M and *D* rotate around *S* in θ–2θ scanning and the profile width is determined by the monochromator. Only the forward-reflection region can be recorded.

(*e*) *M*/S(*T*): This is the diffractometer equivalent of the Guinier camera. A symmetric or asymmetric monochromator is used in the incident beam and the profile width is determined by the *RS*. The incident-beam divergence is limited by ESM.

(*f*) *S*(*R*),(*S*–*B*): The reflections are focused on a fixed-radius circle which measures 4θ. A linkage moves the detector around the focusing circle and always points it to the fixed specimen. The angular range is limited (normally 30–240°4θ) and can be changed by moving the specimen and diffractometer to different positions. The profile width is determined by ES and RS. The same geometry is used with an incident- or diffracted-beam focusing monochromator.

The interaction of the X-ray beam with the specimen varies in different geometries and this may have important consequences on the results, as will be described later. When a reflection specimen is used in θ–2θ or θ–θ scanning, only those crystallites whose lattice planes are oriented nearly parallel to the specimen surface can reflect (Fig. 2.3.1.2) (Parrish, 1974). A transmission specimen in θ–2θ scanning permits reflections only from planes nearly normal to the surface. In the *S*–*B* case, reflections can occur from planes inclined over a range of about 45° to the surface. Transmission specimens must, of course, be mounted on X-ray-transparent substrates. Jenkins (1989) has reviewed the instrumentation and experimental procedures.

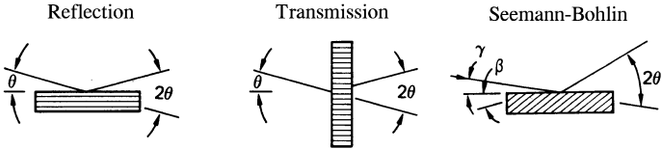

Fig. 2.3.1.2. Specimen orientation for three diffractometer geometries. With θ–2θ scanning, diffraction is possible only from planes nearly parallel to the reflection specimen surface (left), and from planes nearly normal to the transmission specimen surface (middle), and from planes inclined different amounts to the specimen surface in Seemann–Bohlin geometry (right).

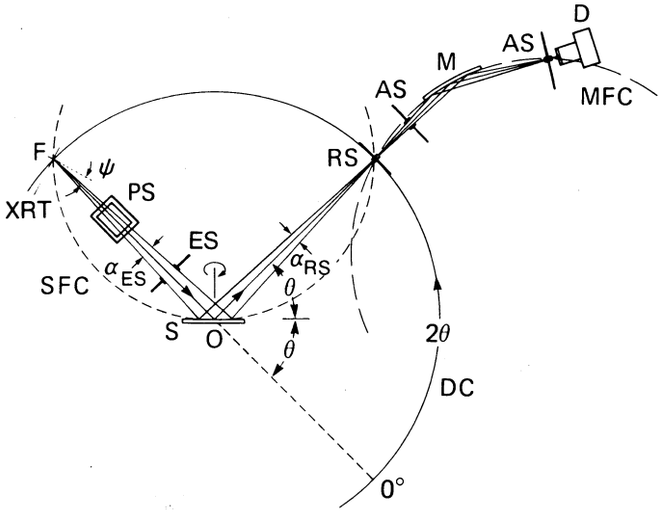

Fig. 2.3.1.3. X-ray optics in the focusing plane of a 'conventional' diffractometer with reflection specimen, diffracted-beam monochromator, and θ–2θ scanning: ψ take-off angle, DC diffractometer circle, MFC monochromator focusing circle, α_{ES} and α_{RS} entrance- and receiving-slit apertures, θ Bragg angle, 2θ reflection angle, *O* diffractometer and specimen rotation axis; other symbols listed in Fig. 2.3.1.1.

2.3.1.1. *Conventional reflection specimen, θ–2θ scan*

The reflection specimen with θ–2θ scanning in the focusing arrangement shown in Fig. 2.3.1.3 is the most widely used powder diffraction method. It is estimated that about 10 000 to 15 000 of these diffractometers have been sold since they were introduced in 1948, which makes it the most widely used X-ray crystallographic instrument. Some authors have called it the Bragg–Brentano parafocusing method (Bragg, 1921; Brentano, 1946), but the X-ray optics (described below) are significantly different from the methods and instruments described by these authors.

The X-ray tube spot focus was first used as the source and gave broad reflections. A narrow entrance slit improved the resolution but caused a large loss of intensity. Early diffractometers were described by LeGalley (1935), Lindemann & Trost (1940), and Bleeksma, Kloos & DiGiovanni (1948); see Parrish (1983). The use of the line focus with parallel slits to limit axial divergence was developed in the late 1940's and gave much higher resolution. A collection of papers by Parrish and co-workers (Parrish, 1965) and Klug & Alexander (1974) describe details of the instrumentation and method.

2.3.1.1.1. *Geometrical instrument parameters*

The powder diffractometer is basically a single-axis goniometer with a large-diameter precision gear and worm drive. The detector and receiving-slit assembly are mounted on an arm attached to the gear in a radial position. The specimen is mounted in a holder carried by a shaft precisely positioned at the centre of the gear. 2/1 reduction gears drive the specimen post at one-half the speed of the detector. Some diffractometers have two large gears, making it possible to drive only the detector with the specimen fixed or *vice versa*, or to use 2/1 scanning. Synchronous motors have been used for continuous scanning for ratemeter recording and stepping motors for step-scanning with computer control.

The geometry of the method requires that the axis of rotation of the diffractometer be parallel to the X-ray tube focal line to obtain maximum intensity and resolution. The target is normal to the long axis of the tube; vertically mounted tubes require a diffractometer that scans in the vertical plane while a horizontal tube requires a horizontal diffractometer. The X-ray optics are the same for both. The incident angle θ and the reflection angle 2θ are defined with respect to the central ray that passes through the diffractometer axis of rotation *O*.

The axis of rotation of the specimen is the central axis of the main gear of the diffractometer, as shown in Fig. 2.3.1.3. The centre of the specimen is equidistant from the source *F* and receiving slit RS. The instrument radius $R_{DC} = F - O = O -$ RS. The radius of commercial instruments is in the range 150 to 250 mm, with 185 mm most common. Changing the radius affects the instrument parameters and a number of the aberrations. Larger radii have been used to obtain higher resolution and better profile shapes. For example, the asymmetric broadening caused by axial divergence is decreased because the chord of the diffraction cone intercepted by the receiving slit has less curvature. However, if the same entrance slit is used, moving the specimen further from the source proportionately increases the length of specimen irradiated and decreases the intensity.

The imaginary specimen focusing circle SFC passes through *F*, *O* and the middle of RS and its radius varies with θ:

$$R_{SFC} = R_{DC}/2\sin\theta. \quad (2.3.1.1)$$

The specimen holder is set parallel to the central ray at 0° and the gears drive the RS-detector arm at twice the speed of the specimen to maintain the θ–2θ relation at all angles. The source F is the line focus of the X-ray tube viewed at a take-off angle ψ. The actual width, F'_w, is foreshortened to

$$F_w = F'_w \sin\psi. \quad (2.3.1.2)$$

In a typical case, $F'_w = 0.4$ mm and, at $\psi = 5°$, $F_w = 0.03$ mm and the projected angular width is 0.025° for $R = 185$ mm. The angular aperture α_{ES} of the incident beam in the equatorial (focusing) plane is determined by the entrance slit width ES_w (also called the 'divergence slit' since it limits the divergence of the beam) and its distance D_1 from F:

$$ES_\alpha = 2\arctan[(ES_w + F_w)/2D_1]. \quad (2.3.1.3)$$

Because the beam is divergent, the length of specimen irradiated S_l in the direction of the incident beam normal to O varies with θ:

$$S_l = [\alpha(R - D')]/\sin\theta, \quad (2.3.1.4)$$

where α is in radians and D' is the distance from F to the crossover point before ES and is given by $F_w D_1/(F_w + ES)$. The approximate relation

$$S_l = \alpha R/\sin\theta \quad (2.3.1.5)$$

is close enough for practical purposes (Parrish, Mack & Taylor, 1966). The intensity is nearly proportional to ES_α but the maximum aperture that can be used is determined by S_l and the smallest angle to be scanned $2\theta_{min}$, as shown in Fig. 2.3.1.4. The entrance-slit width may be increased to obtain higher intensity at the upper angular range; for example, ES = 1° for the forward-reflection region and 4° for back-reflection.

Some slit designs are shown in Fig. 2.3.1.5. The base is machined with a pair of rectangular shoulders whose separation A is the sum of the diameters of the two rods (*a*) or bar widths (*b*) and the central spacers on both ends that determine the slit opening. The distance P between the centre of the slit opening and the edge of the slit frame is kept constant for all slits to avoid angular errors when changing slits. The rods may be molybdenum or other highly absorbing metal and are cemented in place. It may also be made in one piece (*c*) using machinable tungsten (Parrish & Vajda, 1966).

A variable ES whose width increases with 2θ so that the irradiated length is about the same at all angles has been described by Jenkins & Paolini (1974). It is called a θ-compensating slit in which a pair of semicircular cylinders with a fixed opening is rotated around the axis of the opening by a linkage attached to the specimen shaft of the diffractometer to vary the aperture continously with θ. The observed intensities must be corrected to obtain the relative intensities and the angular dependence of the aberrations is different from the fixed aperture slit.

Another way to irradiate constantly the entire specimen length is to use a self-centring slit which acts as an entrance and antiscatter slit (de Wolff, 1957). A 1 mm thick brass plate with rounded edge is mounted above the centre of the specimen and is moved in a plane normal to the specimen surface so that the aperture is proportional to sin θ. It can only be used for forward reflections.

Owing to the beam divergence, the geometric centre of the irradiated specimen length shifts a small amount during the scan (see also §2.3.5.1.5). It is generally advisable to centre the beam at the smallest 2θ to be scanned. Below about 20°, the irradiated length increases rapidly and it is essential to use small apertures and to align the entrance and antiscatter slits carefully. Failure to do this correctly could cause (*a*) errors in the relative intensities owing to the primary beam exceeding the specimen area, (*b*) cutoff by the walls of the specimen holder for low-absorbing thick specimens, and (*c*) increased background from scattering by the specimen holder or the primary beam entering the detector. The transmission specimen method (Subsection 2.3.1.2) has advantages in measuring large d's.

The beam converges after reflection on the receiving slit RS, whose width defines the reflection and profile width. Only those rays that are within the θ–2θ setting are in sharp convergence, *i.e.* 'in focus'. The reflections become broader with increasing distance from the RS, and, therefore, this method is not suited for position-sensitive detectors. The RS aperture

$$\alpha_{RS} = 2\arctan(RS_w/2R) \quad (2.3.1.6)$$

is the dominant factor in determining the intensity and resolution. For $RS_w = 0.1$ mm and $R = 185$ mm, $\alpha_{RS} = 0.031°$.

Antiscatter slits AS are slightly wider than the beam and are essential in this and other geometries to make certain the detector

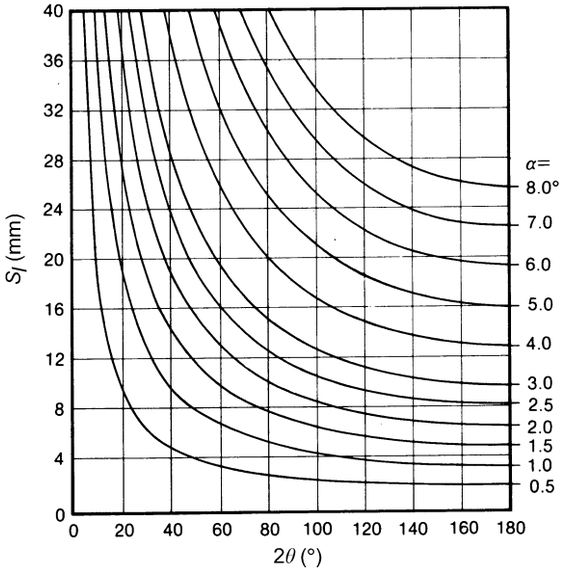

Fig. 2.3.1.4. Length of specimen irradiated, S_l, as a function of 2θ for various angular apertures. $S_l = \alpha R/\sin\theta$, $R = 185$ mm.

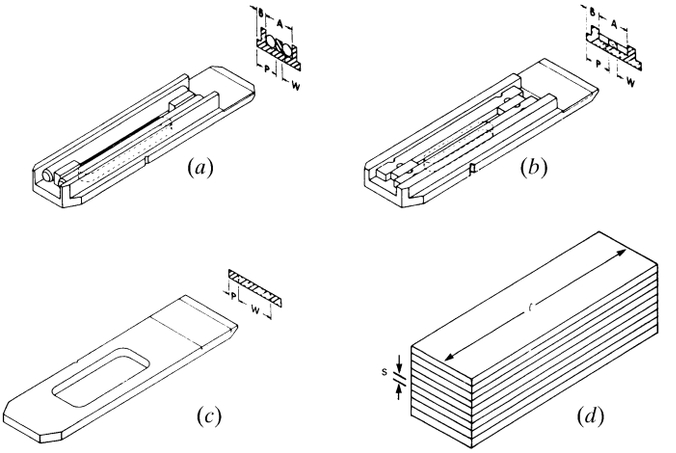

Fig. 2.3.1.5. Slit designs made with (*a*) rods, (*b*) bars, and (*c*) machined from single piece. (*d*) Parallel (Soller) slits made with spacers or slots cut into the two side pieces (not shown) to position the foils.

can receive X-rays only from the specimen area. They must be carefully aligned to avoid touching the beam.

The use of the long X-ray source makes it necessary to reduce the axial divergence, which would cause very large asymmetry. This is done with two sets of thin (25 to 50 μm) parallel metallic foils PS ('Soller slits'; Soller, 1924) placed before and after the specimen. If a monochromator is used, the set on the side of the monochromator is not essential because the crystal reduces the divergence. The angular aperture of a set of slits is

$$\delta = 2\arctan(\text{spacing/length}). \qquad (2.3.1.7)$$

The overall width of the set and δ determine the width of the specimen irradiated in the axial direction, which remains constant at all 2θ's. The construction is illustrated in Fig. 2.3.1.5(*d*). The aperture δ is usually 2 to 5°. Each set of parallel slits reduces the intensity; for example, with 12.5 mm long foils with 1 mm spacings, the intensity is about one-half of that without the parallel slits. The aperture can be selected with any combination of spacings and lengths but the greater the length, the fewer foils are needed, and the less is the intensity loss due to thickness of the metal foils (usually 0.025 mm). These slits can be made as interchangeable units of different apertures.

2.3.1.1.2. *Use of monochromators*

Many diffractometers are equipped with a curved highly-oriented pyrolytic graphite monochromator placed after the receiving slit as shown in Fig. 2.3.1.3. Although graphite has a large mosaic spread (~ 0.35 to 0.6°), the diffracted beam from the specimen is defined by the receiving slit, which determines the profile shape and width rather than the monochromator. The same results are obtained whether the monochromator is set in the parallel or antiparallel position with respect to the specimen. The most important advantage of graphite is its high reflectivity, which is about 25–50% for Cu $K\alpha$. This is much higher than LiF, Si or quartz monochromators that have been used for powder diffraction. The $K\beta$ filter and the parallel slits in the diffracted beam can be eliminated and, since each reduces the $K\alpha$ intensity by about a factor of two, the use of a graphite monochromator actually increases the available intensity. The diffracted-beam monochromator eliminates specimen fluorescence and the scattered background whose wavelengths are different from that of the monochromator setting. For example, a Cu tube can be used for specimens containing Co, Fe, or other elements with absorption edges at longer wavelengths than Cu $K\alpha$ to produce patterns with low background. Several monochromator geometries are described by Lang (1956).

A specimen in the reflection mode may be used with an incident-beam monochromator and θ–2θ scanning as shown in Fig. 2.3.1.1(*c*). One of the principal advantages is that it is possible to adjust the monochromator and slits to remove the $K\alpha_2$ component and produce patterns with only $K\alpha_1$ peaks. The profile symmetry, resolution and instrument function are thus greatly improved; see, for example, Warren (1969), Wölfel (1981), Göbel (1982) and Louër & Langford (1988). The high-quality crystal required causes a large loss of intensity and reduces specimen fluorescence but does not eliminate it. However, Soller slits in the incident beam and a β filter are no longer required and the net loss of intensity can be as low as 20%. Such monochromators can now be provided as standard by diffractometer manufacturers and their use is increasing, but they are not as widely used as the diffracted-beam monochromator.

2.3.1.1.3. *Alignment and angular calibration*

It is essential to align and calibrate the diffractometer properly. Failure to do so degrades the performance of the instrument, leading to a loss of intensity and resolution, increased background, incorrect profile shapes, and errors that cannot be readily diagnosed. Procedures and devices for this purpose are often provided by the manufacturer. The principles and mechanical devices to aid in making a proper alignment have been described by Parrish & Lowitzsch (1959) and the general procedure by Klug & Alexander (1974, p. 280).

The alignment requires setting the diffractometer axis of rotation to the selected X-ray tube take-off angle at a distance equal to the radius of the diffractometer. The long axes of the X-ray tube focal line, entrance, receiving, and antiscatter slits must be centred, be parallel to the axis of rotation, and lie in the same plane when the instrument is at 0°. The slits are made parallel to the axis of rotation in the manufacture of the diffractometer, and these steps require positioning of the instrument with respect to the line focus. The parallel-slit foils must also be normal to the rotation axis. A *flat* fluorescent screen made as a specimen to fit into the diffractometer specimen post is used to centre the primary beam by small movements of the ES and/or diffractometer. The diffracted beam can be centred on the curved monochromator with a narrow slit placed at the centre of the monochromator position (with the monochromator removed). The detector arm is then moved to the highest intensity. The procedure is repeated with the receiving slit in position. This is very close to the 0° position described below.

The angular calibration of the diffractometer is usually made by accurately measuring the 0° position to establish a fiducial point. It assumes that the gear system is accurate and that the receiving-slit arm moves exactly to the angle indicated on the scale at all 2θ positions. The determination of the angular precision of the gear train requires special equipment and methods; see, for example, Jenkins & Schreiner (1986). It is

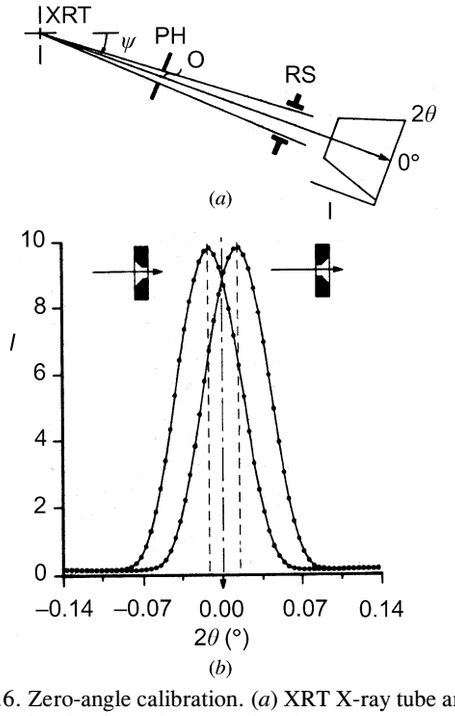

Fig. 2.3.1.6. Zero-angle calibration. (*a*) XRT X-ray tube anode, ψ take-off angle, *O* axis of rotation, PH pinhole, RS receiving slit. Intensity distribution at right. (*b*) 0° position is median of two curves recorded with 180° rotation of PH.

references