

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 $\Delta\theta_i$ (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. 5.3.3.3*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 $50\ \mu\text{m}$ 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 [§5.3.3.3.1, 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

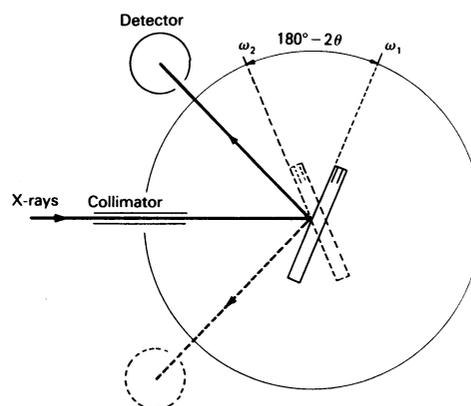


Fig. 5.3.3.4. Schematic representation of the Bond (1960) method.