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:

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

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.

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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:

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

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, 1981a; Grosswig, Jäckel & Kittner, 1986; Gałdecka, 1993a,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, 1981a), 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

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

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 (λ_{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

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