(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