5. DETERMINATION OF LATTICE PARAMETERS

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 & Tomkeieff, 1969; referred to in §5.3.3.4.3.2(4)], the following expression for the angular correction $\Delta\theta_t$ (to be added to the measured value of θ) is obtained:

$$\Delta\theta_t = \frac{\alpha\gamma}{2\sin 2\theta} + \frac{\alpha^2 + \gamma^2}{4\tan 2\theta}, \tag{5.3.3.21}$$

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 $\pm 0.1°$, the scanning step $\Delta\theta = 0.01°$. 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-LiIO$_3$ 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. 5.3.3.3*b*), 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 $50\,\mu m$ 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 [§5.3.3.3.1, 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

$$\theta = |180° - |\omega_1 - \omega_2|/2|. \tag{5.3.3.22}$$

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
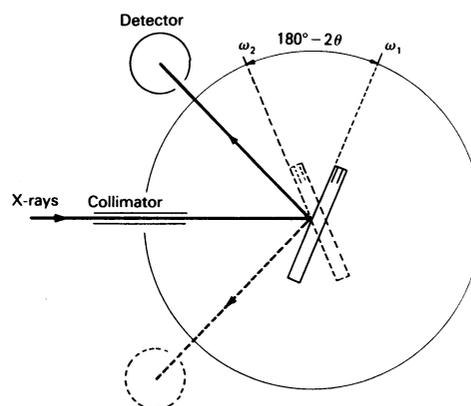

Fig. 5.3.3.4. Schematic representation of the Bond (1960) method.

errors, reported the a_0 values (in kXU), which related to these measurements (standard deviations are given in parentheses), as 5.419770 (0.000019), 5.419768 (0.000031), 5.419790 (0.000149). These values are referred to $\lambda = 1.537395$ kXU. These results were then tested by Beu, Musil & Whitney (1962) by means of the likelihood-ratio method to test the hypothesis of 'no remaining systematic errors'. They proved that the estimate for this sample of silicon is accurate within the stated precision (1 part in 390 000).

The results reported in Bond (1960) – very high accuracy and remarkable reproducibility (low standard deviation), obtained by use of a relatively simple device, which can be realized on the basis of a standard diffractometer – encourage experimenters to perform similar measurements. However, many problems arise with the adaptation of the Bond method to other kinds of samples and/or to other purposes than those described by Bond (1960) in his original paper. Both theoretical and experimental work have increased the accuracy and the precision of the method during the last 35 years.

5.3.3.4.3.2. *Systematic errors*

As mentioned above (§5.3.3.4.1), some systematic errors that affect the asymmetric diffractometer are experimentally eliminated in the Bond (1960) arrangement. According to Beu (1967), who has supplemented the list of errors given by Bond, the following systematic errors are eliminated at the $0.001°\theta$ level:

(*a*) absorption, source profile, radial divergence and surface flatness; removed since the detectors are used only to measure intensities and not angular positions;

(*b*) zero, eccentricity, misalignment and diffractometer radius; eliminated since θ depends only on the difference in the crystal-angle positions and not on these geometrical factors;

(*c*) ratemeter recording does not affect the measurements since the detectors are used only for point-by-point counting;

(*d*) 2:1 tracking error is eliminated because the 2:1 tracking used in most commercial asymmetric diffractometers is not used;

(*e*) dispersion, if the peak position of the profile is determined rather than the centroid or the median, and the wavelength has been determined for the peak position also.

As well as these errors there are other systematic errors, due to both physical and apparatus factors, which should be eliminated by suitable corrections.

(1) *Lorentz–polarization error*. The Lorentz–polarization factor Lp influences the shape of the profile as follows:

$$v_1(x) = \mathrm{Lp}\, v(x), \qquad (5.3.3.23)$$

where $v(x)$ and $v_1(x)$ are the shape functions [see equations (5.3.3.10), (5.3.3.10*a,b*)] of the undistorted and distorted profiles, respectively. It therefore produces a shift ($\Delta\theta_{\mathrm{Lp}}$) in the peak position.

The correction for the Lp factor was estimated, assuming that $v(x)$ is the Cauchy function [equation (5.3.3.19)], by Bond (1960, 1975), Segmüller (1970), and Okazaki & Ohama (1979) for two cases. For perfect crystals, when the Lp factor has the form (James, 1967, p. 59; Segmüller, 1970; Okazaki & Ohama, 1979)

$$\mathrm{Lp} = (1 + |\cos 2\theta|)/\sin 2\theta, \qquad (5.3.3.24)$$

the correction is given by

$$\theta - \theta_p = (\omega_h/2)^2 [\cot 2\theta_p + \sin 2\theta_p/(1 + |\cos 2\theta_p|)], \quad (5.3.3.25)$$

where ω_h is the half-width of the profile, θ_p is the Bragg angle related to the distorted profile, and θ is the corrected Bragg angle. In contrast, the following formulae are valid for mosaic crystals:

$$\mathrm{Lp} = (1 + \cos^2 2\theta)/(2\sin 2\theta), \qquad (5.3.3.26)$$

and

$$\theta - \theta_p = (\omega_h/2)^2 \cot 2\theta_p (2 + \sin^2 2\theta_p)/(2 - \sin^2\theta_p). \quad (5.3.3.27)$$

Because of a notable difference between the values calculated from (5.3.3.25) and (5.3.3.27), the problem is to choose the formulae to be used in practice. However, the Lorentz–polarization error is usually smaller than the rest.

(2) *Refraction*. In the general case, when the crystal surface is not parallel to the reflecting planes but is rotated from the atomic planes around the measuring axis by the angle ε, the correction, which relates directly to the determined interplanar distance, has the form (Bond, 1960; Cooper, 1962; Lisoivan, 1974, 1982)

$$d = d_p \left[1 + \frac{\delta\cos^2\varepsilon}{\sin(\theta + \varepsilon)\sin(\theta - \varepsilon)} \right], \qquad (5.3.3.28)$$

where δ is unity minus the refractive index of the crystal for the X-ray wavelength used, and d_p and d are the uncorrected and corrected interplanar distances, respectively.

(3) *Errors due to axial and horizontal (in-plane) divergence*. The axial divergence of the primary beam, given by an angle $2\Delta_p$ depending on the source and collimator dimensions, causes the angle θ', formed by a separate ray of the beam with a given set of crystallographic planes, to differ from the proper Bragg angle. In general, if the plane of diffraction is not sufficiently perpendicular to the axis of rotation but lacks perpendicularity by an angle Δ, the measured Bragg angle θ' can be described, according to Bond (1960), as

$$\sin\theta' = \sec\Delta\,\sin\theta. \qquad (5.3.3.29)$$

Let us assume that both the crystal and the collimator have been accurately adjusted so that the lack of perpendicularity results from axial divergence only. By averaging the expression (5.3.3.29) over the limits $\pm\Delta_p$, the mean value of $\sin\theta'$ can be found and, as a consequence, the following formula describing the correct d spacing can be obtained:

$$d = d'(1 + \Delta_p^2/6), \qquad (5.3.3.30)$$

where d' is the apparent d spacing.

According to Berger (1984), this correction is valid only for the case of infinitely small focus, when all rays have the same intensity. Taking into consideration the shift of the centroid caused by vertical divergence when the focus emits uniformly within the axial limits $(-F, F)$, he proposes an alternative correction for θ:

$$\Delta\theta_d = \tfrac{1}{6}\tan\theta(P^2 + F^2), \qquad (5.3.3.31)$$

where $2P$ is the sample height.

As tested using computer modelling (Urbanowicz, 1981*b*) and estimated analytically (Härtwig & Grosswig, 1989), the effect of the horizontal divergence on the peak position of the recorded profiles cannot be neglected, contrary to suggestions of Bond (1960). The respective systematic error is dependent on asymmetries of both the focus-tube emissivity and the spectral line, and so it is difficult to express it with a simple formula [*cf.* point (7) below]. In practice (Härtwig, Grosswig, Becker & Windisch, 1991), it proves to be the second largest error. (The first is the one caused by refraction.)

(4) *Specimen-tilt and beam-tilt error*. Since the three main sources of systematic error in diffractometer measurements, *i.e.* zero, eccentricity, and absorption, have been eliminated in the Bond method, two errors due to misalignment of the crystal and the collimator can strongly influence results of lattice-parameter