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,

Piermarini & Block, 1975; Leszczyński, Podlasin & Suski, 1993).

By introduction of synchrotron radiation to a Bond-system diffractometer (Ando *et al.*, 1989), a highly collimated and very narrow beam has been obtained, so lattice-parameter measurements can be accomplished reliably and quickly with a routinely achieved precision of 2 parts in 10^6; these can be combined with X-ray topographs made in selected areas of the sample.

(1) *Crystals with different symmetry*. Cooper (1962) used the Bond (1960) diffractometer and method for absolute measurements of lattice parameters of several crystals belonging to various orthogonal systems. Special attention was paid to preparing the samples, *i.e.* cutting and polishing, to obtain crystal surfaces parallel to the planes of interest. One sample of a given substance was sufficient to find the lattice in the case of cubic crystals but two samples were required for tetragonal and hexagonal systems, and three were necessary for the orthorhombic system. This difficulty increases when non-orthogonal lattices have to be examined. This problem was resolved by Lisoivan (1974, 1982), who used very thin single-crystal slabs, which made possible measurements both in reflection and in transmission. Lisoivan (1981, 1982), developing his first idea, derived the requirements for a precision determination of all the interaxial angles for an arbitrary system. The coplanar lattice parameters can also be determined in one crystal setting when only reflection geometry is used (Grosswig *et al.*, 1985).

Superlattices can be determined using the system proposed by Bond; a simple method for this purpose was derived by Kudo (1982).

(2) *Different sample areas*. A separate problem is to adapt the Bond method for measurement of small spherical crystals, commonly used in structure investigations. A detailed analysis of this problem is given by Hubbard & Mauer (1976), who indicate that the effect of absorption and horizontal divergence has to be taken into account if the sample dimensions are less than the cross section of the primary beam. As has been mentioned above (§§5.3.3.4.1, 5.3.3.4.3.2), these factors, as well as eccentricity and uncertainty of the zero point, could be neglected in Bond's (1960) experiment. Kheiker (1973) considered systematic errors resulting from the latter two factors when small crystals are used. He proposed a fourfold measurement of the sample position (rather than a twofold one used by Bond), in which 'both sides' of a given set of planes are taken into account, so that measurement by the Bond method is performed for two pairs of specimen positions: ω_1 and $\omega_2 = \omega_1 - 2\theta$, and $\omega_3 = 180^\circ + \omega_1$ and $\omega_4 = 180^\circ + \omega_2$. The corresponding positions of the counter are also determined and used in calculations of the Bragg angle (*cf.* §5.3.3.4.1). The mean value of the θ angle is not subject to the errors mentioned. A similar idea has been presented by Mauer *et al.* (1975).

In many practical cases, it is necessary to determine lattice parameters of thin superficial layers. One of the possibilities is to use the Bond method for this purpose. Wołcyrz, Pietraszko & Łukaszewicz (1980) used asymmetric Bragg reflections with small angles of incidence, to reduce the penetration depth of X-rays. This rather simple method permits high accuracy if proper corrections (the formulae are given by the authors) resulting from the dynamical theory of diffraction of X-rays are carefully determined. This method was used to estimate the gradient of the lattice parameter inside diffusion layers. The penetration depth was changed by rotation of the sample. Golovin, Imamov & Kondrashkina (1985) achieved a penetration depth as small as about 1 to 10 nm, using X-ray total-reflection diffraction (TRD) from the planes normal to the surface of the specimen. The sample was oriented in such a way that the conditions for total external reflection were satisfied when the X-ray beam fell on the sample at a small angle of incidence, about 0.5°.

The homogeneity of the crystal in a direction parallel to its surface may be examined by means of local measurements, described by Lisoivan & Dikovskaya (1969) and Lisoivan (1974), in which the goniometer head was specially designed so that the sample could be precisely set and displaced.

(3) *Determination of lattice-parameter changes*. Baker, George, Bellamy & Causer (1968) have shown that a carefully manufactured and adjusted Bond-system diffractometer (mentioned above) with good stability of environmental conditions (temperature, pressure, power voltage) may be a suitable tool for the investigation of lattice-parameter changes. A static method of thermal-expansion measurement is proposed, in which changes in angle of an *in situ* specimen due to changes in the lattice parameter with temperature are quickly determined. If it is assumed that the intensity and the shape of the peak have not altered with the change of conditions (*cf.* the method based on double-crystal diffractometers in §5.3.3.7.1), the change in angle can be determined by intensity measurement alone. The reported precision of the relative measurement is 1 part in 10^7. Since the shape of the profile may change with the change of conditions, the whole profile must be determined accurately and precisely, so that the whole experiment, consisting of a series of measurements, is time-consuming. The optimization problems resulting from this inconvenience have been discussed above (§5.3.3.3.2; Barns, 1972; Urbanowicz, 1981*a*,*b*).

In particular, thermal-expansion studies can detect phase transitions and the resulting changes in crystal symmetry (Kucharczyk, Pietraszko & Łukaszewicz, 1976; Kucharczyk & Niklewski, 1979; Pietraszko, Waśkowska, Olejnik & Łukaszewicz, 1979; Horváth & Kucharczyk, 1981; Pietraszko, Tomaszewski & Łukaszewicz, 1981; Keller, Kucharczyk & Küppers, 1982; Åsbrink, Wołcyrz & Hong, 1985).

Another group of applications of the Bond method is connected with single-crystal characterization problems (homogeneity, doping, stoichiometry) resulting from technological operations (epitaxy, diffusion, ion implantation) producing changes in lattice spacings, $\delta d/d = 10^{-2}$ to 10^{-5}. The examples cited below show a variety of applications.

Stępień, Auleytner & Łukaszewicz (1972) and Stępień-Damm, Kucharczyk, Urbanowicz & Łukaszewicz (1975) examined γ-irradiated $NaClO_3$. The effect of X-ray irradiation on the lattice parameter of TGS crystals in the vicinity of the phase transition was studied by Stępień-Damm, Suski, Meysner, Hilczer & Łukaszewicz (1974). Pihl, Bieber & Schwuttke (1973) dealt with ion-implanted silicon, using a Bond-system diffractometer for local measurements. The effect of silicon doping on the lattice parameters of gallium arsenide was studied by Fewster & Willoughby (1980). Crystal-perfection studies by the Bond method were reported by Grosswig, Melle, Schellenberger & Zahorowski (1983), and Wołcyrz & Łukaszewicz (1982). In the latter paper, the measurements were performed on a superficial single-crystal layer by the use of the geometry described above [paragraph (2)] (Wołcyrz, Pietraszko & Łukaszewicz, 1980). Lattice distortion in LiF single crystals was examined by Dressler, Griebner & Kittner (1987), who used the method of Grosswig *et al.* (1985) [*cf.* paragraph (1)]. The use of anomalous dispersion in studies of microdefects was considered by Holý & Härtwig (1988).

references