5.3.3.4. *One-crystal spectrometers*

5.3.3.4.1. *General characteristics*

A diffractometer in which both 2θ and ω scans are available, intended for precise and accurate lattice-parameter determination, is sometimes called a one-crystal spectrometer, by analogy with a similar device used for wavelength determination. This name has been used by Lisoivan (1982), who in his review paper described various properties and applications of such a device.

Bragg-angle determination with the one-crystal spectrometer can be performed in an asymmetric as well as in a symmetric arrangement (Arndt & Willis, 1966, pp. 262–264). In the asymmetric arrangement (Fig. 5.3.3.3*a*), the angle 2θ is the difference between two detector positions, related to the maximum intensity of the diffracted and the primary beam, respectively. Bragg-angle determination in such an arrangement is subject to several systematic errors; among these zero error, eccentricity, and absorption are of great importance. As shown by Berger (1984), the latter two errors can be eliminated when Soller slits are used.

To eliminate the zero error, a symmetric diffractometer may be used, in which each measurement of the Bragg angle is performed twice, for two equivalent diffracting positions of the sample, symmetrical in relation to the primary-beam direction (Fig. 5.3.3.3*b*). The respective positions of the counter (or counters, since sometimes two counters are used) are also symmetrical. Such an arrangement may be considered to be (Beu, 1967), in some ways, the diffractometer counterpart of the Straumanis film method (Straumanis & Ieviņš, 1940). From geometric considerations, the absolute value of the angle between the two counter positions is 4θ and the absolute value of the angle between the two sample positions, ω_1 and ω_2, is $180^\circ - 2\theta$, so that both 2θ and ω scans can be used for the Bragg-angle determination.

As was mentioned in §5.3.2.3.4(vi), the idea of calculating the θ angle from the two sample positions has been used with photographic methods (Bragg & Bragg, 1915; Weisz, Cochran & Cole, 1948). Bond (1960), in contrast, was the first to apply this to measurements on the counter diffractometer, and proved that, owing to the geometry, not only the zero error but also the eccentricity, absorption, and several other errors can be reduced.

5.3.3.4.2. *Development of methods based on an asymmetric arrangement and their applications*

Although the Bond (1960) method, based on a symmetric arrangement presented in §5.3.3.4.3, makes possible higher accuracy than that obtained by means of a standard diffractometer, an asymmetric arrangement proves to be more suitable for certain tasks connected with lattice-parameter measurement, because of its greater simplicity. The more detailed arguments for the use of such a device result from some disadvantages of the Bond method, discussed in §5.3.3.4.3.4.

One of the earliest and most often cited methods of lattice-parameter determination by means of the counter single-crystal diffractometer (in an asymmetric arrangement) is that of Smakula & Kalnajs (1955). The authors reported unit-cell determinations of eight cubic crystals. The systematic errors due to seven factors were analysed according to the formulae derived by Wilson (1950) and Eastabrook (1952) for powder samples, and valid also for single crystals. The lattice parameters computed for various diffraction angles were plotted *versus* $\cos^2\theta$; extrapolation to $2\theta = 180^\circ$ gave the lattice parameters corrected for systematic errors. Accuracy of 4 parts in 10^5, limited by the uncertainty of the X-ray wavelength, and precision of 1 part in 10^6 were achieved.

A more complete list of factors causing broadening and asymmetry of the diffraction profile, and so affecting statistical and systematic errors of lattice-parameter determination, has been given by Kheiker & Zevin (1963, Tables IV, IVa, and IVb). Since the systematic errors due to the factors causing asymmetry (specimen transparency, axial divergence, flat specimen) are, as a rule, dependent on the Bragg angle and proportional to $\cos\theta$, $\cos^2\theta$, $\cot\theta$ or $\cot^2\theta$, they can be removed or reduced – as in the method of Smakula & Kalnajs (1955) – by means of extrapolation to $\theta = 90^\circ$. The problem has also been discussed by Wilson (1963, 1980) in the case of powder diffractometry [*cf.* §5.3.3.3.1(i)]. When comparing the considerations of Kheiker & Zevin and Wilson [the list of references concerning the subject given by Kheiker & Zevin (1963) is, with few exceptions, contained in that given by Wilson (1963)], it will be noticed that some differences in the formulae result from differences in the geometry of the measurement rather than from the different nature of the samples (single crystal, powder).

As in the photographic methods, the accurate recording of the angular separation between $K\alpha$ and $K\beta$ diffraction lines can be the basis for lattice-parameter measurements with a diffractometer (Popović, 1971). The method allows one to reduce the error in the zero setting of the 2θ scale and the error due to incorrect positioning of the sample on the diffractometer, since the angular separations are independent of the zero positions of the 2θ and ω scales.

An example of a contemporary method of lattice-parameter determination is given by Berger (1984). As has been mentioned in §5.3.3.4.1, the characteristic feature of the device is the Soller slits, which limit the divergence of both primary and diffraction

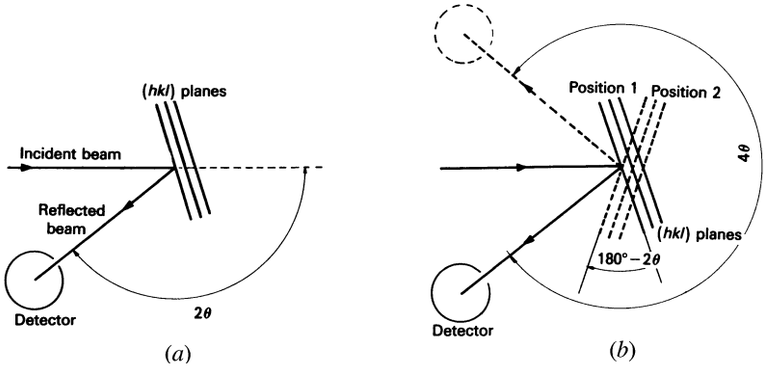

Fig. 5.3.3.3. Determination of the Bragg angle by means of the one-crystal spectrometer using (*a*) an asymmetric or (*b*) a symmetric arrangement. The zero position of the detector arms must be known in (*a*), but not in (*b*). After Arndt & Willis (1966).

Copyright © 2006 International Union of Crystallography

references