easily measured with a standard specimen set to reflect the $K\alpha$ and the specimen to be measured inserted normal to the diffracted beam in front of the detector. It is not critical to achieve the exact value and a range of ±15–20% of the transmission can be tolerated. This minimizes the effect of the absorption change with 2θ, and corrections of the relative intensities are required only when accurate values are required.

The intensity of the incident beam can be measured at 0° in the same geometry and used to scale the relative intensities to 'absolute' values. The flat specimen, transparency, and specimen surface displacement aberrations are similar to those in reflection specimen geometry except that they vary as $\sin\theta$ rather than $\cos\theta$. This is an important factor in the measurement of large-d-spacing reflections. The flat-specimen effect is smaller because the irradiated specimen length is usually smaller. The transparency error is also usually smaller because thin specimens are used.

An important advantage of the method is that the specimen displacement can be directly determined by measuring the peak in the normal position and again after rotating the specimen holder 180°. The correct peak position is at one-half the angle between the two values. The axial divergence has the same effect as in reflection. The limitations are that only the forward-reflection region is accessible, and the intensity is about one-half of the reflection method (except at small angles) because smaller specimen volumes are used.

An alternative arrangement for the transmission specimen mode is to use an incident-beam monochromator as shown in Fig. 2.3.1.12(*b*). This is similar to the geometry used in the Guinier powder camera with the detector replacing the film. A high-quality focusing crystal is required. Wölfel (1981) used a symmetrical focusing monochromator with 260 mm focal length for quantitative analysis. Göbel (1982) used an asymmetric monochromator with a position-sensitive detector for high-speed scanning, see §2.3.5.4.1. By proper selection of the source size and distances, the $K\alpha_2$ can be eliminated and the pattern contains only the $K\alpha_1$ peaks (Guinier & Sébilleau, 1952). This geometry can have high resolution with the FWHM typically about 0.05 to 0.07°. The profile widths are narrower for the subtractive setting of the monochromator than for the additive setting.

The pattern is recorded with θ–2θ scanning. The 0° position can be determined by measuring 4θ, *i.e.* peaks above and below 0°, or calibration can be made with a standard specimen. A slit after the monochromator limits the size of the beam striking the specimen. The width and intensity of the powder reflections are limited by the receiving-slit width. A parallel slit is used between the specimen and detector to limit axial divergence.

The full spectrum from the X-ray tube strikes the monochromator and only the monochromatic beam reaches the specimen, so that it is preferred for radiation-sensitive materials. On the other hand, the radiation reaching the specimen may cause fluorescence (though considerably less than the full spectrum) which adds to the background.

2.3.1.3. *Seemann–Bohlin method*

The Seemann–Bohlin (*S–B*) diffractometer has the specimen mounted on a radial arm instead of the axis of rotation and a linkage or servomechanism moves the detector around the circumference of a fixed-radius focusing circle while keeping it pointed to the stationary specimen. All reflections occur simultaneously focused on the focusing circle as shown in Fig. 2.3.1.13(*a*). The method was originally developed for powder cameras by Seemann (1919) and Bohlin (1920) but was not widely used because of the limited angular range and the broad reflections caused by inclination of the rays to the film. The diffractometer eliminates the broadening and extends the angular range. Diffractometers designed for this geometry have been described by Wassermann & Wiewiorosky (1953), Segmüller (1957), Kunze (1964*a*,*b*), Parrish, Mack & Vajda (1967), King, Gillham & Huggins (1970), Feder & Berry (1970), and others.

The geometry is shown in Fig. 2.3.1.13(*b*) (Parrish & Mack, 1967). Reflections occur from lattice planes with varying inclinations β_H to the specimen surface. The reflecting position of a plane H is $\theta_H = \gamma + \beta_H$, where γ is the incidence angle and $4\theta_H$ the reflection angle. The maximum value of β_H is about 45°. It is essential to align the specimen tangent to FC. This is a critical adjustment because even a small misalignment causes profile broadening and loss of peak intensity.

The source may be the line focus of the X-ray tube [F in Fig. 2.3.1.13(*b*)] or at the focus of a monochromator [ES in Fig. 2.3.1.13(*a*)]; in the latter case, the entrance slit at F' limits the divergent beam reaching the specimen. The source, specimen centre O, and receiving slit RS lie on the specimen focusing circle SFC, which has a fixed radius r. The incidence angle γ is given by

$$\gamma = \arcsin(b/2r), \qquad (2.3.1.21)$$

where b is the distance from F or F' to O, or $2r\sin\gamma$. The γ angle determines the angular range that can be recorded with a given r, decreasing γ decreases $2\theta_{\min}$. The relationships of specimen position on the focusing circle and the recording range

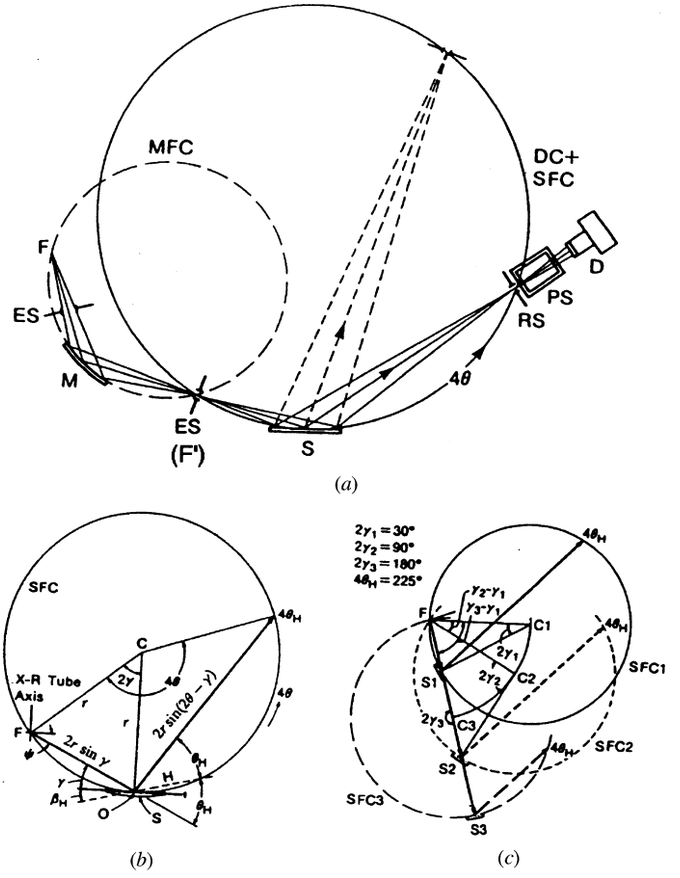

Fig. 2.3.1.13. Seemann–Bohlin method. (*a*) X-ray optics using incident-beam monochromator. (*b*) X-ray tube line-focus source showing geometrical relations: γ mean angle of incident beam, β_H inclination of reflecting plane H to specimen surface, θ_H Bragg angle of H plane, t tangent to focusing circle at O. (*c*) Diffractometer settings for various angular ranges.

are illustrated in Fig. 2.3.1.13(*c*). To change the range requires rotation of the X-ray tube axis or the diffractometer around F. The detector must also be repositioned. For forward-reflection measurements, γ is usually $\leq 10^\circ$. Extreme care must be used in the specimen preparation to avoid errors due to microabsorption (particle-shadowing) effects, which increase with decreasing γ. The 0° position cannot be measured directly and a standard is used for calibration. The range from 0° to about $15^\circ 2\theta$ is inaccessible because of mechanical dimensions. At $\gamma = 90^\circ$, only the back-reflection region can be scanned.

The aperture of the beam striking the specimen is

$$\alpha_{\rm SB} = 2\arctan({\rm ES}_w/2a), \qquad (2.3.1.22)$$

where $\rm ES_{\it w}$ is the entrance slit width and a the distance between F or F' and the slit. The irradiated specimen length l is constant at all angles, $l = 2\alpha r$. A large aperture can be used to increase intensity since the specimen is close to F. However, the selection of α is limited if γ is small, and also because of the large flat-specimen aberration.

The receiving-slit aperture varies with the distance of the slit to the specimen

$$\alpha_{\rm RS}(^\circ 4\theta) = 2\arctan {\rm RS}_w/[2r\sin(2\theta - \gamma)]. \qquad (2.3.1.23)$$

Consequently, the resolution and relative intensity gradually change across the pattern. The S–B has greater widths at the smaller 2θ's and nearly the same widths at the higher angles compared with the θ–2θ diffractometer. The aperture can be kept constant by using a special slit with offset sides (to avoid shadowing) and pointing the opening to C while the detector remains pointed to O (Parrish *et al.*, 1967). The slit opening is tangent to FC and inclined to the beam and rotates while scanning. The constant aperture slit has

$$\alpha_{\rm RS}(^\circ 4\theta) = 2\arctan({\rm RS}_w/2r). \qquad (2.3.1.24)$$

The axial divergence is limited by parallel slits as in conventional diffractometry and the effects are about the same. The equatorial aberrations are also similar but larger in magnitude. The specimen-aberration errors are listed in Table 5.2.7.1. The flat specimen causes asymmetric broadening; the shift is proportional to $\alpha_{\rm ES}^2$ and increases with decreasing θ. It can be eliminated by making the specimen with the same curvature as $r = {\rm FC}$. In this case, one curvature satisfies the entire angular range because the focusing circle has a fixed radius. However, the curvature precludes rotating the specimen. The specimen transparency also causes asymmetric broadening and a peak shift that increases with decreasing θ. For $\mu h \rightarrow 0$, the geometric term is the same as for specimen displacement (Mack & Parrish, 1967).

The diffracted intensity is proportional to $I_0 A(\mu h) TB$, where I_0 is the incident intensity determined by α, δ, and the axial length L of the incident-beam assembly, $A(\mu h)$ is the specimen absorption factor, T the transmission of the air path, and B the length $L_{\rm RS}$ of the diffracted ring intercepted by the slit. The X-rays reflected at a depth x below the specimen surface are attenuated by

$$\exp\{-[\mu x\,{\rm cosec}\,\delta + \mu x\,{\rm cosec}\,(2\theta - \delta)]\}, \qquad (2.3.1.25)$$

where μ is the linear absorption coefficient. The asymmetric geometry causes the absorption to vary with the reflection angle. The air absorption path varies with the distance O to RS and reaches a maximum at $180^\circ + 2\gamma$. The expression for air transmission includes the radius of the X-ray tube R_T, which is needed only for the case where the X-ray tube focal line is used as F. In a typical instrument with X-ray tube source F and $r = 174$ mm, the transmission of Cu $K\alpha$ decreases from 90% at $40^\circ 4\theta$ to 62% at 210°, and Cr $K\alpha$ from 73 to 23% at the same angles.

Some of the advantages of the method include the following: (*a*) the fixed specimen makes it possible to simplify the design of specimen environment devices; (*b*) a large aperture can be used and the intensities are higher than for conventional diffractometers; (*c*) the flat-specimen aberration can be eliminated by a single-curvature specimen; (*d*) a small γ angle can be used to increase the path length l in the specimen, and hence the intensity of low-absorbing thin-film samples ($l = t/\sin\gamma$ and for $\gamma = 5^\circ$, $l = 11.5t$); (*e*) the method is useful in thin-film and preferred-orientation studies because about a 45° range of lattice-plane orientations can be measured and compared with conventional patterns. The limitations include (*a*) the more complicated diffractometer and its alignment, (*b*) limited angular range of about 10 to $110^\circ 2\theta$ for the forward-reflection setting, (*c*) extreme care required in specimen preparation, and (*d*) larger aberration errors.

2.3.1.4. *Reflection specimen, θ–θ scan*

In this geometry, the specimen is fixed in the horizontal plane and the X-ray tube and detector are synchronously scanned in the vertical plane in opposite directions above the centre of the specimen as shown in Fig. 2.3.1.14. The distances source to S and S to RS are equal to that the angles of incidence and diffraction and a constant ${\rm d}\theta/{\rm d}t$ are maintained over the entire angular range. A focusing monochromator can be used in the incident or diffracted beam. High- and low-temperature chambers are simplified because the specimen does not move. The arms carrying the X-ray tube and detector must be counterbalanced because of the unequal weights. The method has advantages in certain applications such as the measurement of liquid scattering without a covering window, high-temperature molten samples, and other applications requiring a stationary horizontal sample (Kaplow & Averbach, 1963; Wagner, 1969).

2.3.1.5. *Microdiffractometry*

There are two types of microdiffraction: (*a*) only a very small amount of powder is available, and (*b*) information is required from very small areas of a conventional-size specimen. Small-volume samples have been analysed with a conventional diffractometer by concentrating the powder over a small spot centred on a single-crystal plate such as silicon (510) or an

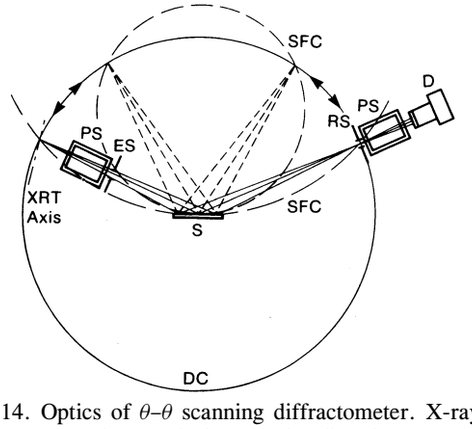

Fig. 2.3.1.14. Optics of θ–θ scanning diffractometer. X-ray tube and detector move synchronously in opposite directions (arrows) around fixed horizontal specimen. A focusing monochromator can be used after the receiving slit.

references