a pinhole

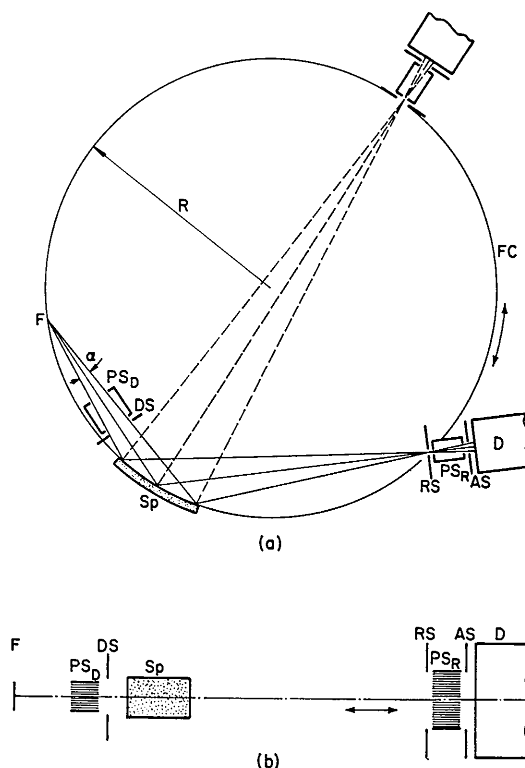


Fig. 1. Seemann–Bohlin focusing diffractometer with counter tube detector. (*a*) Focusing plane, (*b*) axial plane. *F* line focus of X-ray tube, α angular aperture of incident beam, PS_D and PS_R parallel slit assemblies, *DS* divergence slit, *Sp* specimen, *RS* receiving slit (pointed to specimen), *AS* antiscatter slit, *D* detector, *FC* focusing circle, *R* radius of focusing circle (same radius as goniometer).

aperture on the shaft passing through the center of the goniometer (Parrish, 1965).

The source is 8 to 10 mm long (Fig. 1) and a focusing cylinder rather than a focusing circle is a more appropriate model. The divergence in the axial direction (normal to the focusing plane) is limited by two parallel slit assemblies similar to those used in the conventional diffractometer. Each set has a full angular aperture $\delta=4\cdot5°$, and the axial width of the first set is 12 mm and the second 20 mm. The axial width of the cross-fire radiation reaching the specimen is smaller than that of the conventional diffractometer because the specimen is closer to the first set. The position of the second set varies with diffraction angle and hence the axial width of the specimen contributing radiation to each pair of foils also varies.

Specimen position

The selection of the specimen position on the focusing circle depends on the diffraction angle range required as shown in Fig. 3. If γ and/or θ_H are small the microabsorption arising from specimen surface irregularities and particle size roughness may cause large intensity errors. Thus for the back-reflection region a 2γ of approximately 120° is advantageous because γ and θ_H are both relatively large for $4\theta_H > 180°$. The 'symmetric' arrangement, realized when the specimen is opposite the source, $2\gamma=180°$, can be used only for the far back-reflection region, and has the possible advantage that two detectors could be used to measure the same H on both sides of the diffractometer. The 'asymmetric' arrangement, $2\gamma<180°$, is used for the front and part of the back-reflection regions.

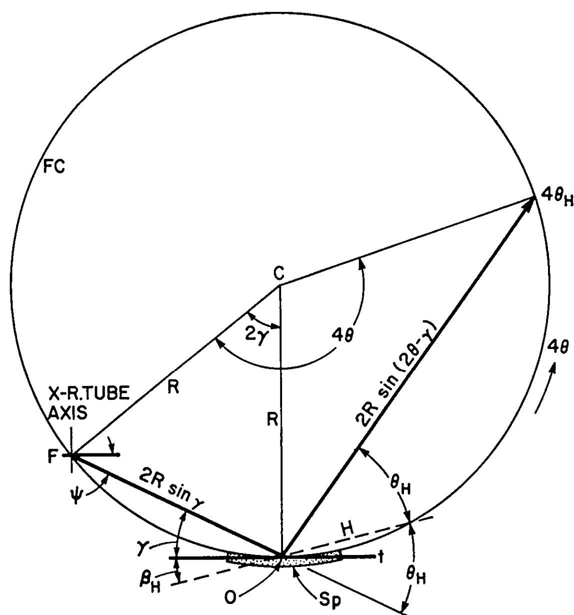


Fig. 2. Geometry in focusing plane. ψ angle-of-view of anode, γ mean angle of incident beam, θ_H Bragg angle of reflecting planes H, and t tangent to FC at O.

If the specimen is moved to a new position, one of the following changes must be made in the alignment in order to maintain the same value of ψ: (*a*) the X-ray tube axis must be rotated around F [Fig. 3(*a*)], or (*b*) the diffractometer must be rotated around F [Fig. 3(*b*)]. Similarly the detector must be repositioned to be normal to the central diffracted ray. For a given goniometer radius the maximum angular aperture α is determined only by the specimen length ($\alpha=l/2R$) and is independent of the distance between F and O.

Multiple detector arrangement

The simultaneous focusing inherent in the S–B geometry makes it possible to scan a pattern with a number of detectors and thereby reduce the recording time. The smallest possible angular separation $\Delta 4\theta=4\theta_2-4\theta_1$ between adjacent detectors depends on the diameter of the detector which determines the maximum number of detectors that can be used. For $R=174$ mm and a scintillation counter diameter of 42 mm, $\Delta 4\theta=41°4\theta$ at $4\theta_1=42°$. Thus three detectors could be used simultaneously, each covering a 60° range (to include overlaps) to scan from 216 to 45°4θ in approximately one-third the time and with the same statistical accuracy as could be achieved with a single detector. The advisability of the procedure must be weighed against the complication of adding separate linkage connections and circuitry for each detector. $\Delta 4\theta$ may be reduced to 19°4θ by rotating the first scintillation counter 90° from its normal position and the X-ray beam would enter a side window scintillation crystal mount. Alternatively, smaller diameter photomultiplier tubes or proportional counters may be used.

To record two closely spaced reflections simultaneously it is necessary to increase R and then $\Delta 4\theta$ would be limited by one-half of the overall dimension X of the receiving slit frame. The expression relating to the pertinent parameters is

$$X=\frac{2R\sin\dfrac{\Delta 4\theta}{2}\sin\left(2\theta_1-\gamma-\dfrac{\alpha}{2}\right)}{\cos\left(\dfrac{\alpha}{2}+\dfrac{\Delta 4\theta}{2}\right)}\,. \tag{3}$$

For example, by doubling R to 348 mm and maintaining the F to O distance at 90 mm, γ is reduced to 7·4° and $\Delta 4\theta$ is reduced to 4°. Sanderson & MacCardle (1966) employed a pair of curved crystal monochromators (each reflecting in opposite directions) after the receiving slits to record the 110 reflections of rutile and anatase ($\Delta 4\theta=8\cdot4°$) for the analysis of titanium dioxide paint pigments.

Focusing

If the specimen curvature and positioning are exact and the specimen and instrument aberrations including axial divergence are negligible, X-rays diffracted by a particular set of planes should converge at the same

point of the focusing circle. In theory it should be possible to use an extremely large aperture beam and long specimen to increase the intensity without loss of resolution. In practice the longer specimen length increases θ_{min}, the specimen preparation becomes somewhat more difficult and requires a larger volume, and the maximum aperture is usually limited to $<10°$ by the X-ray tube window. In the instrument used in these studies $l=23$ mm when $\alpha=4°$ and larger apertures were not used because l increases as $2\alpha R$.

To determine the quality of the focusing four adjacent 6 mm wide strips along the specimen length were irradiated by successive translations of a 1° divergence slit as shown in the insert of Fig. 4. The line profile shapes and positions were essentially the same for each strip provided the specimen was properly prepared and aligned. In fact this proved to be a good method for checking the specimen preparation. If some of the crystallites were relatively large it was sometimes possible to rotate the specimen slightly to obtain a narrower profile from one of the strips but the other strips were broadened indicating the specimen tilt angle was incorrect. This could result if a few large crystallites became the major contributors to the reflected intensity. The difficulty may be overcome by using a large irradiated specimen area and/or small crystallite sizes. This is essential in any case because curved rotating specimens can not be used and flat rotating specimens would cause a large focusing aberration.

The relative net peak and integrated intensities from the four strips varied in several specimens. The variations could not be explained by crystallite size statistics because strip D was always lower than strip A. A 50μ thick beryllium foil was clamped to a curved specimen holder and the 00.2 Cu $K\beta$ profiles recorded from each strip as shown in Fig. 4. When the foil was rotated 180°

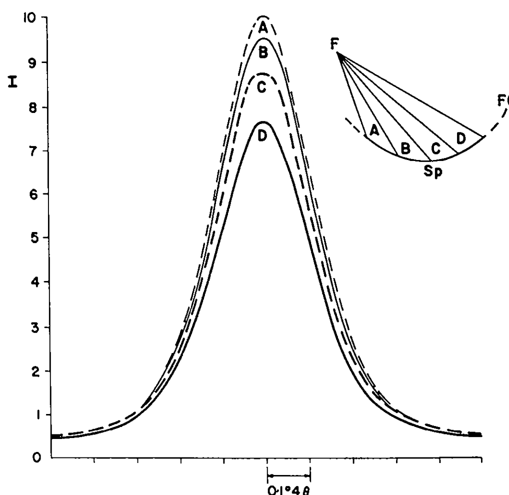
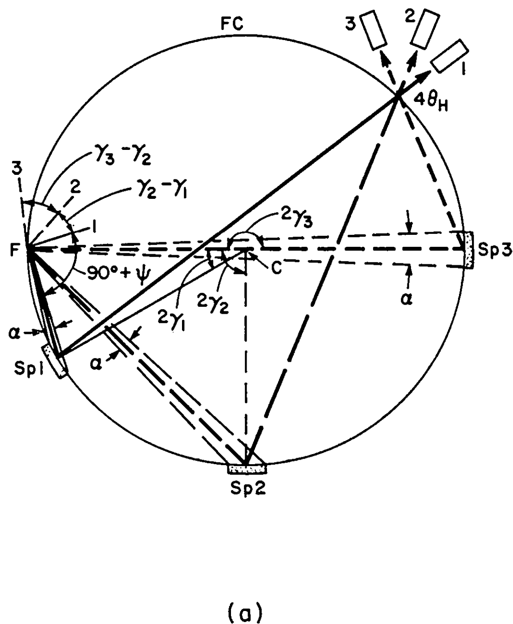


Fig. 4. Line profiles obtained from four irradiated strips (insert) of 50 μ thick curved beryllium foil. 00.2 Cu $K\beta$, $W_{RS}=0{\cdot}075$ mm .



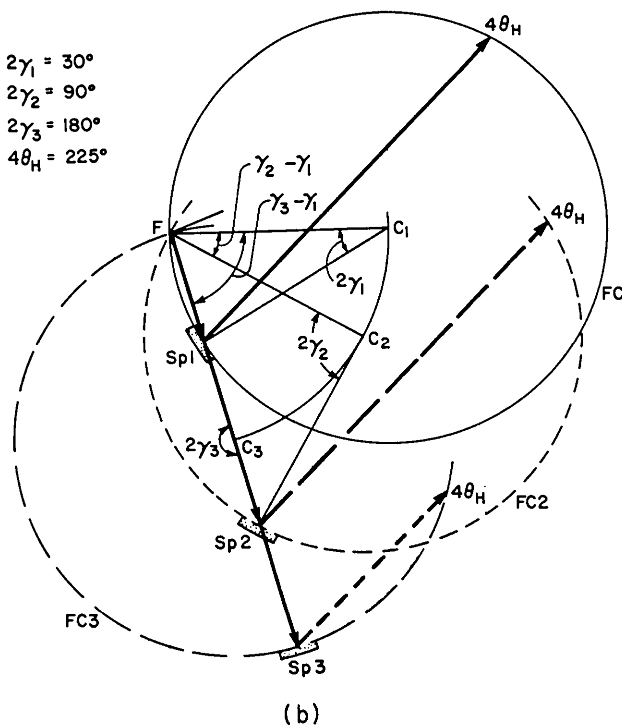


Fig. 3. Diffractometer arrangements for various specimen positions. Angular aperture α is constant for any position of a fixed length specimen on the focusing circle. Changing specimen position requires (a) rotating X-ray tube around F to maintain same ψ, or (b) rotating goniometer around F.

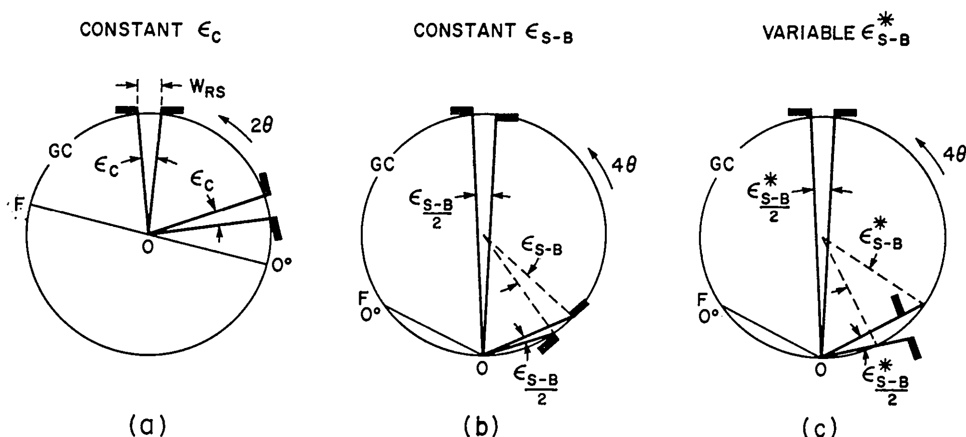


Fig. 5. Schematic drawings of (*a*) conventional diffractometer with constant receiving aperture, (*b*) S–B with constant aperture obtained by pointing receiving slit to center of goniometer, (*c*) S–B with variable aperture obtained by pointing receiving slit to middle of specimen.

Table 1. *Variation of integrated intensity as a function of* ψ *and* γ

Strip	ψ	$I(\psi)$	γ	$I(\gamma)_{\mu\to 0}$	$I(\psi)\,.\,I(\gamma)_{\mu\to 0}$	I(obs.)
A	7·5°	1·00	13·5°	1·00	1·00	1·00
B	6·5	0·97	14·5	0·97	0·94	0·95
C	5·5	0·90	15·5	0·93	0·84	0·87
D	4·5	0·84	16·5	0·90	0·76	0·76

so that the area previously irradiated as strip *D* became strip *A* the results were essentially the same.

The variation of the intensity may be explained in terms of ψ and γ which change in each strip as shown in Table 1, where ψ and γ refer to the median ray for each strip. The incident intensity increases with increasing ψ, and the $I(\psi)$ data are for a copper target X-ray tube operated at 40 kV peak to peak, full-wave rectified (Parrish, Mack & Taylor, 1966). The diffracted intensity varies with γ and θ and for low absorbing specimens

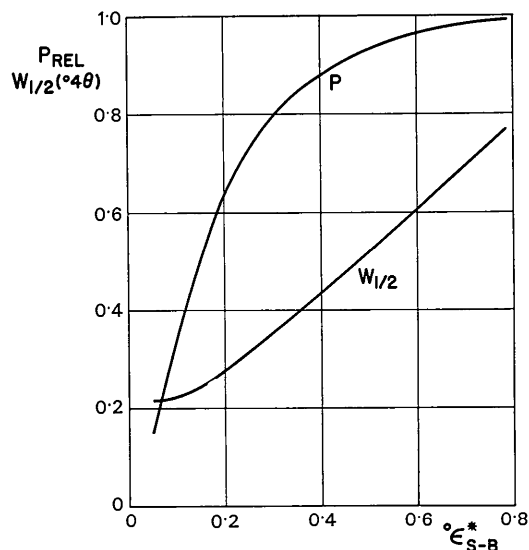


Fig. 6. Dependence of net peak intensity P and line width $W_{1/2}$ at $\frac{1}{2}P$ on receiving slit angular aperture. Curved silicon powder specimen, 111 Cu $K\beta$.

$$I(\gamma)_{\mu\to 0}=K/[\sin\gamma\,.\,\sin(2\theta-\gamma)]\,, \quad (4)$$

where K represents several terms that determine the intensity and is independent of γ. The differential of this equation shows that varying γ results in a considerable change of intensity along the specimen length and that the effect is more pronounced for low γ and high θ. The product $I(\psi)\,.\,I(\gamma)_{\mu\to 0}$ checks well with the observed integrated intensities and the peak intensities show the same dependence because the line profiles have the same widths.

For specimens of high absorption

$$I(\gamma)_{\mu\to\infty}=K/[\sin\gamma+\sin(2\theta-\gamma)] \quad (5)$$

and varying γ has a negligible effect on the intensity across the specimen. Segmüller (1957) derived the same expression as equation (5), which he confirmed experimentally by measuring the intensity with the source and detector positions fixed while γ was varied by moving the specimen around the focusing circle.

Dependence of resolution and intensity on source and receiving apertures in focusing plane

Source aperture

The focal line of the X-ray tube is the geometrical source and the projected width W_F contributes a symmetrical broadening that is independent of diffraction angle. The amount of broadening is determined by the angular aperture of the source which is defined as

$$E_{S-B}(°4\theta)=2\arctan[W_F/(2R\sin\gamma)]\,. \quad (6)$$

For $W_F=0·042$ mm, $R=174$ mm and $\gamma=15°$, $E_{S-B}=0·054\,°4\theta$. In the accompanying paper (Mack & Parrish,

1967) the resolution of the S–B is compared with the conventional (c) diffractometer and it is of interest to compare the equivalent sources of broadening. Thus

$$E_c(°2\theta) = 2 \text{ arc tan}(W_F/2R_c) \quad (7)$$

and $E_c = 0{\cdot}014\,°2\theta$ for the same W_F and R.

The contribution of W_F to the line breadth is about twice as great for the S–B with its smaller source to specimen distance as for the conventional diffractometer. In practice the receiving slit width W_{RS} is often at least twice W_F and contributes a correspondingly greater portion of the breadth.

The incident intensity (for the same X-ray tube voltage and current) may be increased by increasing the angle-of-view ψ of the anode (Parrish *et al.*, 1966) but increasing ψ also increases W_F. The integrated intensity increases linearly and the peak intensity increases at a rate dependent on the resolution.

Receiving aperture

The receiving slit width is a dominant factor in determining the breadth and intensity of line profiles of well-crystallized highly absorbing curved specimens. In the conventional diffractometer the receiving slit moves tangentially around the goniometer circle and the chord length of diffracted radiation intercepted is equal to W_{RS} as shown in Fig. 5(a). The receiving angular aperture in the focusing plane is

$$\varepsilon_c(°2\theta) = 2 \text{ arc tan}(W_{RS}/2R_c) \quad (8)$$

and is constant at all diffraction angles.

In the S–B diffractometer there are two cases. If the slit is pointed to the middle of the specimen surface [Fig. 5(b)] the opening is normal to the central diffracted ray and is always inclined at an angle $2\theta-\gamma$ to the tangent of FC. The aperture varies with the distance of the slit to the specimen

$$\varepsilon^*_{S-B}(°4\theta) = 2 \text{ arc tan } \frac{W_{RS}}{2R\sin(2\theta-\gamma)} \quad (9)$$

and hence varies continually over the scanning range. If the slit is pointed to the center of the goniometer [Fig. 5(c)] the effective width decreases with decreasing θ and the aperture is the same at all diffraction angles,

$$\varepsilon_{S-B}(°4\theta) = 2 \text{ arc tan}(W_{RS}/2R)\,. \quad (10)$$

In the conventional and constant ε S–B diffractometers the receiving slit width broadens each profile symmetrically and the broadening is independent of diffraction angle. Hence the peak and centroid do not shift as W_{RS} is changed provided the center-lines of the slits are exactly the same. In the region where $K\alpha$ doublets are only partially resolved the peak and centroids of the full doublet profile may shift slightly to larger angles with increasing W_{RS} (Parrish, 1965). The broadening is most noticeable at the smaller diffraction angles because at larger angles the breadth arises mainly from spectral dispersion and wider receiving slits may be used to gain intensity with relatively small increase in breadth. The integrated line intensity is proportional to W_{RS} over a wide range of slit widths. The peak intensity of a nearly symmetrical profile such as a $K\beta$ line is proportional over a somewhat smaller range of slit widths.

The broadening of the variable ε^* S–B diffractometer is greater at small and large diffraction angles and falls to a minimum at $180° + 2\gamma$. In the front-reflection region this geometry thus accentuates the decrease of intensity and increase of resolution with increasing diffraction angle which are normal in the conventional and constant ε S–B diffractometers. Fig. 6 shows the increase of $W_{\frac{1}{2}}$ and P with increasing ε^*_{S-B} of the silicon powder 111 Cu $K\beta$ reflection. Essentially the same results were recorded for the 311 and 511/333 Cu $K\beta$ reflections. A calibrated series of slits with W_{RS} varying from 0·03 to 0·45 mm was used (Parrish, 1966). A good compromise between intensity and resolution could be achieved with the constant aperture S–B by using $\varepsilon_{S-B} = 0{\cdot}2\,°4\theta$. This gives 60% of the maximum P and only $0{\cdot}06\,°4\theta$ increase in $W_{\frac{1}{2}}$ over that of the narrowest receiving slit used.

The form of the constant aperture slit which is pointed to the center of the goniometer has been described by Parrish *et al.* (1967). The determination of the antiscatter width is similar to that for the conventional diffractometer (Parrish *et al.*, 1966) but in the case of the constant ε S–B, W_{RS} varies with θ. It is therefore necessary to use in the calculation that value for W_{RS} corresponding to the highest θ-angle to be scanned. Unfortunately the width is then larger than optimum at small θ's where the scattering is usually more troublesome.

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