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5.3. X-ray diffraction methods: single crystal

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5.3.1. Introduction

5.3.1.1. *General remarks*

The starting point for lattice-parameter measurements by X-ray diffraction methods and evaluation of their accuracy and precision is the Bragg law, combining diffraction conditions (the Bragg angle θ and the wavelength λ) with the parameters of the lattice to be determined:

$$2\,d\sin\theta = n\lambda, \qquad (5.3.1.1)$$

in which d is the interplanar spacing, being a function of direct-lattice parameters a, b, c, α, β, γ, and n is the order of interference. Before calculating the lattice parameters, corrections for *refraction* should be introduced to d values determined from (5.3.1.1) [James (1967); Isherwood & Wallace (1971); Lisoivan (1974); Hart (1981); Hart, Parrish, Bellotto & Lim (1988); *cf.* §5.3.3.4.3.2, paragraph (2) below].

Since only d values result directly from (5.3.1.1) and the non-linear dependence of direct-lattice parameters on d is, in a general case, rather complicated (see, for example, Buerger, 1942, p. 103), it is convenient to introduce reciprocal-cell parameters (a^*, b^*, c^*, α^*, β^*, γ^*) and to write the Bragg law in the form:

$$\begin{aligned}4\sin^2\theta/\lambda^2 &= n^2/d^2\\ &= h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2hka^*b^*\cos\gamma^*\\ &\quad +2hla^*c^*\cos\beta^*+2klb^*c^*\cos\alpha^*,\end{aligned} \qquad (5.3.1.2)$$

where h, k and l are the indices of reflection, and then those of the direct cell are calculated from suitable equations given elsewhere (Buerger, 1942, p. 361, Table 2). The minimum number of equations, and therefore number of measurements, necessary to obtain all the lattice parameters is equal to the number of parameters, but many more measurements are usually made, to make possible least-squares refinement to diminish the statistical error of the estimates. In some methods, extrapolation of the results is used to remove the θ-dependent systematic errors (Wilson, 1980, Section 5, and references therein) and requires several measurements for various θ.

Measurements of lattice dimensions can be divided into *absolute*, in which lattice dimensions are determined under defined environmental conditions, and *relative*, in which, compared to a reference crystal, small changes of lattice parameters (resulting from changes of temperature, pressure, electric field, mechanical stress *etc.*) or differences in the cell dimensions of a given specimen (influenced by point defects, deviation from exact stoichiometry, irradiation damage or other factors) are examined.

In the particular case when the lattice parameter of the reference crystal has been very accurately determined, precise determination of the ratio of two lattice parameters enables one to obtain an accurate value of the specimen parameter (Baker & Hart, 1975; Windisch & Becker, 1990; Bowen & Tanner, 1995).

Absolute methods can be characterized by the *accuracy* δd, defined as the difference between measured and real (unknown) interplanar spacings or, more frequently, by using the relative accuracy $\delta d/d$, defined by the formula obtained as a result of differentiation of the Bragg law [equation (5.3.1.1)]:

$$\delta d/d = \delta\lambda/\lambda - \cot\theta\,\delta\theta, \qquad (5.3.1.3)$$

where $\delta\lambda/\lambda$ is the relative accuracy of the wavelength determination in relation to the commonly accepted wavelength standard, and $\delta\theta$ is the error in the Bragg angle determined.

The analogous criterion used for characterization of relative methods may be the *precision*, defined by the variance $\sigma^2(d)$ [or its square root – the standard deviation, $\sigma(d)$] of the measured interplanar spacing d as the measure of repeatability of experimental results.

The relative precision of lattice-spacing determination can be presented in the form:

$$\sigma(d)/d = \cot\theta\,\sigma(\theta), \qquad (5.3.1.4)$$

where $\sigma(\theta)$ is the standard deviation of the measured Bragg angle θ.

Another mathematical criterion proposed especially for relative methods is the *sensitivity*, defined (Okazaki & Ohama, 1979) as the ratio $\delta\theta/\delta d$, *i.e.* the change in the θ value owing to the unit change in d.

The main task in unit-cell determination is the *measurement of the Bragg angle*. For a given θ angle, the accuracy $\delta\theta$ and precision $\sigma(\theta)$ affect those of the lattice parameter [equations (5.3.1.3) and (5.3.1.4)]. To achieve the desired value of $\delta d/d$, the accuracy $\delta\theta$ must be no worse than resulting from the Bragg law (Bond, 1960):

$$|\delta\theta| = (|\delta d|/d)\tan\theta. \qquad (5.3.1.5)$$

An analogous equation can be obtained for $\sigma(\theta)$ as a function of $\sigma(d)/d$. The values $\delta\theta$ and $\sigma(\theta)$ depend not only on the measurement *technique* (X-ray source, device, geometry) and the *crystal* (its structure, perfection, shape, physical properties), but also on the *processing of the experimental data*.

The first two factors affect the measured profile [which will be denoted here – apart from the means of recording – by $h(\theta)$], being a convolution of several distributions (Alexander, 1948, 1950, 1954; Alexander & Smith, 1962; Härtwig & Grosswig, 1989; Härtwig, Hölzer, Forster, Goetz, Wokulska & Wolf, 1994) and the third permits calculations of the Bragg angle and the lattice parameters with an accuracy and a precision as high as possible in given conditions, *i.e.* for a given profile $h(\theta)$.

In the general case, $h(\theta)$ can be described as a convolution:

$$h(\theta) = h_\lambda(\theta) * h_A(\theta) * h_C(\theta), \qquad (5.3.1.6)$$

where $h_\lambda(\theta)$ is an original profile due to wavelength distribution; $h_A(\theta)$ is a distribution depending on various apparatus factors, such as tube-focus emissivity, collimator parameters, detector aperture; and $h_C(\theta)$ is a function (the crystal profile) depending on the crystal, its perfection, mosaic structure, shape (flatness), and absorption coefficient.

The functions $h_A(\theta)$ and $h_C(\theta)$ are again convolutions of appropriate factors.

Each of the functions $h_\lambda(\theta)$, $h_A(\theta)$, and $h_C(\theta)$ has its own shape and a finite width, which affect the shape and the width ω_h of the resulting profile $h(\theta)$.

Since $h_A(\theta)$ and $h_C(\theta)$ are ordinarily asymmetric, the profile $h(\theta)$ is also asymmetric and may be considerably shifted in relation to the original one, $h_\lambda(\theta)$, leading to systematic errors in lattice-parameter determination.

The finite precision $\sigma(d)/d$, on the other hand, results from the fact that the two measured variables – the intensity h and the angle θ – are random variables.

The half-width ω_λ of $h_\lambda(\theta)$ defines the minimum half-width of $h(\theta)$ that it is possible to achieve with a given X-ray source:

$$\omega_h \gtrsim \omega_\lambda. \qquad (5.3.1.7)$$

It can be assumed from the Bragg law that:

$$\omega_\lambda = (w_\lambda/\lambda)\tan\theta, \qquad (5.3.1.8)$$

where w_λ is the half-width of the wavelength distribution. In commonly used X-ray sources, $w_\lambda/\lambda \approx 300 \times 10^{-6}$.

Combination of (5.3.1.5) and (5.3.1.8), and with (5.3.1.7) taken into consideration, gives an estimate of the ratio of the admissible error $\delta\theta$ to the half-width of the measured profile:

$$\frac{|\delta\theta|}{\omega_h} \le \frac{|\delta d|/d}{w_\lambda/\lambda}. \qquad (5.3.1.9)$$

To obtain the highest possible accuracy and precision for a given experiment (given diffraction profile), mathematical methods of data analysis and processing and programming of the experiment are used (Bačkovský, 1965; Wilson, 1965, 1967; Barns, 1972; Thomsen & Yap, 1968; Segmüller, 1970; Thomsen, 1974; Urbanowicz, 1981*a*; Grosswig, Jäckel & Kittner, 1986; Gałdecka, 1993*a*,*b*; Mendelssohn & Milledge, 1999).

Measurements of lattice parameters can be realized both with *powder samples* and with *single crystals*. At the first stage of the development of X-ray diffraction methods, the highest precision was obtained with powder samples, which were easier to obtain and set, rather than with single crystals. The latter were considered to be more suitable in the case of lower-symmetry systems only. In the last 35 years, many single-crystal methods have been developed that allow the achievement of very high precision and accuracy and, at the same time, allow the investigation of different specific features characterizing single crystals only (defects and strains of a single-crystal sample, epitaxic layers).

Some elements are common to both powder and single-crystal methods: the application of the basic equations (5.3.1.1) and (5.3.1.2); the use of the same formulae defining the precision and the accuracy [equations (5.3.1.4) and (5.3.1.3)] and – as a consequence – the tendency to use θ values as large as possible; the means of evaluation of some systematic errors due to photographic cameras or to counter diffractometers (Parrish & Wilson, 1959; Beu, 1967; Wilson, 1980); the methods of estimating statistical errors based on the analysis of the diffraction profile and some methods of increasing the accuracy (Straumanis & Ieviņš, 1940). In other aspects, powder and single-crystal methods have developed separately, though some present-day high-resolution methods are not restricted to a particular crystalline form (Fewster & Andrew, 1995). In special cases, the combination of X-ray powder diffraction and single-crystal Laue photography, reported by Davis & Johnson (1984), can be useful for the determination of the unit-cell parameters.

Small but remarkable differences in lattice parameters determined by powder and single-crystal methods have been observed (Straumanis, Borgeaud & James, 1961; Hubbard, Swanson & Mauer, 1975; Wilson 1980, Sections 6 and 7), which may result from imperfections introduced in the process of powdering or from uncorrected systematic errors (due to refractive-index correction, for example; *cf*. Hart, Parrish, Bellotto & Lim, 1988). The first case was studied by Gamarnik (1990) – both theoretically and experimentally. As shown by the author, the relative increase of lattice parameters in ultradispersed crystals of diamond in comparison with massive crystals was as high as $\Delta d/d = 2.05 \times 10^{-3} \pm 10^{-4}$. Analysis of results of lattice-parameter measurements of silicon single crystals and powders, performed by different authors (Fewster & Andrew, 1995, p. 455, Table 1), may lead to the opposite conclusion: The weighted-mean lattice parameter of silicon powder proved to be about 0.0002 Å smaller ($\Delta d/d \simeq -4 \times 10^{-5}$) than that of the bulk silicon.

5.3.1.2. *Introduction to single-crystal methods*

The essential feature of single-crystal methods is the necessity for the very *accurate setting* of the diffracting planes of the crystal in relation to the axes or planes of the instrument; this may be achieved manually or automatically. The fully automated four-circle diffractometer permits measurements to be made with an arbitrarily oriented single crystal, since its original position in relation to the axes of the device can be determined by means of a computer (calculation of the orientation matrix); the crystal can then be automatically displaced into each required diffracting position. Misalignment of the crystal and/or of element(s) of the device (the collimator, for example) may be a source of serious error (Burke & Tomkeieff, 1968, 1969; Halliwell, 1970; Walder & Burke, 1971; Filscher & Unangst, 1980; Larson, 1974). On the other hand, a well defined single-crystal setting allows the unequivocal indexing of recorded reflections (moving-film methods, counter diffractometer) and the accurate determination of Bragg angles. In the particular case of large, specially cut and set, single crystals and a suitable measurement geometry, it is possible to avoid some sources of systematic error (Bond, 1960).

Single-crystal methods are realized by a great variety of techniques.

(i) Usually, a *single diffraction* phenomenon, which occurs when only one set of planes is in position to diffract the incident X-ray beam at a given moment, is applied in lattice-parameter measurements. A separate group of so-called *multiple-diffraction* methods is formed by methods in which two or more sets of planes simultaneously fulfil the diffraction condition [equations (5.3.1.1) and (5.3.1.2)]. Some photographic divergent-beam methods (Lonsdale, 1947; Heise, 1962; Morris, 1968; Isherwood & Wallace, 1971; Lang & Pang, 1995) and methods with counter recording in which a collimated beam is used (Renninger, 1937; Post, 1975) belong to this group.

(ii) In *traditional methods*, the unit-cell dimensions are determined in relation to the wavelength of a given X-radiation. Their accuracy and precision [equations (5.3.1.3) and (5.3.1.4)] are limited to those determined by the accuracy and precision of the wavelength determination and the width w_λ of the wavelength distribution [see equations (5.3.1.7) and (5.3.1.9)], so that the accuracy cannot exceed the limit of about 1 part in 10^6. To surmount these difficulties, new methods have been introduced. Combined X-ray and optical interferometry (applied simultaneously) permits the determination both of the lattice parameter and of the X-ray wavelength in terms of the visible wavelength standard so that interplanar distances can be 'non-dispersively' (independently of the optical and X-ray wavelength values and their dispersions) measured in metric units with an accuracy of 1 part in 10^7. These methods (Deslattes, 1969; Deslattes & Henins, 1973; Becker *et al.*, 1981; see also Section 4.4.2) are so-called *non-dispersive* methods. Various *pseudo-non-dispersive* methods, in which the width of the diffraction profile has been reduced owing to the use of two- or three-crystal spectrometers (Godwod, Kowalczyk & Szmid, 1974; Hart & Lloyd, 1975; Buschert, 1965) and/or multiple-beam techniques (Hart, 1969; Larson, 1974; Kishino, 1973; Ando, Bailey & Hart, 1978; Buschert, Pace, Inzaghi & Merlini, 1980; Buschert, Meyer, Stuckey Kauffman & Gotwals, 1983; Häusermann & Hart, 1990), are a very suitable tool for high-precision (up to 1 part in 10^9) differential measurements. In multiple-diffraction methods, an interesting type of '*n*-crystal spectrometer' is generated within the specimen (Post, 1975), so that the resulting diffraction profiles are also narrow.

(iii) In traditional methods, usually only *one single crystal* (the specimen) is used to determine a given lattice parameter, while, in the non-dispersive and pseudo-non-dispersive methods, *two, three or more single crystals* are required, which play the role of the monochromator and/or the reference crystal.

(iv) In the majority of methods, a *single X-ray beam* is used, which is usually well *collimated*. In some methods, however, in which the sample remains stationary, a *highly divergent beam* is applied to satisfy the Bragg law for various sets of planes. These are the Kossel (1936) method and the divergent-beam techniques developed by Lonsdale (1947). The original conception of *multiple-beam* measurement was introduced by Hart (1969). The beams may come from two sources (as in the original paper) or may be separated from only one source (Kishino, 1973).

(v) Most frequently, only *one wavelength* of characteristic X-radiation is used. Sometimes, a monochromator is applied – in particular, in two- or three-crystal spectrometers [see, for example, Fewster (1989) and Obaidur (2002)]. *White* X-radiation may also be used in the Laue method, recently introduced for absolute measurements of the unit-cell dimensions (Carr, Cruickshank & Harding, 1992), or in connection with the two-crystal spectrometer (Okazaki & Kawaminami, 1973*a*,*b*; Okazaki & Ohama, 1979; Ohama, Sakashita & Okazaki, 1979; Okazaki & Soejima, 2001), to allow measurements at extremely large θ angles, or in *energy-dispersive* diffractometers (Buras, Olsen, Gerward, Will & Hinze, 1977), which make short exposures possible.

In the second case, the measurement is based on a principle different from that of traditional methods: a continuous incident X-ray spectrum and a fixed Bragg angle $2\theta_0$ are used. The relation between the interplanar spacing d_H and the energy E_H of the scattered photons is given by

$$E_H\, d_H \sin\theta = \tfrac{1}{2}hc = 6.199 \text{ (keV Å)}, \qquad (5.3.1.10)$$

where H denotes *hkl*.

The *resolved* $K\alpha_{1,2}$ *doublet* is often used in various methods (photographic moving-crystal methods as well as divergent-beam diffractometers) to base the measurements on two independent constant values (Main & Woolfson, 1963; Polcarová & Zůra, 1977; Schwartzenberger, 1959; Mackay, 1966; Isherwood & Wallace, 1971; Spooner & Wilson, 1973; Heise, 1962) or to obtain two independent X-ray beams from a single X-ray source (the multiple-beam method proposed by Kishino, 1973). Sometimes, the $K\beta$ line is also applied (Popović, 1971; Kishino, 1973).

(vi) More and more frequently, new sources of radiation are introduced instead of traditional laboratory *Bremsstrahlung* sources. In the case of methods using a divergent beam, the excitation of the characteristic X-rays may be performed both by primary *X-rays* (Lonsdale, 1947) and by *electron* bombardment (Kossel, 1936; Gielen, Yakowitz, Ganow & Ogilvie, 1965; Ullrich & Schulze, 1972), or by *proton* irradiation (Geist & Ascheron, 1984). Also, a *Mössbauer* source (because of its short wavelength) (Bearden, Marzolf & Thomsen, 1968) and *synchrotron radiation* (Buras *et al.*, 1977; Ando, Hagashi, Usuda, Yasuami & Kawata, 1989) may be used (see also §5.3.3.9 below). The latter is considered to be an ideal X-ray source because of the short exposure required.

When making a choice of the method, the aim of the measurement, the required accuracy and/or precision as well as the laboratory equipment available should be taken into account.

(i) In the case when unit-cell parameters of a *standard crystal* are to be determined, the highest accuracy is needed. This special task is sometimes realized by unique, sophisticated and time-consuming methods (Baker, George, Bellamy & Causer, 1968; Deslattes & Henins, 1973; Becker, Seyfried & Siegert, 1982; Härtwig & Grosswig, 1989): the sample has to be of high quality (pure, defect-free, suitably prepared) and should have a small thermal-expansion coefficient. A detailed error analysis is required. Such measurement is often reduced to only one parameter, since high-symmetry crystals are generally used as standard.

(ii) The second special problem is to determine *all the lattice parameters* of a lower-symmetry system with high, though not necessarily the highest, accuracy.

The most suitable tool for this task is the automated four-circle diffractometer, which permits a proper setting of the crystal for each possible *hkl* reflection. *One crystal mounting* is then sufficient to determine the unit cell with rather high (10 parts in 10^6) accuracy. The measurements can also be performed using a two-circle diffractometer (Clegg & Sheldrick, 1984); these are, however, more troublesome since, in this case, only two rotations are motor-driven while the two remaining angles must be set by hand.

When the diffractometer is to be used, preliminary measurements with photographic methods are advisable. A single rotation photograph allows one to determine one lattice parameter only, a single moving-film photograph makes it possible to obtain a two-dimensional picture of the reciprocal cell, and a suitable combination of two photographic techniques can be the basis for the determination of all the lattice parameters from a single mounting of the crystal (Buerger, 1942; Hulme, 1966; Hebert, 1978; Wölfel, 1971) with moderate accuracy (not better than 1 part in 10^4).

The above counter and photographic methods are suitable for small, preferable spherical, crystals. In the case of one-crystal spectrometers, which give better accuracy (from 10 to 1 parts in 10^6), in particular when the Bond (1960) arrangement is used and when all necessary corrections are taken into account, the preferable form of the sample is a large, flat slab, the surface of which is parallel to the planes of interest. Usually, several samples from one single crystal are needed in order to determine the unit cell of a lower-symmetry system (Cooper, 1962). It is possible, however, to determine coplanar lattice parameters using a single sample, in one crystal mounting, when reflections from different crystal planes are taken into consideration (Luger, 1980, Section 4.2.2; Grosswig, Jäckel, Kittner, Dietrich & Schellenberger, 1985), and a special combination of reflection and transmission geometries enables one to determine all the lattice parameters from a single sample (Lisoivan, 1974, 1981, 1982).

Multiple-diffraction methods, both photographic and with counter recording, can provide a large number of reflections from one crystal mounting. In spite of this, these methods are as yet applied to mainly cubic lattices and exceptionally to other (orthogonal) lattices, because the interpretation of multiple-diffraction patterns is rather complicated (Chang, 1984; and references therein).

High-precision multiple-crystal spectrometers are suitable for comparison measurements in which differences in interplanar spacings rather than absolute values of the spacings are determined.

(iii) When the *lattice-parameter changes* caused by changes of environmental conditions are to be determined, high precision and sensitivity are more important than high accuracy.

In the case of temperature dependence, an additional low- and/or high-temperature attachment is necessary for the precise establishment and control of the temperature (Baker, George, Bellamy & Causer, 1968; Łukaszewicz, Kucharczyk, Malinowski & Pietraszko, 1978; Okazaki & Ohama, 1979; Okada, 1982; Soejima, Tomonaga, Onitsuka & Okazaki, 1991), so that the basic instrument should be relatively simple (Glazer, 1972; Berger, 1984; Clegg & Sheldrick, 1984). Since measurements at many temperatures are then performed, the problem is to obtain the desired precision in as short a time as possible by using automatic control (Baker, George, Bellamy & Causer, 1968), special strategy of measurement (Barns, 1972; Urbanowicz, 1981*a*), and special sources of radiation [synchrotron radiation used by Buras *et al.* (1977) and Ando, Hagashi, Usuda, Yasuami & Kawata (1989)]. Analogous problems appear when the effects of other factors such as pressure (Mauer, Hubbard, Piermarini & Block, 1975; d'Amour, Denner, Schulz & Cardona, 1982; Leszczyński, Podlasin & Suski, 1993), or electric field (Kobayashi, Yamada & Nakamura, 1963) are examined.

(iv) To detect *small differences of lattice parameter* between the sample and the standard or between two points of the same specimen, the highest precision is required. To improve resolution in traditional methods, a finely collimated X-ray beam (Kobayashi, Yamada & Nakamura, 1963) and cameras with large radius (Kobayashi, Yamada & Azumi, 1968) are required. Really high precision, which reaches 1 part in 10^9, can be obtained with multiple-crystal (pseudo-non-dispersive) techniques (Hart, 1969; Buschert, Meyer, Stuckey Kauffman & Gotwals, 1983).

In the present review, all the methods are classified with respect to the measurement technique, in particular into photographic and counter-diffractometer techniques. Moreover, the methods will be described in approximately chronological sequence,* *i.e.* from the earliest and simplest rotating-crystal method to the latest more-complex non-dispersive techniques, and at the same time from those of poor accuracy and precision to those attaining the highest precision and/or accuracy. In each of the methods realizing a given technique, first the absolute and then the relative methods will be described.

5.3.2. Photographic methods

5.3.2.1. *Introduction*

Photographic single-crystal techniques used for unit-cell determination can be divided into three main groups:

(1) the Laue method with a well collimated beam of polychromatic X-radiation with a stationary crystal;

(2) methods with a well collimated beam of characteristic radiation and a moving crystal;

(3) methods with a highly divergent X-ray beam of monochromatic radiation (usually combined with white radiation).

In the past, only techniques belonging to groups (2) and (3) were used in absolute lattice-parameter measurements. As recently shown by Carr, Cruickshank & Harding (1992), a single synchrotron-radiation Laue photograph can provide all necessary information for the determination of unit-cell dimensions on an absolute scale (though with low accuracy for the present).

The methods of the second group are popular moving-crystal methods or their modifications especially adapted for lattice-parameter determination. Cameras and other equipment for performing these measurements – with the exception of special designs – are available in every typical X-ray diffraction laboratory. At present, these methods of poor (1 part in 10^2) or moderate (up to 1 part in 10^4) accuracy are suitable only for preliminary measurements.

Less popular and more specific divergent-beam methods (third group) give satisfactory accuracy (1 part in 10^4 or 1 part in 10^5), comparable with that obtained by counter-diffractometer methods, by means of very simple equipment.

In spite of the common use of counter diffractometers, and of the increasing use of imaging plates (and synchrotron radiation), traditional photographic methods of the second and the third groups are still popular and new designs are reported.

5.3.2.2. *The Laue method*

As based on polychromatic radiation, the Laue method is, in principle, useless for accurate lattice-parameter determination. It is true that, from a single Laue diffraction pattern (in transmission), one can determine precisely the axial ratios and interaxial angles (a method based on the gnomonic projection is described by Amorós, Buerger & Amorós, 1975), but the unit cell determined will differ from the true cell by a simple scale factor.

The problem of absolute scaling of the cell is important nowadays, when synchrotron-radiation Laue diffraction patterns are currently being used for collecting X-ray data (from single-crystal systems including proteins, for example). As shown by Cruickshank, Carr & Harding (1992), it is possible to estimate the scale factor using the minimum wavelength present in the incident X-ray beam. A method proposed by the authors (Carr, Cruickshank & Harding, 1992) allows one to determine the unit cell and orientation of an unknown crystal (in a general orientation) from a single Laue pattern. The accuracy of the absolute lattice-parameter determination depends on the accuracy with which the minimum wavelength is known for the experiment and is, at present, about 5% in favourable cases (while the error in axial ratio determination after refinement is typically 0.25%). To increase the accuracy, the authors propose either to record the Laue patterns with an attenuator in the incident beam that has a suitable absorption edge ($\lambda_{\min}$ can become a sharp and accurately known limit) or to locate the bromine-absorption edge, if the X-ray detector contains bromine, as in photographic films and image plates.

5.3.2.3. *Moving-crystal methods*

Moving-crystal methods of lattice-parameter determination apply basic photographic techniques, such as:

(1) the rotating- or oscillating-crystal method;

(2) the Weissenberg method;

(3) the technique of de Jong–Bouman; or

(4) the Buerger precession method.

In the first of these methods, the film remains stationary, while in the others it is moved during the exposure. The principles and detailed descriptions of these techniques have been presented elsewhere (Buerger, 1942; Henry, Lipson & Wooster, 1960; Evans & Lonsdale, 1959; Stout & Jensen, 1968, Chapter 5; Sections 2.2.3, 2.2.4, and 2.2.5 of this volume) and only their use in lattice-parameter measurements will be considered here.

5.3.2.3.1. *Rotating-crystal method*

The rotating-crystal method – the simplest of the moving-crystal methods – determines the identity period I along the axis of rotation (or oscillation), $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, from the formula

$$I(uvw) = n\lambda / \sin \nu, \qquad (5.3.2.1)$$

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* With some exceptions; for example, multiple-diffraction methods introduced by Renninger (1937) are placed after the Bond (1960) method.

in which n is the number of the layer line and ν is the angle between the directions of the primary and diffracted beams.

The angle ν is determined from the measurement of the distance l_n between two lines corresponding to the same layer number n from the equation

$$\tan \nu = l_n / R, \qquad (5.3.2.2)$$

where R is the camera radius.

All the lattice parameters may be determined from separate photographs made for rotations of the crystal along different rotation axes, *i.e.* the system axis, plane and spatial diagonals (Evans & Lonsdale, 1959), without indexing the photographs. In practice, however, this method is rarely used alone and is most often applied together with other photographic methods (for example, the Weissenberg method), but it is a useful preliminary stage for other methods. In particular, the length of a unit-cell vector may be directly determined if the rotation axis coincides with this vector.

Advantages of this method are:

(*a*) simple equipment (only rotation of the crystal is required, since the film is stationary);

(*b*) immediate determination of direct-cell parameters (photographs obtained with other cameras afford information about reciprocal-lattice parameters only);

(*c*) indexing of the photographs is unnecessary.

Drawbacks of the method are:

(*a*) poor precision and accuracy of the measurement ($|\delta d|/d \approx 10^{-2}$);

(*b*) small amount of information from a single photograph (one parameter only);

(*c*) necessity of taking several photographs in the case of a lower-symmetry system if this method is the only one used.

5.3.2.3.2. *Moving-film methods*

A two-dimensional picture of a reciprocal cell from one photograph can be obtained by the methods in which rotation of the crystal is accompanied by movement of the film, as in the Weissenberg, the de Jong–Bouman, and the Buerger precession techniques. These methods give greater precision ($|\delta d|/d \approx 10^{-4}$) than the previous one (§5.3.2.3.1).

The advantages of the Weissenberg method in relation to the other two are:

(*a*) a simpler camera;

(*b*) a larger range of reciprocal-lattice points recorded on one photograph (larger range of θ angles, up to 90° for the zero layer).

On the other hand, the disadvantage, in contrast to the de Jong–Bouman and the Buerger precession methods, is that it gives deformed pictures of the reciprocal lattice. This is not a fundamental problem, especially now that computer programs that calculate lattice parameters and draw the lattice are available (Luger, 1980). In lattice-parameter measurements, both the zero-layer Weissenberg photographs and the higher-layer ones are used. The latter can be made both by the normal-beam method and by the preferable equi-inclination method. Photographs in the de Jong–Bouman and precession methods give undeformed pictures of the reciprocal lattice, but afford less information about it than do Weissenberg photographs.

5.3.2.3.3. *Combined methods*

The most effective photographic method of lattice-parameter measurement is a combination of two techniques (Buerger, 1942; Luger, 1980), which makes it possible to obtain a *three-dimensional picture* of the reciprocal lattice; for example: the rotation method with the Weissenberg (lower accuracy); or the precession (or the Weissenberg) method with the de Jong–Bouman (higher accuracy).

A suitable combination of the two methods will determine all the lattice parameters, even for monoclinic and triclinic systems, *from one crystal mounting*. This problem has been discussed and resolved by Buerger (1942, pp. 388–390), Hulme (1966), and Hebert (1978). Wölfel (1971) has constructed a special instrument for this task, being a combination of a de Jong–Bouman and a precession camera.

5.3.2.3.4. *Accurate and precise lattice-parameter determinations*

To measure with a precision and an accuracy better than is possible in routine photographic methods, additional work has to be performed. The first methods allowing precise measurement of lattice parameters were photographic powder methods (Parrish & Wilson, 1959). Special single-crystal methods with photographic recording to realize this task (earlier papers are reviewed by Woolfson, 1970, Chap. 9) combine elements of basic single-crystal methods (presented in §§5.3.2.3.1 and 5.3.2.3.2) with ideas more often met in powder methods (asymmetric film mounting). A similar treatment of some systematic errors (extrapolation) is met in both powder and single-crystal methods.

(i) The relative accuracy $\Delta I/I$ of the identity period I in the rotating-crystal method, estimated by differentiation of formula (5.3.2.1), is given by

$$\Delta I/I = -\cot \nu \Delta \nu. \qquad (5.3.2.3)$$

This formula shows that the highest accuracy is obtained for ν tending to 90°. Since reflections with large values of ν are difficult to record in commonly used cameras, a special camera may be used for this task, in which a flat film is placed perpendicular to the rotation axis, or a different one, whose axis coincides with the primary beam (Umansky, 1960). The accuracy achieved with these improvements is still no better than 5 parts in 10^3.

(ii) The asymmetric film mounting proposed by Straumanis & Ieviņš (1940) in the case of powder cameras can also be used in a simple oscillating camera (Farquhar & Lipson, 1946). In particular, this idea can be realized in a precision Debye–Scherrer camera adapted to single-crystal measurements by mounting in it a goniometer head (Popović, 1974). The Straumanis mounting allows the recording of the high-angle reflections close together on the film, thus reducing the effect of film shrinkage and making it possible to measure the effective camera radius.

(iii) Sometimes, to eliminate systematic errors (uncertainty of the camera radius), the separations resulting from the wavelength differences of the $K\alpha_1$ and $K\alpha_2$ doublet are measured rather than the absolute distances on the film (Main & Woolfson, 1963; Alcock & Sheldrick, 1967). The first reference related to the zero-layer normal-beam photograph, the second to higher layer lines (in the equi-inclination method also) and oscillation photographs.

(iv) Systematic errors connected with film shrinkage can also be eliminated by means of the *ratio method*, introduced by Černohorský (1960) for powder samples and adapted by Polcarová & Zůra (1977) for single crystals. In this method, pairs of reflections that differ from one another in wavelength and/or in *hkl* indices are used and the ratio of the two diameters of the diffraction rings corresponding to these reflections is taken into account. The accuracy of the method is about 1 part in 10^4

if systematic errors due to absorption, refraction, Lp factor, temperature, changes of the camera radius, and misalignment of the sample and the goniometer are corrected. The ratio method was generalized by Horváth (1983) to the monoclinic crystal system.

(v) Graphical extrapolation, similar to that used in powder methods (Parrish & Wilson, 1959), can also be used for single crystals (Farquhar & Lipson, 1946; Weisz, Cochran & Cole, 1948), to reduce systematic errors proportional to $\sin\theta$. Least-squares refinement, on the other hand, permits a reduction of the standard deviations of the results (Main & Woolfson, 1963; Clegg, 1981). Mathematical methods of processing the data obtained from oscillation photographs, including 'eigenvalue filtering' and profile fitting (Rossmann, 1979; Reeke, 1984) have been applied to the refinement of unit-cell parameters, crystal orientation, and reflecting-range parameters needed to process oscillation photographs.

(vi) By measuring the *angle between two reflecting crystal positions*, symmetrical in relation to the primary beam [the idea used in the original Bragg spectrometer (Bragg & Bragg, 1915)], one can eliminate some sources of systematic errors. Such a spectrometer with photographic recording was used by Weisz, Cochran & Cole (1948). In spite of the great simplicity of the arrangement, the accuracy obtained was about 1 part in 10^4. The authors indicated the need for introducing counter recording to the method. 12 years later, their idea was realized by Bond (1960) (*cf.* Subsection 5.3.3.4, in particular §5.3.3.4.3).

(vii) The other way of reducing some systematic errors is to introduce a *reference crystal*. Singh & Trigunayat (1988) adapted the idea to the oscillation method. By mounting the specimen crystal and the reference crystal, properly centred and set, on two identical goniometer heads with a screw-type base, they recorded layer lines of the two crystals simultaneously. The identity period I of the crystal was then determined from the formula that results from a combination of (5.3.2.1) and (5.3.2.2) for layer lines of the two crystals (notation of the present Section):

$$I = n\lambda \left[\frac{l_n^2 (I_r^2 - m^2\lambda^2)}{l_{m,r}^2 m^2 \lambda^2} + 1 \right]^{1/2}, \qquad (5.3.2.4)$$

in which l_n and $l_{m,r}$ are the measured distances between nth layer lines of the crystal and between mth layer lines of the specimen, respectively, and I_r is the identity period of the reference crystal. The result is thus independent of the camera radius. When the differences between l_n and $l_{m,r}$ are no greater than a few mm, the error due to film shrinkage is automatically taken care of, and the error due to a parallel shift of the axis of the cylindrical cassette in relation to the axis of rotation is negligible in practice. The other possible misalignments related to the cassette and the collimator can be readily detected beforehand by taking a complete rotation photograph.

Reference crystals are commonly used in multiple-crystal methods reviewed in Subsection 5.3.3.7.

5.3.2.3.5. *Photographic cameras for investigation of small lattice-parameter changes*

Small changes of lattice parameters caused by thermal expansion or other factors can be investigated in *multiple-exposure cameras*.

Bearden & Henins (1965) used the double-crystal spectrometer with photographic detection to examine *imperfections* and *stresses* of large crystals. The technique allowed the detection of angle deviations as small as 0.5″. A nearly perfect calcite crystal was used as the first crystal (monochromator), the sample was the second. The device distinguished itself with very good sensitivity. The use of the long distance (200 cm) between the focus and the second crystal made possible resolution of the doublet $K\alpha_{1,2}$, and elimination of the $K\alpha_2$ radiation. An additional advantage was that the arrangement was less time-consuming, so that it was suitable for controlling the perfection of growing crystals and useful for choosing adequate samples for the wavelength measurements.

Kobayashi, Yamada & Azumi (1968) have described a special 'strainmeter' for measuring small strains of the lattice. The strain x_i along an axis normal to the i plane results in a change δd_i of the interplanar distance d_i:

$$x_i = \delta d_i / d_i = -\cot\theta_i \delta_i. \qquad (5.3.2.5)$$

The use of a large camera radius $R = 2639$ mm makes it possible to obtain both high sensitivity and high precision (2 parts in 10^6) even in the range of lower Bragg angles ($\theta \simeq 55^\circ$). The device is suitable for the investigation of defects resulting from small strains and may be used in measurements of thermal expansion.

Glazer (1972) described an automatic arrangement, based on the Weissenberg goniometer, for the photographic recording of high-angle Bragg reflections as a function of temperature, pressure, time, *etc*. A careful choice of the oscillation axis and oscillation range makes it possible to obtain a distorted but recognizable phase diagram (Fig. 5.3.2.1) within several hours. The method had been applied by Glazer & Megaw (1973) in studies of the phase transitions of $NaNbO_3$.

Popović, Šljukić & Hanic (1974) used a Weissenberg camera equipped with a thermocouple mounted on the goniometer head for precise measurement of lattice parameters and thermal expansion in the high-temperature range.

5.3.2.4. *The Kossel method and divergent-beam techniques*

5.3.2.4.1. *The principle*

Another group of methods with photographic recording has been developed in parallel with those discussed in Subsection 5.3.2.3. These are the methods in which the crystal remains stationary and the diffraction conditions are fulfilled, simultaneously for more than one set of crystallographic planes, by the use of a highly divergent beam, dispersed from a point source (Fig. 5.3.2.2). The Kossel method (Kossel, 1936, and references therein), the divergent-beam techniques initiated by Lonsdale (1947), and their numerous modifications belong to this group.

The excitation of the characteristic X-rays used in these methods can be performed by X-radiation (Lonsdale, 1947), by electron bombardment (Kossel, 1936; Gielen *et al.*, 1965; Ullrich & Schulze, 1972) or by proton irradiation (Geist & Ascheron, 1984) of a single crystal. The source of emitted X-rays may be located either *in* the sample itself (the Kossel method), *on* the surface of the sample in a layer of target material (the pseudo-Kossel method), or *outside* the sample (the divergent-beam techniques). The divergent X-ray beam diffracts from sets of crystallographic planes. The diffracted rays for each Bragg reflection form a conical surface whose semivertical angle is equal to $90^\circ - \theta$ and whose axis is normal to the Bragg plane (*i.e.* coincides with the reciprocal-lattice vector).

The conical surface of an *hkl* reflection can be described in the form (Morris, 1968; Chang, 1984):

$$x'^2 + y'^2 = z'^2 \tan^2\alpha, \qquad (5.3.2.6)$$

where (x', y', z') is an orthogonal coordinate system with its origin at the vertex of the cone and with z' along the axis of the cone and normal to the plane of interest, and α is the semivertical angle. Since α depends on the Bragg angle, it is possible to combine (5.3.2.6) with the Bragg law [equations (5.3.1.1) or (5.3.1.2)], and so with the lattice parameters. In particular, the dependence can be presented as:

$$\frac{r}{z'} = \frac{1}{\sin\theta} = \frac{2d}{n\lambda}, \qquad (5.3.2.6a)$$

where $r = (x'^2 + y'^2 + z'^2)^{1/2}$.

In another convenient coordinate system (x, y, z) common for all the cones, say with z along the direction of the incident beam, (5.3.2.6a) will take the form:

$$\frac{r}{c_x x + c_y y + c_z z} = \frac{2d}{n\lambda}, \qquad (5.3.2.6b)$$

where c_x, c_y, c_z are direction cosines of the angles between the z' axis and the axes x, y and z, respectively. Since the origin of the coordinate system has not been changed,

$$r = (x^2 + y^2 + z^2)^{1/2}. \qquad (5.3.2.6c)$$

The Kossel lines (Fig. 5.3.2.3) are formed at the intersections of the cones with a flat film placed parallel to the specimen surface (Fig. 5.3.2.2). When the film plane is normal to the z axis, and the focus-to-film distance is equal to Z, putting $z = Z$ in

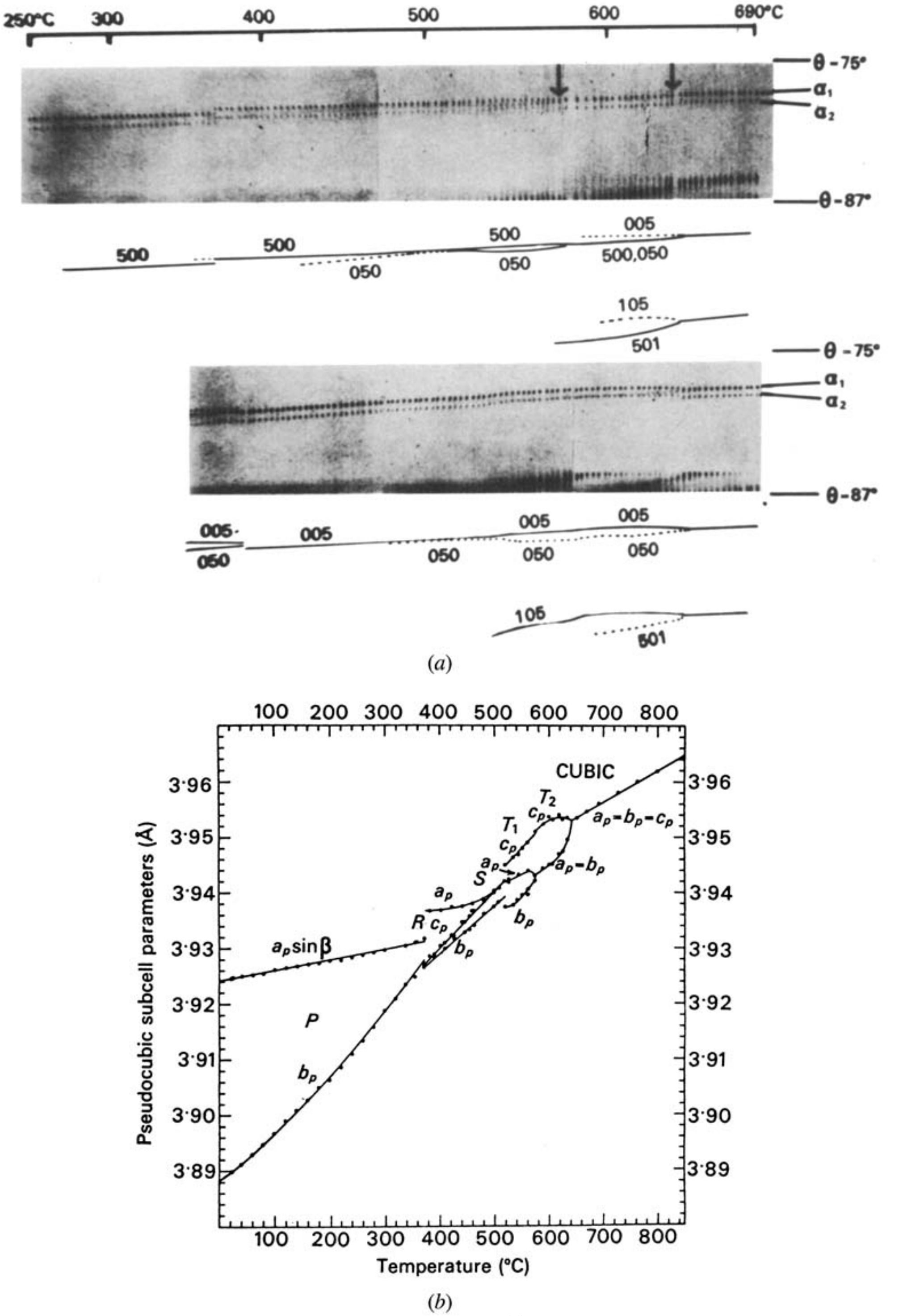


Fig. 5.3.2.1. (a) Photographic recording of lattice-parameter changes. (b) Corresponding diagram of the variation of lattice parameters in pseudocubic $NaNbO_3$ (Glazer & Megaw, 1973).

(5.3.2.6*b*,*c*) gives the formulae describing the conic section on the film.

A high-precision Kossel camera is described by Reichard (1969) and the generation of pseudo-Kossel patterns by the divergent-beam method has been described by Imura, Weissmann & Slade (1962), Ellis, Nanni, Shrier, Weissmann, Padawer & Hosokawa (1964), and Berg & Hall (1975).

The photographs may be in either the transmission or the back-reflection region (Fig. 5.3.2.2). The second arrangement seems to be (Lutts, 1968) more suitable for lattice-parameter determination, since the background is less intensive and the lines on the photographs have greater contrast. Both possibilities are used in practice. Photographs in the back-reflection region have been reported by Imura, Weissmann & Slade (1962), Ullrich (1967), Newman & Weissmann (1968), Newman & Shrier (1970), and Berg & Hall (1975). Examples of the use of the transmission region are given by Yakowitz (1966*a*), Reichard (1969), and Glass & Weissmann (1969).

The recommended *crystal thickness t* for work in the transmission region, according to Hanneman, Ogilvie & Modrzejewski (1962), is given by:

$$t = 1/0.2\mu_L, \qquad (5.3.2.7)$$

where μ_L is the linear absorption coefficient for $K\alpha$ radiation generated in the crystal. A more detailed study of the effect of sample thickness, as well as operating voltage, on the contrast of Kossel transmission photographs is given by Yakowitz (1966*a*).

The picture geometry does not depend, in principle, on whether the Kossel, pseudo-Kossel, or divergent-beam technique is applied. Imura (1954) has studied in detail the form of the curves of the light or deficiency type, and recorded both in the transmission and in the back-reflection region. The curves on transmission patterns can be considered to be conics; those recorded in the back-reflection region are related to ellipses, but of higher order. In general, the photograph has to be indexed before performing measurement on the film. For this purpose, the pattern may be compared with a calculated pattern (gnomonic, orthogonal, cylindrical, or stereographic projection). For lattice-parameter determination, various features of the photographs may be used, *i.e.* intersections or near-intersections of Kossel lines, their near-tangency, lens-shaped figures, and the whole lines approximated with a function.

5.3.2.4.2. *Review of methods of accurate lattice-parameter determination*

The basis of lattice-parameter determination involves measurements performed on the film. There are various methods covering most of the different geometrical features of the cones and recorded pictures. These were reviewed by Lutts (1968), Yakowitz (1966*b*, 1969) and Tixier & Waché (1970). In each case, the wavelength of the excited radiation has to be known. Often, the resolved $K\alpha_{1,2}$ doublet and/or $K\beta$ radiation is applied rather than a single (but most pronounced) $K\alpha_1$ line. The other data needed (a sufficient number of equations, the solution of which leads to lattice-parameter determination; camera geometry; crystal system; and indices) depend on the method.

Biggin & Dingley (1977) propose a classification of all the methods using a divergent beam based on the information required.

(i) All the kinds of information mentioned above are needed in the earliest method (Kossel, 1936), in which near-tangency of Kossel lines is taken into account.

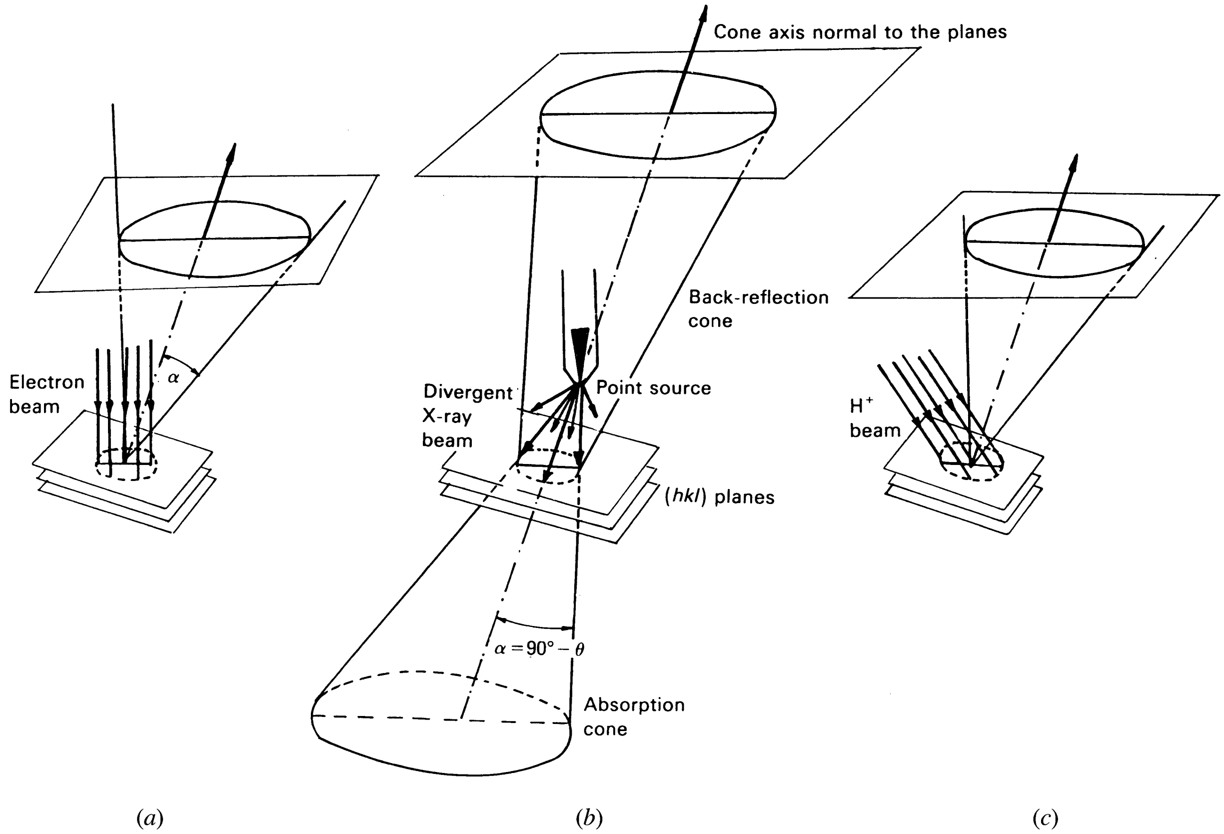
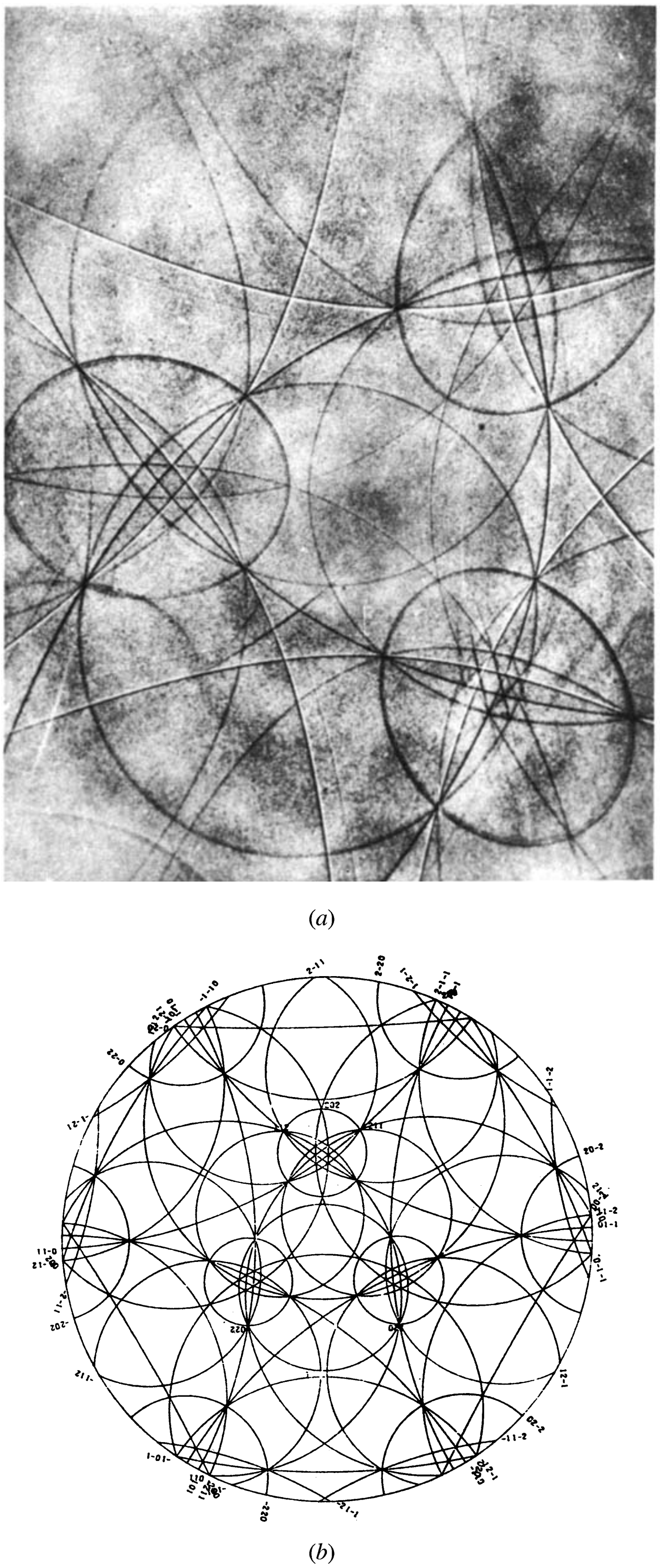


Fig. 5.3.2.2. Schematic representation of the origin of the Kossel lines. (*a*) The Kossel (1936) method. (*b*) The divergent-beam method developed by Lonsdale (1947). (*c*) The proton-induced Kossel effect (Geist & Ascheron, 1984). In (*b*), the divergent X-ray beam is directed onto the sample from a point source while in the remaining cases it is generated within a crystal by (*a*) electrons or (*c*) protons.

(ii) As has been shown in successive papers that appeared from 1947 to the early 1970's, information on camera dimensions can be eliminated if the crystallographic system is known and the photograph is indexed. Some dependence between crystal planes and, as a consequence, between lines on the photograph, is then taken into consideration. This is of great importance, since camera dimensions, in particular the distance from the focus to the centre of the photograph, are difficult to measure accurately and negatively influence the precision and accuracy of the determined lattice parameters.


(*a*)

(*b*)

Fig. 5.3.2.3. (*a*) The Kossel pattern from iron and (*b*) the corresponding stereographic projection (Tixier & Waché, 1970).

The Lonsdale (1947) method is based on triple *intersections* of the Kossel lines resulting from **multiple-diffraction** effects (*cf.* Subsection 5.3.3.6), which are *dependent on the wavelength*, so first the particular wavelength has to be determined by an extrapolation. Two or three lines with known indices produced by different wavelengths ($K\alpha_1$, $K\alpha_2$, and/or $K\beta$) are used for this task (Schwartzenberger, 1959; Mackay, 1966; Isherwood & Wallace, 1971; Spooner & Wilson, 1973). Similar problems arise when near-tangency of two lines is taken into consideration (Kossel, 1936; Mackay, 1966).

With the use of reciprocal-lattice geometry, the equation of the so-called Kossel plane (Isherwood & Wallace, 1971) for a diffracting plane (*hkl*) is given by (Spooner & Wilson, 1973; Chang, 1984):

$$L_1x^* + L_2y^* + L_3z^* = \frac{1}{d}, \qquad (5.3.2.8)$$

where L_1, L_2, and L_3 are direction cosines between the reciprocal vector $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ and the unit-cell vectors $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$, *i.e.*

$$L_1 = \frac{ha^*}{H}, \quad L_2 = \frac{kb^*}{H}, \quad L_3 = \frac{lc^{*\prime}}{H}, \qquad (5.3.2.8a)$$

where $H = |\mathbf{H}| = 1/d, a^* = |\mathbf{a}^*|, b^* = |\mathbf{b}^*|, c^* = |\mathbf{c}^*|$.

In the case of the triple intersection, (5.3.2.8) is satisfied simultaneously by three sets of diffracting planes, the Miller indices of those being $(h_ik_il_i)$, $i = 1, 2, 3$. From the Ewald construction, it follows that the triple point (x_0^*, y_0^*, z_0^*) must lie on the sphere of reflection:

$$x^{*2} + y^{*2} + z^{*2} = \frac{4}{\lambda_0^2}. \qquad (5.3.2.8b)$$

The radius of the sphere, $2/\lambda_0$, is the modulus of the double wavevector defined by Isherwood & Wallace (1971).

For cubic crystals, where $H = (h^2 + k^2 + l^2)^{1/2}/a$, the set of equations to be solved, resulting from (5.3.2.8) and (5.3.2.8*a*), which relates to the triple point, takes the form

$$h_ix_0^* + k_iy_0^* + l_iz_0^* = (h_i^2 + k_i^2 + l_i^2)/a, \qquad (5.3.2.9)$$

where $i = 1, 2, 3$.

First, coordinates x_0^*, y_0^*, z_0^* dependent on a are determined from (5.3.2.9), and next a is calculated from (5.3.2.8*b*). It should be noted that the measurements performed on the film are used here for determination of the wavelength only. As shown (theoretically and experimentally) by Brühl & Rhan (1985) for cubic lattices, positions of the lines on the film that result from the multiple-diffraction phenomenon are insensitive to lattice-parameter changes (caused by thermal expansion, for example), while positions of the primary reflections depend on actual lattice-parameter values. Practical examples of photographic multiple-diffraction methods are given by Lonsdale (1947) (see also Tixier & Waché, 1970; Chang, 1984), Isherwood & Wallace (1966), Isherwood (1968), Isherwood & Wallace (1970), Spooner & Wilson (1973), Brown, Halliwell & Isherwood (1980), and Isherwood, Brown & Halliwell (1981, 1982).

The technique, in which triple intersections of Kossel lines are analysed, can be used both for back-reflection and for transmission. In the second case, the thickness t of the crystal should be such that $\mu_L t \simeq 1$ [*cf.* equation (5.3.2.7)]. However, thicker crystals, for which $\mu_L t \gtrsim 10$, can be examined by anomalous transmission, if the degree of crystal perfection is high (Glass & Moudy, 1974). A correction for displacement of the conics due to wafer thickness t is necessary in the case when the intersection lies along the normal to the specimen surface. One triple intersection allows the determination of the lattice parameter of a cubic crystal, but for a structure in the orthorhombic system three such intersections would be required.

Two intersecting Kossel lines sometimes form a *lens configuration* (Fig. 5.3.2.4*a*). The use of such a figure, consisting of two lenses (Fig. 5.3.2.4*b*) owing to the resolved doublet of $K\alpha_1$ and $K\alpha_2$ (or $K\beta$) radiation, makes it possible to determine lattice parameters without a knowledge of the distance between the source and the film. Lattice parameters are then calculated from the ratio L_1/L_2 of the distances L_1 and L_2 between pairs of the sections. Heise (1962) used this method for cubic crystals in the simplest case, in which the cone axes are perpendicular to the film (symmetrical method). His idea had been generalized by Gielen *et al.* (1965), who formed a theory of the lens in the case of arbitrarily situated diffracting planes and arbitrary wavelengths, but for cubic crystals only. Lutts (1968) derived suitable formulae for cubic, tetragonal, and hexagonal systems by combining the ratio L_1/L_2 with interplanar spacings and lattice parameters.

Several features of the Kossel pattern may be jointly taken into account for its interpretation and lattice-parameter determination. Hanneman, Ogilvie & Modrzejewski (1962) used the conic sections formed by $K\alpha_1$ and $K\beta$ radiation and the lens figures.

Lang & Pang (1995) observed and analysed fine streaks in the transmitted pseudo-Kossel patterns caused by both the coherent multiple diffraction and the enhanced Borrmann (anomalous) transmission. As they have found, these fine-scale features of a few arcseconds in angular width, which add markers to the broad-line Kossel patterns, may be taken into account in accurate lattice-parameter measurements.

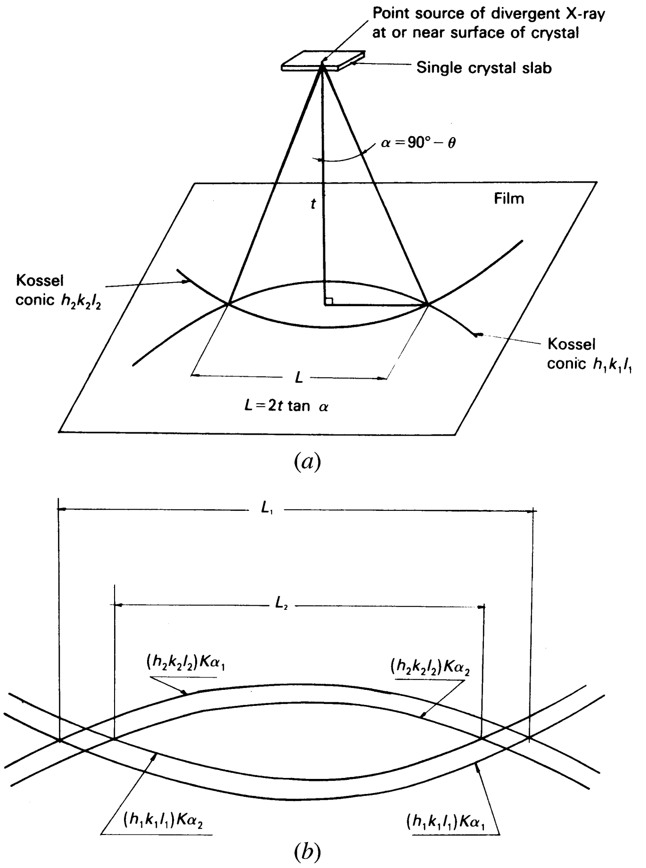


Fig. 5.3.2.4. Lens-shaped figures formed by pairs of intersecting conics. (*a*) Schematic representation of the method of Heise (1962). (*b*) The use of the $K\alpha_{1,2}$ doublet for precise and accurate lattice-parameter determination.

(iii) Determination of lattice parameters by means of techniques utilizing a highly divergent beam becomes much more complicated if there is no information about indices and the *crystal system.* Such a problem arises in the case when the crystal system of the specimen is *unknown* or when the lattice is deformed. Then, a three-dimensional array of intersecting cones with a common vertex should be taken into consideration.

It is difficult to dispense with the data concerning the camera geometry. However, the distance of X-ray source from the film center may be eliminated in calculations when the *multiple-exposure technique* is used. This technique, introduced by Ellis *et al.* (1964) for back-reflection patterns, depends on recording the Kossel lines at variable but controlled distances from the focus to the film (Fig. 5.3.2.5), so that three or more positions of a cone generator can be established and, as a consequence, the cone axis and the semivertical angle are determined. The interpretation of the multiple-exposure pictures is based, in principle, on the coordinates of general points of lines rather than on their special properties.

The basic formula valid for all the methods applying the Kossel idea,

$$\mathbf{P} \cdot \mathbf{N} = \cos\alpha, \qquad (5.3.2.10)$$

where $\mathbf{P}$ is the unit vector defining the cone generator and $\mathbf{N}$ is the axial direction of a cone, can now be fully utilized, since multiple-exposure techniques make possible accurate calculations of direction cosines. Lengthy and complicated calculations resulting from measurements performed on the film may be realized by means of a computer. A suitable program is given by Fischer & Harris (1970). This technique has also been applied and developed by Slade, Weissmann, Nakajima & Hirabayashi (1964), Shrier, Kalman & Weissmann (1966), Newman & Weissmann (1968), Schneider & Weik (1968), Fischer & Harris (1970), Newman & Shrier (1970), Aristov, Shekhtman & Shmytko (1973), and Soares & Pimentel (1983) for both the back-reflection and the transmission region.

As mentioned above, the Kossel lines occurring in the back-reflection region are similar to ellipses; they can be described using an equation of the fourth degree (Newman, 1970). In general, the major axes of such ellipse-shaped figures have been

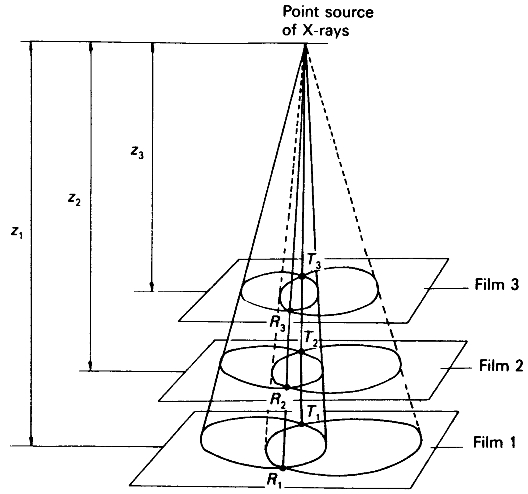


Fig. 5.3.2.5. Schematic representation of the multiple-exposure technique (after Fischer & Harris, 1970).

taken into account in lattice-parameter determination. A novelty introduced by Lider & Rozhansky (1967) was to also use the minor axes in the calculations. The essential feature of their method is the location of the X-ray source in the plane of a flat film.

(iv) The other possibility for gathering the necessary information for the recorded picture is a more detailed study of the form of the Kossel lines. Morris (1968) proposed a method based on the mathematical analysis of a cone, which makes possible the determination of lattice parameters in any crystal system, with a relative accuracy as high as 10 parts in 10^6. The necessary calculations can be made by a computer program. A conic section can usually be expressed by a general equation of the second degree (Bevis, Fearon & Rowlands, 1970; Harris & Kirkham, 1971; Morris, 1968):

$$x^2 + Ay^2 + Bxy + Cx + Dy + E = 0, \qquad (5.3.2.11)$$

which results from a combination and a transformation of (5.3.2.6*b*) and (5.3.2.6*c*). The coefficients A, B, C, D, and E, being functions of the direction cosines and of the ratio $2d/n\lambda$, can be found by the method of least squares. Methods based on *Kossel-line fitting* can be realized both in the single-exposure (Harris & Kirkham, 1971) and in the multiple-exposure technique (Aristov, Shekhtman & Shmytko, 1973; Aristov & Shmytko, 1978).

(v) From theoretical considerations based on the shape of pseudo-Kossel lines (Harris & Kirkham, 1971), it is possible to eliminate the need for information concerning camera geometry if the source and the pattern centre are accurately located. Lattice parameters of an unknown or deformed crystal can thus be determined with no information other than measurements on the film and a knowledge of the *wavelength*.

A general method for locating the X-ray source and the centre of the pattern – which permits the realization of the above idea – has been developed by Biggin & Dingley (1977). Its characteristic feature is the introduction of steel balls between the specimen and the film; these cast sharp shadows on the film by blocking the diffuse radiation. Coordinates of points along the Kossel lines as well as the shadow ellipses recorded on the film are taken into account in calculations.

5.3.2.4.3. *Accuracy and precision*

Although the precision theoretically obtainable by means of the Lonsdale (1947) method is of the order of 1 part in 10^6, this limit is unattainable in practice. The reported values are in the range of about 10^{-4}–10^{-5} Å, depending not only on the method but also on the crystal – its symmetry and perfection. The highest accuracy known by the author was achieved by Lonsdale [(1947), $\pm 5 \times 10^{-5}$ Å, for diamond], Morris [(1968), 2 parts in 10^5] and Aristov & Shmytko [(1978), $|\delta d|/d \sim 3 \times 10^{-5}$, 1–$5 \times 10^{-5}$ rad for angles between crystallographic directions].

Systematic errors due to the methods in which a divergent beam is applied have been discussed by Hanneman, Ogilvie & Modrzejewski (1962), Gielen, Yakowitz, Ganow & Ogilvie (1965), Beu (1967), Lutts (1968), and Aristov & Shmytko (1978). The main sources of systematic error are:

(i) those common to all X-ray methods, resulting from a finite depth of X-ray penetration, wavelength dispersion, refraction (Isherwood & Wallace, 1966; Isherwood, 1968), and from the real structure (substructures and mosaic blocks; and

(ii) those common to methods with photographic recording, resulting from film shrinkage and inaccurate determination of camera dimensions and distances on the film.

The errors of the second group may be to some extent removed if small differences of the length resulting from the resolved $K\alpha_{1,2}$ doublet are measured on the film rather than distances due to only one wavelength, and/or if the camera dimensions can be eliminated from the equations used in the calculations of lattice parameters (see §5.3.2.4.2). A relative misorientation between the specimen and the flat film has been analysed by Lutts (1973).

An error typical for methods realized by means of an electron microscope or an electron-beam probe may result from the thermal effects of the electron beam generating a divergent X-ray beam at the crystal surface. Uncontrolled thermal effects may also occur in the case of the Kossel method, since the sample is situated inside the X-ray tube. In the latter method, the wavelength of the radiation emitted depends on the chemical composition of the sample, since the sample plays the role of the anode of the X-ray tube.

The reported precision of the methods, limited by the finite width of the lines on the photograph, and depending also on the geometrical features taken into account, is 1 part in 10^3 to 1 part in 10^5. The highest $[\sigma(d)/d = 10^{-5}]$ is reported by Hanneman, Ogilvie & Modrzejewski (1962), Gielen, Yakowitz, Ganow & Ogilvie (1965), and Lider & Rozhansky (1967). On the other hand, the lowest (1 part in 10^3), obtained by Harris & Kirkham (1971), is attributed to the method in which neither the indexing of the lines nor a knowledge of the crystallographic system or camera geometry is required.

For precision determination of lattice-parameter differences, a 'point' source (*i.e.* as small as possible) is required and the high-order Kossel lines should be used to obtain both well resolved $K\alpha_{1,2}$ doublets and 'thin' figures. The near-intersections of conic sections, applied in Lonsdale's (1947) method, the major axes of lens-shaped figures, used in Heise's (1962) method, and the small spherical polygons formed by several Kossel cones are very sensitive to lattice-parameter changes, so that these figures can be taken into account in the precise measurements reported in §5.3.2.4.4.

5.3.2.4.4. *Applications*

As was mentioned in §5.3.2.4.3, the methods in which a highly divergent beam is used are applied both to the accurate determination of the unit cell and to the precision detection of lattice-parameter changes or differences. It should be added that the Kossel method is especially suitable for small single crystals or fine-grained polycrystals, whereas the other divergent-beam techniques need larger specimens (Lutts, 1968).

Since all the methods are relatively simple (stationary specimen, stationary film, simple construction of the camera) and, on the other hand, are applicable mainly for highly symmetric systems, they proved to be particularly useful in studies of metals and semiconductors. Various applications of the Kossel method and other divergent-beam techniques for this task have been discussed by Ullrich (1967), Ullrich & Schulze (1972), and Geist & Ascheron (1984). The latter paper relates especially to semiconductors.

A task that arises both in metallurgy and in the semiconductor industry is the examination of the real structure – in particular, measurements of strains introduced by variation in temperature, pressure, mechanical stress (elastic strains) or by point defects, deviation from exact stoichiometry, irradiation damage, and phase changes (permanent strains).

Measurements of small changes in interplanar spacings of independent sets of crystal planes enable a stress–strain analysis to be made (Imura, Weissmann & Slade, 1962; Elllis *et al.*, 1964; Slade *et al.*, 1964; Newman & Weissmann, 1968; Berg & Hall, 1975). A special case of strains is an extensional deformation of the lattice in the direction of crystal growth (Isherwood, 1968).

A typical metallurgical problem is the effect of heat treatment on the microstructure of alloys. An example of the application of the Kossel method to the task is given by Shinoda, Isokawa & Umeno (1969), who reported a study of precipitation of α from β in copper–zinc alloys. The lattice parameters and thermal expansion of α-iron and its alloys were examined by Lutts & Gielen (1971). Structure defects resulting from over-pressure experiments and annealing were investigated by Potts & Pearson (1966). Irradiation effects caused by neutrons were the subject of papers of Hanneman, Ogilvie & Modrzejewski (1962), Yakowitz (1972), and Spooner & Wilson (1973); those caused by electron bombardment were reported by Ullrich (1967).

Divergent-beam techniques are considered to be a suitable tool for studying strains in epitaxic layers (Hart, 1981), since corresponding lines of the layer and substrate, observed on one photograph, can be readily identified. Relevant examples are given by Brühl (1978), Chang, Patel, Nannichi & de Prince (1979), and Chang (1979), who examined lattice mismatch in LPE heterojunction systems, and by Brown, Halliwell & Isherwood (1980), and Isherwood, Brown & Halliwell (1981, 1982), who reported characterization of distortions in heteroepitaxic structures together with a theoretical basis (multiple diffraction) for the method.

Another task of real-structure examination is the determination of angles between crystal blocks. A method has been worked out by Aristov, Shmytko & Shulakov (1974*a*,*b*).

Divergent-beam techniques can also be used in X-ray topographic studies, realized either by means of Kossel-line scanning (Rozhansky, Lider & Lyutzau, 1966) or by line-profile analysis (Glass & Weissmann, 1969).

Schetelich & Geist (1993) used the Kossel method for lattice-parameter determination and a qualitative estimation of the crystal perfection of *quasicrystals* and showed that the fine structure of Kossel lines of quasicrystals is the same as observed for conventional crystals.

Mendelssohn & Milledge (1999) used a Dingley–Kossel camera for quick and simple computer-aided measurements of cell parameters of isotopically distinct samples of LiF over a wide temperature range of 15–375 K.

5.3.3. Methods with counter recording

5.3.3.1. *Introduction*

Although, theoretically, the limit of accuracy in all methods based on the Bragg law [equation (5.3.1.1)] is given by the accuracy of the wavelength measurement ($\delta\lambda/\lambda \sim 10^{-6}$), with photographic recording this limit is not attained. Surprisingly high accuracy may be offered by accurately applied Kossel or divergent-beam techniques. In practice, however, even in this case the accuracy achieved is poorer by an order of magnitude.

The use of Geiger–Müller, proportional, or scintillation counters together with a step-scanning motor makes it possible to record the diffraction profile in a quantitative numerical form convenient for data processing, to locate it with better accuracy and precision and, as a consequence, to obtain better accuracy and precision for the Bragg angle and thus for the lattice parameter. To make the most of this possibility, theoretical papers concerning methods of peak location, estimation of systematic and statistical errors, and optimization of the measurement were developed in parallel with constructional and experimental methods.

Methods of lattice-parameter determination with counter recording form a large and heterogeneous group. As well as measurements on two- or four-circle standard diffractometers, a separate method developed by Bond (1960) and a variety of non-dispersive (X-ray and optical interferometry) and pseudo-non-dispersive methods (two- and three-circle spectrometers, multiple-beam techniques, and combined methods) are included in this group.

5.3.3.2. *Standard diffractometers*

The determination of lattice parameters by the use of a standard diffractometer is based, as in the case of photographic methods, on (5.3.1.1) and (5.3.1.2), and the main task is to measure a sufficient number of reflections (the θ values for various *hkl* indices) for determining and solving the equations and for calculating the unknown parameters. The reflections can be chosen arbitrarily or in a special way (high θ angle, axial or non-axial reflections).

The characteristic feature of measurements performed on a diffractometer is, however, that to satisfy the Ewald condition for a given reflection the crystal and the detector are rotated or, depending on the geometry (equatorial or inclination), shifted round their axes as well. Basic and more detailed information about the geometry of diffractometers is given elsewhere (Arndt & Willis, 1966, Chap. 3; Stout & Jensen, 1968, Section 6.3; Kheiker, 1973, Chap. 4; Luger, 1980, Chap. 4; Section 2.2.6 of this volume). For calculating the *setting angles* for given *hkl* reflections, the lattice parameters (at least preliminary values) have to be known, and conversely, if the setting angles are known, it is possible to calculate or to refine lattice parameters. Therefore, not only the θ values (given by the angle 2θ of rotation of the detector about the goniometer axis) but also the values of the remaining setting angles (*i.e.* ω, φ, and χ of the crystal rotation in equatorial geometry, or μ and φ for the crystal and ν for the detector in inclination geometry) can be used for lattice-parameter determination. This problem can be treated by a matrix analysis.

5.3.3.2.1. *Four-circle diffractometer*

In the case of an automated four-circle (equatorial geometry) diffractometer, the setting angles are calculated by means of the orientation matrix $\boldsymbol{U}$, *i.e.* a matrix such that

$$\boldsymbol{A}^* = \boldsymbol{U}\boldsymbol{A}_G, \qquad (5.3.3.1)$$

where

$$\boldsymbol{A}^* = \begin{bmatrix} a^* \\ b^* \\ c^* \end{bmatrix} \qquad (5.3.3.1a)$$

is the reciprocal-axis system with metric

$$\boldsymbol{G}^{-1} = \begin{bmatrix} a^{*2} & a^*b^*\cos\gamma^* & a^*c^*\cos\beta^* \\ a^*b^*\cos\gamma^* & b^{*2} & b^*c^*\cos\alpha^* \\ a^*c^*\cos\beta^* & b^*c^*\cos\alpha^* & c^{*2} \end{bmatrix} \qquad (5.3.3.1b)$$

and

$$\boldsymbol{A}_G = \begin{bmatrix} a_G \\ b_G \\ c_G \end{bmatrix} \qquad (5.3.3.1c)$$

is the crystal-fixed orthonormal system. As can be proved (Busing & Levy, 1967; Hamilton, 1974; Luger, 1980, Section

4.1.1; Gabe, 1980), the reciprocal-cell parameters are related to the orientation matrix by the following equation:

$$\boldsymbol{A}^*\boldsymbol{A}^{*\prime} = \boldsymbol{U}\cdot\boldsymbol{U}', \qquad (5.3.3.2)$$

where $\boldsymbol{A}^*\boldsymbol{A}^{*\prime} = \boldsymbol{G}^{-1}$ is given by (5.3.3.1*b*). It is thus possible to calculate the lattice parameters from the terms of the orientation matrix.

The determination of the orientation matrix is usually the first step in measurements performed on the four-circle diffractometer. This task can be accomplished when the preliminary lattice-parameter values are known, and even when they are unknown. In the first case, the setting angles of two reflections, and, in the second, of three reflections, have to be determined. The procedure (Busing & Levy, 1967; Hamilton, 1974) is usually accomplished by the software of the four-circle diffractometer. Least-squares refinement of the lattice and orientation parameters may be performed when the setting angles of several reflections have been observed (Clegg, 1984). Appropriate constraints, resulting from the presence of symmetry elements in the given crystal structure, to be introduced during the refinement, are discussed by Bolotina (1989).

In a particular case, the four-circle diffractometer can be used for lattice-parameter measurements performed in the plane perpendicular to the main goniometer axis (say, the horizontal plane), for which $\chi = 0^\circ$, so that, in practice, only 2θ and ω values are used for lattice-parameter determination (see also §5.3.3.4.1). The equations to be solved can be simplified if only axial reflections are taken into account. In an example described by Luger (1980, Section 4.2.2), the $\mathbf{b}^*$ axis of a monoclinic crystal is oriented in the direction of the main axis. Then each of the two axial lengths, a^* and c^* (see Fig. 5.3.3.1), can be obtained from only one measurement:

$$a^* = \frac{2\sin\theta}{|h|\lambda}, \qquad (5.3.3.3a)$$

$$c^* = \frac{2\sin\theta}{|l|\lambda}, \qquad (5.3.3.3b)$$

whereas φ values of two reflections are used to determine the β^* angle between $\mathbf{a}^*$ and $\mathbf{c}^*$ axes, since

$$\beta^* = \varphi_{h00} - \varphi_{00l}. \qquad (5.3.3.3c)$$

This method is more suitable for orthogonal systems than for non-orthogonal ones, because of the difficulties in obtaining the proper orientation in the case of the monoclinic and, particularly, the triclinic system. In the latter case, the crystal has to be set three times.

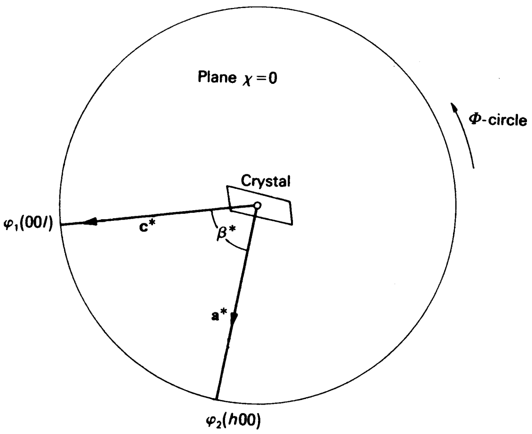


Fig. 5.3.3.1. Determination of reciprocal-lattice angles on the θ circle (after Luger, 1980).

5.3.3.2.2. *Two-circle diffractometer*

Lattice-parameter determination by the use of the two-circle (inclination) diffractometer, the so-called 'Weissenberg diffractometer', is more troublesome than by means of the four-circle one, because only two rotations [ω (or φ) of the crystal, and 2θ (or γ) of the detector] are motor-driven under computer control, while two inclination angles (μ for the crystal and ν for the detector) must be set by hand.

The problem of application of the popular two-circle (Eulerian-cradle) diffractometer for measurements similar to those presented in §5.3.3.2.1 was discussed by Clegg & Sheldrick (1984). The main idea of their paper was to introduce equations combining setting angles, obtained for selected reflections, with reciprocal-cell parameters, for calculating the latter. The authors started with zero-layer reflections for which, for a crystal mounted about the c axis,

$$\sin\theta = (x^2 + y^2)^{1/2}, \qquad (5.3.3.4a)$$

$$\omega = \omega_0 + \theta - \tan^{-1}(y, x), \qquad (5.3.3.4b)$$

where

$$x = \lambda(ha^* + kb^*\cos\gamma^*)/2, \qquad (5.3.3.4c)$$

$$y = (\lambda kb^*\sin\gamma^*)/2, \qquad (5.3.3.4d)$$

and ω_0 is a zero-point correction.

The remaining parameter c had to be determined from the inclination angle μ, measured by hand. The use of zero-layer reflections was advantageous, apart from the simplicity of the formulae (5.3.3.4*a*,*b*,*c*,*d*), because they were less affected by crystal misalignment than were upper-layer reflections. However, a zero-point correction ω_0 for ω had to be performed. For this purpose, the ω_0 value was treated as an additional parameter in off-line least-squares refinement.

As the next step, the authors introduced equations for a general crystal orientation instead of an aligned crystal (*cf.* §5.3.3.2.1) and derived equations defining the setting angles for an arbitrary reflection useful for data collection from a randomly oriented crystal if preliminary lattice-parameter values had been assumed. This made possible measurements of reflections on a range of layers; only one crystal mounting was required. The matrix formulae suitable for Eulerian-geometry diffractometers are also given by Kheiker (1973, Chap. 3, Section 9) and Gabe (1980).

In order to perform precise refinement of all six cell parameters, Clegg & Sheldrick (1984) used least squares with empirical weights:

$$W_{hkl} = 1/\sqrt{\omega_{hkl}}, \qquad (5.3.3.5)$$

where ω_{hkl} is the width of the *hkl* reflection. An additional (third) motor to control the μ circle was proposed.

The authors point out that the two-circle diffractometer, owing to its simpler construction in comparison with the four-circle one, is well suited to operations that require additional attachments; for example, for low-temperature operation.

5.3.3.3. *Data processing and optimization of the experiment*

5.3.3.3.1. *Models of the diffraction profile*

Every measurement is based on a certain model of its object. By 'model' we understand here* all the systematized *a priori*

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* Statisticians (Schwarzenbach, Abrahams, Flack, Gonschorek, Hahn, Huml, Marsh, Prince, Robertson, Rollett & Wilson, 1989) define model as 'conjecture about physical reality used to interpret the observations'. Based on their definition, the author proposes its operative interpretation.

knowledge concerning the given measurement, necessary for planning and performing the experiment and for estimating parameters being determined. The use of an incorrect model results in a bias, *i.e.* an additional systematic error that may appear aside from physical and geometric aberrations. Therefore, the choice of a well founded model is essential in accurate measurements.

In the case of lattice-parameter determination, the object of direct measurements is a diffraction profile, already mentioned in Subsection 5.3.1.1, and the quantity that is directly determined from the experiment is the Bragg angle θ.

The *a priori* information about the diffraction profile should define: (i) the way in which the Bragg angle θ is related to the measured profile $h(\omega)$, *i.e.* a measure of location; (ii) the mean values of the measured intensities within the profile; and (iii) their variances.

(i) In traditional photographic methods, the Bragg angle is determined from the measurement of distance on the film, where points or lines of the most intense blackening are taken into account. The blackening, which corresponds to the recorded intensity, may be estimated qualitatively ('by eye') or quantitatively, by means of a special device. In the second case, the intensity is determined as a function of the coordinates on the photograph, which, in turn, are related to the angular positions of diffracted beams. The distribution so obtained, *i.e.* the line profile or the diffraction profile, allows more precise measurements of the distances and the determination of θ angles, if a definition of the point (θ_0, h_0) of the profile $h(\theta)$, corresponding to the Bragg angle, *i.e. a measure of location*, is accepted. The analogous situation appears when the diffraction profile is recorded by means of the counter diffractometer. Then the intensities are measured by a counter, while the angular positions of the detector (2θ scan) or the sample (θ scan), or both (ω–2θ scan), are controlled by stepping motor. The device is normally combined with a computer, which facilitates the data processing.

There are various measures of location of the diffraction profile (Wilson, 1965; Thomsen & Yap, 1968). The most popular are:

(1) the centroid or the centre of gravity, defined as

$$\theta_c = \int\limits_{\Omega_1}^{\Omega_2} \theta h(\theta)\,\mathrm{d}\theta \Big/ \int\limits_{\Omega_1}^{\Omega_2} h(\theta)\,\mathrm{d}\theta, \qquad (5.3.3.6)$$

where Ω_1 and Ω_2 are the selected truncation limits;

(2) the median, the value θ_m that equally divides some specified portion of the line profile, *i.e.*

$$\int\limits_{\Omega_1}^{\theta_m} h(\theta)\,\mathrm{d}\theta = \int\limits_{\theta_m}^{\Omega_2} h(\theta)\,\mathrm{d}\theta; \qquad (5.3.3.7)$$

(3) the geometrical peak – the abscissa value θ_p for which the maximum occurs, *i.e.*

$$[\mathrm{d}h(\theta)/\mathrm{d}\theta]_{\theta=\theta_p} = 0; \qquad (5.3.3.8)$$

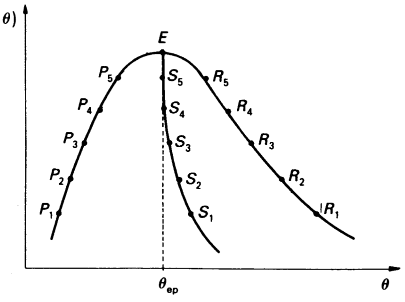


Fig. 5.3.3.2. The extrapolated-peak procedure (after Bearden, 1933).

(4) the extrapolated peak or the midchord peak, introduced by Bearden (1933) – the point $\theta_{\rm ep}$ of intersection of two curves, one of them approximating the midpoints of chords drawn through the profile parallel to the abscissa axis (or to the background) and the other approximating the data points (Fig. 5.3.3.2);

(5) the single midpoint of a chord $\theta_{\rm mc}$ drawn horizontally at the defined height, αH, where H is the peak height and α is the truncation level, $0 < \alpha < 1$.

The advantages and disadvantages of these measures of location have been widely discussed (Wilson, 1965, 1967; Thomsen & Yap, 1968; Segmüller, 1970; Kirk & Caulfield, 1977; Grosswig, Jäckel & Kittner, 1986; Gałdecka, 1994), the errors, both systematic (biases) and statistical (variances), resulting from each of these definitions being taken into account. The dependence of these errors on the scanning range (truncation limits) is of great importance. Such features of the definitions as their simplicity or current usage were also considered.

The geometrical peak of the least-squares parabola, approximating the data points near the top of the profile, distinguishes itself with the best precision but rather large bias (because of the asymmetry of the profiles met in practice); the extrapolated peak – commonly used in the case of the Bond (1960) method (definition 4) – permits location of the peak with better accuracy and omitting the dispersion error (*cf.* §5.3.3.4.3.2). The centre of gravity, very useful in theoretical considerations (Wilson, 1963), is strongly dependent on the truncation limits and requires a rather large scanning range. The choice of the definition of the measure of location is the first step of lattice-parameter calculations and also of systematic and statistical error estimation.

In the papers that appeared in the mid-1950's, and which were mainly concerned with powder samples, the centre of gravity as a measure of location was more often used than the peak, probably owing to its property of additivity (the total systematic error in the Bragg angle is a sum of the partial errors related to various physical and apparatus factors) and the estimated errors were consequently referred to this point. The papers were reviewed by Wilson (1963, 1980), one of the authors, in the form of a homogeneous mathematical theory of X-ray powder diffractometry. Some of the formulae describing corrections for displacements of the centroid caused by physical and geometrical factors (collected in convenient tables) proved to be useful for single-crystal methods as well (Smakula & Kalnajs, 1955; Kheiker & Zevin, 1963). Wilson (1963) derived the general formula for calculations of the peak displacements due to various factors. As results from this, the displacements are not additive and, in the case when at least one of the partial distributions is asymmetric, the convolution of the curves [see equation (5.3.1.6)] may lead to an appreciable peak shift, if the distributions are not known. The problem has been treated by Berger (1984, 1986*a*), who used computer modelling.

In later single-crystal methods, in particular in the Bond (1960) method, the peak position of the profile was determined rather than the centroid and the respective corrections referred to the peak (§5.3.3.4.3.2). As a rule, the corrections that related to the peak position were treated as being independent. In practice, this simplifying assumption can be sufficient in measurements with moderate and even high accuracy. However, if the highest accuracy, say of 1 part in 10^7, is required, the joint effect of all the aberrations should be considered (the so-called 'cross terms' are used besides the main terms). Such considerations [Härtwig & Grosswig, 1989; *cf.* §5.3.3.4.3.2, point (7)] must be based on a well-founded physical model of the diffraction profile.

(ii) As already mentioned in Subsection 5.3.1.1, the diffraction profile can be described as a convolution of several factors (distributions), namely the wavelength distribution, crystal profile and certain aberration profiles. To the so-obtained *net* profile [equation (5.3.1.6)], a background should be added – constant in the case of an ω scan (as in one-crystal spectrometers, for example), and more complex (but usually approximated with a straight line within a narrow angular range) in other cases. Thus, to describe accurately the distribution of the mean values of measured intensities, all individual distributions must be given.

Such complete syntheses of the diffraction profile are rarely performed, and only for the highest-accuracy absolute measurements (Härtwig, Hölzer, Förster, Goetz, Wokulska & Wolf, 1994). Since one of the basic factors of the convolution model is the wavelength distribution that characterizes a given source of radiation, its accurate determination and proper scaling in metric units is of primary importance in high-accuracy lattice-parameter measurements. At present, only a few such measurements are reported, which relate to the Cu $K\alpha$ emission line (Berger, 1986*b*; Härtwig, Hölzer, Wolf & Förster, 1993; Härtwig, Bąk-Misiuk, Berger, Brühl, Okada, Grosswig, Wokulska & Wolf, 1994) and to the Cu $K\beta$ line (the latter paper). Owing to a relatively simple analytical model proposed by Berger (1986*b*) to describe the $K\alpha_{1,2}$ doublet, the measurement results are easy to handle.

Profiles connected with individual apparatus factors (collimation, for example) can also be, in principle, described analytically, under some simplifying assumptions. Examples of such profiles are distributions related to the vertical divergence of the beam (Eastabrook, 1952) and to the horizontal (in-plane) divergence (Urbanowicz, 1981*a*). These are general enough, so can be calculated for given apparatus parameters. While performing high-accuracy measurements, however, the validity of all respective accompanying assumptions must be carefully considered (Urbanowicz, 1981*b*; Härtwig & Grosswig, 1989; Härtwig *et al.*, 1993).

In wider practice, there is a tendency towards using simpler descriptions of the diffraction profile. Often, one of the factors, apart from the spectral distribution, is dominant, and the influence of the other ones can be neglected. Berger (1986*b*), for example, neglecting small effects of both the vertical divergence and the crystal profile, obtained an analytical model of the measured Cu $K\alpha$ emission spectrum, with several adjusted parameters, and so managed to determine the pure Cu $K\alpha$ emission-spectrum profile without the necessity of calculating the deconvolution of the measured spectrum in relation to the horizontal-divergence profile.

The choice of model of the *shape* of the diffraction profile depends, of course, on the purpose for which it is applied. The simplest possible descriptions are used in low- or medium-accuracy measurements, in which first the *measured* values of Bragg angles are determined by approximation of the measured profiles with simple analytical functions (polynomials or so-called *shape functions*), the parameters of which have no physical meaning, and then all necessary corrections are calculated and subtracted from the *measured* Bragg angles – under the assumption of their additivity, mentioned in (i) – to obtain their *true* values. Another application of the simple models is just the estimation of systematic and statistical errors of the Bragg-angle determination. The choice and use of such simple models will be shown in §5.3.3.3.2.

(iii) The knowledge of variances (and covariances) of recorded counts is needed to evaluate the goodness of fit while approximating the measured profile with a given model function (appropriate criteria have been formulated by Gałdecka, 1993*a*,*b*) and to estimate the precision of the Bragg-angle determination.

Most often, one assumes that the variances of measured intensities are defined by the Poisson statistic, *i.e.*

$$\sigma^2(h) = h, \qquad (5.3.3.9)$$

where h is the intensity in number of counts.

Other factors affecting the statistics of recorded counts and the validity of the assumption [equation (5.3.3.9)] have been taken into consideration by Bačkovský (1965) [see also equations (5.3.3.17) and (5.3.3.18) and the comments on these], Wilson (1965), and Gałdecka (1985). The factors are mostly errors in the angle setting and reading and also fluctuations of the primary-beam intensity, of the counting time, and of the temperature of the sample. The use of automatic scanning can cause correlations between intensities measured at different points in the profile (Gałdecka, 1985).

5.3.3.3.2. *Precision and accuracy of the Bragg-angle determination; optimization of the experiment*

The analysis of the variance $\sigma^2(\theta_0)$ of a chosen measure of location permits a combination of the precision of the Bragg-angle determination, and so of the lattice-parameter determination [equation (5.3.1.4)], with the scanning range $2\Omega = \Omega_2 - \Omega_1$ [see definition (1), §5.3.3.3.1] or truncation level α [see definition (5)], the number of measuring points n (usually $n = 2p + 1$), the parameters of the profile (number of counts H in the peak position, the half-width ω_h), and its shape. It is convenient to present the profile $h(\theta)$ in a standardized form (Thomsen & Yap, 1968) as:

$$h(\theta) = Hv[x(\theta)], \qquad (5.3.3.10)$$

where

$$x(\theta) = 2\frac{\theta - \theta_0}{\omega_h} \qquad (5.3.3.10a)$$

are standardized angle values and

$$v(x) = h/H \qquad (5.3.3.10b)$$

is the shape function, not dependent on the parameters H and ω_h. For each measure of location [definitions (1)–(5) of §5.3.3.3.1(i)], there is the dependence:

$$\sigma^2(\theta_0) = F\frac{\omega_h^2}{I_pT}, \qquad (5.3.3.11)$$

where I_p is the peak intensity, T is the total counting time, and F is a dimensionless factor that depends on the measure of location and the shape of the profile.

Since, in the case of fixed-time counting, the total counting time T is proportional to the number n of measuring points:

$$T = n\Delta t, \qquad (5.3.3.12)$$

where Δt is the counting time, and since the number of counts h is proportional to the intensity I:

$$h = I\Delta t, \qquad (5.3.3.13)$$

and, in particular, the number of counts H in the peak position is proportional to the peak intensity I_p:

$$H = I_p\Delta t, \qquad (5.3.3.13a)$$

the dependence (5.3.3.11) can be presented as

$$\sigma^2(\theta_0) = \frac{F}{n}\frac{\omega_h^2}{H}. \qquad (5.3.3.14)$$

Thus, for a given measure of location and given shape of the profile [equations (5.3.3.10), (5.3.3.10*b*)], the variance $\sigma^2(\theta_0)$ depends on the ratio ω_h^2/H of the profile parameters (ω_h, H) and decreases with an increase of the number of points, n.

In particular, the variance $\sigma^2(\theta_p)$ of the peak [definition (3), §5.3.3.3.1] of the least-squares parabola has been estimated (Wilson, 1965) as

$$\sigma^2(\theta_p) = \frac{3H}{2p\Omega^2[h''(\theta_p)]^2}, \qquad (5.3.3.15)$$

where $h''(\theta_p)$ is the second derivative of $h(\theta)$ in the peak position and p is a number such that $n = 2p + 1$ ($n \approx 2p$, if p is sufficiently large).

Taking into account the standardization performed [equations (5.3.3.10), (5.3.3.10*a,b*)], equation (5.3.3.15) can be rewritten in the form:

$$\sigma^2(\theta_p) = \frac{1}{n}\,\frac{3}{4X^2[v''(0)]^2}\,\frac{\omega_h^2}{H}, \qquad (5.3.3.16)$$

where X is the standardized scanning range

$$X = 2\Omega/\omega_h \qquad (5.3.3.16a)$$

and $v''(0)$ is the second derivative of the shape function in the peak positions. By comparing (5.3.3.16) and (5.3.3.14), we find the factor F in this case to be

$$F = \frac{3}{4X^2[v''(0)]^2}. \qquad (5.3.3.16b)$$

From (5.3.3.14) and (5.3.3.16*b*), the variance of the peak of the least-squares parabola decreases with an increase of the scanning range. On the other hand, the bias of the peak position, resulting from the asymmetry of the profile, is proportional to Ω^2 (Wilson, 1965):

$$\Delta\theta_p = 2(\Omega^2/\omega_h)[v'''(u_p)/v''(u_p)], \qquad (5.3.3.16c)$$

where $v''(u_p)$ and $v'''(u_p)$ are the second and third derivatives of a function describing the profile at its peak position u_p. These two aspects should be taken into account in choosing the scanning range. Yet, as shown by Gałdecka (1993*b*; Section 5), (5.3.3.16*c*) may be applied to reduce the bias by extrapolating to $\Omega = 0$ the results obtained within various scanning ranges.

In the case of polynomials of higher (and even) degrees ($m = 4, 6, 8$) and $0.5 \ll X \ll 1$, the factor F can be expressed by a semi-empirical dependence (Thomsen, 1974; Gałdecka, 1993*b*):

$$F = 0.0017\, m^2 (\tan^{-1} X)/X^3, \qquad (5.3.3.16d)$$

but it is difficult to evaluate the bias. Therefore, as shown by Gałdecka (1993*b*), polynomials of higher degrees have no advantage over a least-squares parabola.

To minimize the bias, a reasonable shape function may be used rather than a polynomial (Gałdecka, 1993*a,b*). The function should be continuous (including its derivatives), not negative and closely related to known physical models of the diffraction profiles. Since the measured diffraction profiles are, as a rule, asymmetric, the proper selection of a description of asymmetry is of primary importance. The use of the so-called 'split functions', consisting of two 'half' functions of the same (or different) shape and different half-widths, leads to a noticeable bias, so such functions must not be used for accurate lattice-parameter determination.

The variance $\sigma^2(\theta_{\rm mc})$ of a single midpoint of a chord [definition (5), §5.3.3.3.1] has been estimated by Bačkovský (1965) as

$$\sigma^2(\theta_{\rm mc}) = \sigma^2(\theta_i) + \sigma^2(h_i)/[h'(\theta_i)]^2, \qquad (5.3.3.17)$$

where $\sigma^2(\theta_i)$ and $\sigma^2(h_i)$ are the variances of the coordinates θ and h, respectively, and $h'(\theta)$ is the first derivative at the ith point. If it is assumed that $\sigma^2(\theta_i)$ is small in relation to the second component of (5.3.3.17) and if (5.3.3.9) and the standardizations (5.3.3.10), (5.3.3.10*a,b*) are taken into consideration, (5.3.3.17) can be rewritten in the form:

$$\sigma^2(\theta_{\rm mc}) = \frac{v_i}{4[v'(x_i)]^2}\,\frac{\omega_h^2}{H}, \qquad (5.3.3.18)$$

where $v'(x_i)$ is the first derivative of the shape function in the ith position.

Comparison of (5.3.3.18) and (5.3.3.14), with $n = 2$, leads to

$$F = \frac{v_i}{2[v'(x_i)]^2}. \qquad (5.3.3.18a)$$

For an arbitrary shape function $v(x)$ describing the diffraction profile, it is thus possible to find such a truncation level $\alpha = \alpha_{\rm opt}$ [§5.3.3.3.1, definition (5)], for which F is a minimum. If the shape function is the Cauchy function,

$$v = \frac{1}{1 + x^2}, \qquad (5.3.3.19)$$

the optimum truncation level is $\alpha_{\rm opt} = 2/3$, and the resulting F factor, $F = F_{\rm min} = 0.84$.

In spite of a large bias introduced by the midpoint of a single chord (the difference between its position and the peak position), this measure of location is preferred by Barns (1972), because the calculations are less time-consuming than those for other points of the profile. Barns takes $\alpha = 0.5$ [$F = 1$ for the Cauchy function; equations (5.3.3.18*a*), (5.3.3.19)] and compensates the bias at this level by determining an effective value of the wavelength based on a silicon standard.

The estimators of the variance for the centroid and the median given by Wilson (1967), or estimators of both the variance and the bias of the extrapolated-peak position given by Gałdecka (1994) can also be the basis of the choice of the scanning range if these measures of location are applied.

The other possibility of affecting the precision of the measurements is to change the shape and the parameters of the profile [see equations (5.3.3.14), and (5.3.3.16*b*) or (5.3.3.18*a*)] by changing the apparatus parameters [the influence on $h_A(\theta)$, equation (5.3.1.6)], or the X-ray source profile $h_\lambda(\theta)$, or the crystal profile $h_C(\theta)$.

An example of the first possibility is the optimization of the parameters of in-plane collimation in the case when the peak of the least-squares parabola is used as the measure of the location (Urbanowicz, 1981*a*). Since both the shape and the parameters of the profile depend on the collimation parameters, the task is to choose collimator-slit dimensions to minimize the value $(\omega_h^2/H)\{1/[v''(0)]^2\}$ [*cf.* equation (5.3.3.16)]. As a result of detailed considerations, under the assumption given by (5.3.3.9), the optimum exists and is defined by the following formula:

$$d_1 = d_2 = 0.565\, L\omega_\lambda, \qquad (5.3.3.20)$$

where d_1 and d_2 are the widths of the slits, L is the collimator length, and ω_λ is the half-width of the original profile $h_\lambda(\theta)$ [*cf.* equations (5.3.1.6), (5.3.1.7), and (5.3.1.8)]. Systematic errors connected with collimation have been discussed separately (Urbanowicz, 1981*b*).

The width of the original profile $h_\lambda(\theta)$ can be reduced by means of spectrally narrow sources or by the use of additional crystal(s) in multiple-crystal methods (Subsection 5.3.3.7). The latter also affects the crystal profile $h_C(\theta)$.

5.3.3.4. *One-crystal spectrometers*

5.3.3.4.1. *General characteristics*

A diffractometer in which both 2θ and ω 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 2θ 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 4θ and the absolute value of the angle between the two sample positions, ω_1 and ω_2, is 180°–2θ, so that both 2θ and ω scans can be used for the Bragg-angle determination.

As was mentioned in §5.3.2.3.4(vi), the idea of calculating the θ 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*

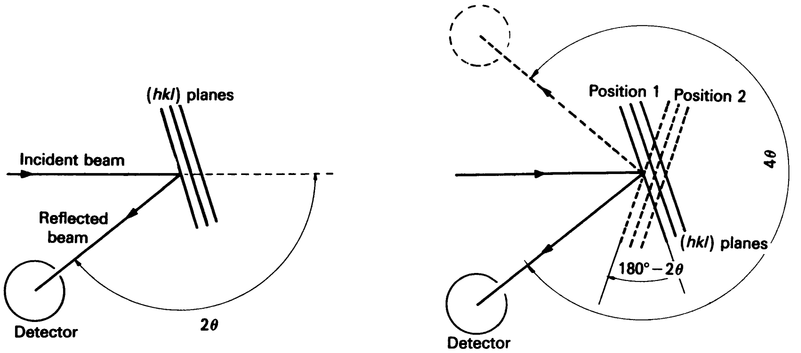
Although the Bond (1960) method, based on a symmetric arrangement presented in §5.3.3.4.3, makes possible higher accuracy than that obtained by means of a standard diffractometer, an asymmetric arrangement proves to be more suitable for certain tasks connected with lattice-parameter measurement, because 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.* §5.3.3.3.1(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 2θ 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 2θ and ω 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



(*a*) (*b*)

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).

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:

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

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 ±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 µm 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

$$\theta = |180° - |\omega_1 - \omega_2|/2|. \qquad (5.3.3.22)$$

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

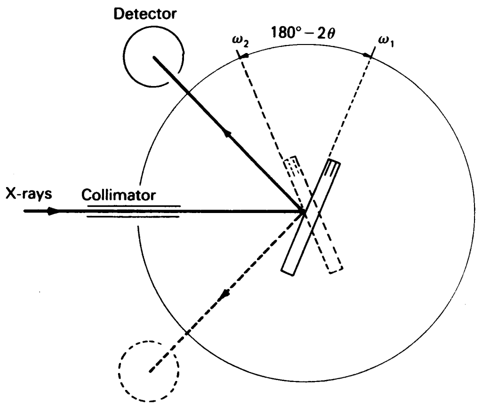


Fig. 5.3.3.4. Schematic representation of the Bond (1960) method.

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°θ 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

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

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

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

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

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

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

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 ±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):

$$\Delta d_T = d\,\alpha_d\,\Delta T, \tag{5.3.3.33}$$

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).

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 (Wołcyrz, 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 θ 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 $h_\lambda(\omega)$. 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 λ. 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

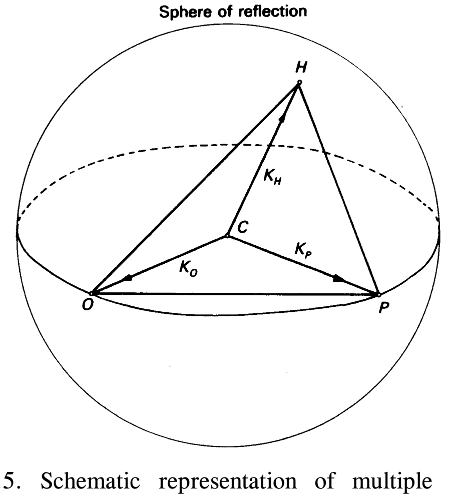
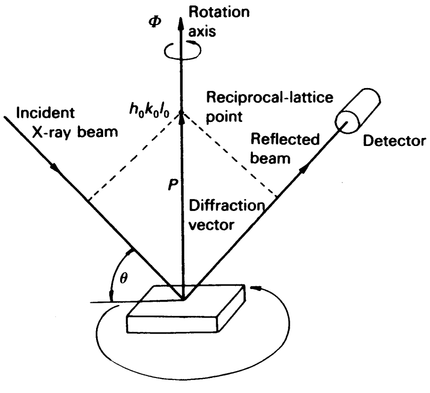


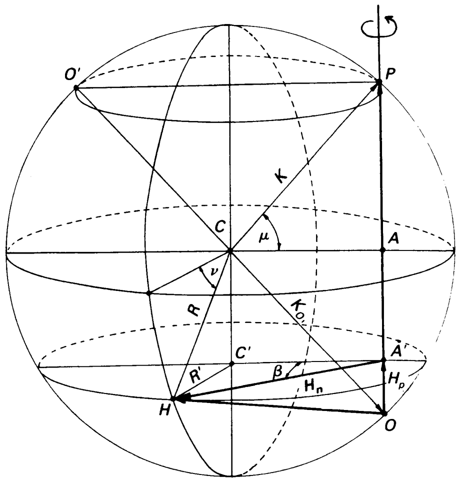
Fig. 5.3.3.5. Schematic representation of multiple diffraction in reciprocal space (after Post, 1975).

simultaneous reflection or (after Renninger, 1937) '*Umweganregung*', may be observed in both X-ray and neutron experiments. In the first case, it occurs both in methods with counter recording, initiated by Renninger (1937), and in methods with photographic recording in which a highly divergent beam is used (§5.3.2.4.2). The intersections of conic sections encountered in the methods developed by Kossel (1936) and Lonsdale (1947) are the cases of multiple-diffraction phenomena in photographic methods.

Simultaneous reflection, undesirable in some cases ('forbidden' reflections in measurements of intensities) can be very useful in others. Its various applications have been reviewed by Terminasov & Tuzov (1964) and Chang (1984). Only the utility of multiple diffraction in lattice-parameter determination will be discussed here.



(*a*)



(*b*)

Fig. 5.3.3.6. Schematic representation of the multiple-diffraction method. (*a*) Experimental set-up (after Cole, Chambers & Dunn, 1962; Post, 1975). (*b*) Geometric representation in reciprocal space.

The principle of Renninger's (1937) experiment, which is also the basis of the method described by Post (1975), is shown in Fig. 5.3.3.6. The crystal in the shape of a slab is at first set in a position to diffract the primary X-ray beam. A primary reflection whose intensity is very low or which is forbidden by the space group of the crystal is usually selected. Its intensity determines the background intensity of the pattern, which should be low. The detector, with a wide-open window, is situated in the appropriate position and remains fixed throughout the experiment while the crystal is rotated around the axis perpendicular to the crystal planes (and its surface) to record successive reflections.

The multiple-diffraction pattern (an example is shown in Fig. 5.3.3.7) has next to be indexed. The principle of the method of indexing, known as the reference-vector method (Cole, Chambers & Dunn, 1962; Post, 1975; Chang, 1984), is shown in Fig. 5.3.3.6(*b*). Directions of the primary and diffracted beams are marked by vectors $\mathbf{K}_0$ and $\mathbf{K}$. The ends of the vectors lie on the Ewald sphere, the radius of which is equal to $1/\lambda$. The reciprocal vector $\mathbf{P} = h_0\mathbf{a}^* + k_0\mathbf{b}^* + l_0\mathbf{c}^*$, being the difference between the vectors $\mathbf{K}$ and $\mathbf{K}_0$, represents the first diffraction phenomenon, which is observed for setting angles equal to φ_0 and μ (usually $\mu = \theta$). Let us assume that the reciprocal vector $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, observed for setting angles $\varphi_0 + \beta$ and ν, represents the next diffraction. The vector components of $\mathbf{H}$, parallel and normal to $\mathbf{P}$, are denoted by $\mathbf{H}_p$ and $\mathbf{H}_n$, respectively. For a given wavelength, the lengths P, H, H_p, H_n of respective vectors $\mathbf{P}$, $\mathbf{H}$, $\mathbf{H}_p, \mathbf{H}_n$ are functions of lattice parameters and diffraction indices.

The task is to find the relationship between the difference β of angles of rotation (or between two values of the setting angles, β and ν) and the lengths of the reciprocal vectors. The following relations result from Fig. 5.3.3.6(*b*):

$$\begin{aligned}\cos\beta &= \frac{(C'A')^2 + H_n^2 - R'^2}{2H_n(C'A')},\\ (C'A')^2 &= R^2 - P^2/4,\\ H_p &= P/2 - R\sin\nu,\\ R' &= R\cos\nu.\end{aligned}$$

Taking these into consideration, and remembering that $H^2 = H_p^2 + H_n^2$, we finally obtain

$$\cos\beta = \frac{H^2 - H_pP}{2H_n(R^2 - P^2/4)^{1/2}}. \qquad (5.3.3.34)$$

Since $\cos(-\beta) = \cos\beta$, the appearance of successive reflections does not depend on the direction of rotation. A detailed discussion of (5.3.3.34) is given by Cole, Chambers & Dunn (1962) and Chang (1984). When preliminary values of the lattice parameters are known, (5.3.3.34) can be applied for indexing multiple-diffraction patterns. A computer program (Rossmanith, 1985) can be very useful in rather complicated calculations and in the graphical representation of the multiple-diffraction

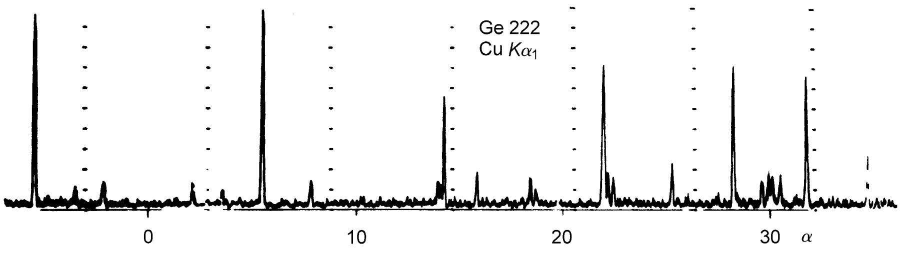


Fig. 5.3.3.7. The multiple-diffraction pattern at the 222 position in germanium (Cole, Chambers & Dunn, 1962).

pattern. Formula (5.3.3.34), since $C'A' = R\cos\mu$, can be presented in another form:

$$R = \frac{H^2 - H_pP}{2H_n\cos\mu\cos\beta}, \qquad (5.3.3.35)$$

where two setting angles, μ and β, are taken into account. When the indices are known, both (5.3.3.34) and (5.3.3.35) can be used for the determination or refinement of lattice parameters.

Another analytical method for indexing multiple-diffraction patterns, based on the determination of the Lorentz point, has been described by Kshevetsky, Mikhailyuk, Ostapovich, Polyak, Remenyuk & Fomin (1979).

Formulae (5.3.3.34) and (5.3.3.35) are valid for all crystal systems. In practice, however, the rather complicated method is used mainly for cubic crystals, and a special approach proved to be needed in order to adapt the method to other (rectangular) systems (Kshevetsky, Mikhalchenko, Stetsko & Shelud'ko, 1985). In the case of a cubic lattice, it is convenient to substitute

$$R = a/\lambda \qquad (5.3.3.35a)$$

into (5.3.3.34) and (5.3.3.35) rather than $R = 1/\lambda$ used in the general case, so that the lengths of the reciprocal vectors, being now functions of the indices only, are:

$$P = (h_0^2 + k_0^2 + l_0^2)^{1/2}, \qquad (5.3.3.35b)$$

$$H = (h^2 + k^2 + l^2)^{1/2}, \qquad (5.3.3.35c)$$

$$H_pP = \mathbf{HP} = h_0h + k_0k + l_0l. \qquad (5.3.3.35d)$$

The lengths of the components of **H** can be determined from (5.3.3.35*b*,*c*,*d*) taking $H_p = H_pP/P$ and $H_n = (H^2 - H_p^2)^{1/2}$. After introducing the alterations [equation (5.3.3.35*a*) and the resulting equations (5.3.3.35*b*,*c*,*d*)], (5.3.3.35) now describes a simple dependence between the ratio a/λ, the indices, and the setting angles.

The accuracy of the lattice-parameter determination resulting from (5.3.3.35) in the cubic case can be assumed to be:

$$\frac{\Delta a}{a} = \tan\mu\Delta\mu + \tan\beta\Delta\beta; \qquad (5.3.3.36)$$

this thus depends on the values of the setting angles β, μ and their accuracies $\Delta\beta$, $\Delta\mu$. The latter depend on various systematic errors.

Since the differences between the two angular settings at which a given set of planes diffracts are measured rather than their absolute values, the systematic errors due to absorption, specimen displacement, and zero-setting are eliminated. In contrast, errors due to vertical divergence, refraction and the change of wavelength of the incident radiation (when it enters the crystal), alignment, and dynamical effects should be taken into account. In the case described by Post (1975), when a fine focus (effective size 0.4 × 0.5 mm) and collimation limiting the beam divergence to 2′ were used, the vertical divergence causing the relative error in d of about 5×10^{-8} could be ignored.

The errors due to the real structure (inhomogeneity, mosaicity and internal stress) were discussed by Kshevetsky *et al.* (1979).

The accuracy possible by this method (from 1 to 4 parts in 10^6) is comparable with that obtained with the Bond (1960) method. The advantages of this method from the point of view of lattice-parameter determination are as follows:

(*a*) a large number of reflections can be measured without realigning or removing the crystal;

(*b*) all the lattice parameters can be determined and not only one, as in the Bond (1960) method;

(*c*) the narrow diffraction profiles can be located with very high accuracy and precision;

(*d*) the arrangement makes it possible to remove some systematic errors;

(*e*) the high accuracy resulting from (*a*)–(*d*), which is comparable with that obtained by means of the Bond (1960) method;

(*f*) the high precision that results from (*a*) and (*c*).

A disadvantage, on the other hand, is the complicated interpretation (indexing) of multiple-diffraction patterns, so that this method is less popular than the Bond (1960) method.

The Post (1975) method has been applied to the accurate lattice-parameter determination of germanium, silicon, and diamond single crystals (Hom, Kiszenick & Post, 1975).

5.3.3.7. *Multiple-crystal – pseudo-non-dispersive techniques*

5.3.3.7.1. *Double-crystal spectrometers*

Detailed information concerning the double-crystal spectrometer, which consists of two crystals successively diffracting the X-rays, can be found in James (1967, pp. 306–318), Compton & Allison (1935), and Azároff (1974). This device, usually used for wavelength determination, may also be applied to lattice-parameter determination, if the wavelength is accurately known. The principle of the device is shown in Fig. 5.3.3.8. The first crystal, the monochromator, diffracts the primary beam in the direction defined by the Bragg law for a given set of planes, so that the resulting beam is narrow and parallel. It can thus be considered to be both a collimator (or an additional collimator, if the primary beam has already been collimated) and a wavelength filter. The final profile $h(\theta)$, obtained as a result of the second diffraction by the specimen when the first crystal remains stationary and the second is rotated, is narrower than that which would be obtained with only one crystal. The final crystal profile $h_C(\theta)$ [*cf.* equation (5.3.1.6)] is due to both crystals, which, if it is assumed that they are cut from the same block, can be described by the autocorrelation function (Hart, 1981):

$$h_C(\theta) = K \int_{-\infty}^{\infty} R(\theta')R(\theta' - \theta)\,\mathrm{d}\theta', \qquad (5.3.3.37)$$

where $R(\theta)$ is an individual reflectivity function of one crystal and K is a coefficient of proportionality. Its half-width is 1.4 times larger than that related to only one crystal. In spite of this, the recorded profile can be as narrow as, for example, 2.6″ (Godwod, Kowalczyk & Szmid, 1974), since the profile due to the wavelength $h_\lambda(\theta)$, modified by the first crystal, is extremely narrow. Additional advantages of the diffraction profile are: its symmetry, because $h_C(\theta)$ is symmetric as an effect of autocorreletion, and smoothness, as an effect of additional integration. The profile can thus be located with very high accuracy and precision.

When there is a small difference in the two lattice spacings, so that one has a value d and the other $d + \delta d$, if $\delta\lambda/\lambda$ is small enough, it can be assumed that the profile does not alter in shape but in its peak position [*cf.* §5.3.3.4.3.3, paragraph (3)]. If for two identical crystals this were located at θ_0, the peak position

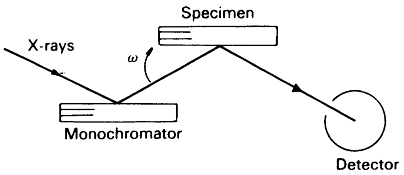


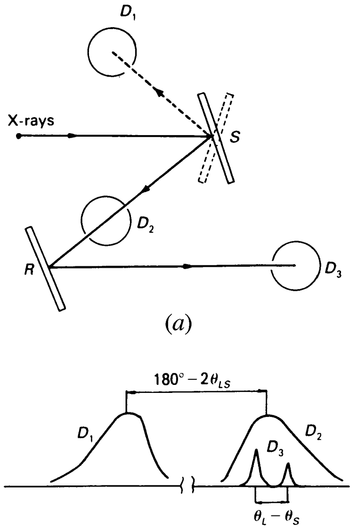
Fig. 5.3.3.8. Schematic representation of the double-crystal spectrometer.

shifts to $\theta_0 - \tan\theta\,\delta d/d$. The measurement of this shift rather than the absolute position of the rocking curve is the basis of all the double-crystal methods. An example of the application of a double-crystal spectrometer with photographic recording has been given in §5.3.2.3.5 (Bearden & Henins, 1965).

The basic requirements that should be fulfilled to make the most of the double-crystal spectrometer are: limitation of the primary beam by means of a collimator, parallelism of the two axes [precision as high as 1″ obtained by Godwod, Kowalczyk & Szmid (1974)], and high thermal stability (0.1 K; Godwod, Kowalczyk & Szmid, 1974). Alignment procedure, errors, and corrections valid for the double-crystal spectrometer have been considered by Bearden & Thomsen (1971).

The double-crystal diffractometer, because of the small width of the diffraction profile, is a very suitable tool for local measurements of lattice-parameter differences, for example between an epitaxic layer and its substrate. Hart & Lloyd (1975) carried out such a measurement on a standard single-axis diffractometer (APEX) to which a simple second axis, goniometer head, and detector were added (Fig. 5.3.3.9). The diffracted beam was recorded simultaneously by three detectors. A *symmetric arrangement* with two detectors, D_1 and D_2, with no layer present, makes possible the determination of the absolute value of the lattice parameter of the substrate, as in the Bond (1960) method. The third detector makes it possible to record the double-crystal rocking curve, which usually fully resolves the layer and substrate profiles. The changes in the lattice parameter between the two components can be used for determination of strain (at 1 part in 10^4).

The very important advantage of this method, from the point of view of local measurements, is that single- or double-crystal diffraction can be selected, simultaneously if needed, on exactly the same specimen area. Other examples of strain measurements by means of a double-crystal spectrometer are given by Takano & Maki (1972), who measured lattice strain due to oxygen diffusing into a silicon single crystal; by Fukahara & Takano (1977), who compared experimental rocking curves and theoretical ones computed within the frame of the dynamical theory; and Barla, Herino, Bomchil & Pfister (1984), who examined the elastic properties of silicon.



(*a*)

(*b*)

Fig. 5.3.3.9. Schematic representation of the double-crystal arrangement of Hart & Lloyd (1975) for the examination of epitaxic layers. (*a*) Experimental set-up. (*b*) Diffraction profiles recorded by detectors D_1, D_2, and D_3.

The standard double-crystal technique does not allow determination of relatively small strains, *i.e.* ones that affect the lattice parameter by, for example, less than 2–3 parts in 10^5, as in the case of (004) Si reflection and Cu $K\alpha$ radiation. To overcome this difficulty, Zolotoyabko, Sander, Komem & Kantor (1993) propose a new method that combines double-crystal X-ray diffraction with *high-frequency ultrasonic excitation*. Since ultrasound has a wavelength a little less than the X-ray excitation length, it affects the diffraction profile close to the Bragg position and so permits the detection of very small profile broadenings caused by lattice distortions. With this method, lattice distortion as small as 5 parts in 10^6 can be measured.

As has been shown in the case of the device used by Hart & Lloyd (1975), the symmetric arrangement due to Bond (1960) proves to be very useful when the double-crystal spectrometer is to be used for absolute lattice-parameter determination, since such an arrangement combines the high precision and sensitivity of a double-crystal spectrometer with the high absolute accuracy of the Bond method. Other examples of a similar idea are presented by Kurbatov, Zubenko & Umansky (1972), who report measurements of the thermal expansion of silicon; Godwod, Kowalczyk & Szmid (1974), who also discuss the theoretical basis of their arrangement; Ridou, Rousseau & Freund (1977), who examine a phase transition; Sasvári & Zsoldos (1980), and Fewster (1982). The latter two papers are concerned with epitaxic layers. A rapid method is proposed by Sasvári & Zsoldos (1980) for deconvoluting the overlapping peaks due to the layer and the substrate. A particular feature of the arrangement proposed in the first of these papers (Kurbatov, Zubenko & Umansky, 1972) is the use of a germanium-crystal monochromator with anomalous transmission, to obtain a nearly parallel primary beam (the horizontal divergence is 28″ and the vertical 14″).

The error analyses given by Godwod, Kowalczyk & Szmid (1974) and Sasvári & Zsoldos (1980) show that systematic errors due to eccentricity, absorption, and zero position are eliminated experimentally, owing to the symmetric arrangement, as in the Bond (1960) method. In contrast, the errors due to crystal tilt, refraction and the Lorentz–polarization factor [their uncertainties in lattice parameters, as evaluated by Sasvári & Zsoldos (1980), are 10^{-6} Å each], axial divergence (2×10^{-6} Å), angle reading (10^{-4} Å), and instrument correction and calculations (each to 5×10^{-5} Å) should be taken into account. The effect of absorption, discussed by Kurbatov, Zubenko & Umansky (1972), proved to be negligible. The final accuracy achieved for silicon single crystals by Godwod, Kowalczyk & Szmid (1974) is comparable with that obtained by Bond (1960).

A specific group of double-crystal arrangements is formed by those in which *white X-radiation* is used instead of characteristic. Such an arrangement makes possible very large values of the Bragg angle (larger than about 80°), which increases the accuracy, precision, and sensitivity of measurement of the lattice parameters and their change with change of temperature. This task is rather difficult to realize by means of

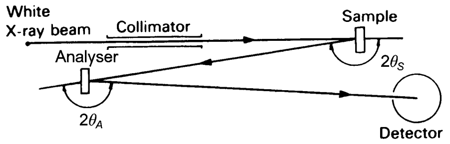


Fig. 5.3.3.10. Schematic representation of the double-crystal arrangement of Okazaki & Kawaminami (1973*a*); white incident X-rays are used.

traditional methods, in which both the wavelengths and the lattice parameters are fixed, and it is difficult to find a suitable combination of their values.

The principle of the method presented by Okazaki & Kawaminami (1973*a*) is shown in Fig. 5.3.3.10. The first crystal (the specimen to be measured) remains fixed during a single measurement, the second (the analyser) is mounted on the goniometer of an X-ray diffractometer and can be operated with either an ω or a θ–2θ scan. As diffraction phenomena appear for both the specimen and the analyser (in general of different materials) whose interplanar spacings are equal to d_s and d_A, respectively, the following relation results from Bragg's law:

$$d_s \sin\theta_s = d_A \sin\theta_A, \qquad (5.3.3.38)$$

where θ_s and θ_A are the respective Bragg angles. Since d_A and θ_s are kept constant, a change in d_s as a function of temperature is determined from a change in θ_A. The relative error $\delta d/d$ resulting from (5.3.3.38) with $\theta_A \approx 90^\circ$ is

$$\begin{aligned}\frac{\delta d_s}{d_s} &= \cot\theta_A\,\delta\theta_A = \tan(\pi/2-\theta_A)\,\delta\theta_A\\ &\approx (\pi/2-\theta_A)\,\delta\theta_A. \qquad (5.3.3.39)\end{aligned}$$

The method initiated by Okazaki & Kawaminami (1973*a*) has been developed by Okazaki & Ohama (1979), who constructed the special diffractometer HADOX (the positions of the specimen and the analyser were interchanged) and discussed systematic errors. Precision as high as 1 part in 10^7 was reported. Examples of the application of such an arrangement for measuring the temperature dependence of lattice parameters were given by Okazaki & Kawaminami (1973*b*) and Ohama, Sakashita & Okazaki (1979). Various versions of the HADOX diffractometer are still reported. By introducing two slits (Soejima, Tomonoga, Onitsuka & Okazaki, 1991) – one to limit the area of the specimen surface to be examined and the other to define the resolution of 2θ – it is possible to combine ω and 2θ scans and obtain a two-dimensional intensity distribution in the plane parallel to the plane of the diffractometer, and to determine the temperature dependence of lattice parameters on a selected area of the specimen (avoiding the effects of the surroundings). The HADOX diffractometer may work with both a rotating-anode high-power X-ray source (examples reported above) and a sealed-tube X-ray source. In the latter case (Irie, Koshiji & Okazaki, 1989), to increase the efficiency of the X-ray tube, the distance between the X-ray source and the first crystal has been shortened by a factor of five. As is implied by (5.3.3.39), one can increase the relative precision of the method by using the analyser angle close to $\pi/2$. This idea has been realized by Okazaki & Soejima (2001), who achieved the relative accuracy of determination of lattice-parameter changes as high as 1 part in 10^9–10^{10} by extending the Bragg angle from 78° (previous versions) to 89.99° and by elimination of systematic errors due to crystal tilt, crystal displacement, temperature effects and radiation damage.

An original method for the measurement of lateral lattice-parameter variation by means of a double-crystal arrangement with an oscillating slit was proposed by Korytár (1984). This method permitted simultaneous recording of two rocking curves from two locations on a crystal. Precision of 3 parts in 10^7 was reported. The method has been applied for the measurement of growth striations in silicon.

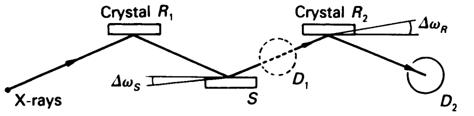


Fig. 5.3.3.11. Schematic representation of the triple-crystal spectrometer developed by Buschert (1965) (after Hart, 1981).

The main disadvantage of double-crystal spectrometers, in their basic form (Fig. 5.3.3.8), is that they cannot be used for measurements on an absolute scale. Combination of the double-crystal arrangement with the system proposed by Bond (1960) makes it possible to recover the origin of the angular scale and thus such an absolute measurement, but the reported precision is rather moderate.

There are two other ways to overcome this difficulty in pseudo-non-dispersive methods: addition either of a third crystal (more accurately, a third reflection) (§5.3.3.7.2) or of a second source (a second beam) (§5.3.3.7.3). Such arrangements require additional detectors. Combinations of both techniques are also available (§5.3.3.7.4).

5.3.3.7.2. *Triple-crystal spectrometers*

Higher precision than that obtained with the double-crystal arrangements (§5.3.3.7.1) can be achieved by means of triple-crystal diffractometers. Arrangements specially designed for the determination of lattice-parameter changes are described by Buschert (1965) and Skupov & Uspeckaya (1975), and reviewed by Hart (1981).

The principle of the triple-axis spectrometer is shown in Fig. 5.3.3.11. The arrangement consists of one standard crystal S, ultimately replaced by the sample under investigation, and two reference crystals R_1 and R_2. The principle of the measurement is as follows. First, the crystals S, R_1, and R_2 are set to their diffraction (peak) positions using two detectors D_1 and D_2. Then the standard crystal S is replaced by the sample and the new peak position is found by means of D_1 when the sample is turned from its original position to its reflecting position. The angle of rotation of the sample $\Delta\omega_s$ depends on the lattice-parameter difference Δd between the sample and the standard. The relation is given by (Hart, 1981)

$$\Delta\omega_s = -\tan\theta\,\Delta d/d. \qquad (5.3.3.40)$$

Next, the second reference crystal R_2 is turned through the angle $\Delta\omega_R$ to its diffracting position, the intensity being controlled with the second detector D_2. From the geometry of the arrangement,

$$\Delta\omega_R = 2\Delta\omega_s. \qquad (5.3.3.41)$$

Because the origin of the ω_s scale is lost during the crystal exchange, this second angle of rotation ($\Delta\omega_R$) is used to determine Δd rather than the first one ($\Delta\omega_s$), by using (5.3.3.41) and (5.3.3.40).

The diffraction profiles observed in the second detector, described by Hart (1981),

$$h(\theta)_R = \int\limits_{-\infty}^{\infty} R^2(\theta')R(\theta'-\theta)\,\mathrm{d}\theta, \qquad (5.3.3.42)$$

are not symmetric but can be as narrow as 0.1–1″, so that a precision of 2 parts in 10^8 is possible.

The main experimental problem here is to adjust the tilts of the crystals. The errors resulting both from the crystal tilts and from the vertical divergence were discussed by Skupov & Uspeckaya (1975).

Triple-crystal spectrometers are often applied as lattice-spacing comparators, when very small changes of lattice parameters ($10^{-8} \le |\Delta d|/d \le 10^{-6}$) are to be detected, in particular for the examination of a correlation between lattice parameter and the dopant or impurity concentration (Baker, Tucker, Moyer & Buschert, 1968). Such an arrangement can also be a very suitable tool in deformation studies, since it allows the separation of the effect of deformation on the Bragg angle from that due to lattice-parameter change (Skupov & Uspeckaya, 1975).

The basis of the accurate lattice-parameter comparison proposed by Bowen & Tanner (1995) is the use of a high-purity silicon standard (*cf.* §5.3.3.9 below) with a well known lattice parameter. To compensate an error that may result from a slight misalignment of crystal planes in relation to the axes of the instrument, the authors recommend a twofold measurement of the diffraction-peak position of the reference crystal (for a given diffraction position and after rotating the specimen holder through 180° about the axis normal to its surface) and a similar twofold measurement of the diffraction-peak position of the sample – after replacing the reference crystal by the sample. The mean positions of the reference crystal and of the sample are used in calculations of the Bragg-angle difference and then of the unknown interplanar spacing. The method uses a standard double-crystal diffractometer fitted with a monochromator (therefore, a third crystal), which provides a well defined wavelength, and with a specimen rotation stage. The measurement is accompanied by a detailed error analysis. The accuracy of absolute lattice-parameter determination as high as a few tens of parts in 10^6, and a much greater relative sensitivity are reported.

By combining a triple-axis spectrometer with the Bond (1960) method, the device can be used for absolute measurements (Pick, Bickmann, Pofahl, Zwoll & Wenzl, 1977). The device described in the latter paper is an automatic triple-crystal diffractometer that permits intensity measurement to be made in any direction in reciprocal space in the diffraction plane with step sizes down to $0.01''$ and therefore can be used for very precise measurements [see also §5.3.3.4.3.2, paragraph (5)].

5.3.3.7.3. *Multiple-beam methods*

The other possibility of recovering the crystal-angle scale in differential measurements with a double-crystal spectrometer (*cf.* §§5.3.3.7.1, 5.3.3.7.2) is to obtain reflections from two crystal planes [for example, from (hkl) and $(\bar{h}\bar{k}\bar{l})$ planes] by means of a double-beam arrangement and to measure them simultaneously.

The second X-ray beam may come from an additional X-ray source (Hart, 1969) or may be formed from a single X-ray source by using a beam-splitting crystal (Hart, 1969, second method; Larson, 1974; Cembali, Fabri, Servidori, Zani, Basile, Cavagnero, Bergamin & Zosi, 1992). In particular, two beams with different wavelengths ($K\alpha_1, K\beta_1$) separated with a slit system can be used for this purpose (Kishino, 1973, second technique). The principle of the double-beam method is shown in Fig. 5.3.3.12. The beams are directed at the first crystal (the reference crystal) so that the Bragg condition is simultaneously fulfilled for both beams, and they then diffract from the second crystal (the specimen). As the second crystal is rotated, a double-crystal diffraction profile is recorded first in one detector and then in the other. The angle $\Delta\theta$ of crystal rotation between the two rocking curves is given by (Baker & Hart, 1975):

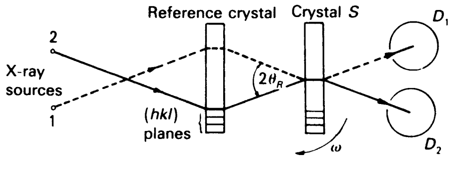


Fig. 5.3.3.12. Schematic representation of the double-beam comparator of Hart (1969).

$$\Delta\theta = (\theta_1 - \theta_2) = \tan\theta\,\Delta d/d. \qquad (5.3.3.43)$$

This formula leads to the lattice-parameter changes Δd.

A double-beam diffractometer can be used for the examination of variations in lattice parameters of about 10 parts in 10^6 within a sample in a given direction. An example was reported by Baker, Hart, Halliwell & Heckingbottom (1976), who used Larson's (1974) arrangement for this task.

The highest reported sensitivity (1 part in 10^9) can be achieved in the double-source double-crystal X-ray spectrometer proposed by Buschert, Meyer, Stuckey Kauffman & Gotwals (1983). The device can be used for the investigation of small concentrations of dopants and defects.

The method can also be applied for the absolute determination of a lattice parameter, if that of the reference crystal is accurately known and the difference between the two parameters is sufficiently small. Baker & Hart (1975), using multiple-beam X-ray diffractometry (Hart, 1969, first technique), determined the d spacing of the 800 reflection in germanium by comparing it with the d spacing of the 355 reflection in silicon. The latter had been previously determined by optical and X-ray interferometry (Deslattes & Henins, 1973; the method is presented in Subsection 5.3.3.8).

In the case of two different wavelengths and diffraction from two different diffraction planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$, the lattice parameter a_0 of a cubic crystal can be determined using the formula (Kishino, 1973)

$$a_0 = \tfrac{1}{2}\{(L\lambda_1)^2 + [(M\lambda_2 - L\lambda_1\cos\theta_{1-2})/\sin\theta_{1-2}]^2\}^{1/2}, \qquad (5.3.3.44)$$

where $L = (h_1^2 + k_1^2 + l_1^2)^{1/2}$, $M = (h_2^2 + k_2^2 + l_2^2)^{1/2}$, and θ_{1-2} is the difference between the two Bragg angles for the specimen crystal, estimated from the measurement of $\Delta\theta = |\theta_{1-2} - \theta'_{1-2}|$ if the difference θ'_{1-2} for the first (reference crystal) is known beforehand. The idea of Kishino was modified by Fukumori, Futagami & Matsunaga (1982) and Fukumori & Futagami (1988), who used the Cu $K\alpha$ doublet instead of $K\alpha_1$ and $K\beta_1$ radiation. Owing to the change, they could use only one detector (Kishino's original method needs two detectors), but a special approach is sometimes needed to resolve two peaks that relate to the components of the doublet. A similar problem of separation of two peaks (recorded by two detectors) is reported by Cembali *et al.* (1992). By introducing a computer simulation of the reflecting curves (using a convolution model), the authors managed to determine the separation with an error of $0.01''$ and to achieve a precision of some parts in 10^7. The same precision is reported by Fukumori, Imai, Hasegawa & Akashi (1997), who introduced a precise positioning device and a position-sensitive proportional counter to their instrument.

As in the other multiple-crystal methods, the most important experimental problem is accurate crystal setting. Larson (1974), as a result of detailed analysis, gave the dependence between the angular separation of two peaks and angles characterizing misalignment of the first and second crystals.

5.3.3.7.4. *Combined methods*

The idea of multiple-beam measurement (§5.3.3.7.3) can be applied to other arrangements that combine the features of the double-beam comparator with those of the triple-crystal spectrometer; there are additional advantages in such a system.

The application of the double-beam technique makes it possible to realize a triple-reflection scheme for comparing lattice parameters on the basis of a double-axis spectrometer. The arrangement proposed by Ando, Bailey & Hart (1978), shown in Fig. 5.3.3.13, consists of a sample and a reference crystal, which are made from the same material but differ in purity (or strain, stoichiometry, vacancy concentration, *etc*). The angular difference $\Delta\theta$ in the Bragg angles of the sample and the reference crystal, θ_S and θ_R, respectively,

$$\Delta\theta = \theta_S - \theta_R, \qquad (5.3.3.45a)$$

is measured as the sample angle $\Delta\omega$ between the double-reflected peak D and the triply diffracted peak T:

$$\Delta\theta = \Delta\omega, \qquad (5.3.3.45b)$$

$$\Delta\omega = \omega_D - \omega_T. \qquad (5.3.3.45c)$$

Assuming that $\Delta\theta$ is entirely due to changes Δd in atomic spacings, the authors use the following relation for determination of the latter:

$$\Delta d/d = -\cot\theta\Delta\theta. \qquad (5.3.3.46)$$

The experimental requirements are simple and inexpensive, owing to simple shapes of both the reference crystal and the sample crystal, so that the measurement can be made quickly. By combining the two reference crystals into a single monolithic reference crystal, excellent stability, difficult to achieve with triple-axis arrangements (*cf.* §5.3.3.7.2), is obtained at the same time. The disadvantage of the method is that it covers a smaller range of lattice parameters than the other double-beam methods (Hart, 1969; Larson, 1974) described in §5.3.3.7.3. A new version of the double-crystal triple-reflection scheme (Häusermann & Hart, 1990) allows one to achieve a precision of 1 part in 10^8 in 2 min of measurement time, which includes the data analysis; 30 min are needed to change the sample. Errors due to the crystal tilt and thermal drifts are considered.

Another example of the triple-reflection scheme realized by means of the double-beam technique has been presented by Kovalchuk, Kovev & Pinsker (1975), who realized the triple-crystal arrangement on the basis of a double-crystal spectrometer by parallel mounting of the two crystals to be compared (the sample and the reference crystal) on one common axis. The advantage of this system is that Bragg angles as high as 80° are available. The device can be applied in studies of the real structure of a single crystal.

High-sensitivity ($\Delta d/d$ up to $\pm 3 \times 10^{-8}$) lattice-parameter-comparison measurement over a wide range of temperatures can be performed by means of the triple-crystal (more accurately, triple-axis) X-ray spectrometer realized by Buschert, Pace, Inzaghi & Merlini (1980). The arrangement (Fig. 5.3.3.14) consists of four crystals. The first is used for obtaining a very wide but extremely parallel exit beam, which is incident on both the standard crystal S and an unknown crystal X, placed side by side on a common axis in the cryostat. The reflected beams from S and X are recorded by partially transmitting detectors DA_2 and DB_2, so that the beams reflect from the third crystal and are detected by the counters DA_3 and DB_3. There is a small, sensitive, angle adjustment to rotate the crystal X with respect to the standard S and it is used to bring the peaks of S and X into approximate coincidence. The angular difference in the peak positions on the third axis is used for determination of lattice-parameter changes from (5.3.3.46), so that

$$\Delta\theta = \Delta\theta_3/2 - \Delta\theta_2, \qquad (5.3.3.47)$$

where $\Delta\theta_2$ and $\Delta\theta_3$ are the differences in peak positions at axes (2) and (3), respectively. The device was used, for example, to study the effect of isotope concentration on the lattice parameter of germanium perfect crystals (Buschert, Merlini, Pace, Rodriguez & Grimsditch, 1988). The measured differences in the lattice parameter, of the order of 1 part in 10^5, were compared with those evaluated theoretically, and a very good agreement was obtained.

Another variant of a multiple-beam arrangement, based on a triple-crystal spectrometer, was proposed by Kubena & Holý (1988). The authors compared the distances of lattice planes in a direction perpendicular to the surface of the sample while studying the growth striations. One well collimated and monochromated beam coming from the first crystal was directed into the sample, and then two beams – one transmitted and one diffracted in the sample – diffracted in the reference crystal. Intensities of the diffracted beams were measured by two detectors. The difference of lattice spacings of the sample and the reference crystal was determined from the difference in positions of respective peaks. The accuracy of the lattice-spacing comparison of 2 parts in 10^7 and the precision of 1 part in 10^7 were obtained.

A four-crystal six-reflection diffractometer (Fewster, 1989) was built to study crystals distorted by epitaxy and defects in nearly perfect crystals. Fig. 5.3.3.15 is a schematic diagram of this device. The two-crystal four-reflection Bartels monochromator (Bartels, 1983) defines a narrow reflectivity profile. The analyser selects the angular range diffracted from the sample. The device may be used for recording both near-perfect rocking curves from distorted crystals (when rotations of the sample and the analyser are coupled) and a diffraction-space map for studying the diffuse scattering (when the two rotations are

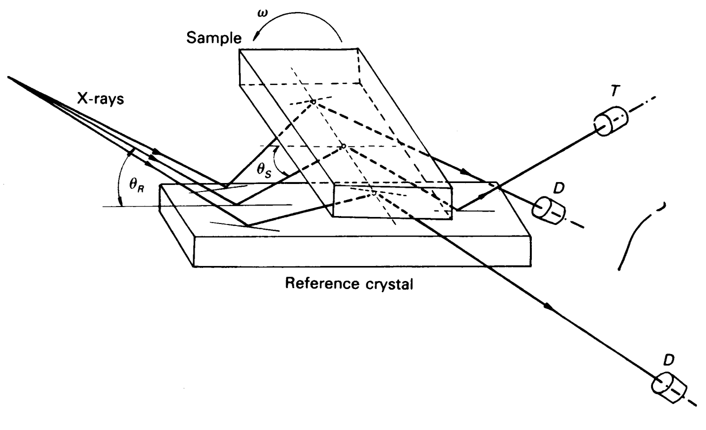


Fig. 5.3.3.13. The double-axis lattice-spacing comparator of Ando, Bailey & Hart (1978); a triple-diffracted beam is used.

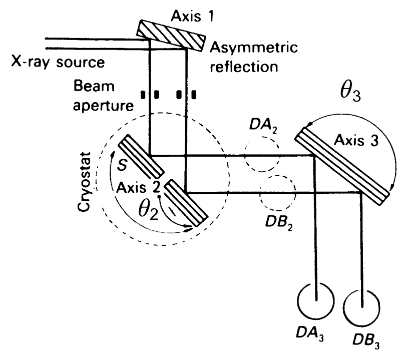


Fig. 5.3.3.14. Schematic representation of the double-beam triple-crystal spectrometer of Buschert *et al.* (1980).

uncoupled). Various applications of such high-sensitivity multiple-crystal X-ray spectrometers for reciprocal-space mapping and imaging (topography), which are outside the scope of the present paper, are reviewed by Fewster (1993, and references therein).

As was shown a few years later by Fewster & Andrew (1995), the device can also be used for absolute lattice-parameter measurements of single-crystal and polycrystalline materials with a relative accuracy of a few parts in 10^6. The authors checked the angular resolution and the sample centring of their instrument, and discussed systematic errors due to refraction, the Lorenz and polarization factor, the diffracting-plane tilt and the peak-position determination.

5.3.3.8. *Optical and X-ray interferometry – a non-dispersive technique*

The accuracy of an absolute measurement can be improved, in relation to that obtained in traditional methods (*cf.* Subsection 5.3.3.5), either if the wavelength of the radiation used in an experiment is known with better accuracy [*cf.* equation (5.3.1.3)] or if a high-quality standard single crystal is given, whose lattice spacing has been very accurately determined (Baker & Hart, 1975; mentioned in §5.3.3.7.3). The two tasks, *i.e.* very accurate determination of both lattice spacings and wavelengths in metric units, can be realized by use of combined optical and X-ray interferometry. This original concept of absolute-lattice-spacing determination directly in units of a standard light wavelength has been proposed and realized by Deslattes (1969) and Deslattes & Henins (1973).

The principle of the method is presented in Fig. 5.3.3.16. The silicon-crystal X-ray interferometer is a symmetric Laue-case type (Bonse & te Kaat, 1968). The parallel translation device consists of the stationary assembly (*a*) formed by two specially prepared crystals, and a moveable one (*b*), to which belongs the third crystal. One of the two mirrors of a high-resolution Fabry–Perot interferometer is attached to the stationary assembly and the second to the moving assembly. A stabilized He–Ne laser is used as a source of radiation, the wavelength of which has been established relative to visible standards. The first two crystals produce a standing wavefield, which is intercepted by the third crystal, so that displacement of the third crystal parallel to the diffraction vector (as suggested by the large arrow) produces alternate maxima and minima in the diffracted beams, detected by X-ray detector (*c*). Resonant transmission maxima of the optical interferometer are detected simultaneously by the photomultiplier indicated at (*d*). Analysis of the fringes (shown in Fig. 5.3.3.17) is the basis for the calculation of the lattice-spacing-to-optical-wavelength ratio (d/λ), which is given by

$$\frac{2d}{\lambda} = \frac{n}{m}\frac{\cos\alpha}{\cos\beta}, \qquad (5.3.3.48)$$

where n and m are the numbers of optical and X-ray diffraction fringes, respectively, and α and β are the measured angular deviations of the optical and X-ray diffraction vectors from the direction of motion. The measurements are carried out in two steps. First, the lattice parameter of silicon along the [110] crystallographic direction was measured in the metric system, independently of the X-ray wavelength used in the experiment. As the next step, a specimen of known lattice spacing, treated as a reference crystal, was used for the accurate wavelength determination of Cu $K\alpha_1$ and Mo $K\alpha_1$. Accuracy better than 1 part in 10^6 was reported (see Section 4.2.2).

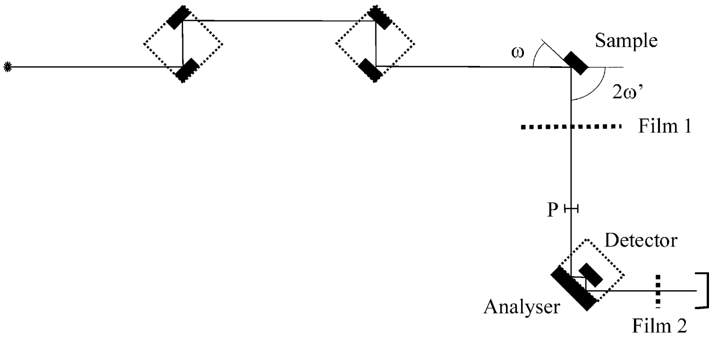


Fig. 5.3.3.15. The geometry of the diffractometer used by Fewster & Andrew (1995). The scattering angle, $2\omega'$, is the fundamental angle for determination of the interplanar spacing and P is the analyser-groove entrance.

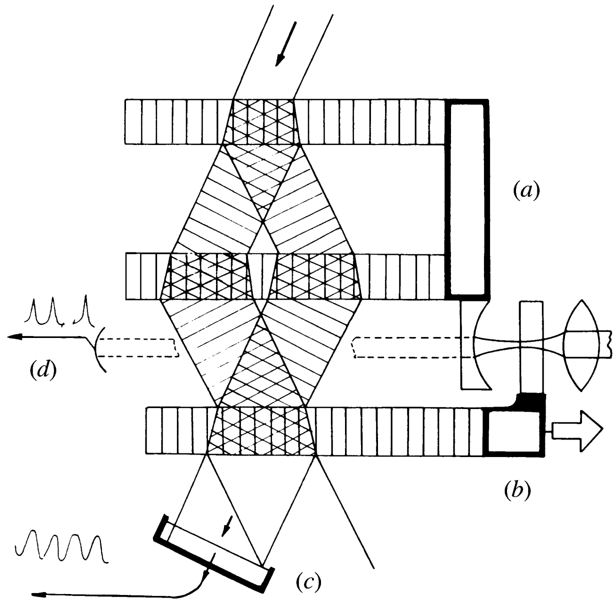


Fig. 5.3.3.16. Optical and X-ray interferometry. Schematic representation of the experimental set-up (after Deslattes & Henins, 1973; Becker *et al.*, 1981).

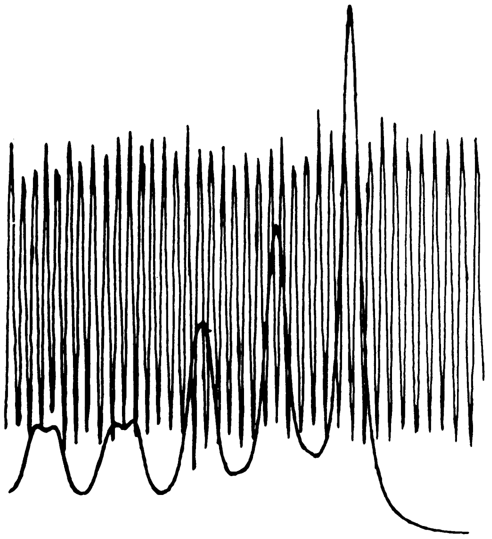


Fig. 5.3.3.17. Portion of a dual-channel recording of X-ray and optical fringes (Deslattes, 1969).

The above experiment was a turning point in accurate measurements of both wavelengths and lattice parameters. Owing to the idea of Deslattes & Henins, it became possible to determine the wavelength in nanometres rather than in troublesome XU or Å* units (*cf.* §4.2.1.1.1). However, the results obtained and the method itself needed verification and some adjustments. These were performed by another group of experimenters with a similar but different measuring device (Becker, Seyfried & Siegert, 1982, and references therein; Siegert, Becker & Seyfried, 1984).

5.3.3.9. *Lattice-parameter and wavelength standards*

An extended series of measurements performed by means of the optical and X-ray interferometry (*cf.* §5.3.3.8) led, among other things, to evaluation of the lattice spacing of a highly perfect silicon sample WASO 4.2.A (Becker *et al.*, 1981). Such silicon samples may be used as reference crystals in successive lattice-spacing comparison measurements – with a double-source double-crystal spectrometer (Windisch & Becker, 1990), for example. The latter measurements provided new excellent lattice-spacing standards (WASO 9, for example) of the well known lattice-parameter values. As shown by the authors, the differences in lattice parameters of different samples of float-zone silicon (due to oxygen or carbon content) were not greater than a few parts in 10^8. Finally, the lattice parameter of silicon, $a = 5.43102088(16)$ Å, has been accepted as the atomic scale length standard (Mohr & Taylor, 2000).

Another reference material reported is crystals of pure rhombohedral corrundum (α-Al_2O_3), *i.e.* of ruby or sapphire (Herbstein, 2000, and references therein; Shvyd'ko *et al.*, 2002).

With silicon standards, measurements or remeasurements of $K\alpha_{1,2}$ and/or $K\beta_{1,3}$ X-ray emission lines and absolute wavelength determinations of most of the 3*d* transition metals (Cr, Mn, Fe, Co, Ni and Cu) have been performed [Härtwig, Grosswig, Becker & Windisch, 1991; Hölzer, Fritsch, Deutsch, Härtwig & Förster, 1997 (see §4.2.2)].

The standard crystals may also be used for determination of such physical quantities as the Avogadro constant (Deslattes *et al.*, 1994; Deslattes, Henins, Schoonover, Caroll & Bowman, 1976). The single accurate wavelength values, on the other hand, may be used both in simple measurements of lattice parameters [based directly on the Bragg law, equation (5.3.1.1)] and for accurate scaling of the wavelength spectra, in order to use them, for example, in high-accuracy lattice-parameter measurements based on complete convolution models [*cf.* §5.3.3.3.1, point(ii)].

Unlike the X-rays emitted from an X-ray tube, for which the spectral line and the characteristic wavelength are known, there are no such characteristic features in synchrotron radiation. Therefore, special energy-selective monochromators should be applied in relative lattice-spacing measurements using synchrotron radiation. Obaidur (2002) proposes two measurement schemes, using two types of high-resolution channel-cut monolithic monochromators. The first scheme (see Fig. 5.3.3.18) is a modification of the Bond method. The second one (see Fig. 5.3.3.19) uses the simultaneous Bragg condition for the indices (5,1,3), $(\bar{5},\bar{1},\bar{3})$, (1,5,3) and $(\bar{1},5,\bar{3})$. The lattice-spacing differences in Si wafers were determined in the sub-parts in 10^6 range of 0.6 parts in 10^6 (in the first scheme) and of 0.2 parts in 10^6 (second scheme).

Recently, a new atomic scale wavelength standard was proposed by Shvyd'ko *et al.* (2000), instead of the wavelength of the Cu $K\alpha_1$ emission line or of the lattice parameter of a silicon standard. It is the wavelength, λ_M, of the ^{57}Fe Mössbauer radiation, *i.e.* of γ radiation of natural linewidth from nuclear transitions. It has been measured to the sub-parts in 10^6 accuracy: $\lambda_M = 0.86025474(16)$ Å (relative accuracy 0.19 parts in 10^6). Its advantage, in relation to the previous standards, is the high spectral sharpness of the Mössbauer radiation of 3.5×10^{-13} in relative units, which makes its wavelength λ_M extremely well defined. This standard wavelength value, which lies a little outside of scope of the present review (X-ray methods), was next used for the lattice-parameter determination of sapphire single crystals with a relative accuracy of about 0.5 parts in 10^6 (Shvyd'ko *et al.*, 2002). Fig. 5.3.3.20 is a diagram of the measurement arrangement.

5.3.4. Final remarks

Let us review the most important problems concerning accurate and precise lattice-parameter determination.

The first, commonly known, requirement for obtaining the highest accuracy and precision is the use of high-Bragg-angle reflections. The tendency to obtain, record, and use in calculation such reflections can be met in rotating-crystal cameras in which Straumanis mounting is applied (Farquhar &

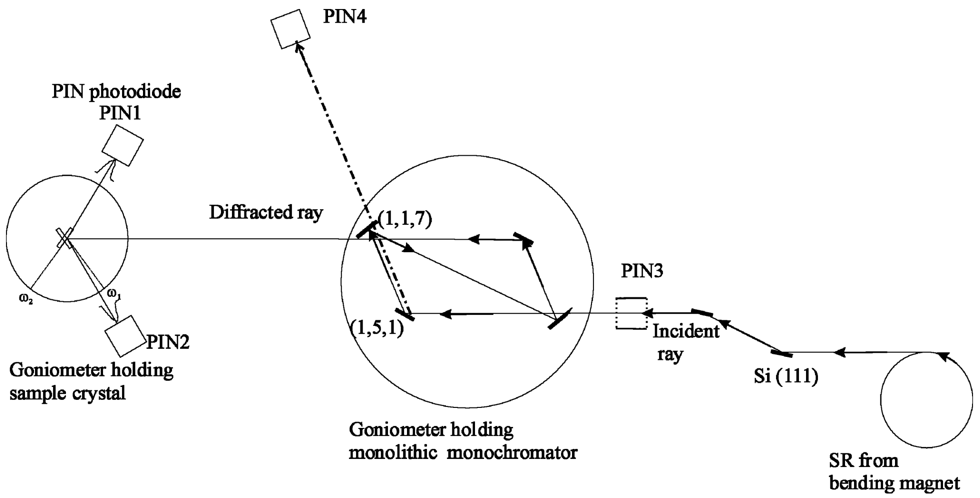


Fig. 5.3.3.18. Synchrotron radiation, SR, from the bending magnet incident on the Si(111) double-crystal monochromator and, after four reflections from the monolithic monochromator (0.1410 nm), impinges on sample Si(444). Two diffractions are recorded at the photodiode detectors, PIN1 and PIN2. The ω_1 and ω_2 values of the crystal positions are recorded using a Heiden height encoder.

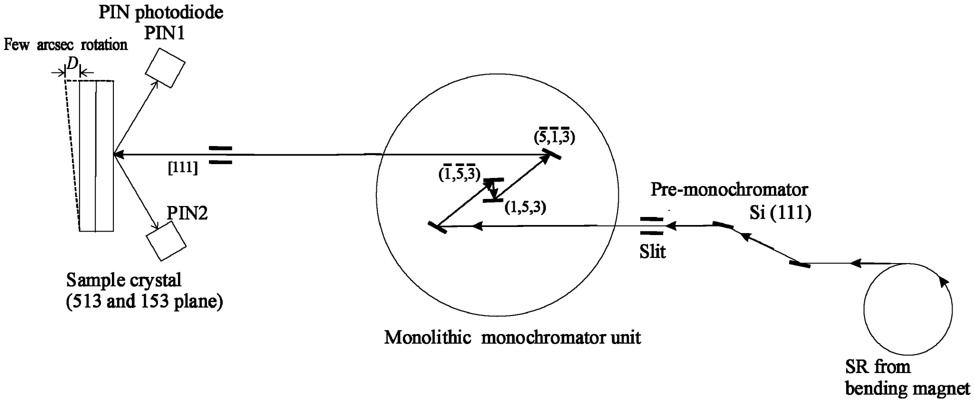


Fig. 5.3.3.19. Synchrotron radiation, SR, from the bending magnet incident on the Si(111) double-crystal monochromator and, after four reflections from the monolithic monochromator (0.1612 nm), impinges on sample Si(153). Two diffractions are recorded at the photodiode detectors, PIN1 and PIN2. The differences between the two peaks' D values are recorded using a Heiden height encoder.

Lipson, 1946; Popović, 1974), in the Weissenberg method (the use of zero-layer photographs), in multiple-exposure cameras (Glazer, 1972; Popović, Šljukić & Hanic, 1974), in standard and special diffractometers (Kobayashi, Yamada & Nakamura, 1963), in double-crystal arrangements with white X-radiation (Okazaki & Kawaminami, 1973*a*,*b*; Okazaki & Ohama, 1979; Ohama, Sakashita & Okazaki, 1979; Okazaki & Soejima, 2001), and in the triple-reflection scheme realized by means of the double-beam technique, proposed by Kovalchuk, Kovev & Pinsker (1975).

Increasing the θ value, in the case of photographic cameras or counter diffractometers, not only reduces the value of $\cot\theta$ in the formulae describing accuracy and precision, but also decreases several systematic errors proportional to $\cos\theta$, $\cos^2\theta$, $\cot\theta$ or $\cot^2\theta$ (Kheiker & Zevin, 1963; Wilson, 1963, 1980). To find the minimum total systematic error, which would occur for $\theta = 90^\circ$ (not attainable in practice), extrapolation of the results is used (Farquhar & Lipson, 1946; Weisz, Cochran & Cole, 1948; Smakula & Kalnajs, 1955; Kobayashi, Yamada & Azumi, 1968; Pierron & McNeely, 1969).

The problem of the choice of suitable reflections for the measurement, calculation, and reduction of systematic errors could be generalized. Not only are such reflections for which θ values are close to 90° desired but also those for which ν tends to 90° in rotating-crystal cameras (Umansky, 1960), high-order Kossel lines in divergent-beam techniques, axial or non-axial reflections in counter-diffractometer methods, *etc.* Zero-layer reflections in Weissenberg photographs or in two-circle ('Weissenberg') diffractometers are preferable to upper-layer ones, because they are less affected by crystal misalignment (Clegg & Sheldrick, 1984) and a larger range of reciprocal-lattice points can be recorded (Luger, 1980); they are not sufficient, however, for the determination of all the lattice parameters in the less-symmetric crystal systems.

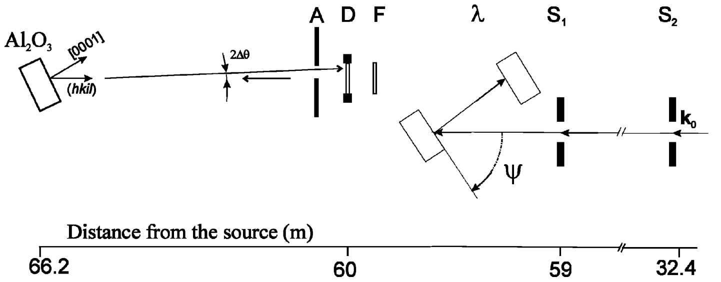


Fig. 5.3.3.20. Experimental set-up for measuring lattice parameters. X-rays after a high-heat-load monochromator (not shown) pass through the vertical slits S_1 and S_2 at a distance of 26.6 m. λ is a 'λ-meter'; F is a ^{57}Fe foil used as a source of the Mössbauer radiation of high brightness; D is a semi-transparent avalanche photodiode with 0.7 ns time resolution; Al_2O_3 is a sapphire single crystal in a furnace on a four-circle goniometer.

Use of the orientation matrix makes possible accurate crystal setting for an arbitrary reflection and identification of recorded reflections not only in the case of the automated four-circle diffractometer or the two-circle diffractometer but also in photographic methods.

For obtaining high accuracy of lattice-parameter determination, systematic errors depending on the radiation, the crystal, and the technique should be known, evaluated, and reduced or corrected. As a rule, those systematic errors whose part in the total systematic error is the most important should be removed first. Looking at the development of the X-ray diffraction techniques, the following remarks can be made.

As far as the photographic methods are concerned, the errors due to the means of recording (film shrinkage, uncertainty of measurement of distances on the film) and camera construction (radius in the moving-crystal methods and the source-to-film distance in divergent-beam techniques) play a major role. They can be reduced to some extent by using the Straumanis mounting or the ratio method, or the resolved doublet $K\alpha_{1,2}$. Various methods have been introduced for reducing the error due to the source-to-film distance in divergent-beam techniques.

In counter-diffractometer methods, which give more accurate determinations of the Bragg angles and intensities, several instrumental and physical factors should be taken into account (Kheiker & Zevin, 1963; Wilson, 1963, 1980; Berger, 1984, 1986*a*; Härtwig & Grosswig, 1989). The effects of some can be diminished by the use of Soller slits (Berger, 1984) and the effects of most can be reduced by the Bond (1960) geometry, in its basic form or in its various modifications (Kheiker, 1973; Mauer *et al.*, 1975; Hubbard & Mauer, 1976; Wołcyrz, Pietraszko & Łukaszewicz, 1980; Kudo, 1982; Lisoivan, 1982; Grosswig *et al.*, 1985), in particular in combination with double- or triple-crystal spectrometers (Kurbatov, Zubenko & Umansky, 1972; Godwod, Kowalczyk & Szmid, 1974; Hart & Lloyd, 1975; Sasvári & Zsoldos, 1980; Fewster, 1982; Pick *et al.*, 1977; Obaidur, 2002). Another arrangement giving a partial reduction of systematic errors is that proposed by Renninger (1937) and developed by Post (1975) and Kshevetsky *et al.* (1979, 1985), in which multiple-diffraction phenomena are applied. In most one- or double-crystal asymmetric spectrometers, the uncertainty of the origin of the angular (ω) scale is the important problem, which can be resolved by introducing either the Bond (1960) symmetrical arrangement (combinations mentioned above) or an additional instrumental axis (or axes) for obtaining a multiple-crystal arrangement (Buschert, 1965; Skupov & Uspeckaya, 1975; Hart, 1981), or a second beam, used in multiple-beam methods (Hart, 1969; Kishino, 1973; Larson, 1974; Baker & Hart, 1975; Buschert *et al.*, 1983) or in various combined methods (Ando, Bailey & Hart, 1978; Kovalchuk, Kovev & Pinsker, 1975; Buschert *et al.*, 1980; Fewster, 1989; Shvyd'ko *et al.*, 2000; Obaidur, 2002).

The other important problem in single-crystal methods, in the case when high accuracy is desired, is the misalignment of the crystal(s) and some elements of the device. The errors due to the misalignment can be reduced to some extent experimentally, if a respective dependence is known (Baker, George, Bellamy & Causer, 1968; Burke & Tomkeieff, 1968, 1969; Bowen & Tanner, 1995), or by calculation of the exact correction (Burke & Tomkeieff, 1968, 1969; Gruber & Black, 1970; Filscher & Unangst, 1980; Larson, 1974) if the inclinations of the beam(s) and the crystal(s) can be determined (Halliwell, 1970; Nemiroff, 1982).

Along with an increase in the accuracy of the θ-angle determination, the error due to the wavelength determination becomes more important and a correction for the refraction should be introduced [the problem has been more intensively argued by Hart (1981, Section 2.3)]. Among others, measurement performed in the case of the Kossel method and divergent-beam techniques can be strongly affected by uncertainty of the wavelength, especially when the exact value of the wavelength is to be determined from the experiment. The combination of X-ray and optical interferometry (Deslattes, 1969; Deslattes & Henins, 1973; Becker *et al.*, 1981), the use of new lattice-parameter standards (Hölzer *et al.*, 1997), and new X-ray or γ-ray sources and wavelength standards (Shvyd'ko *et al.*, 2000; Obaidur, 2002) gives new possibilities for very accurate lattice-spacing measurements, up to the sub-parts in 10^6 range.

The accuracy of the method can be evaluated theoretically taking into account and estimating the errors that have not yet been eliminated. In the case of some θ-dependent errors, the maximum-likelihood method proves useful for this task (Beu, Musil & Whitney, 1962). Sometimes computer simulation is used to estimate some errors difficult to express in an analytical form (Hubbard & Mauer, 1976; Urbanowicz, 1981*b*; Berger, 1986*a*; Härtwig & Grosswig, 1989). A more objective test of the accuracy would be an inter-laboratory comparison, like that reported by Parrish (1960) many years ago. Usually, the authors introducing new methods, techniques or devices try to compare the results of their lattice-parameter determination with those obtained by other experimenters (Batchelder & Simmons, 1965, p. 2868; Hubbard, Swanson & Mauer, 1975, p. 46; Hubbard & Mauer, 1976, p. 2; Łukaszewicz *et al.*, 1976, p. 70; 1978, p. 566; Lisoivan, 1982, p. 94; Grosswig, Härtwig, Alter & Christoph, 1983, p. 506; Chang, 1984, p. 254; Härtwig, Bąk-Misiuk, Berger, Brühl, Okada, Grosswig, Wokulska & Wolf, 1994; Fewster & Andrew, 1995, p. 455; Herbstein, 2000).

In view of the new achievements in high-accuracy absolute lattice-parameter measurements, such as the results reviewed in §§5.3.3.8 and 5.3.3.9, and the accurate error analysis [Härtwig & Grosswig (1989); §5.3.3.4.3.2, point (7)], Härtwig, with his co-workers, initiated and organized an interlaboratory comparison of various 'traditional' methods and techniques, including the Bond method (*cf.* §5.3.3.4.3), the 'Soller-slit' method (§5.3.3.4.2) and the photographic multiple-diffraction (*Umweganregung*) method (§5.3.2.4.2). In all measurements performed, a common silicon standard (WASO 9, mentioned above) of accurately known lattice parameter was used as the specimen, so it was possible to check independently the validity of all corrections introduced for systematic errors. As shown by Härtwig, Bąk-Misiuk, Berger, Brühl, Okada, Grosswig, Wokulska & Wolf (1994), the agreement of their independent results was not worse than 3 parts in 10^6. The quantity defines the present-day possibilities of accurate 'dispersive' methods.

Herbstein (2000) concluded, 'there has been little improvement in claimed precision over the past 40–60 years', but his analysis relates to widely used 'dispersive' methods [including the Bond (1960) method] rather than to present-day high-precision comparison methods, which are also used for absolute measurements.

For obtaining high precision, a monochromatic and well collimated X-ray beam is desired. The first requirement can be fulfilled by using a filter or monochromator, the second can be satisfied by introducing a point source and a choice of collimation parameters, and both can be accomplished by introducing one or more additional crystals. It is not necessary for a well collimated beam to be very narrow if local measurements in selected small areas of the specimen are not the object of the experiment. The use of a large, parallel X-ray beam may be advantageous in some comparative measurements (Buschert, Pace, Inzaghi & Merlini, 1980).

Very high accuracy and high-precision measurements are, however, expensive; they need additional instrumental axes and detectors, and sometimes additional sources. Relatively simple divergent-beam techniques (photographic recording, stationary crystal) require fine X-ray sources (an electron microscope or an electron-beam probe) if high precision is to be attained.

Some authors have managed to reduce the cost of the experiment using simpler equipment. An example may be the triple-reflection scheme realized by the use of a double-axis spectrometer proposed by Ando, Bailey & Hart (1978) and Häusermann & Hart (1990). An additional advantage of the device is excellent stability.

Apart from the magnificent development of measuring techniques, an increasing role of mathematics is noticeable in contemporary papers. Matrix algebra is used for description of the crystal orientation in relation to the instrumental axes. Mathematical interpretation of the results is a very important part of the measurement, in particular in multiple-diffraction methods, both divergent-beam photographic and collimated-beam counter diffractometric. Syntheses of diffraction profiles are easily done with the aid of a computer. Algebraic and geometrical considerations make it possible to calculate proper corrections for systematic errors. Statistical methods give a tool for estimating and increasing the precision, in particular by means of least-squares refinement, and also for testing the hypothesis of 'no remaining systematic errors'. Commonly used computers are useful in numerous calculations and in controlling automatic devices.

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