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

$$\boldsymbol{A}^*\boldsymbol{A}^{*\prime} = \boldsymbol{U}\cdot\boldsymbol{U}', \tag{5.3.3.2}$$

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:

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

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

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

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

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.

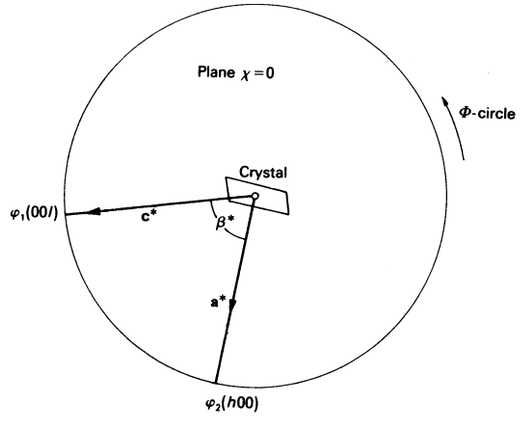

Fig. 5.3.3.1. Determination of reciprocal-lattice angles on the θ circle (after Luger, 1980).

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,

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

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

where

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

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

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:

$$W_{hkl} = 1/\sqrt{\omega_{hkl}}, \tag{5.3.3.5}$$

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*

* 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

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

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.*

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

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

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

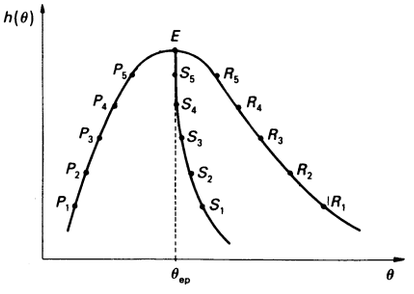

Fig. 5.3.3.2. The extrapolated-peak procedure (after Bearden, 1933).

(4) the extrapolated peak or the midchord peak, introduced by Bearden (1933) – the point θ_{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 θ_{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.*

$$\sigma^2(h) = h, \tag{5.3.3.9}$$

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:

$$h(\theta) = Hv[x(\theta)], \tag{5.3.3.10}$$

where

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

are standardized angle values and

$$v(x) = h/H \tag{5.3.3.10b}$$

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:

$$\sigma^2(\theta_0) = F\frac{\omega_h^2}{I_p T}, \tag{5.3.3.11}$$

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:

$$T = n\Delta t, \tag{5.3.3.12}$$

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

$$h = I\Delta t, \tag{5.3.3.13}$$

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

$$H = I_p\Delta t, \tag{5.3.3.13a}$$

the dependence (5.3.3.11) can be presented as

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

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

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

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:

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

where X is the standardized scanning range

$$X = 2\Omega/\omega_h \tag{5.3.3.16*a*}$$

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

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

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):

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

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*):

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

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

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

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:

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

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

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

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,

$$v = \frac{1}{1 + x^2}, \tag{5.3.3.19}$$

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:

$$d_1 = d_2 = 0.565\, L\omega_\lambda, \tag{5.3.3.20}$$

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 $h_C(\theta)$.

references