Note that since $(N^{(k)}+N^{(k)}) \bmod 2\pi$ is a zero vector, the phase set $P[P(\bar{\varphi}+N^{(k)})+N^{(k)}]$ is expected to be nearly identical to $\bar{\varphi}$. Analogously for $N^{(k)}=(N^{(i)}+N^{(j)}) \bmod 2\pi$ we can expect $P(\bar{\varphi}+N^{(k)})$ to be very close to $P[P(\bar{\varphi}+N^{(i)})+N^{(j)}]$ or to $P[P(\bar{\varphi}+N^{(j)})+N^{(i)}]$. It is useful to take heed of this fact in the implementation of step 5 of the algorithm and to generate sets of shifting vectors that are not only different but also 'independent'.

5. Application

The decomposition scheme presented may be simply incorporated into the direct-methods routines. It was verified with real structures by the program system *TRYMIN*90. This system and a detailed definition of the form of the function $\bar{G}$ used here (the so-called centrosymmetric approximation) is presented by Kříž (1992). The form of centrosymmetric approximation is derived from Cochran's (1955) distribution. Examples (of real structures) show that there are a number of independent shifting vectors that change about 50% of phases and keep about 90% of triplet invariants unchanged. Further numerical experiments show that we can expect similar results for other combinations of phases, for example, the traditional tangent formula or quartets.

References

COCHRAN, W. (1955). *Acta Cryst.* **8**, 473-478.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B**26**, 274-285.
KŘÍŽ, V. (1989). *Acta Cryst.* A**45**, 456-463.
KŘÍŽ, V. (1992). In preparation.
WHITE, P. S. & WOOLFSON, M. M. (1975). *Acta Cryst.* A**31**, 53-56.
YAO, J. (1981). *Acta Cryst.* A**37**, 642-644.

Acta Cryst. (1993). A**49**, 106-115

Description and Peak-Position Determination of a Single X-ray Diffraction Profile for High-Accuracy Lattice-Parameter Measurements by the Bond Method. I. An Analysis of Descriptions Available

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Abstract

The accuracy of lattice-parameter measurements is defined by the actual error of Bragg-angle determination. The total error in the angular position determined (peak position) - corresponding to the Bragg angle - depends on the experiment itself (physical and geometrical aberrations) and on the method of calculation used. The aim of this paper is to find the best method of approximation of the measurement data to ensure a given accuracy - here, 1 part in 10^6 - with the assumption that the technique and the method used for correcting the aberrations allow this accuracy. Considering some disadvantages of interpolation and approximation with polynomials, commonly used in practice, it is suggested the calculations are based on a model of the measured diffraction profile. In the present paper (paper I), desired properties of such a model are discussed. Various possible descriptions of the diffraction profile - including popular 'shape functions' widely used in practice - are collected in a unified and standardized form and classified and analysed, with account taken of (i) physical aspects, (ii) mathematical aspects, (iii) statistical aspects and (iv) practical aspects (applications), with premises resulting from the measurement method, the Bond method [Bond (1960). *Acta Cryst.* **13**, 814-818]. A special emphasis has been put on the best description of the moderate asymmetry characterizing the reflections from nearly perfect single crystals and on statistical properties of the model.

1. The problem

1.1. *Precision and accuracy of the lattice-spacing determination*

To ensure a given accuracy $|\Delta d|/d$ of the lattice-parameter determination, the error, $d\theta$, in the Bragg angle, θ, cannot exceed that resulting from differentiation of the Bragg law, *i.e.*

$$|d\theta| \leq (|\Delta d|/d) \tan\theta. \quad (1)$$

For example, to achieve the accuracy of 1 part in 10^6 of the d_{111}-spacing measurement of a silicon single crystal when Cu $K\alpha$ radiation is used, the error in θ

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must be less than 1″ ($3\times10^{-4\circ}$) for the 444 interference ($\theta=78.31°$) but cannot exceed 0.05″ ($2\times10^{-5\circ}$) for the 111 interference ($\theta=14.25°$).

In brief, the actual (total) error $d\theta$ consists of a component, $d\theta_E$, dependent on the experiment (physical and geometrical aberrations) and of a component, $d\theta_c$, dependent on the method of calculation used for interpretation of the measurement data. The latter component alone is the subject of the present analysis, with the provision that the measurement technique and the method used would allow a desired accuracy, *i.e.* $|d\theta_E|\ll|d\theta|$, so the problem is then to find a suitable method of calculation that would make the achievement of the desired accuracy possible, *i.e.* for which

$$|d\theta_E+d\theta_c|\leq(|\Delta d|/d)\tan\theta. \quad (2)$$

In (2) the additivity of the errors $d\theta_E$ and $d\theta_c$ is assumed; this is an approximation commonly used in practice. It will thus also be used in the present paper. Another approach to the problem will be discussed in § 6 of paper II (Gałdecka, 1993).

In the Bond (1960) method the Bragg angle θ is determined from a series of counts $h_1,\dots h_n$, recorded in the region of maximum intensity, as a function of angular values $\omega_1,\dots\omega_n$. The measured diffraction profile is usually approximated by an analytical function using the method of least squares and then the peak position ω_P, *i.e.* the position for which the function achieves its maximum, is calculated. Measurements of intensity as a function of the angle ω of rotation of the specimen are made twice, for two diffracting positions of the specimen, ω_{P1} and ω_{P2}, symmetrical in relation to the direction of the primary beam. The Bragg angle is then calculated from the formula:

$$\theta=|90°-|\omega_{P1}-\omega_{P2}|/2|. \quad (3)$$

The twofold measurement causes aberrations (systematic errors) that are typical for other arrangements (such as zero error, eccentricity and absorption) but which are eliminated experimentally in the Bond (1960) arrangement, while other aberrations (due to refraction, Lp factor and axial divergence, for example) must be removed by calculating appropriate corrections (for a complete list of such corrections see Härtwig & Grosswig, 1989; Gałdecka, 1992).

1.2. *The need for a model of the recorded diffraction profile*

Let us consider now the total error connected with calculations, $d\theta_c$ [(2)]. It consists of a statistical part $\delta\theta_c$ and a systematic part, the bias, $\Delta\theta_c$,

$$d\theta_c=\Delta\theta_c+\delta\theta_c. \quad (4)$$

Later, since subsequent formulae will relate solely to the method of calculation, we shall dispense with the index *c*. The twofold measurement used (*cf.* § 1.1) leads to a reduction of the standard deviation $\sigma(\theta)$ of the Bragg angle determined, in relation to the standard deviation $\sigma(\omega_P)$ of a single peak position,

$$\sigma(\theta)=2^{1/2}\sigma(\omega_P)/2, \quad (5)$$

where $\sigma(\omega_P)\simeq\sigma(\omega_{P1})\simeq\sigma(\omega_{P2})$, but it does not lead to a reduction of a possible bias that might result from an incorrect model of the diffraction profile used in calculations, since the two profiles recorded are symmetrical to each other in relation to $\omega=0$. Thus the two biases would sum to

$$|\Delta\theta|=|\Delta\omega_{P2}+\Delta\omega_{P1}|/2=|\Delta\omega_P|, \quad (6)$$

so, in terms of absolute values, the bias of the Bragg-angle determination is approximately equal to the bias $\Delta\omega_P$ of the peak-position determination.

There are two basic purposes of approximation of the measurement data by a continuous analytical function for accurate peak-position determination:

(*a*) reduction of the statistical errors of observations (recorded counts);

(*b*) calculation of the expected (unbiased) values of intensities at intermediate points between measurement points.

When the total error in the peak position,

$$d\omega_P=\Delta\omega_P+\delta\omega_P, \quad (7)$$

is to be reduced, two different approaches are used in relation to its statistical part $\delta\omega_P$ and its systematic part $\Delta\omega_P$. It is relatively easy to reduce the statistical error by increasing (i) the number of measurement points, (ii) the number M of repetitions of a given measurement, (iii) the number of counts recorded (by increasing the primary-beam intensity or the counting time) or (iv) by a suitable choice of collimation conditions (Urbanowicz, 1981*a*, *b*). The bias $\Delta\omega_P$ is independent of the above factors and, if neither recognized nor corrected, remains in the results obtained. The essential problem for the high-accuracy lattice-parameter determination is therefore to find the proper model of the diffraction profile to provide the results free from any bias, or to estimate and reduce the bias, and, more generally, to find criteria of correctness of a model considered.

From the point of view of applications, what is needed is a possibly simple and universal function capable of approximating an arbitrary collection of measurement data. It is, however, clear that the function cannot be an interpolative function and that even rational spline functions, used succesfully in Rietveld refinement (Hepp & Baerlocher, 1988), were useless for the present task. Such descriptions, based on actual rather than expected values of intensity, are not likely to satisfy requirements (*a*) and (*b*) above. The function to be used for accurate measurements must represent a model of the diffraction profile, which, according to suggestions of Oatley & French

(1982), who used the Bayesian three-stage regression model, should have well defined mathematical and statistical properties.

A polynomial, thought of as an expansion in a power series about the peak of an unknown function describing the real diffraction profile, could be, in principle, treated as a 'model'. However, assumptions that would accompany the expansion (which is also an element of the model) are difficult to reconstruct in practice. This causes the results of polynomial approximation to be strongly dependent on the scanning range and the degree of the polynomial (*cf.* Wilson, 1965; Thomsen & Yap, 1968; Grosswig, Jäckel & Kittner, 1986). To obtain accurate results, the scanning range and/or the degree of the polynomial should be carefully selected, based on reasonable criteria resulting from a statistical model of recorded counts (discussed in § 2.6 below). Thus, polynomial approximation alone cannot be treated as an objective and universal method. We shall return to the problem in paper II (Gałdecka, 1993). A further disadvantage of polynomials, in various applications, is that, in contrast with some 'shape functions', their coefficients have neither a physical meaning nor a simple connection with the parameters of the measured profile (*i.e.* the peak coordinates and the half-widths).

On the other hand, there is a variety of rather simple 'shape functions' used for an analysis of the diffraction profiles recorded both in powder diffractometry (reviewed by Young & Wiles, 1982) and in single-crystal diffractometry (Urbanowicz, 1981*a*; Oatley & French, 1982). But can the popular shape functions be treated as models of the diffraction profile? Are these descriptions capable of introducing new qualities to the problem? What criteria should be used to select the best function?

In order to answer the questions it is useful to consider some basic physical premises to ensure objectivity and generality of description. Furthermore, as the function considered should serve as a tool for calculations, it is advisable to analyse its important mathematical and computational features. For final evaluation of correctness of description, some statistical criteria are needed, based on a statistical model of recorded counts. Let us discuss the various aspects of descriptions available.

2. Descriptions of the diffraction profile

2.1. *Assumptions*

Since present considerations relate to the Bond (1960) method, the following prerequisites and assumptions will be taken into account.

(1) An ω scan is used rather than a 2θ or $\omega/2\theta$ scan, as already mentioned in § 1.1 above. This implies a constant background (Alexander & Smith, 1962; Kheiker, 1969). Since, for the purpose discussed, the diffraction profile is recorded within a limited scanning range (not wider than, say, two half-widths), it is justifiable to assume that the function used as a model of the diffraction profile will describe the profile together with its background.

(2) Separate diffraction profiles are recorded rather than the whole diffraction pattern (used, for example, in powder diffraction). The dependence of parameters of the profile (such as the half-width or a coefficient of asymmetry) on the Bragg angle is thus not important in the appropriate descriptions.

(3) Recorded diffraction profiles show, as a rule, a moderate but appreciable asymmetry that must be taken into account in their descriptions. Since functions describing the diffraction profile are usually given in an idealized symmetric form, the present discussion will contain two stages:

(i) description of the symmetric profile;

(ii) corrections for asymmetry.

2.2. *A standardization of descriptions*

To discuss the shape of the diffraction profile $h(\omega)$ separately from the actual parameters of the profile – the maximum intensity H, the peak position ω_P and the half-width ω_h – the profile can be described using the following standarization [used by Thomsen & Yap (1968) and generalized by the author of the present paper]:

$$h(\omega) = Hv(u)/v_P, \tag{8}$$

$$u = u_P + w(\omega - \omega_P)/\omega_h, \tag{9}$$

where $v(u)$ is a function describing the shape of the profile (the shape function), u_P and v_P are coordinates of its peak position and w is its half-width. Usually, in the case of simple symmetric shape functions, $u_P = 0$, $v_P = 1$ and $w = 2$.

2.3. *Physical model – the substance of description*

The X-ray diffraction profile can be accurately described using complex convolution formulae. In the description, the influences of various physical and apparatus factors, causing broadening and/or asymmetry of the measured profile in relation to the original profile corresponding to the wavelength distribution, are taken into consideration (see, for example, Klug & Alexander, 1959, and references therein). Such a specific description usually relates to one particular measurement (radiation, crystal, order of interference, measurement device *etc.*). Thus, the 'complete physical model' of the diffraction profile is a hypothetical idea rather than an available formula; there is no simple analytical function that could be used as a physical model valid for each case. However, in some particular cases such simple descriptions are available.

If the crystal is of high perfection and the influence of the device is to be neglected, the complete convolution formula might be approximated by the Cauchy function

$$v(u) = 1/(1+u^2) \quad (10)$$

due to the wavelength distribution. The shape of the spectral line [(10)] results from the classical theory of an electronic simple harmonic oscillator with electromagnetic damping (see, for example, Compton & Allison, 1935), and the half-width of the spectral line w_λ is a function of physical constants. The half-width of the resultant diffraction profile, ω_h [*cf.* the standardization given by (9)], for a given Bragg angle θ can be approximated by the half-width ω_f due to the wavelength distribution,

$$\omega_h \simeq \omega_f = w_\lambda\,(\tan\theta)/\lambda. \quad (11)$$

If, conversely, the contributions of all (numerous enough, say K) factors in the distribution are approximately equal and have finite variances, the profile may be described, according to the central-limit theorem, by the Gaussian function

$$v(u) = \exp(-u^2 \ln 2) \quad (12)$$

and the half-width ω_h of the resultant profile is the square root of the sum of squares of half-widths $\omega_{h,k}$ of respective factors,

$$\omega_h = \left(\sum_{k=1}^{K} \omega_{h,k}^2\right)^{1/2}. \quad (13)$$

In applications, the Gaussian function is considered to be more suited for mosaic crystals than for perfect crystals.

Equations (10) and (12) can thus be treated as two opposed extreme cases of one general convolution model. The X-ray diffraction profiles recorded are, as a rule, intermediate cases, and can be sometimes described using relatively simple 'physical' models, in which the effect of some selected factors is considered. The effect of the in-plane collimation on the shape of the diffraction profile, for example, can be described by the model function (Urbanowicz, 1981*a*)

$$\begin{aligned} v(u) = {} & (u+u_1)\tan^{-1}(u+u_1) + (u-u_1)\tan^{-1}(u-u_1) \\ & -(u+u_2)\tan^{-1}(u+u_2) \\ & -(u-u_2)\tan^{-1}(u-u_2) \\ & -\ln[1+(u+u_1)^2]/2 - \ln[1+(u-u_1)^2]/2 \\ & +\ln[1+(u+u_2)^2]/2 + \ln[1+(u-u_2)^2]/2, \end{aligned} \quad (14a)$$

where

$$u_1 = (d_1+d_2)/L_2\omega_f, \quad u_2 = |d_1-d_2|/L_2\omega_f, \quad (14b)$$

d_1 and d_2 are widths of the collimator slits, L_2 is the collimator length and

$$u = 2(\omega - \omega_P)/\omega_f. \quad (14c)$$

Note that the standardization in the case relates to the parameters of the original profile and not to those of the final profile (*cf.* § 2.2).

The effect of collimation may also be described using a simpler, and thus less accurate, model (Urbanowicz, 1981*a*):

$$v(u) = u_4[\tan^{-1}(u+u_3) - \tan^{-1}(u-u_3)], \quad (15a)$$

where

$$\begin{aligned} u_3 &= (d_1^2+d_2^2)^{1/2}/L_2\omega_f, \\ u_4 &= 2d_1d_2/(d_1^2+d_2^2)^{1/2}L_2\omega_f. \end{aligned} \quad (15b)$$

The above two models have been derived with the assumptions that the crystal is of high perfection, the in-plane collimation used for controlling the primary-beam intensity does not introduce any appreciable systematic errors and the influence of other apparatus functions is to be neglected. The functions are capable of describing only a particular class of experimental profiles. They do not include the limiting Gaussian form [(12)]. This is, however, the best class of diffraction profiles recorded in terms of accurate lattice-parameter measurements. One cannot expect high-accuracy results if the crystal is imperfect and the apparatus functions cause a remarkable deformation of the original profile.

The above equations (10) and (11), (12) and (13), (14*a*), (14*b*) and (14*c*), (15*a*) and (15*b*) are the only simple mathematical formulae known to the author that describe the shape of a single-crystal X-ray diffraction profile by means of parameters that have defined physical meanings. Another example of such a physical model, used in neutron powder diffraction, is that introduced by Ikeda & Carpenter (1985).

If some partial distributions of the complete convolution model have the shape of the Cauchy function while others are more likely to be of Gaussian shape, one can accept the Voigt function as a model of the diffraction profile (Langford, 1978). This is a conceptual rather than a physical model (as the Gaussian function itself), unless the parameters (the half-widths, for example) of the partial distributions are expressed by means of physical or geometrical (apparatus) quantities. In the simplest case, when the Cauchy function in the model corresponds to the wavelength distribution entirely [compare with (10) and (11) and the comments on them], the convolution model can be presented in the form

$$v(u) = \int_{-\infty}^{\infty} (1+u'^2)^{-1} \exp\{-[(u-u')/r]^2 \ln 2\}\, du', \quad (16a)$$

where u is given by (14*c*), r is the ratio of the

half-width of the Gaussian function, ω_g, to that of the Cauchy function, ω_f,

$$r = \omega_g / \omega_f. \quad (16b)$$

2.4. Mathematical models - approximating functions

The idealized physical models of collimation, taken by way of example in § 2.3 [(14*a*), (14*b*), (14*c*) and (15*a*), (15*b*)], well described the mechanism of collimation but were insufficient for an interpretation of a given set of experimental data. To explain the differences between the real and the calculated diffraction profiles, such factors as the real distribution of the tube-focus emissivity and the actual inaccuracy in the adjustment of the source and the collimator had to be taken into account (Urbanowicz, 1981*b*). After the introduction of these factors, the description (available this time in a numerical rather than analytical form) became much more complex than before. On the other hand, the measured profiles and the idealized profiles did not, in principle, vary in shape. Integration, used in calculations of the convolution product, causes the resultant function to be much smoother than before. The differences were in their parameters (peak position, peak height, half-width) and their asymmetry, which did not occur in the idealized case. As will be shown in § 2.5 below, the asymmetry characterizing real diffraction profiles can be expressed in a simpler way (analytically) than *via* the complete (physical) convolution model. Thus what is needed for the purpose of the present paper is a function that approximates the physical model, including all known and important mathematical and statistical premises.

The models discussed in § 2.3, equations (14), (15) and (16), are examples of functions with shapes defined by parameters related to physical and apparatus quantities. Yet such functions, even if a correction allowing for asymmetry (discussed in § 2.5) is used, are unserviceable for approximation of an arbitrary recorded profile when preliminary values of the physical parameters are unknown. Therefore there is a tendency towards using functions with shapes defined by parameters that do not have physical interpretations. Some such functions, for example the Voigt function [(16)], are capable of expressing the continuous change of shape from the Cauchy function to the Gaussian. It should be emphasized that, while making the transition from the physical to a mathematical model, the 'complete physical model' must still be remembered. In this case, the complete physical model is represented by a collection of corrections for respective aberrations. The corrections, being a result of detailed analysis of individual factors of the complete convolution model, are reported elsewhere (see references at the end of § 1.1).

In practice, two fairly simple shape functions are used that include a Cauchy function and a Gaussian function as the extreme cases. As has been shown (David, 1986; see also Gałdecka, 1993, § 4.2), the Voigt functions - well founded theoretically but inconvenient for applications - can be well approximated by pseudo-Voigt functions, being sums of the two limiting functions,

$$v(u) = c/(1+u^2) + (1-c)\exp(-u^2 \ln 2), \quad (17a)$$

where c is an adjustable parameter that defines the shape; $c=1$ relates to the pure Cauchy shape, $c=0$ relates to the pure Gaussian, so the limitation

$$0 \le c \le 1 \quad (17b)$$

is necessary from the point of view of the physical model.

The second possibility is use of the Pearson VII functions, borrowed from a system of frequency curves (Elderton & Johnson, 1969), which have the form

$$v(u) = (1 + au^2)^{-m}, \quad (18a)$$

where

$$a = 2^{1/m} - 1 \quad (18b)$$

and m is a parameter that defines the shape, the so-called decay rate; $m=1$ corresponds to the Cauchyian shape, and $m=\infty$ corresponds to the Gaussian shape, so the limitation

$$1 \le m \le \infty \quad (18c)$$

is physically justified.

All the functions, being physical models of the diffraction profile (see § 2.3), and appropriate approximating functions considered here (§ 2.4) are characterized by the common features:

(*a*) continuity;

(*b*) non-negativity;

(*c*) showing one maximum;

(*d*) having two inflection points at their slopes;

(*e*) having v values that tend to zero for $|u|$ tending to infinity.

Moreover, all functions listed in §§ 2.3 and 2.4 are symmetric, which is the first approximation in the description of the diffraction profile. There are, certainly, other possible distributions with the features listed above (further examples will be given in § 2.5 below). Ordinarily, authors who use particular shape functions do not give the motivation for their choice. The functions can probably provide a good fit to actual observed data. But are the shape functions capable of approximating the complete physical model, and hence an arbitrary set of data, with an adequate goodness of fit? What criteria should be used when selecting the description? The agreement between selected shape functions and the models discussed in § 2.3 will be tested in paper II (Gałdecka, 1993).

2.5. *Asymmetry – further specification of the description*

If at least one of the distributions that are the factors of the final convolution product is asymmetric, the resulting diffraction profile is asymmetric. Illustrative examples are given by Berger (1986*a*). One can distinguish the following sources of asymmetry of the diffraction profile recorded in the Bond method:

(*a*) intrinsic asymmetry of a separate spectral line;

(*b*) asymmetry that results from the nonlinear transition from the λ scale to the θ (or ω) scale (it has been found by the author that this asymmetry is to be neglected since the profiles recorded are relatively narrow);

(*c*) asymmetry that is the result of overlapping reflections;

(*d*) asymmetry of some other physical functions and apparatus functions, such as the Lorentz-polarization factor, the absorption profile, the tube-focus emissivity and the vertical (axial) and horizontal (in-plane) collimation.

There are various mathematical methods used for description of the resultant asymmetry of the final diffraction profile. These are:

(i) a sum of several symmetric functions with different peak positions;

(ii) a simple asymmetric multiplier;

(iii) the so-called split functions;

(iv) some other asymmetric functions.

In case (i), a sum of two or more superimposed symmetric functions with different peak positions, the distance between the peaks being treated as an adjustable parameter, can be used as an entirely mathematical method for expressing the asymmetry, irrespective of the origin of the latter (Hecq, 1981; Howard, 1982). A sum of two or more symmetric functions when the distance(s) between the peaks is (are) defined by the wavelengths, structure and interference order could be treated as a physical model of the diffraction profile. However, such descriptions are usually complex and hence inconvenient for the present task. Berger (1986*b*), for example, used a sum of four profiles to describe the spectral distribution alone, corresponding to $K\alpha_1$–$K\alpha_2$ radiation, and Howard (1982) needed a sum of five components to approximate the complete convolution model (in neutron powder diffraction).

For case (ii), another example of a description of asymmetry is a simple asymmetric multiplier, $P(u)$, such that

$$v(u) = P(u)v_s(u), \tag{19}$$

where $v_s(u)$ is an idealized symmetric profile and $v(u)$ is the resultant asymmetric shape function.

In particular, a quadratic function modified by the function 'sign' is used,

$$P(u) = 1 - \text{sign}\,(u)\varphi u^2, \tag{20a}$$

where φ is a coefficient of asymmetry. This form of multiplier is a result of physical considerations and expresses the effect of the vertical (axial) divergence (Klug & Alexander, 1959; Rietveld, 1969). [In more accurate calculations the axial divergence is represented by a 'truncated exponential function' (Enzo, Fagherazzi, Benedetti & Polizzi, 1988).] Originally, φ was proportional to tan θ; here, according to assumption (2) in § 2.1, the dependence on θ is not taken into account.

For moderate asymmetry, a simpler linear factor (Thomsen & Yap, 1968),

$$P(u) = 1 + \xi u, \tag{20b}$$

may be sufficient in (19). The description could be treated as the first approximation of a more complex description of asymmetry dependent on various factors if the underlying symmetric profile $v_s(u)$ is given. If so, an assumption would be needed that either the asymmetry is small enough or the scanning range is narrow enough, *viz* $\xi u \ll 1$, to dispense with higher terms of the supposed expansion.

Further examples of such asymmetric factors are given by Ersson (1979). These are, however, more complex and more specific, so they will not be considered here.

For case (iii), a practical rather than a theoretical approach to the description of asymmetry is the use of so-called 'split functions' consisting of two 'halves' of functions of the same shape but different half-widths, set in such a way (Thomsen & Yap, 1968) that the full half-width is equal to 2:

$$v(u) = v_s(u^*), \tag{21a}$$

where

$$u^* = u/[1 + \chi\ \text{sign}\,(u)] \tag{21b}$$

and χ is a coefficient of asymmetry, defined by

$$\chi = (u_2 + u_1 - 2u_P)/(u_2 - u_1), \tag{21c}$$

where u_1 and u_2 are given by

$$v(u_1) = v(u_2) = v_p/2, \quad u_1 < u_2. \tag{21d}$$

Sometimes two different values of the parameter defining the shape (for example, m for a Pearson VII) are used for each 'half' of the split functions (Brown & Edmonds, 1980; Toraya, 1986). In any case, descriptions consisting of such segments defined by different formulae and/or parameters are simple examples of spline functions, already mentioned in § 1.2.

A disadvantage of some simple corrections for asymmetry (*e.g.* an asymmetric multiplier or a pair of split functions) is that they can introduce some formal 'defects' to resultant physical or mathematical models. Functions defined by (19) and (20*a*) or (19) and (20*b*) may take negative, and hence physically

unrealistic, values. The defect is particularly troublesome when the functions are to be used in calculations of integrated intensities (for a more detailed discussion, see Howard, 1982). To meet the aim of the present paper, the correct description of the profile near its peak is of primary importance. The analysis of functions defined by (19) and (20*a*), and by (21*a*) and (21*b*), reveals that their second derivatives, $v''(u)$, at the peak ($u=\delta$, $|\delta|\to 0$) are discontinuous and depend on the sign of the argument. Namely, in the case of a modified quadratic factor [(19), (20*a*)],

$$v''(\delta)=v''_s(0)-2\varphi \text{ sign }(\delta) \tag{22}$$

and for a pair of split functions [(21*a*), (21*b*), (21*c*)],

$$v''(\delta)=v''_s(0)/[1+\chi \text{ sign }(\delta)]^2. \tag{23}$$

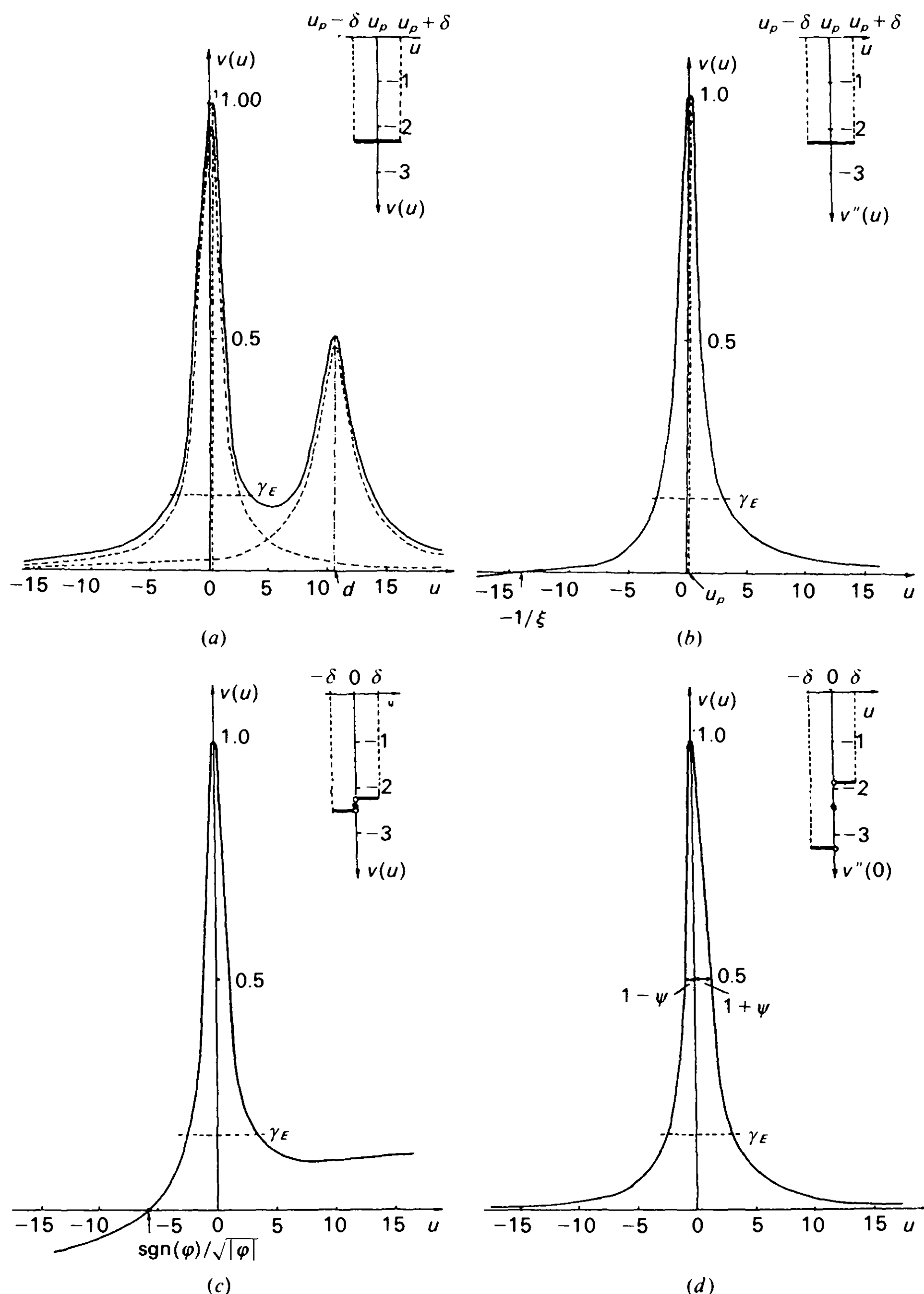

Fig. 1. Various asymmetric shape functions obtained from a basic symmetric function (a Pearson VII function) by the modifications: (*a*) a sum of two symmetric functions of one shape and different peak positions (d is the distance between the peaks); (*b*) a linear multiplier; (*c*) a quadratic multiplier; (*d*) a pair of split functions. The plot of the second derivative $v''(\delta)$ at the peak, $u=\delta$, $\delta^2 \ll 1$, is shown in the upper right corner of each diagram. γ_E is the truncation level of the approximated experimental data.

As shown in Fig. 1, the discontinuity is particularly remarkable in the case of a pair of split functions (Fig. 1d). The defect mentioned by Thomsen & Yap (1968), may lead [and it does, as will be shown in paper II, § 4.3] to a systematic error (bias) of the peak-position determination. Another defect of a model may be an increase of intensity values for $|u|$ distant from the peak and tending to infinity. An example is shown in Fig. 1(c), which relates to a modified quadratic asymmetric factor, and, as may easily be proved, occurs when the parameter m of the underlying Pearson VII function is less than 1 (here, $m = 0.78$).

For case (iv), descriptions that avoid the drawbacks mentioned above are derived by Johnson (1949). Using the notation of the present paper (and after some transformations), the distributions can be presented in the form

$$v(u) = f'(u)\exp\{-0.5B^2[1+\varepsilon f(u)]^2\}, \quad (24a)$$

where B^2 and ε are parameters (the latter, in the present notation, expressing the asymmetry), $f(u)$ is an arbitrary simple enough continuous and non-decreasing function (a kind of 'cumulative density function'; see § 2.4); its first derivative, $f'(u)$, corresponds to a 'probability density function'.

Then $f(u)$ can be defined by

$$f(u) = \int f'(u)\,\mathrm{d}u. \quad (24b)$$

On the other hand, $f'(u)$, if symmetric, could be treated as $v_s(u)$ in (19),

$$f'(u) = v_s(u). \quad (24c)$$

Two examples of Johnson (1949) distributions (given in the original paper) that the functions

$$f(u) = \ln[u + (u^2+1)^{1/2}],$$

so

$$f'(u) = (1+u^2)^{-1/2}, \quad (24d)$$

and

$$f(u) = \sinh u, \quad \text{so} \quad f'(u) = \cosh u \quad (24e)$$

were applied by Oatley & French (1982) for approximation of particular experimental data (intensity values for various proteins). The first of the functions is shown in Fig. 2. Their drawback is (as will be shown in paper II, § 4.2) that they are not directly related to the physical convolution model discussed in § 2.3.

There is, of course, a possibility of using some other functions $f'(u) = v_s(u)$, such as a pseudo-Voigt or a Pearson VII function, to construct further distributions defined by (24a). A particular problem may occur when the corresponding integral [(24b)] is not available in a simple analytical form. Then an approximate expression may be used. For moderate asymmetry, *i.e.* $\varepsilon u \ll 1$, one may put

$$\varepsilon f(u) \simeq \varepsilon u. \quad (24f)$$

The final version of the best asymmetric distribution will then have the form

$$v(u) = v_s(u)\exp[-0.5B^2(1+\varepsilon u)^2], \quad (25)$$

where $v_s(u)$ is given by (17a) or (18a).

Results of approximation by means of the function given in (25) are almost identical with those obtained using a linear factor [(19), (20b)] for narrow scanning ranges (differences in the peak position, its standard deviation and the R factor do not exceed 1%). The use of the exponential factor [(25)] allows the resultant description, free from formal defects, to be used within a large range of arguments.

For applications, the range of values of the 'macroscopic' coefficient of asymmetry, χ [(21c), (21d)], appropriate for a given formula may be important. Relations between respective parameters of asymmetry used in the descriptions discussed, ξ, φ and ε, and the macroscopic parameter, χ, limitations for the parameters and permitted ranges of arguments are given in Table 1.

2.6. *The statistical component as a criterion of correctness of a model considered*

Any correct model of the measured diffraction profile should include, in accordance with the suggestions expressed by Oatley & French (1982), a defined statistical part, describing statistical errors of recorded intensities, in addition to its substantial 'deterministic' part. The statistical information might then be used for testing the correctness of the deterministic mathematical description.

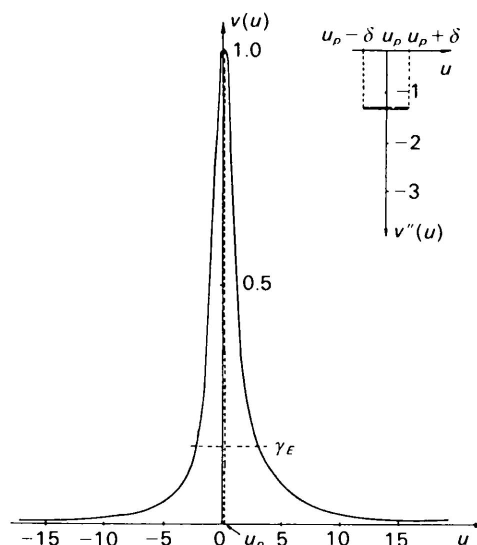

Fig. 2. An asymmetric Johnson distribution [(24a)]. The plot of the second derivative $v''(u)$ at the peak, $u = \delta$, $\delta^2 \ll 1$, is shown in the upper right corner.

Table 1. *Relations between coefficients of asymmetry used in various descriptions and the macroscopic parameter of asymmetry, χ, under the assumption that the shape $v_s(u)$ of the underlying symmetric profile is a Cauchy function*

Description of asymmetry $v(u)$	Resultant 'macroscopic' coefficient of asymmetry, χ, for $v_s=(1+u^2)^{-1}$	The range of u values for which $v(u)\geq 0$
$(1+\xi u)v_s(u)$	$\chi(\xi)=\xi[3\xi^2+2(1+\xi^2)^{1/2}+2]^{-1/2}$, ξ theoretically unlimited, $\lim_{\xi\to\infty}\lvert\chi(\xi)\rvert\leq 0.58$	$u\in[-1/\xi,\infty)$ for $\xi>0$; $u\in(-\infty,-1/\xi]$ for $\xi<0$
$[1-\operatorname{sign}(u)\varphi u^2]v_s(u)$*	$\chi(\varphi)=-1/\varphi+\operatorname{sign}(\varphi)(1/\varphi^2-1)^{1/2}$ for $\varphi\neq 0$, $\lim_{\lvert\varphi\rvert\to 0}\chi(\varphi)=0, \lvert\varphi\rvert\leq 1$, $\lvert\chi(\varphi)\rvert\leq 1$	$u\in(-\infty,\varphi^{-1/2})$ for $\varphi>0$; $u\in[-\lvert\varphi\rvert^{-1/2},\infty)$ for $\varphi<0$
$\exp\{\frac{1}{2}[1-(1+\varepsilon u)^2\}v_s(u)$	$\chi(\varepsilon)\simeq-\varepsilon(1-1.15\varepsilon^2)/2, \lvert\varepsilon\rvert\leq 0.54$, $\lvert\chi(\varepsilon)\rvert\leq 0.18$	$u\in(-\infty,\infty)$

* Note that the second derivative is discontinuous at the peak.

One can consider a given model to be correct if:

(i) the differences between calculated intensities $\bar{h}_i$ and observed intensities h_i have random character, *i.e.* the expected values of the differences are equal to zero:

$$E(\bar{h}_i-h_i)=0, \quad i=1,2,\ldots,n; \tag{26}$$

(ii) the expected values of the squares of the differences are equal to the variances of the recorded counts:

$$E[(\bar{h}_i-h_i)^2]=\sigma^2(h_i). \tag{27a}$$

Moreover, in the case of appreciable correlations between measurements, there is the relation:

$$E[(\bar{h}_i-h_i)(\bar{h}_j-h_j)]=\operatorname{cov}(h_i,h_j), \quad i\neq j, \tag{27b}$$

where cov (h_i, h_j) are covariances of the measurement intensities.

The above requirements can be combined with such statistical parameters, defining the goodness of fit, as the discrepancy factor,

$$R=\left[\sum_{i=1}^{n}\sum_{j=1}^{n}w_{i,j}(\bar{h}_i-h_i)(\bar{h}_j-h_j)\right]^{1/2}\Big/\sum_{i=1}^{n}\sum_{j=1}^{n}w_{i,j}h_ih_j \tag{28}$$

or the mean deviance

$$\sigma_h^2=(n-m)^{-1}\sum_{i=1}^{n}\sum_{j=1}^{n}w_{i,j}(\bar{h}_i-h_i)(\bar{h}_j-h_j), \tag{29a}$$

where $w_{i,j}$ are the weights of observations; σ_h^2 corresponds to the variance of observation of unit weight.

Knowledge of individual variances and covariances of the recorded counts may be used for estimating the expected mean variance, $\hat{\sigma}_h^2$, and the expected discrepancy factor, $\hat{R}$, which should be obtained in the course of approximation, when the approximating function is a 'model'. It can be proved that, if the weights matrix is the inverse of the variance-covariance matrix and the requirements given by equations (26), (27*a*) and (27*b*) are satisfied, then [*cf.*, for example, Hamilton (1964, § 4.4)]

$$E\left[\sum_{i=1}^{n}\sum_{j=1}^{n}w_{i,j}(\bar{h}_i-h_i)(\bar{h}_j-h_j)\right]=(n-m)\hat{\sigma}_h^2, \tag{29b}$$

so

$$E(\sigma_h^2)=\hat{\sigma}_h^2. \tag{29c}$$

To introduce the correct weights, individual variances and covariances must be known or assumed. The recorded counts obey Poisson statistics, hence

$$\sigma^2(h_i)=h_{i,0}, \tag{30a}$$

$$\operatorname{cov}(h_i,h_j)=0, \quad i\neq j, \tag{30b}$$

where $h_{i,0}$ is the expected value of h_i.

In the case when the proper weighting scheme is used, *i.e.* $w_{i,i}=1/h_{i,0}$, $w_{i,j}=0$, the expected value of the R factor is

$$E(R^2)\simeq(n-m)\hat{\sigma}_h^2\Big/\sum_{i=1}^{n}h_i \tag{30c}$$

and the mean deviance is given by (29*c*).

In the general case, variances of recorded counts can be greater than those described by (27), and some correlations between measured intensities may occur (Gałdecka, 1985),

$$\sigma^2(h_i)=h_{i,0}+h_{i,0}^2\sigma^2(I)/I^2+\sigma^2(\omega_i)h_i'^2, \quad -p\leq i\leq p, \tag{31a}$$

$$\operatorname{cov}(h_i,h_j)=\operatorname{cov}(\omega_i,\omega_j)h_i'h_j', \quad i\neq j, \tag{31b}$$

where $2p+1=n$ is the number of points; $\sigma(I)/I$ is the instability of the primary beam; $h_i'=h'(\omega_i)$, $\sigma^2(\omega_i)=\operatorname{cov}(\omega_i,\omega_i)$ and $\operatorname{cov}(\omega_i,\omega_j)$ are the variances and covariances of the angular positions defined by

$$\begin{aligned}\operatorname{cov}(\omega_i,\omega_j)=&(1+ij/p^2)\sigma^2(\omega)_R/2\\&+p(1-ij/p^2)\sigma^2(\Delta_\omega)/2\\&-\lvert i-j\rvert\sigma^2(\Delta_\omega)/2, \quad -p\leq i,j\leq p,\end{aligned} \tag{31c}$$

where $\sigma^2(\omega)_R$ characterizes the angle-reading error and $\sigma^2(\Delta_\omega)$ characterizes the error in angle setting (positioning).

When individual variances (and covariances) are unknown but an approximate level of statistical errors is given, defined by the mean variance $\hat{\sigma}_h^2$ of recorded

counts within a given scanning range, uniform weights, $w_{i,i} = 1$, $w_{i,j} = 0\ (i \neq j)$ may then be used. With the assumption that

$$\sigma^2(h_1) \simeq \sigma^2(h_2) \simeq \ldots \simeq \sigma^2(h_n) \simeq \hat{\sigma}_h^2 = (1/n) \sum \sigma^2(h_i), \quad (32)$$

one can show (Rao, 1982) that

$$E[\sum (h_i - \bar{h}_i)^2] = (n - m)\hat{\sigma}_h^2. \quad (33a)$$

When the approximating function is a model of the diffraction profile, the calculated mean deviance σ_h^2 [(29a)] will provide an unbiased estimator of the mean variance $\hat{\sigma}_h^2$ of observations,

$$E(\sigma_h^2) = E[\sum (h_i - \bar{h}_i)^2]/(n - m) = \hat{\sigma}_h^2, \quad (33b)$$

and the square of the calculated R factor will be equal to its estimated value, given by

$$E(R^2) = \sum \sigma^2(h_i)/\sum h_i^2 = (n - m)\hat{\sigma}_h^2/\sum h_i^2 = \hat{R}^2. \quad (34)$$

Thus, the equality $\sigma_h^2 = \hat{\sigma}_h^2$ (or $R^2 = \hat{R}^2$) may be a criterion for acceptance of the model considered. Statistical tests, such as the χ^2 test (for comparing the calculated and the expected σ_h^2 or R^2) or the F distribution for two variances (for comparing pairs of calculated values, $\sigma_{h,1}^2$ and $\sigma_{h,2}^2$ or R_1^2 and R_2^2, obtained for different models), are helpful in deciding whether to accept or reject a model considered. Further details connected with the use of the χ^2 test will be given in paper II, § 2.2.

2.7. *Practical aspect - applications*

From the point of view of applications, the function to be used for approximation of the measurement data should be:

(i) universal, capable of describing every possible shape of the measured profile (here obtained using the Bond method),

(ii) convenient for calculations.

Moreover, with regard to the problem of the present paper, results of the peak-position determination should be unbiased, independent of the scanning range (stable) and undispersed (showing as small as possible variance).

One may ask why, for the problem in question, one description used is a 'physical model' or gives a good approximation to the model, while another only provides a good fit to a given set of data? What are the consequences of some formal 'defects' of descriptions discussed in § 2.5? Is it necessary to base the goodness-of-fit criteria on a statistical model of recorded counts?

As will be shown in paper II (Gałdecka, 1993), each of the elements of description have some influence on the accuracy of the peak-position determination. On the other hand, the accuracy of results obtained may be treated as an additional criterion of correctness of a model considered, apart from the statistical criteria discussed in § 2.6.

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References

ALEXANDER, L. E. & SMITH, G. S. (1962). *Acta Cryst.* **15**, 983-1004.
BERGER, H. (1986*a*). *J. Appl. Cryst.* **19**, 34-38.
BERGER, H. (1986*b*). *X-ray Spectrom.* **15**, 241-243.
BOND, W. L. (1960). *Acta Cryst.* **13**, 814-818; erratum: (1975), **A31**, 698.
BROWN, A. & EDMONDS, J. W. (1980). *Adv. X-ray Anal.* **23**, 361-374.
COMPTON, A. H. & ALLISON, S. K. (1935). *X-rays in Theory and Experiment.* New York: Van Nostrand.
DAVID, W. I. F. (1986). *J. Appl. Cryst.* **19**, 63-64.
ELDERTON, W. D. & JOHNSON, N. L. (1969). *System of Frequency Curves*, pp. 77-78. Cambridge Univ. Press
ENZO, S., FAGHERAZZI, G., BENEDETTI, A. & POLIZZI, S. (1988). *J. Appl. Cryst.* **21**, 536-542, 543-549.
ERSSON, N. O. (1979). *J. Appl. Cryst.* **12**, 295-302.
GAŁDECKA, E. (1985). *Structure and Statistics in Crystallography*, edited by A. J. C. WILSON, pp. 137-149. New York: Adenine Press.
GAŁDECKA, E. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, ch. 5.3. Dordrecht: Kluwer Academic Publishers.
GAŁDECKA, E. (1993). *Acta Cryst.* **A49**, 116-126.
GROSSWIG, S., JÄCKEL, K.-H. & KITTNER, R. (1986). *Cryst. Res. Tech.* **21**, 133-139.
HAMILTON, W. C. (1964). *Statistics in Physical Science.* New York: Ronald Press.
HÄRTWIG, J. & GROSSWIG, S. (1989). *Phys. Status Solidi A*, **115**, 369-382.
HECQ, M. (1981). *J. Appl. Cryst.* **14**, 60-61.
HEPP, A. & BAERLOCHER, CH. (1988). *Aust. J. Phys.* **41**, 229-236.
HOWARD, C. J. (1982). *J. Appl. Cryst.* **15**, 615-620.
IKEDA, S. & CARPENTER, J. M. (1985). *Nucl. Instrum. Methods Phys. Res.* **A239**, 536-544.
JOHNSON, N. L. (1949). *Biometrika*, **36**, 149-169.
KHEIKER, D. M. (1969). *Acta Cryst.* **A25**, 82-88.
KLUG, H. P. & ALEXANDER, L. E. (1959). *X-ray Diffraction Procedures*, 2nd ed., p. 251. New York: John Wiley.
LANGFORD, J. I. (1978). *J. Appl. Cryst.* **11**, 10-14.
OATLEY, S. & FRENCH, S. (1982). *Acta Cryst.* **A38**, 537-549.
RAO, C. R. (1982). *Linear Statistical Inference and its Applications*, § 4.1.5, Polish ed. Warszawa: PWN.
RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65-71.
THOMSEN, J. S. & YAP, F. Y. (1968). *J. Res. Natl Bur. Stand. Sect. A*, **72**, 187-205.
TORAYA, H. (1986). *J. Appl. Cryst.* **19**, 440-447.
URBANOWICZ, E. (1981*a*). *Acta Cryst.* **A37**, 364-368.
URBANOWICZ, E. (1981*b*). *Acta Cryst.* **A37**, 369-373.
WILSON, A. J. C. (1965). *Br. J. Appl. Phys.* **16**, 665-674.
YOUNG, R. A. & WILES, D. B. (1982). *J. Appl. Cryst.* **15**, 430-438.