

## 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  $2\theta$  and  $\omega$  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  $2\theta$  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  $4\theta$  and the absolute value of the angle between the two sample positions,  $\omega_1$  and  $\omega_2$ , is  $180^\circ - 2\theta$ , so that both  $2\theta$  and  $\omega$  scans can be used for the Bragg-angle determination.

As was mentioned in §5.3.2.3.4(vi), the idea of calculating the  $\theta$  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 Eastabrook (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.* §5.3.3.1(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  $2\theta$  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  $2\theta$  and  $\omega$  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

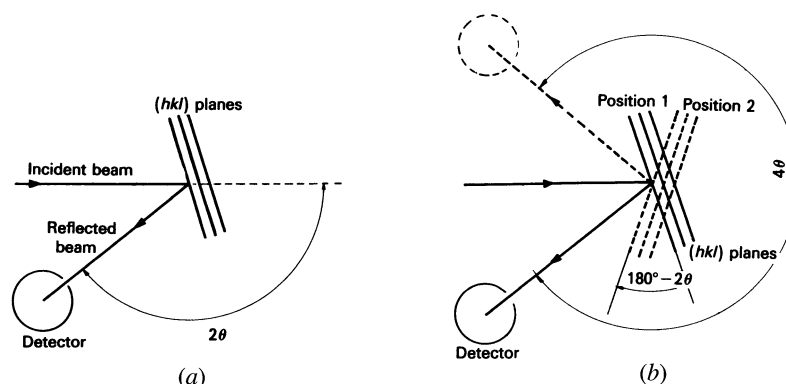


Fig. 5.3.3.3. Determination of the Bragg angle by means of the one-crystal spectrometer using (a) an asymmetric or (b) a symmetric arrangement. The zero position of the detector arms must be known in (a), but not in (b). After Arndt & Willis (1966).

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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 & 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  $\theta$ ) 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  $\alpha$  and  $\gamma$  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  $180^\circ$ ) and by means of extrapolation. The correction for refraction was introduced separately. The method was used in studies of the antiparallel  $180^\circ$  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  $\alpha$ -LiIO<sub>3</sub> 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  $\zeta$  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,  $\omega_1$  and  $\omega_2$ , 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  $\theta$  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

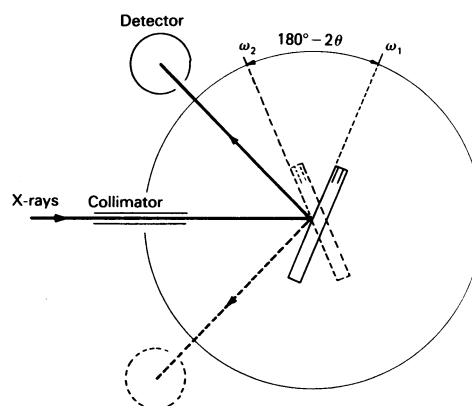


Fig. 5.3.3.4. Schematic representation of the Bond (1960) method.

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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  $\theta$  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  $L_p$  influences the shape of the profile as follows:

$$v_1(x) = L_p v(x), \quad (5.3.3.23)$$

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

The correction for the  $L_p$  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  $L_p$  factor has the form (James, 1967, p. 59; Segmüller, 1970; Okazaki & Ohama, 1979)

$$L_p = (1 + |\cos 2\theta|) / \sin 2\theta, \quad (5.3.3.24)$$

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  $\omega_h$  is the half-width of the profile,  $\theta_p$  is the Bragg angle related to the distorted profile, and  $\theta$  is the corrected Bragg angle. In contrast, the following formulae are valid for mosaic crystals:

$$L_p = (1 + \cos^2 2\theta) / (2 \sin 2\theta), \quad (5.3.3.26)$$

and

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

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  $\varepsilon$ , the correction, which relates directly to the determined interplanar distance, has the form (Bond, 1960; Cooper, 1962; Lisoivan, 1974, 1982)

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

where  $\delta$  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  $\theta'$ , 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  $\Delta$ , the measured Bragg angle  $\theta'$  can be described, according to Bond (1960), as

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

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:

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

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  $\theta$ :

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

where  $2P$  is the sample height.

As tested using computer modelling (Urbanowicz, 1981b) 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

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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 & Causser, 1968) derived a formula for the real value of the angle between two reflecting positions [*i.e.*  $\omega_1$  and  $\omega_2$  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  $\alpha$  and the beam tilt  $\beta$  and the relative error  $\Delta a/a$  in lattice parameter  $a$  in the form

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

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 & Causser (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;  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  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  $\pm 0.5$  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 & Causser (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 ( $\pm 0.15$  K).

(6) *Temperature correction.* An error  $\Delta d_T$  in the lattice parameter  $d$  owing to the uncertainty  $\Delta T$  of the temperature  $T$

can be estimated from the formula (Łukaszewicz, Pietraszko, Kucharczyk, Malinowski, Stępień-Damm & Urbanowicz, 1976):

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

if the thermal-expansion coefficient  $\alpha_d$  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  $\pm 0.05$  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 & Causser, 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 & Causser, 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,

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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:  $\omega_1$  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  $\theta$  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. Wołczyrz, 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  $0.5^\circ$ .

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, Wołczyrz & 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  $\gamma$ -irradiated  $\text{NaClO}_3$ . 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 Wołczyrz & 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)] (Wołczyrz, 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).

## 5. DETERMINATION OF LATTICE PARAMETERS

### 5.3.3.4.3.4. Advantages and disadvantages of the Bond method

The significant advantages of the Bond (1960) method, such as:

- (a) very high accuracy;
  - (b) rather high precision;
  - (c) well elaborated analysis of errors;
  - (d) a simple arrangement, which may be realized on the basis of a standard diffractometer with computer control and, if necessary, supplemented with suitable attachment; and
  - (e) variety of applications;
- make this method one of the most popular at present.

The method, however, has the following limitations:

- (i) Special requirements concerning the sample are difficult to satisfy in some cases.
- (ii) Problems arise with determination of all the lattice parameters of non-cubic crystals. Multiple-sample preparation or a special approach is needed in such cases.
- (iii) Lattice-spacing determination from small spherical crystals requires additional corrections or fourfold measurements.
- (iv) Displacement of the irradiated area on the sample surface (Wołczyrz, Pietraszko & Łukaszewicz, 1980; Berger, 1984) complicates examination of the real structure (for example, by local measurements).
- (v) The method is rather time-consuming, since twofold scanning of the profile is required for determination of a single  $\theta$  value.
- (vi) Because two detectors, or a wide range of rotations of only one detector, are required, measurement with additional attachments is more difficult than on an asymmetric diffractometer.

Nevertheless, the geometry proposed by Bond (1960), owing to its advantages, is commonly used in precise and accurate multiple-crystal spectrometer methods (§§5.3.3.7.1, 5.3.3.7.2).

Other limitations concerning the precision and accuracy of the method are common to it and to all the 'traditional' methods (Subsection 5.3.3.5).

### 5.3.3.5. Limitations of traditional methods

As 'traditional' are considered the methods that depend on a comparison of the lattice spacings to be determined with the wavelength values of characteristic X-radiation that comes directly from laboratory (*Bremsstrahlung*) sources. The *emission lines* are *wide and asymmetric*, which limits both the accuracy and precision of lattice-parameter measurements (as discussed in Subsection 5.3.1.1). One of the limiting factors is the *uncertainty of the wavelength value*. For many years, the wavelength values determined by Bearden (1965, 1967) with an accuracy of 5 parts in  $10^6$  were widely used. At present, owing to remarkable progress in the measurement technique, it is possible to achieve an accuracy in wavelength of an order better, and nowadays remeasurements of some characteristic emission X-ray wavelengths are reported [cf. §5.3.3.3.1(iii) and Subsection 5.3.3.8]. Yet, even after reducing the uncertainty in wavelength, and after introducing all necessary corrections for systematic errors, the highest accuracy of traditional methods does not exceed 1 part in  $10^6$  (cf. Subsection 5.3.3.8).

The accuracy of an order better is possible with X-ray and optical interferometry. This *non-dispersive method* (cf. Subsection 5.3.3.8) is used for accurate lattice-spacing determination of highly perfect standard crystals; the standards are next used for both lattice-parameter determination with a double-beam comparison technique (Baker & Hart, 1975; see also

§5.3.3.7.3) and for the accurate wavelength determination mentioned above.

Another problem is the limited precision attainable by traditional methods. As was discussed in Subsection 5.3.1.1, the width of the diffraction profile depends on the spectral distribution of the wavelength, (5.3.1.6), (5.3.1.7), (5.3.1.8), and cannot be less than this owing to the wavelength dispersion. However, much has been done to approach this limit and to attain the precision and accuracy of the diffraction profile location (cf. Subsection 5.3.3.3). The highest precision of lattice-parameter determination that it is possible to achieve with traditional methods is about 1 part in  $10^7$ . For some problems connected with single-crystal characterization, such as the effect of irradiation, stress, defect concentration, including local measurement (topography), better precision is required.

From (5.3.1.9), the other possibility of increasing precision, besides choosing optimum parameters for the measurement and improvement of profile-location methods, is to influence the original profile  $h_i(\omega)$ . This aim can be attained either by applying spectrally narrower X-ray sources or by reducing the width of the original profile by means of arrangements with additional crystals playing the role of monochromator and reference crystal. This second possibility is applied in double- or triple-crystal spectrometry, in multiple-beam methods, or in combined methods. These methods are called '*pseudo-non-dispersive*' methods, since the width of the diffraction profile is considerably limited in them owing to considerable limitation of the width of the original profile. A similar situation to that in *n*-crystal spectrometers, in which the beam reflected from one set of crystal planes is the source of radiation for the second (or the next) diffraction phenomena, arises in multiple-diffraction methods; this is described in Subsection 5.3.3.6.

A systematic and well illustrated review of pseudo-non-dispersive and other differential methods is given by Hart (1981), who is the author of numerous papers on this subject.

### 5.3.3.6. Multiple-diffraction methods

Multiple diffraction occurs when two or more sets of planes simultaneously satisfy the Bragg law for a single wavelength  $\lambda$ . The beam diffracted from one set of planes becomes the incident beam within the crystal for the next diffraction. In the reciprocal-space representation, this means that three or more reciprocal-lattice points lie simultaneously on the Ewald sphere (Fig. 5.3.3.5). These points can be detected by successive rotations of the crystal, as described below. This phenomenon, known also as

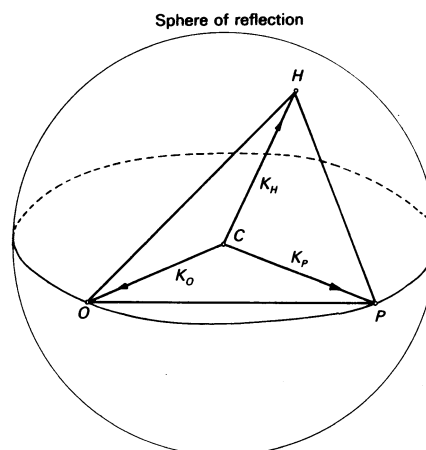


Fig. 5.3.3.5. Schematic representation of multiple diffraction in reciprocal space (after Post, 1975).