

5.3. X-RAY DIFFRACTION METHODS: SINGLE CRYSTAL

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 diffrac-

tometer, 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 Eastbrook (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

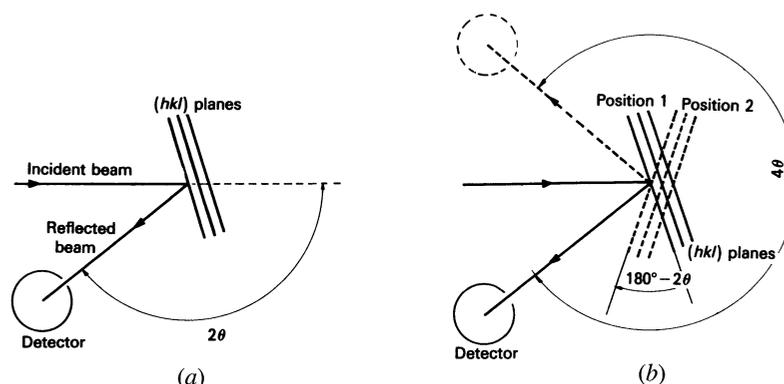


Fig. 5.3.3.3. Determination of the Bragg angle by means of the one-crystal spectrometer using (a) an asymmetric or (b) a symmetric arrangement. The zero position of the detector arms must be known in (a), but not in (b). After Arndt & Willis (1966).

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beams and, at the same time, eliminate errors due to eccentricity and absorption. On the other hand, systematic errors due to refraction, vertical inclination, vertical divergence, and Soller-slit inaccuracy, as well as asymmetry of profiles and crystal imperfection, have to be analysed.

Since, in this case, the angle between the incident and the reflected beam is measured, the inclinations of both beams must be considered. As a result of the analysis [analogous to that of Burke & Tomkiewic, 1969; referred to in §5.3.3.4.3.2(4)], the following expression for the angular correction $\Delta\theta_i$ (to be added to the measured value of θ) is obtained:

$$\Delta\theta_i = \frac{\alpha\gamma}{2 \sin 2\theta} + \frac{\alpha^2 + \gamma^2}{4 \tan 2\theta}, \quad (5.3.3.21)$$

where α and γ are the vertical inclinations of the incident and reflected beams, respectively. The correction for vertical divergence is presented in §5.3.3.4.3.2(3).

The Soller-slit method, the accuracy and precision of which are comparable to those obtained with the Bond method, is suitable both for imperfect crystals, since only a single diffracting position of the sample is required, and for perfect samples, when an exactly defined irradiated area is required. It is applicable to absolute and to relative measurements. Examples are given by Berger, Rosner & Schikora (1989), who worked out a method of absolute lattice-parameter determination of *superlattices*; by Berger, Lehmann & Schenk (1985), who determined lattice-parameter variations in PbTe single crystals; and by Berger (1993), who examined point defects in II-VI compounds.

An original method, based on determining the Bragg angle from a two-dimensional map of the intensity distribution (around the reciprocal-lattice point) of high-angle reflections as a function of angular positions of both the specimen and the counter, was described by Kobayashi, Yamada & Nakamura (1963) and Kobayashi, Mizutani & Schmidt (1970). A finely collimated X-ray beam, with a half-width less than $3'$, was used for this purpose. The accuracy of the counter setting was $\pm 0.1^\circ$, the scanning step $\Delta\theta = 0.01^\circ$. Systematic errors depending on the depth of penetration and eccentricity of the specimen were reported, and were corrected both experimentally (manifold measurements of the same planes for different diffraction ranges, and rotation of the crystal around its axis by 180°) and by means of extrapolation. The correction for refraction was introduced separately. The method was used in studies of the antiparallel 180° domains in the ferroelectric barium titanate, which were combined with optical studies.

The determination of variations in the cell parameter of GaAs as a function of homogeneity, effects of heat treatments, and surface defects has been presented by Pierron & McNeely (1969). Using a conventional diffractometer, they obtained a precision of 3 parts in 10^6 and an accuracy better than 2 parts in 10^6 . The systematic errors were removed both by means of suitable corrections (Lorentz-polarization factor and refraction) and by extrapolation.

A study of the thermal expansion of α -LiIO₃ over a wide range of temperatures (between 20 and 520 K) in the vicinity of the phase transition has been reported by Abrahams *et al.* (1983). Lattice-parameter changes were examined by means of a standard diffractometer (CAD-4); absolute values at separate points were measured by the use of a Bond-system diffractometer.

An apparatus for the measurement of uniaxial stress based on a four-circle diffractometer has been presented by d'Amour *et al.* (1982). The stress, produced by turning a differential screw, can be measured *in situ*, *i.e.* without removing the apparatus from

the diffractometer. An example of lattice-parameter measurement of Si stressed along [111] is given, in which the stress parameter ζ is calculated from intensity changes of the chosen 600 reflection.

5.3.3.4.3. The Bond method

5.3.3.4.3.1. Description of the method

By the use of the symmetric arrangement presented in §5.3.3.4.1 (Fig. 5.3.3.3b), it is possible to achieve very high accuracy, of about 1 part in 10^6 (Bond, 1960), and high precision (Baker, George, Bellamy & Causer, 1968) but, to make the most of this, some requirements concerning the device, the sample, the environmental conditions, the measurement itself, and the data processing have to be fulfilled; this problem will be continued below.

Bond (1960) in his notable work used a large, highly pure and perfect single crystal (zone-refined silicon) in the shape of a flat slab. The scheme of the method is given in Fig. 5.3.3.4. The crystal was mounted with the reflecting planes accurately parallel to the axis of the shaft on a graduated circle (clinometer), the angular position of which could be read accurately (to $1''$). The X-ray beam travelling from the tube through a collimator (two $50 \mu\text{m}$ slits, 215 mm apart, so that the half-width of the primary beam was $0.8'$) fell directly upon the crystal, set in one of the two diffracting positions. The diffracted beam was intercepted by one of two detectors [Geiger-Müller (G-M) counters], which were fixed in appropriate positions. The detectors were wide open, so that their apertures were considerably wider than the diffracted beam, which eliminated some systematic errors depending on the counter position. The crystal was rotated step by step through the reflecting position to record the diffraction profile. Next, the peak positions of both profiles were determined by the extrapolated-peak procedure [§5.3.3.1, definition (4)] to find the accurate positions of the sample, ω_1 and ω_2 , from which the Bragg angle was calculated by use of a formula that can be written in a simple form as

$$\theta = |180^\circ - |\omega_1 - \omega_2|/2|. \quad (5.3.3.22)$$

Before calculating the interplanar distance [equation (5.3.1.1)] or, in the simplest case, the lattice parameter directly, the systematic errors have to be discussed and evaluated. Sometimes, corrections are made to the parameters themselves rather than to the θ values. The reader is referred to §5.3.3.4.3.2, in which present knowledge is taken into account, rather than to Bond's original paper.

Bond performed measurements at room temperature (298 K) for reflections 444, 333, and 111 and, after detailed discussion of

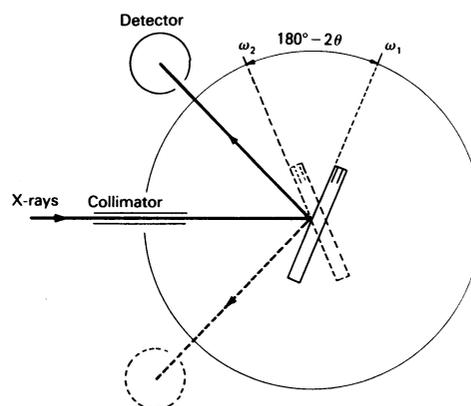


Fig. 5.3.3.4. Schematic representation of the Bond (1960) method.