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Extended pseudo-Voigt function for approximating the Voigt profile

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The formula of the pseudo-Voigt function expressed by a weighted sum of Gaussian and Lorentzian functions is extended by adding two other types of peak functions in order to improve the accuracy when approximating the Voigt profile. The full width at half-maximum (FWHM) values and mixing parameters of the Gaussian, the Lorentzian and the other two component functions in the extended formula can be approximated by polynomials of a parameter $\rho = \Gamma_L/(\Gamma_G + \Gamma_L)$, where Γ_G and Γ_L are the FWHM values of the deconvoluted Gaussian and Lorentzian functions, respectively. The maximum deviation of the extended pseudo-Voigt function from the Voigt profile is within 0.12% relative to the peak height when sixth-order polynomial expansions are used. The systematic errors of the integrated intensity Γ_G and Γ_L, estimated by fitting the extended formula to Voigt profiles, are typically less than 1/10 of the errors arising from the application of the original formula of the pseudo-Voigt approximation proposed by Thompson *et al.* [*J. Appl. Cryst.* (1987), **20**, 79–83], while the time required for computation of the extended formula is only about 2.5 relative to the computation time required for the original formula.

1. Introduction

The Voigt function, which is defined by the convolution of Gaussian (normal distribution) and Lorentzian (Cauchy distribution) functions, is the most important description of the symmetric feature of a diffraction peak profile because of its theoretical significance as well as the practical goodness of fit to experimental data (Langford, 1992). Not only are the X-ray emission spectra of transition metals naturally Lorentzians (Hölzer *et al.*, 1997), but the particle-size broadening is also suggested to be described by a Lorentzian (de Keijser *et al.*, 1982), while the instrumental contributions can roughly be approximated by a Gaussian (Rietveld, 1969), according to the central limit theorem, and strain broadening may also possess a Gaussian form (David & Matthewman, 1985). Therefore, the Voigt profile is a theoretically natural description of diffraction peak shape.

Although experimentally observed diffraction peak profiles are often asymmetric, by multiply convoluting asymmetric instrumental functions with the symmetric profile function, asymmetric model functions can be constructed systematically (Ida & Kimura, 1999). However, the computation of profile fitting applying the Voigtian-based function may generally become quite time consuming, especially when it is calculated by multiple numerical convolutions with asymmetric instrumental functions.

The pseudo-Voigt function, which is a linear combination of Gaussian and Lorentzian functions with the same full width at half-maximum (FWHM) values, is a simple approximation for the Voigt profile function (Wertheim *et al.*, 1974). It has been claimed that the maximum deviation between the exact Voigt profile and the optimized pseudo-Voigt approximation is 0.77% relative to the peak height, and it is adequate for data containing $\leq 2 \times 10^4$ counts channel^{-1}, for which one standard deviation is $\geq$0.7% of the counts. Furthermore, it is advantageous that an efficient algorithm (Ida & Kimura, 1999) is applicable to the numerical evaluation of the convolutions of the pseudo-Voigt-based functions with instrumental functions, because for the Gaussian and Lorentzian functions, the primitive function and its inverse are both available.

Thompson *et al.* (1987) have proposed a convenient expression of the pseudo-Voigt function for approximating the Voigt profile, in which the FWHM and Lorentzian weight of the pseudo-Voigt function are related to the FWHM values of the deconvoluted Gaussian and Lorentzian functions, Γ_G and Γ_L. However, the accuracy of the approximation may not be adequate for analysing high-precision data collected with a synchrotron radiation source.

In this paper, we propose an extended formula of the pseudo-Voigt function for precisely approximating the Voigt profile and demonstrate that it can significantly improve the accuracy of the integrated intensity, Γ_G and Γ_L, estimated by fitting to a Voigt profile.

2. The Voigt profile

2.1. The Voigt and complex error functions

The Voigt profile defined by the convolution of Gaussian and Lorentzian functions, with FWHM values of Γ_G and Γ_L, is expressed by the following equations:

$$f_V(x;\Gamma_G,\Gamma_L) = (2/\Gamma_G)[(\ln 2)/\pi]^{1/2} \times K[2(\ln 2)^{1/2}x/\Gamma_G\,,(\ln 2)^{1/2}\Gamma_L/\Gamma_G], \quad (1)$$

$$K(x,y) = (y/\pi)\int_{-\infty}^{\infty} \exp(-t^2)/[y^2+(x-t)^2]\,\mathrm{d}t = \Re[w(x+iy)], \quad (2)$$

$$w(z) = \exp(-z^2)\,\mathrm{erfc}(-iz), \quad (3)$$

where $K(x,y)$ is usually referred to as the Voigt function, $w(z)$ is a scaled complex error function called the Faddeeva function, and $\mathrm{erfc}(z)$ is the complementary complex error function. $\Re[z]$ means the real part of z.

An efficient algorithm to evaluate the Faddeeva function has been proposed by Poppe & Wijers (1990), the accuracy of which is 14 significant digits throughout almost the whole of the complex plane.

2.2. Specification of the Voigt profile

Although the variable shape of the Voigt function $K(x,y)$ is specified by a single parameter y taking x as abscissa, it seems numerically inconvenient because we need $x\to\infty$ and $y\to\infty$ to reproduce a pure Lorentzian profile using the formula of $K(x,y)$. Thus here we define a parameter $\rho\equiv\Gamma_L/(\Gamma_G+\Gamma_L)$ instead of y and take the Voigt profile for $\Gamma_G+\Gamma_L=1$ as a reference profile, without loss of generality. From the reference Voigt profile defined by

$$p(x;\rho)\equiv f_V(x;1-\rho,\rho), \quad (4)$$

the general Voigt profile for arbitrary Γ_G and Γ_L is derived straightforwardly as

$$f_V(x;\Gamma_G,\Gamma_L) = [1/(\Gamma_G+\Gamma_L)]p[x/(\Gamma_G+\Gamma_L);\rho]. \quad (5)$$

The Voigt profiles calculated by the algorithm of Poppe & Wijers (1990) on variation of the parameter ρ are shown in Fig. 1.

3. Extension of the pseudo-Voigt approximation

3.1. Pseudo-Voigt function

The normalized pseudo-Voigt function is given by

$$f_{\mathrm{pV}}(x) = (1-\eta)f_G(x;\gamma_G)+\eta f_L(x;\gamma_L), \quad (6)$$

where $f_G(x;\gamma_G)$ and $f_L(x;\gamma_L)$ are the normalized Gaussian and Lorentzian functions, with FWHM $\Gamma = 2(\ln 2)^{1/2}\gamma_G = 2\gamma_L$,

$$f_G(x;\gamma_G) = (1/\pi^{1/2}\gamma_G)\exp(-x^2/\gamma_G^2), \quad (7)$$

and

$$f_L(x;\gamma_L) = (1/\pi\gamma_L)(1+x^2/\gamma_L^2)^{-1}, \quad (8)$$

and η is a parameter which mixes the two functions.

Thompson *et al.* (1987) have proposed the following expression for the pseudo-Voigt approximation for the convolution of the Gaussian and Lorentzian functions, with FWHM values of Γ_G and Γ_L, respectively:

$$\eta = 1.36603(\Gamma_L/\Gamma) - 0.47719(\Gamma_L/\Gamma)^2 + 0.11116(\Gamma_L/\Gamma)^3, \quad (9)$$

$$\Gamma = (\Gamma_G^5 + 2.69269\Gamma_G^4\Gamma_L + 2.42843\Gamma_G^3\Gamma_L^2 + 4.47163\Gamma_G^2\Gamma_L^3 + 0.07842\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{1/5}, \quad (10)$$

which we abbreviate as the TCH formula.

Fig. 2 is a plot of the difference relative to the peak height between the profile calculated by the TCH formula and the reference Voigt profile; we find the maximum deviation to be about 1.2% at $\rho\simeq 0.5$. It is expected that the goodness of fit to the Voigt profile would be improved by the addition of other functions, with intermediate shape between Gaussian and Lorentzian, into the formula of the pseudo-Voigt function.

3.2. Application of intermediate functions

We can find only a few functions that satisfy both of the following requirements: (i) intermediate shape between Gaussian and Lorentzian; (ii) availability of both the primitive function and its inverse. The latter is required for application of the efficient numerical method for evaluating the convolutions with instrumental functions (Ida & Kimura, 1999). One candidate is an irrational function with the following normalized formula:

$$f_I(x;\gamma_I) = (1/2\gamma_I)[1+(x/\gamma_I)^2]^{-3/2}. \quad (11)$$

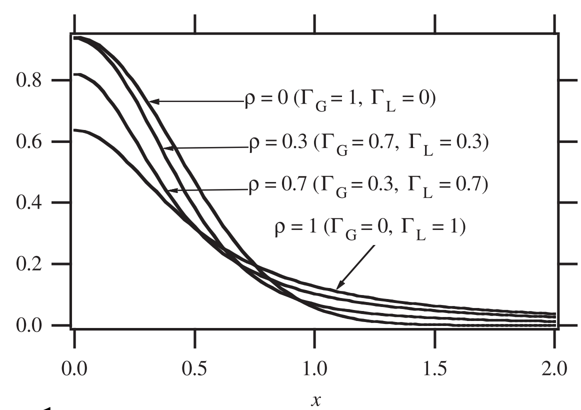

Figure 1
The Voigt profiles on variation of the Gaussian and Lorentzian FWHM values, Γ_G and Γ_L.

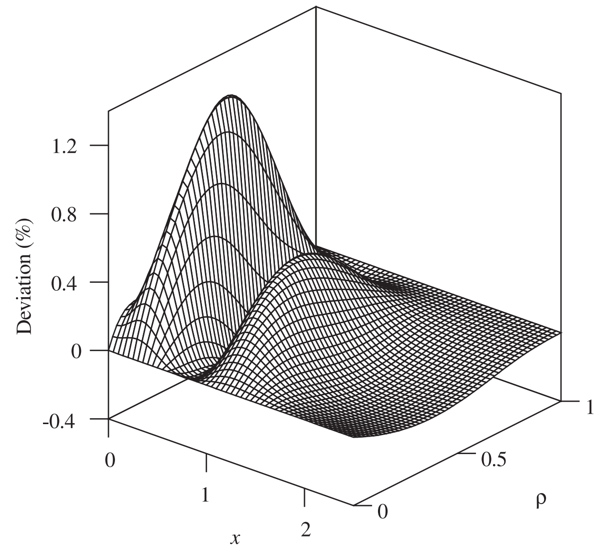

Figure 2
Three-dimensional plot of the deviation of the pseudo-Voigt function calculated by the formula proposed by Thompson *et al.* (1987) from the Voigt profile relative to the peak height.

The FWHM of this function is given by $(2^{2/3}-1)^{1/2}\gamma_I$, and the primitive function and its inverse are

$$F_I(x) = (x/\gamma_I)/2[1+(x/\gamma_I)^2]^{1/2} \tag{12}$$

and

$$F_I^{-1}(\xi) = 2\xi\gamma_I/(1-4\xi^2)^{1/2}, \tag{13}$$

respectively. Another candidate is the squared hyperbolic secant function defined by

$$f_P(x;\gamma_P) = (1/2\gamma_P)\,\mathrm{sech}^2\,(x/\gamma_P), \tag{14}$$

$$\mathrm{sech}\,x \equiv 2/[\exp(x)+\exp(-x)], \tag{15}$$

of which the FWHM is given by $2[\ln(2^{1/2}+1)]\gamma_P$, and the primitive function and its inverse are given by

$$F_P(x) \equiv (1/2)\tanh\,(x/\gamma_P) \tag{16}$$

and

$$F_P^{-1}(\xi) = (\gamma_P/2)\ln[(1+2\xi)/(1-2\xi)], \tag{17}$$

respectively, with

$$\tanh x \equiv [\exp(x)-\exp(-x)]/[\exp(x)+\exp(-x)]. \tag{18}$$

The profiles of the above two functions are shown in Fig. 3. Since the irrational and hyperbolic functions are roughly equidistantly spaced between Gaussian and Lorentzian functions, it is suggested that addition of both terms would considerably improve the goodness of fit to the Voigt profile.

Thus we propose a formula of the extended pseudo-Voigt function:

$$f_{\mathrm{epV}}(x) = (1-\eta_L-\eta_I-\eta_P)f_G(x;\gamma_G)+\eta_L f_L(x;\gamma_L) + \eta_I f_I(x;\gamma_I)+\eta_P f_P(x;\gamma_P). \tag{19}$$

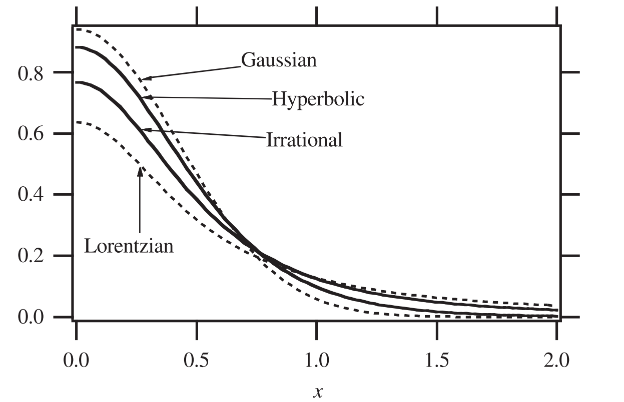

Figure 3
Profiles of the Gaussian, Lorentzian, irrational and hyperbolic functions with FWHM = 1.

The FWHM values of the components are given by $W_G = 2(\ln 2)^{1/2}\gamma_G$, $W_L = 2\gamma_L$, $W_I = 2(2^{2/3}-1)^{1/2}\gamma_I$ and $W_P = 2[\ln 2^{1/2} + 1)]\gamma_P$.

3.3. Least-squares optimization of the FWHM and mixing parameters

As the first step, we determine the least-squares optimized values of the FWHM parameters W_G, W_L, W_I and W_P and the mixing parameters η_L, η_I and η_P of the extended pseudo-Voigt function for approximating the reference Voigt profiles, varying the parameter $\rho = 0.01, 0.02, \ldots, 0.99$. We denote the FWHM optimized in this process as w_i ($i = \{G, L, I, P\}$) instead of W_i to clarify that it is to be optimized for the Voigt profile with $\Gamma_G + \Gamma_L = 1$. Once w_i is determined, the FWHM W_i for arbitrary Γ_G and Γ_L is simply given by $W_i = (\Gamma_G + \Gamma_L)w_i$.

The reference Voigt profile data $\{y_i\}$ are calculated at $x_i = 0, 0.05, 0.010, \ldots, 9.95$ (200 data points) by using the Poppe–Wijers algorithm, and numerical least-squares optimization of the extended pseudo-Voigt function is achieved by the Levenberg–Marquardt method (Press *et al.*, 1986), applying the weight $y_i^{-1/2}$. All FWHM parameters, w_G, w_L, w_I and w_P, and mixing parameters, η_L, η_I and η_P, in the extended formula of the pseudo-Voigt function are treated as independent variable parameters.

3.4. Approximation of dependence of w_i and η_i on ρ

The dependence of the optimized w_i and η_i on ρ is, as shown in Figs. 4 and 5, suggested to be quite well approximated by polynomials of ρ.

Taking the behaviour of w_i and η_i towards $\rho \to 0$, 1 into account, we apply the following polynomial expansion formulae:

$$w_G = 1 - \rho\sum_{i=0}^{N} a_i\,\rho^i, \tag{20}$$

$$w_L = 1 - (1-\rho)\sum_{i=0}^{N} b_i\,\rho^i, \tag{21}$$

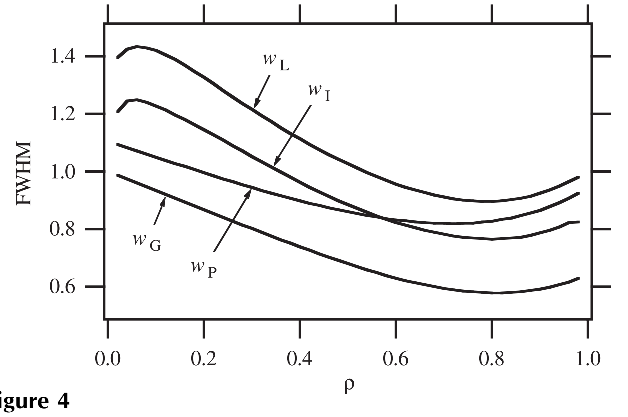

Figure 4
The optimized values of extended pseudo-Voigt parameters w_G, w_L, w_I and w_P.

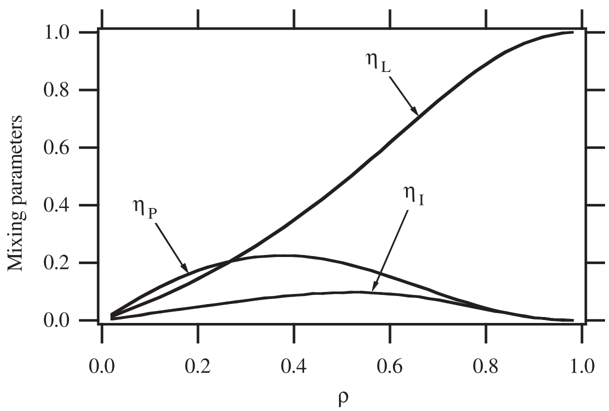

Figure 5
The optimized values of extended pseudo-Voigt parameters η_L, η_I and η_P.

$$w_I = \sum_{i=0}^{N} c_i \, \rho^i, \tag{22}$$

$$w_P = \sum_{i=0}^{N} d_i \, \rho^i, \tag{23}$$

$$\eta_L = \rho \Big[1 + (1 - \rho) \sum_{i=0}^{N} f_i \, \rho^i \Big], \tag{24}$$

$$\eta_I = \rho(1 - \rho) \sum_{i=0}^{N} g_i \, \rho^i, \tag{25}$$

$$\eta_P = \rho(1 - \rho) \sum_{i=0}^{N} h_i \, \rho^i. \tag{26}$$

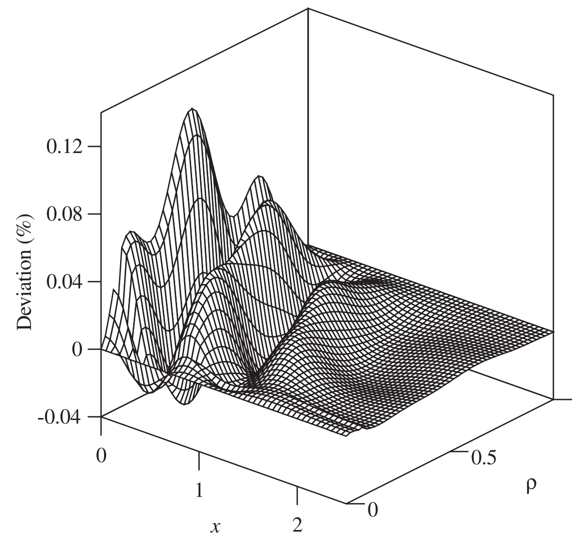

Figure 6
Three-dimensional plot of the deviation of the extended pseudo-Voigt function from the Voigt profile relative to the peak height.

The optimized values of the coefficients $\{a_i\}$, $\{b_i\}$, $\{c_i\}$, $\{d_i\}$, $\{f_i\}$, $\{g_i\}$ and $\{h_i\}$ for $N = 6$ are listed in Table 1, and the deviation of the extended pseudo-Voigt function, calculated with these coefficients, from the Voigt profile is plotted in Fig. 6. The maximum deviation relative to the peak height is found to be about 0.12% at $\rho \simeq 0.46$, which is just 1/10 of the maximum deviation according to the TCH formula.

The computing speed of the algorithms was compared by using a compiled macro procedure (*WaveMetrics*, Igor Pro) on a personal computer (Apple, Power Macintosh 7600/200). The computing time required for evaluating the extended formula of the pseudo-Voigt function is roughly 2.5 relative to the computing time required by the TCH formula, while the relative time required for the evaluation of the Voigt profiles by the Poppe–Weijers algorithm is about 20.

4. Errors in estimation of profile parameters by a fitting method

The accuracy of profile parameters estimated by least-squares fittings by applying the TCH form and the extended form of the pseudo-Voigt function to a Voigt profile is discussed in this section.

Table 1
The optimized polynomial coefficients $\{a_i\}$, $\{b_i\}$, $\{c_i\}$, $\{d_i\}$, $\{f_i\}$, $\{g_i\}$ and $\{h_i\}$.

i	$\{a_i\}$	$\{b_i\}$	$\{c_i\}$	$\{d_i\}$	$\{f_i\}$	$\{g_i\}$	$\{h_i\}$
0	0.66000	−0.42179	1.19913	1.10186	−0.30165	0.25437	1.01579
1	0.15021	−1.25693	1.43021	−0.47745	−1.38927	−0.14107	1.50429
2	−1.24984	10.30003	−15.36331	−0.68688	9.31550	3.23653	−9.21815
3	4.74052	−23.45651	47.06071	2.76622	−24.10743	−11.09215	23.59717
4	−9.48291	29.14158	−73.61822	−4.55466	34.96491	22.10544	−39.71134
5	8.48252	−16.50453	57.92559	4.05475	−21.18862	−24.12407	32.83023
6	−2.95553	3.19974	−17.80614	−1.26571	3.70290	9.76947	−10.02142

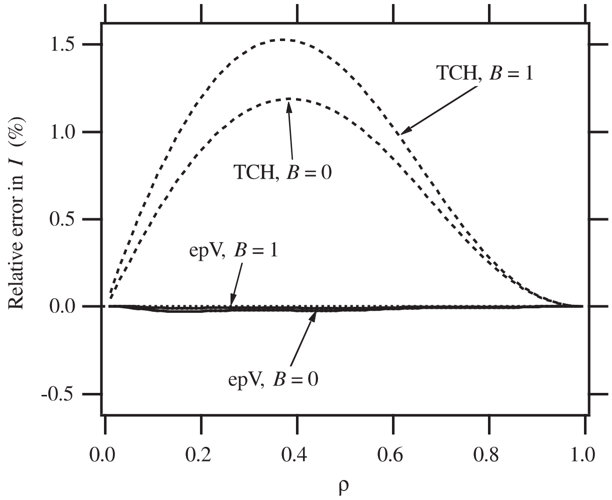

Figure 7
Errors in estimation of the integrated intensity I from Voigt profile data. The data labelled 'TCH' were calculated by the formula proposed by Thompson *et al.* (1987), and those labelled 'epV' were calculated by the extended pseudo-Voigt function. B is the height of the background added to the Voigt profile.

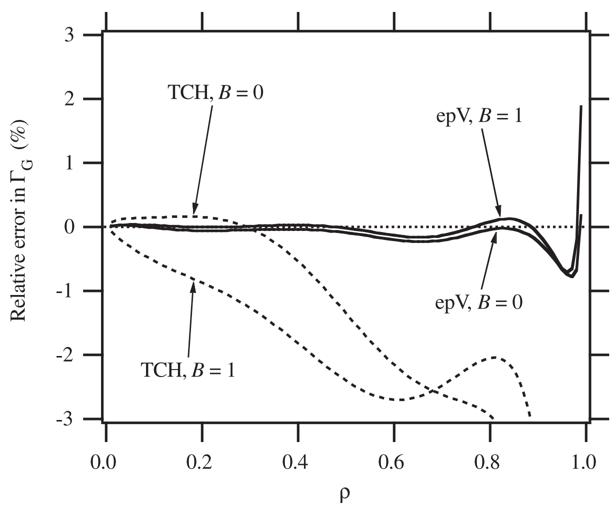

Figure 8
Errors in estimation of the Gaussian FWHM Γ_G from Voigt profile data.

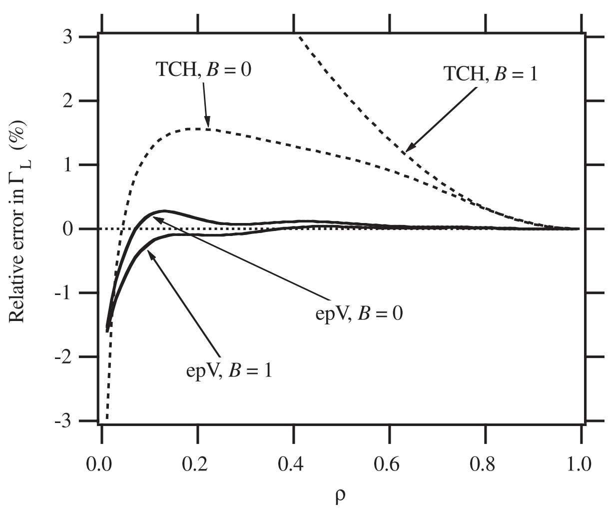

Figure 9
Errors in estimation of the Lorentzian FWHM Γ_L from Voigt profile data.

Sample data $\{y_i\}$ were prepared by using the reference Voigt profile as follows:

$$y_i = B + p(x_i, \rho),$$
$$x_i = -5.0, -4.9, -4.8, \ldots, 5.0,$$

the data points of which roughly satisfy the Rietveld refinement guidelines proposed by McCusker *et al.* (1999). In order to elucidate the effect of background, two sets of data, $B = 0$ (no background) and $B = 1$ (large background), were examined. Note that the peak height of the reference Voigt profile varies from ~0.64 to ~0.94 depending on ρ; that is, $B = 1$ means that the background is similar to or higher than the top of the peak function.

The constant background b, integrated intensity I, and Gaussian and Lorentzian FWHM values Γ_G and Γ_L, are treated as variable fitting parameters. The function to be minimized is

$$S = \sum_i [y_i - b - I f(x_i; \Gamma_G, \Gamma_L)]^2 / y_i, \qquad (27)$$

where $f(x_i; \Gamma_G, \Gamma_L)$ is the pseudo-Voigt function based on the TCH formula or the extended formula.

Table 2
Relative errors in profile parameters estimated by a profile fitting based on the TCH formula of the pseudo-Voigt function to Voigt profiles without background ($B = 0$).

ΔI, $\Delta\Gamma_G$ and $\Delta\Gamma_L$ are the relative errors in the estimated integrated intensity, and in the Gaussian and Lorentzian FWHM values, respectively. R_P is the R factor for profile fitting.

ρ	ΔI (%)	$\Delta\Gamma_G$ (%)	$\Delta\Gamma_L$ (%)	R_P (%)
0.1	0.50	0.15	1.23	0.43
0.2	0.90	0.15	1.56	0.72
0.3	1.13	−0.03	1.45	0.94
0.4	1.19	−0.54	1.29	1.05
0.5	1.08	−1.35	1.12	1.02
0.6	0.85	−2.15	0.91	0.84
0.7	0.54	−2.62	0.63	0.55
0.8	0.25	−2.95	0.31	0.25
0.9	0.06	−5.32	0.08	0.06

Table 3
Relative errors in profile parameters estimated by a profile fitting based on the TCH formula of the pseudo-Voigt function to Voigt profiles with large background ($B = 1$).

See Table 2 for definitions.

ρ	ΔI (%)	$\Delta\Gamma_G$ (%)	$\Delta\Gamma_L$ (%)	R_P (%)
0.1	0.70	−0.53	6.96	0.03
0.2	1.20	−0.87	5.52	0.06
0.3	1.47	−1.27	4.24	0.09
0.4	1.52	−1.82	3.12	0.09
0.5	1.35	−2.40	2.17	0.09
0.6	1.02	−2.70	1.39	0.07
0.7	0.63	−2.48	0.76	0.05
0.8	0.28	−2.05	0.32	0.02
0.9	0.06	−3.68	0.07	0.00

Table 4
Relative errors in profile parameters estimated by a profile fitting based on the extended pseudo-Voigt function to Voigt profiles without background ($B = 0$).

See Table 2 for definitions.

ρ	ΔI (%)	$\Delta\Gamma_G$ (%)	$\Delta\Gamma_L$ (%)	R_P (%)
0.1	−0.006	−0.014	0.220	0.038
0.2	−0.008	−0.058	0.158	0.057
0.3	−0.004	−0.046	0.072	0.070
0.4	−0.008	−0.037	0.115	0.073
0.5	−0.010	−0.091	0.094	0.072
0.6	−0.005	−0.200	0.043	0.064
0.7	−0.002	−0.208	0.031	0.045
0.8	−0.003	−0.042	0.019	0.024
0.9	0.000	−0.231	0.001	0.006

Table 5
Relative errors in profile parameters estimated by a profile fitting based on the extended pseudo-Voigt function to Voigt profiles with large background ($B = 1$).

See Table 2 for definitions.

ρ	ΔI (%)	$\Delta\Gamma_G$ (%)	$\Delta\Gamma_L$ (%)	R_P (%)
0.1	−0.021	0.026	−0.216	0.004
0.2	−0.027	−0.003	−0.095	0.005
0.3	−0.020	0.010	−0.069	0.006
0.4	−0.023	0.028	0.019	0.007
0.5	−0.022	−0.020	0.034	0.006
0.6	−0.013	−0.131	0.012	0.006
0.7	−0.006	−0.134	0.014	0.004
0.8	−0.007	0.082	0.008	0.002
0.9	−0.001	−0.106	−0.001	0.001

The relative errors of the estimated profile parameters (I, Γ_G, Γ_L) are plotted in Figs. 7–9 and summarized in Tables 2–5. The R factors for the profile fitting (R_P), defined by

$$R_P = \sum_i |y_i - b - I f(x_i; \Gamma_G, \Gamma_L)| \Big/ \sum_i y_i, \qquad (28)$$

are also listed in Tables 2–5.

The extended pseudo-Voigt function clearly gives improved accuracy in the estimation of the profile parameters for any shape of the Voigt profile. The errors in the profile parameters estimated by fitting based on the extended pseudo-Voigt function are typically less than 1/10 of the errors arising from application of the TCH formula. When a large background is included in the experimentally observed profile, application of the TCH formula may result in a considerable amount of systematic error, especially in the estimation of Γ_L, while no significant reduction of accuracy is found in the estimation based on the extended formula.

5. Conclusions

We propose a practical formula of an extended pseudo-Voigt function optimized for approximating the Voigt profile. The systematic errors of the profile parameters estimated by fitting the extended formula to Voigt profiles are typically less than 1/10 of the errors resulting from the application of the original formula of the pseudo-Voigt approximation proposed by Thompson *et al.* (1987), while the time required for computation of the extended formula is only about 2.5 relative to the computation time required for the original formula.

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