CROATICA CHEMICA ACTA CCACAA 57 (4) 749—755 (1984)

YU ISSN 0011—1643
CCA-1489 UDC 548.73
Original Scientific Paper

Application of Bell-Shaped Functions in X-ray Diffraction Broadening Analysis*

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Received December 15, 1983

Graphical and analytical solutions for the crystallite size and strain parameters, causing diffraction broadening, are given using two or more orders of the reflexion from the same set of crystal lattice planes and representing diffraction profiles with simple bell-shaped functions. The effect of the inevitable truncation of the profile tails on the derived values of the size and strain parameters is also discussed. It has been found that the truncation more considerably affects the functions describing the size parameter than the ones describing the strain parameter, this being in agreement with the experimental evidence.

INTRODUCTION

An observed X-ray diffraction line profile, $h(\varepsilon)$, is the convolution of the instrumental profile (»standard line profile«), $g(\varepsilon)$, inherent in the diffraction method, and the pure diffraction profile, $f(\varepsilon)$, produced by small crystallite sizes, by faultings on lattice planes and by strains in the crystal lattice:[1,2]

$$h(\varepsilon) = \int f(\varepsilon - t)\, g(t)\, \mathrm{d}t. \qquad (1)$$

The derivation of $f(\varepsilon)$ (deconvolution) can be done by the Fourier transform method, commonly referred to as the Stokes[1] method. This procedure does not require assumptions in the mathematical descriptions of the profile shapes $h(\varepsilon)$ and $g(\varepsilon)$. The analysis of the pure diffraction profile, $f(\varepsilon)$, can be done by the Warren and Averbach[2] method using directly the Fourier coefficients of $f(\varepsilon)$ obtained by deconvolution. Each coefficient is the product of the »size« parameter (including both the crystallite size and faulting contributions) and the »strain« parameter. Since the latter parameter depends on the order of the reflexion it can be separated from the former parameter using two or more orders of the reflexion from the same set of crystal lattice planes. Hence, this analysis gives in principle such information about the sample as the mean crystallite size, distribution of sizes, deformation and twin faulting and the nature and extent of the lattice strains.[2]

On the other hand, simplified methods, circumventing the deconvolution process, may be used, especially in routine measurements, wherein the numerical results are required speedily and a good relative accuracy suffices. These methods are based on direct measurements of (*i*) the integral width (the area

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

under the diffraction profile divided by the profile height), (*ii*) the width at the half of the diffraction profile height, and (*iii*) the variance (the second moment of the profile).[3] Much work has been done using the widths of the profiles and these techniques have been recently promoted.[4] Let the integral widths alone be considered in the present paper. The observed integral widths B_i and b_i of the $K\alpha_1$ profiles* $h(\varepsilon)$ and $g(\varepsilon)$, respectively, and the unknown width β_i of profile $f(\varepsilon)$ are related as follows (e. g. ref.[5]):

$$b_i \beta_i = B_i \int g(\varepsilon) f(\varepsilon) \, \mathrm{d}\varepsilon. \tag{2}$$

In order to find the relationship between B_i, b_i and β_i in an explicit form, one must assume analytical functions for $g(\varepsilon)$ and $f(\varepsilon)$ in (2) (e. g. ref.[5,6,8]). Such assumptions, however, affect the value obtained for β_i. Instead, the following empirical relation can be used:[9,10]

$$B_i^2 = B_i \beta_i + b_i^2. \tag{3}$$

The width β_i can also be found if the Stokes correction[1] is performed and the profile $f(\varepsilon)$ is synthesized. In the following text it is understood that β_i is determined from the observed values for B_i and b_i, or from the found $f(\varepsilon)$.

The pure diffraction profile $f(\varepsilon)$ can be considered (analogously to (1)) as the convolution of the crystallite size profile (supposing that the faultings are not present), $p(\varepsilon)$, and the lattice strain profile, $s(\varepsilon)$:[11]

$$f(\varepsilon) = \int p(\varepsilon - t) \, s(t) \, \mathrm{d}t. \tag{4}$$

The relation among the corresponding integral widths β_{pi} and β_{si} (unknowns) and β_i (derived from (2) or (3) or by the Stokes method[1]) is (analogously to (2)):

$$\beta_{pi} \beta_{si} = \beta_i \int p(\varepsilon) \, s(\varepsilon) \, \mathrm{d}\varepsilon. \tag{5}$$

In order to find the relation (5) in an explicit form one may assume analytical expressions for $p(\varepsilon)$ and $s(\varepsilon)$ in the form of bell-shaped functions. According to Ruland,[8] $s(\varepsilon)$ can be described by the Gaussian function, $\exp(-k_s^2 \varepsilon^2)$ [or by $(1 + k_s^2 \varepsilon^2)^{-2}$ as suggested by other authors[11]], while $p(\varepsilon)$ can be described by the Cauchy function, $(1 + k_p^2 \varepsilon^2)^{-1}$, for a wide crystallite size distribution, or by $\sin^2(k_p \varepsilon)/(k_p^2 \varepsilon^2)$ for a narrow size distribution. Recently, the diffraction profiles have been described by the Voigt function, which is represented as the convolution of m Cauchy and n Gaussian functions.[12,13]

In the present paper only simple bell-shaped functions are considered. Graphical and analytical solutions are given (in the cases where they have been missing in literature) for the crystallite size and strain parameters, using two or more orders of the reflexion from the same set of the crystal lattice planes. The other part of the paper deals with the effect of the inevitable truncation of the profile tails on the derived values of the parameters which cause broadening.

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* If one deals with the profiles obtained using the spectral doublet $K\alpha_1\alpha_2$, then it is understood that the contribution to the observed profile due to the α_2 component is eliminated (e. g. ref.[4-7]).

SEPARATION OF THE SIZE AND STRAIN PARAMETERS

The integral widths of the crystallite size profile, $p(\varepsilon)$, and the strain profile, $s(\varepsilon)$, in (5) are given by well-known expressions (e. g. ref.[5,9]):

$$\beta_{pi} = \frac{\lambda}{L_{hkl} \cos \Theta}, \quad \beta_{si} = 4\, e_{hkl} \tan \Theta, \tag{6}$$

where λ is the vawelength of the radiation used, Θ is the Bragg angle, and L_{hkl} and e_{hkl} are the volume average of the crystallite size and the lattice strain, respectively, in the direction normal to the reflecting lattice plains (hkl). If (at least two or) several orders of the reflexion are available, it is in principle possible to conclude whether one source or two sources of the broadening is/are present, by checking the dependence of β_i on Θ. If β_i increases with Θ as $1/\cos\Theta$, then the crystallite size broadening alone is present ($\beta_{pi} = \beta_i$). If β_i increases with Θ as $\tan\Theta$, then the lattice strain causes broadening. In either case the parameter causing broadening can be found from the pure diffraction width β_i of any order of the reflexion (eq. (6)). If both size and strain broadenings are present, the unknowns L_{hkl} and e_{hkl} can be found from the relations among β_i, β_{pi} and β_{si}, which can be obtained by using eq. (5) and making assumptions for the crystallite size and strain profiles, $p(\varepsilon)$ and $s(\varepsilon)$. Two assumptions are considered here.

[1] $p(\varepsilon) = (1 + k_p{}^2\, \varepsilon^2)^{-1}$, $s\,(\varepsilon) = \exp\,(-\,k_s{}^2\, \varepsilon^2)$

In this case the exact expression relating β_i, β_{pi} and β_{si} was given by Schoening.[11] As this exact expression in rather complicated and cannot be handled conveniently,[11,10] Schoening[11] in the same paper suggested a simple graphical solution for L_{hkl} and e_{hkl} for two orders of the reflexion having $\sin\Theta_2 = 2\,\sin\Theta_1$: from the graphs relating $(L_{hkl}\, B_2)^{-1}$ and $(B_1/B_2 - 0.5)$ (where B_j are the measured quantities $\beta_{ij} \cos\Theta_j/\lambda$, $j = 1,2$) against $u_2 = 4\, L_{hkl}\, e_{hkl}$ $\sin\Theta_2/\lambda$ one first determines $(L_{hkl}\, B_2)^{-1}$ and u_2, and then L_{hkl} and e_{hkl}. Instead of the exact expression, Halder and Wagner[10] gave a good approximate relation (analogously to (3)) for estimation of the crystallite size and strain parameters:

$$\beta_i{}^2 = \beta_i\, \beta_{pi} + \beta_{si}{}^2. \tag{7}$$

Substituting (6) in the approximate relation (7) it follows

$$\frac{\gamma^2}{\sin^2\Theta} = \frac{\lambda}{L_{hkl}} \frac{\gamma}{\sin^2\Theta} + (4\, e_{hkl})^2, \tag{8}$$

where $\gamma = \beta_i \cos\Theta$.

Eq. (8) provides a means for the graphical solution. All available orders of a given reflexion are used to construct a linear plot of $\gamma^2/\sin^2\Theta$ against $\gamma/\sin^2\Theta$. The size and strain parameters are found from the slope, λ/L_{hkl}, and the ordinate intercept, $(4\, e_{hkl})^2$. In case of an isotropic material, all available reflexions can be used.

Eq. (8) can be also written in the form

$$(4\, e_{hkl})^2 \left(\frac{\sin\Theta}{\lambda}\right)^2 = \left(\frac{\gamma}{\lambda}\right)^2 - \frac{\gamma}{\lambda} \cdot \frac{1}{L_{hkl}}.$$

By plotting $y = (\sin \Theta/\lambda)^2$ as a function of $x = \gamma/\lambda$ and approximating it with a parabola one can obtain the value of L_{hkl} from the intercept on the x axis, equaling $x_0 = 1/L_{hkl}$, and the value of e_{hkl} from the slope of the curve in the point $(x_0, 0)$, which is given by $dy/dx = L_{hkl}^{-1} (4\, e_{hkl})^{-2}$.

The explicit analytical expressions for L_{hkl} and e_{hkl} can be found from (7) for two orders of the reflexion having $\sin \Theta_2 = 2 \sin \Theta_1$:

$$L_{hkl} = \frac{\lambda (\gamma_2 - 4\gamma_1)}{\gamma_2^2 - 4\gamma_1^2}, \quad (4\, e_{hkl})^2 = \frac{\gamma_1 \gamma_2 (\gamma_2 - \gamma_1)}{\sin^2 \Theta_1 (4\gamma_1 - \gamma_2)},$$

where

$$\gamma_j = \beta_{ij} \cos \Theta_j, \; j = 1,2.$$

[2] $p(\varepsilon) = (1 + k_p^2\, \varepsilon^2)^{-1}$, $s(\varepsilon) = (1 + k_s^2\, \varepsilon^2)^{-2}$

In this case the following expression relating β_i, β_{pi} and β_{si} can be found from (5) (e. q. ref.[11]):

$$\beta_i = \frac{(\beta_{pi} + 2\,\beta_{si})^2}{\beta_{pi} + 4\,\beta_{si}}. \tag{9}$$

Schoening[11] gave the graphical solution of (9) for L_{hkl} and e_{hkl} in a similar way as in the case [1].

Substituting (6) in (9) one obtains for the two orders of the reflexion, having $\sin \Theta_2 = 2 \sin \Theta_1$:

$$e_{hkl} = \frac{\lambda (4\, L_{hkl}\, \gamma_1 - L_{hkl}\, \gamma_2 - 3\lambda)}{32\, L_{hkl} \sin \Theta_1 (L_{hkl}\, \gamma_2 - 2\, L_{hkl}\, \gamma_1 + \lambda)}, \tag{10}$$

$$a\, L^3_{hkl} + b\, L^2_{hkl} + c\, L_{hkl} + d = 0, \tag{11}$$

where the coefficients in (11) are known quantities,

$$a = 8\, \gamma_1 \gamma_2 (\gamma_2 - 2\, \gamma_1), \qquad c = -6\, \lambda^2 \gamma_2,$$

$$b = 3\, \lambda\, \gamma_2 (8\, \gamma_1 - 3\, \gamma_2), \qquad d = -\lambda^3,$$

with

$$\gamma_j = \beta_{ij} \cos \Theta_j, \; j = 1,2.$$

Eq. (11) can be solved graphically for L_{hkl}; then e_{hkl} follows from (10). Or, eq. (11) can be rewritten in the form

$$D^3 + 3\, pD + 2\, q = 0, \tag{12}$$

where

$$D = L_{hkl} + \frac{b}{3a}, \quad 3\, p = \frac{3\, ac - b^2}{3\, a^2}, \quad 2\, q = \frac{2\, b^3}{27\, a^3} - \frac{bc}{3\, a^2} + \frac{d}{a}.$$

The solutions of (12) are as follows (Cardan's formulae):

$$D_1 = u + v, \; D_2 = w_1 u + w_2 v, \; D_3 = w_2 u + w_1 v,$$

where

$$u = \sqrt[3]{-q + \sqrt{q^2 + p^3}}, \quad v = \sqrt[3]{-q - \sqrt{q^2 + p^3}}, \quad w_{1,2} = -\frac{1}{2} \pm i \frac{\sqrt{3}}{2}.$$

The number of real solutions of D, and therefore of L_{hkl}, depends on the sign of $q^2 + p^3$. For $q^2 + p^3 > 0$ there are one real and two complex solutions.

For $q^2 + p^3 < 0$ there are three different real solutions. If $q^2 + p^3 = 0$ there are two cases: (*i*) $p = 0$, $q = 0$: $D_1 = D_2 = D_3 = 0$; (*ii*) $p^3 = -q^2 \neq 0$: here one has three real solutions, but two of them are the same. If one obtains for L_{hkl} a value, which is not expected (too high or too low), or which is negative, or if one obtains two or three real solutions for L_{hkl}, then the assumption [2] is not correct.

It is obvious that assumptions [1] and [2], like others appearing in literature, affect the final results of the separation of the line profile broadening sources. Moreover, the definitions of the crystallite size and strain parameters are different in various approaches to the broadening analysis. Therefore, the numerical values of the parameters obtained by the same author, who uses different methods, may be mutually in disagreement.[5] The Warren-Averbach and integral width methods define the crystallite size as the dimension normal to the reflecting planes, averaged in the crystallite (coherently diffracting domain) volume, whereas the variance method gives the cube root of the crystallite volume. Besides, the size parameter also depends on the extent of faultings and whether or not they are specifically allowed for. The Warren-Averbach method provides the root-mean-squared strain averaged over a distance normal to the reflecting planes, whereas the integral width method yields an approximate upper limit of the lattice strain. One has to bear in mind all these when comparing the values of the size and strain parameters as derived using different methods. For a detailed discussion on the accuracy of the size and strain parameters obtained from the diffraction broadening analysis, the reader is referred to excellent reviews existing in literature (e. g. ref.[2-5,9,14]).

TRUNCATION OF PROFILE TAILS

The effect of the truncation of the profile tails on the broadening analysis has been investigated by many authors (e. g. ref.[14,4]). The truncation necessarily occurs because the range of the observation of the experimental profile is finite. A profile $I(\varepsilon)$ of inherently infinite extent is truncated at arbitrary points ε_T and $-\varepsilon_T$. This inevitable truncation can be considered as a multiplication of the profile $I(\varepsilon)$ with the rectangular function, $r(\varepsilon)$, implied in experiment and defined as:[14,4]

$$r(\varepsilon) = \begin{cases} 1 \text{ if } -\varepsilon_T \leqslant \varepsilon \leqslant \varepsilon_T, \\ 0 \text{ elsewhere.} \end{cases},$$

The truncation distorts the Fourier coefficients of the profile and contributes to the so-called »hook« effect, thus introducing errors in the obtained size and strain parameter values (e. g. ref.[2,4,5,14]). For example, an error of 20% would be made in the crystallite size value, if the truncation were made at the points, where the profile ordinate falls to 5% of its maximum value.[14] An accompanying error, which is often considered together with the truncation, is the background level error. In practice the background level is more readily over rather than underestimated, owing to overlapping tails of neighbouring reflexions. This causes the apparent net intensity to fall to zero well within the observation range. Such a profile can be considered as truncated at the points where the intensity apparently falls to zero.[4]

In the present work the integral widths have been calculated for several simple bell-shaped functions, $I(\varepsilon)$, truncated at the points where the profile

ordinates fall to the one hundredth of the profile maximum. These values have been compared with the widths for the infinite range of definition. That is, the following expressions have been solved:

$$B_i = \frac{\int_{-\infty}^{\infty} I(\varepsilon)\,\mathrm{d}\varepsilon}{I(0)}, \tag{13}$$

$$B_{i\,(-\varepsilon_T,\,\varepsilon_T)} = \frac{\int_{-\varepsilon_T}^{\varepsilon_T} I(\varepsilon)\,\mathrm{d}\varepsilon}{I(0)}, \tag{14}$$

where $I(\pm\,\varepsilon_T) = I(0)/100$. The obtained results are given in Table I, together with the half-maximum widths. It follows from Table I, that the truncation

TABLE I

Influence of the Truncation of the Profile Tails on the Integral Width

bell-shaped function, $I(\varepsilon)$	integral width for the infinite range of definition, B_i (13)	half-maximum width	$k\varepsilon_T$, where $I(\varepsilon_T)=I(0)/100$	the ratio of the integral width of the profile truncated at the points $\pm\,\varepsilon_T$, and the integral width for the infinite range of definition, $B_i\,(-\varepsilon_T,\,\varepsilon_T)/B_i$, i. e. (14)/(13)
$\frac{\sin^2(k\varepsilon)}{(k\varepsilon)^2}$	$\frac{\pi}{k}$	$\frac{0.885888\pi}{k}$	$2.852342=$ $=\pi-0.289251$	0.902234 0.902822 (for $B_{i(-\pi,\,\pi)}$)
$(1+k^2\varepsilon^2)^{-1}$	$\frac{\pi}{k}$	$\frac{2}{k}$	$\sqrt{99}=9.949874$	0.936231
$(1+k^2\varepsilon^2)^{-2}$	$\frac{\pi}{2k}$	$\frac{2\sqrt{\sqrt{2}-1}}{k}$	3	0.986153
$\exp(-k^2\varepsilon^2)$	$\frac{\sqrt{\pi}}{k}$	$\frac{2\sqrt{\ln 2}}{k}$	$\sqrt{\ln 100}=$ $=2.145966$	0.997597

much more affects the functions, which describe approximately the size parameter $[\sin^2(k\varepsilon)/(k\varepsilon)^2,\ (1+k^2\varepsilon^2)^{-1}]$, than the ones describing approximately the strain parameter $[(1+k^2\varepsilon^2)^{-2},\ \exp(-k^2\varepsilon^2)]$. This is in agreement with the experimental evidence: the methods for the diffraction broadening analysis show that the crystallite size parameter is much more dependent on the accuracy with which the profile tails are measured, than it is the strain parameter (e. g. ref.[5,4]). In parallel to this conclusion it is, therefore, very important to avoid a tendency to overestimate the background level, either due to the overlapping of the tails of the neighbouring profiles, or due to the fact that for the small crystallite sizes and for a wide size distribution the tails of the profiles are very long.

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SAŽETAK

Primjena zvonolikih funkcija u analizi rendgenskoga difrakcijskog proširenja

S. Popović

Predočena su grafička i analitička rješenja za parametre veličine kristalita i deformacije kristalne rešetke, koji uzrokuju difrakcijsko proširenje, kada se u obzir uzimaju dva ili više redova refleksa od istog skupa mrežnih ravnina, a difrakcijski se profili opisuju jednostavnim zvonolikim funkcijama. Diskutira se i utjecaj neizbježnog kresanja repova profila na izvedene vrijednosti parametara veličine kristalita i deformacije rešetke. Nađeno je da kresanje repova mnogo više utječe na funkcije koje opisuju parametar veličine kristalita, nego na funkcije koje opisuju parametar deformacije, što je u skladu s eksperimentalnim činjenicama.