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 $0.001^\circ\theta$ 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:

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

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)

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

the correction is given by

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

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:

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

and

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

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)

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

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

$$\sin\theta' = \sec\Delta \sin\theta. \tag{5.3.3.29}$$

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:

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

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:

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

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

determination. They are difficult to control because of the random character; numerous authors analysing the Bond method have tried to cope with them. A review is given by Nemiroff (1982).

Bond (1960) considered the crystal-tilt error separately from the collimator tilt. However, in subsequent papers on this subject it was shown that the errors connected with the crystal tilt and the collimator tilt, *i.e.* with the angles that the normals to the crystal and collimator make, respectively, with the plane of angular measurement, are dependent and should be treated jointly.

Foreman (in Baker, George, Bellamy & Causer, 1968) derived a formula for the real value of the angle between two reflecting positions [*i.e.* ω_1 and ω_2 in equation (5.3.3.22)] when affected by both tilts. Burke & Tomkeieff (1968, 1969), in contrast, have found a dependence between the crystal tilt α and the beam tilt β and the relative error $\Delta a/a$ in lattice parameter a in the form

$$\Delta a/a = \alpha\beta/\sin\theta - (\alpha^2 + \beta^2)/2. \qquad (5.3.3.32)$$

A separate analysis is given by Gruber & Black (1970) and by Filscher & Unangst (1980).

Two approaches are used to eliminate the systematic errors considered, based on the above formula:

(i) The error resulting from the crystal tilt and the collimator tilt can be reduced experimentally. Baker, George, Bellamy & Causer (1968) have given a simple procedure that allows a collimator tilt of small but unknown magnitude to be tolerated and, at the same time, the tilt of the crystal to be adjusted to its optimum value. Burke & Tomkeieff (1968, 1969) propose a method for setting the crystal so that $\alpha = \beta$, since, as is obvious from (5.3.3.32), the error has then its minimum value; α and β have to be of the same sign. Then the influence of crystal tilt and beam tilt on the accuracy of lattice-parameter determination is negligible at the level of 1 part in 10^6.

(ii) Equation (5.3.3.32) permits calculation of the exact correction due to both crystal and collimator tilts, if the respective values of α and β are known. Halliwell (1970) proposed a method for determining the beam and the crystal tilt that requires measuring reflections from both the front and back surfaces of the crystal. In a method described by Nemiroff (1982), the two tilts are measured and adjusted independently within ± 0.5 mrad.

(5) *Errors connected with angle reading and setting*. Errors in angle reading and angle setting depend both on the class of the device and on the experimenter's technique. Some practical details are discussed by Baker, George, Bellamy & Causer (1968). Since the angles are measured by counting pulses to a stepping motor connected to a gear and worm, the errors due to angle setting and reading depend on the fidelity with which the gear follows the worm. To diminish errors affected by the gearwheel (notably eccentricity), the authors propose a closed error-loop method, which involves using each part of the gear in turn to measure the angle and averaging the results. In the diffractometer reported in the above paper, there was, originally, an angular error of about $+15''$ around the gearwheel, and this can be corrected by means of a cam so that the residual error is reduced to about $\pm 5''$.

Another example of a high-precision drive mechanism is given by Pick, Bickmann, Pofahl, Zwoll & Wenzl (1977). In the diffractometer described in their paper (see also §5.3.3.7.2), the gear was shown to follow the worm with fidelity even down to $0.01''$ steps, and a drift of $\pm 10\%$ per step was traced to insufficient stability of temperature (± 0.15 K).

(6) *Temperature correction*. An error Δd_T in the lattice parameter d owing to the uncertainty ΔT of the temperature T can be estimated from the formula (Łukaszewicz, Pietraszko, Kucharczyk, Malinowski, Stępień-Damm & Urbanowicz, 1976):

$$\Delta d_T = d\,\alpha_d\,\Delta T, \qquad (5.3.3.33)$$

if the thermal-expansion coefficient α_d in the required direction is known.

In the case of the 111 reflection of silicon, for which $\alpha_d \approx 2.33 \times 10^{-6}$, to obtain a relative accuracy (precision) of 1 part in 10^6, the temperature has to be controlled with accuracy (precision) not worse than ± 0.05 K if the temperature correction is to be neglected (Segmüller, 1970; Hubbard & Mauer, 1976; Łukaszewicz *et al.*, 1976).

(7) *Remarks*. The above list of corrections, sufficient when the Bond (1960) method is applied under the conditions similar to those described by him (large, perfect, specially cut single crystal; well collimated primary beam; large open detector window) has to be sometimes complemented in the case of different specimens and/or different measurement conditions (§5.3.3.4.3.3). When an asymmetric diffractometer is used, all the systematic errors listed in this section (see also §5.3.3.4.1) must be taken into account.

Using a complete convolution model of the diffraction profile, Härtwig & Grosswig (1989) were able to derive all known aberrations (and so respective corrections) in a rigorous, analytical way. The analytical expressions given by the authors, though based on some simplifying assumptions, are usually much more complex than the ones shown in points (1)–(6) above. Some coefficients in their equations depend on physical parameters characterizing the particular device and experiment. So, to follow the idea of Härtwig & Grosswig, one must individually consider all preliminary assumptions. As shown by the authors, to achieve the accuracy of 1 part in 10^7, all aberrations mentioned by them must be taken into account. The most important aberrations prove to be those related to refraction and to horizontal divergence.

5.3.3.4.3.3. *Development of the Bond method and its applications*

The Bond (1960) method, in its first stage, was meant for large, specially cut and set samples. In principle, only one lattice parameter can be determined in one measuring cycle. As has been shown, the method can also be adapted to other samples, with non-cubic symmetry, and to geometries of the illuminated area, different from those used by Bond. This task needs, however, some additional operations and often some additional corrections for systematic errors.

The basic application of the Bond (1960) method, because its geometry reduced several systematic errors, was to absolute lattice-parameter measurements. The method also proved useful in precise investigations of lattice-parameter changes.

Bond-system diffractometers were most often realized in practice on the basis of standard diffractometers under computer control (Baker, George, Bellamy & Causer, 1968; Segmüller, 1970; Pihl, Bieber & Schwuttke, 1973; Kucharczyk, Pietraszko & Łukaszewicz, 1993). Some were designed for special investigations, such as high-precision measurements, $\sigma(d)/d = 10^{-7}$ (Baker, George, Bellamy & Causer, 1966; Grosswig, Härtwig, Alter & Christoph, 1983; Grosswig *et al.*, 1985; Grosswig, Härtwig, Jäckel, Kittner & Melle, 1986); local measurements at chosen points of a specimen (Lisoivan & Dikovskaya, 1969; Lisoivan, 1974, 1982); examination of lattice-parameter changes over a wide temperature range (Łukaszewicz *et al.*, 1976, 1978; Okada, 1982); or the effect of high pressure on lattice parameters (Mauer, Hubbard,

references