Profile Refinement of Powder Diffraction Patterns Using the Voigt Function

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Abstract
The Voigt function has been incorporated as a peak-shape description into a program for the refinement of constant-wavelength X-ray and neutron diffraction patterns. The results obtained for neutron diffraction are encouraging and indicate that the Voigt function describes the symmetrical component of the profile peak shape to high accuracy even in the presence of substantial line broadening from particle-size effects. In contrast with approximations to the Voigt function, such as the pseudo-Voigt and Pearson VII functions, the present treatment allows the angular dependences of line-broadening effects resulting from particle-size and instrumental contributions to be coded independently from each other in the Rietveld technique. The present treatment, which details improvements to the symmetrical component of the peak shape, does not offer a fully rigorous description of the peak shape as asymmetry corrections such as those given by Howard [J. Appl. Cryst. (1982), 15, 615-620] are not included.

Introduction
The Rietveld profile refinement technique (Rietveld, 1969) has, over the past decade, proved to be an important method for the refinement of crystal structures from powder diffraction patterns and has been particularly successfully applied to the analysis of constant-wavelength neutron diffraction data. This success is, in no small part, a result of the assumption that the constant-wavelength neutron diffraction peak shape may, to a good approximation, be described by a Gaussian function. Recent high-resolution experiments (e.g. Suortti, Ahtee & Unonius, 1979), however, have indicated deficiencies in this assumption and, indeed, a considerable catalogue of work now exists (e.g. Young & Wiles, 1982; Hill & Howard, 1984) that indicates that there is a Lorentzian (Cauchy) component to the peak shape arising from particle-size effects. Given that particle-size broadening may be well described by a Lorentzian function (de Keijser, Langford, Mittemeijer & Vogels, 1982) and instrumental contributions may be described by a Gaussian (Rietveld, 1969), the recognized natural candidate for a more general description of the constant-wavelength neutron diffraction peak shape is a convolution of Gaussian and Lorentzian functions (the Voigt function) (Suortti, Ahtee & Unonius, 1979; de Keijser, Mittemeijer & Rozendaal, 1983). However, no profile refinement code to date has included this function as a peak-shape description (David & Matthewman, 1984). Instead, a variety of simpler functions (a catalogue is given in the paper by Young & Wiles, 1982) have been used. Although many of these functions, such as the intermediate and modified Lorentzians, lack any physical significance and provide purely empirical peak fits, two functions, the Pearson VII and pseudo-Voigt functions, closely resemble the Voigt function and may be continuously varied between Gaussian and Lorentzian limits. In particular the pseudo-Voigt function has been shown to model the Voigt function to a high accuracy (Wertheim, Butler, West & Buchanan, 1974) and has led, in a number of cases, to significant improvements over Gaussian-based refinements (Young & Wiles, 1982; Hill & Howard, 1984). The principal shortcoming, however, of any approximation to the Voigt function is that there is no simple way of allowing the half-width parameters of the Gaussian and Lorentzian components of the peak shape to vary as a function of angle in their separate and different ways. (Although, in this paper, strain broadening is assumed to possess a Gaussian form this need not be demanded; strain effects may be separately coded in terms of a Voigt function without loss of generality of the Voigt as an improved peak description over the Gaussian.)

In this paper it is shown that it is not necessary to resort to approximations to the Voigt function in profile refinement. A refinement code based on the Cambridge Crystallographic Subroutine Library (CCSL) (Matthewman, Thompson & Brown, 1982) is presented and the analysis of neutron diffraction data sets is discussed. The principal advantages of using the Voigt peak shape in profile refinement are, firstly, that the function is physically reasonable and, secondly, that the angular dependence of the Lorentzian and Gaussian contributions to the Voigt function may be independently and correctly coded and that, consequently, particle-size effects may be simply separated...
from the instrumental contributions. Additionally it is worth noting that profile refinement with Voigt peak shapes is not computationally disadvantageous, being roughly only 50% slower than the equivalent refinement using Gaussians.

The Voigt peak shape

Given that the instrumental contribution to a diffraction peak centred at \( \theta = 2\theta_0 \) may be described by a normalized Gaussian function of the form

\[
G_i = \left[ \frac{1}{\sigma(2\pi)^{1/2}} \right] \exp \left[ -\frac{(\theta_i - 2\theta_0)^2}{(2\sigma^2)} \right],
\]

Caglioti, Paoletti & Ricci (1958) have shown that the angular dependence of the Gaussian half-width parameter, \( \sigma \), can be written as

\[
\sigma_i^2 = u \tan^2 \theta_i + v \tan \theta_i + w,
\]

where \( u, v \) and \( w \) are constant half-width parameters. Other workers (e.g. Suortti, Ahtee & Unonius, 1979) have shown that the full width at half maximum, \( \Gamma \), of the normalized Lorentzian function

\[
L_i = (\Gamma/2\pi)/\left[ (\Gamma/2)^2 + (2\theta_i - 2\theta_0)^2 \right]
\]

describing particle-size effects varies as \( 1/\cos \theta_i \), which may, to emphasize the correspondence with (1), be written as

\[
\Gamma_i^2 = t(\tan^2 \theta_i + 1).
\]

The angular dependence of the normalized Voigt function obtained by convolution of the above two functions may thus be described by four half-width parameters, \( u, v, w \) and \( t \). From Batty, Hoath & Roberts (1976) the normalized Voigt function may be simply related to the real part of the complex error function,

\[
V_i = \left[ \frac{1}{\sigma(2\pi)^{1/2}} \right] \text{Re} \left[ w(x + iy) \right],
\]

where

\[
x = (2\theta_i - 2\theta_0)/(\sigma\sqrt{2})
\]

and

\[
y = \Gamma/(\sigma\sqrt{2})
\]

and with

\[
z = x + iy
\]

\[
w(z) = \exp(-z^2)\text{erfc}(-iz).
\]

In contrast with the work of Suortti, Ahtee & Unonius (1979) the half-width parameters are simply related to the arguments of the complex error-function formulation and thus the function and its derivatives, which are simple functions of the complex error function, may be easily incorporated into the profile refinement code.

Comparison of Gaussian- and Voigt-based profile refinements

The de-intercalated spinel \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) \((x \approx 0.9)\)

In recent years there has been a growing interest in novel materials that have been prepared by intercalation or deintercalation of small mobile cations such as \( H^+ \), \( Li^+ \) and \( Na^+ \). \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) \((x \approx 0.9)\) is one of many non-stoichiometric phases based on the \( AB_2\text{O}_4 \) spinel structure. \( Li^+ \) ions may be chemically or electrochemically removed from the cubic spinel \( \text{LiMn}_2\text{O}_4 \) leaving a structure in which the \( \text{Mn}_2\text{O}_4 \) framework remains intact and the stoichiometry approaches \( \text{MnO}_2 \) (David, Thackeray & Goodenough, 1985). This deintercalation reaction is, not surprisingly, rather severe and results in a breakdown of individual crystallites and a substantial reduction in particle size. \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) is thus an ideal candidate for testing the Voigt refinement procedure and comparing the relative merits of Gaussian- and Voigt-based refinements where particle sizes play a significant role in line broadening. Although the presence of a small amount of impurities (particularly unreacted \( \text{LiMn}_2\text{O}_4 \)) in the sample of \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) used in the present work is undesirable, nevertheless, the quality of the following results justify the use of \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) as a test material for the investigation of Voigt-based profile refinements. The results of both Gaussian- and Voigt-based profile refinements of \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) are presented in Table 1: the observed and calculated profiles are displayed in Figs. 1(a) and (b) respectively. The data were obtained from a 12 h run on the D1a diffractometer at the ILL, Grenoble, using a wavelength of 1.5082 Å. The improved quality of fit of the Voigt refinement over the Gaussian refinement is immediately apparent from a comparison of the two profiles and is reflected in the significant reduction in \( R \) factors (Table 2): in particular, the reductions in profile \( R \) factor from 21.9 to 11.9% and ‘Bragg’ \( R \) factor from 9.7 to 4.8% indicate that the Voigt refinement has resulted in a significantly superior profile fit. This point is also apparent from inspection of Figs. 2(a) and (b), which show an expanded plot of the diffraction profile around \( \theta = 100^\circ \) for the Gaussian- and Voigt-based refinements respectively. Comparison of Figs. 2(a) and (b) further highlights the inability of the Gaussian function and the success of the Voigt function in describing the symmetrical peak-shape component resulting from both instrumental contributions and particle-size broadening.

In addition to confirming that the Voigt-based refinement results in an improved fit, a detailed analysis of the refined parameters in Table 1 further reveals that there are substantial systematic differences between the two refinements. The differences, having been expressed as multiples of the square root of the sum of the squares of the estimated standard
Table 1. Refined parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Gaussian-based refinement</th>
<th>Voigt-based refinement</th>
<th>Difference†</th>
</tr>
</thead>
<tbody>
<tr>
<td>asym</td>
<td>$5.4(1.4) \times 10^{-5}$</td>
<td>$2.25(9) \times 10^{-5}$</td>
<td>2.3</td>
</tr>
<tr>
<td>$u$</td>
<td>2240(150)</td>
<td>172(9)</td>
<td>7.4</td>
</tr>
<tr>
<td>$v$</td>
<td>$-3670(300)$</td>
<td>$-446(20)$</td>
<td>3.4</td>
</tr>
<tr>
<td>$w$</td>
<td>4430(130)</td>
<td>376(10)</td>
<td>15.7</td>
</tr>
<tr>
<td>$t$</td>
<td></td>
<td>456(10)</td>
<td>—</td>
</tr>
<tr>
<td>zero</td>
<td>$-10(6)$</td>
<td>$-11.64(15)$</td>
<td>2.7</td>
</tr>
<tr>
<td>$a$</td>
<td>80224(4) Å</td>
<td>80215(1) Å</td>
<td>2.2</td>
</tr>
<tr>
<td>$A(Li)$</td>
<td>0.23(4) Å²</td>
<td>0.087(15) Å²</td>
<td>3.3</td>
</tr>
<tr>
<td>$B(Li)$</td>
<td>1.00 Å²</td>
<td>1.00 Å²</td>
<td>—</td>
</tr>
<tr>
<td>$B(Mn)$</td>
<td>0.48(5) Å²</td>
<td>0.44(2) Å²</td>
<td>0.7</td>
</tr>
<tr>
<td>$\chi(O)$</td>
<td>0.2677(10) Å²</td>
<td>0.26258(5) Å²</td>
<td>1.3</td>
</tr>
<tr>
<td>$B(O)$</td>
<td>0.86(3) Å²</td>
<td>0.76(1) Å²</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*The $u$, $v$ and $w$ parameters obtained from the Gaussian-based refinement have been divided by $8\ln2$ for direct comparison with the parameters derived from the Voigt-based refinement.

†The difference between equivalent refined parameters is expressed as a multiple of the square root of the sum of the squares of the e.s.d.'s of the two parameters.

‡The temperature factor of the Li ion was fixed at 1.00 Å².

![Fig. 1. Observed, calculated and difference profiles of Li$_{1-x}$Mn$_2$O$_4$ using (a) a Gaussian peak shape and (b) a Voigt peak shape.](image)

![Fig. 2. Selected region ($88 < 2\theta < 106^\circ$) of the diffraction profile of Li$_{1-x}$Mn$_2$O$_4$. (Small unfitted peaks result from impurities.)](image)
Table 2. R factors

<table>
<thead>
<tr>
<th></th>
<th>Gaussian-based refinement</th>
<th>Voigt-based refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_I$</td>
<td>9.7%</td>
<td>4.8%</td>
</tr>
<tr>
<td>$R_F$</td>
<td>18.5%</td>
<td>12.6%</td>
</tr>
<tr>
<td>$R_{w_F}$</td>
<td>21.9%</td>
<td>11.9%</td>
</tr>
<tr>
<td>$R_e$</td>
<td>5.0%</td>
<td>6.2%</td>
</tr>
<tr>
<td>$N - P + C$</td>
<td>1561*</td>
<td>2427*</td>
</tr>
</tbody>
</table>

Weighted profile R factor:

$$R_{w_F} = \left( \sum w_i (Y_i \text{obs} - Y_i \text{calc})^2 / \sum w_i Y_i \text{obs}^2 \right)^{1/2}$$

Profile R factor:

$$R_F = \left( \sum |Y_i \text{obs} - Y_i \text{calc}| / \sum Y_i \text{obs} \right)$$

`Bragg` R factor:

$$R_t = \left( \sum I_i \text{obs} / \sum I_i \text{calc} \right) / \sum I_i \text{obs}$$

`Expected` R factor:

$$R_e = \left( (N - P + C) / \sum w_i Y_i \text{obs}^2 \right)^{1/2}$$

$N - P + C = \text{number of observations} - \text{number of variables} + \text{number of constraints}$

$\alpha = \text{scale factor}$

*The large increase in the value of $N - P + C$ in the Voigt refinement results from the significant Lorentzian component to the line shape and the fact that all points between $\pm 5F$ (equation 3) were considered to contribute to a Bragg peak.*

Examination of the correlation sub-matrix referring to half-width parameters alone (Table 3) obtained from the Voigt-based refinement shows that although, as with the Gaussian-based refinement, the $u$, $v$ and $w$ parameters are heavily correlated with one another the $t$ parameter is relatively free from correlation. This is an important observation as it indicates that the Lorentzian component of the peak shape is, to a good approximation, uncoupled to other parameters, and that the physical significance of the Lorentzian component, particle-size broadening, may be interpreted with some confidence. The refined parameter, $t$, which is defined in (4) may be used to obtain a measure of the average particle size of the material. From Henry, Lipson & Wooster (1960) and de Keijser, Langford, Mittemeijer & Vogels (1982) the integral breadth, $\beta_L$, (expressed in radians) of the Lorentzian component of a diffraction peak may be related to the apparent average crystallite (or domain) size, $D$, through the equation

$$D = \lambda / (\beta_L \cos \theta),$$

where $\lambda$ is the neutron wavelength. As the integral breadth, $\beta_L$, of a Lorentzian is related to the full width at half maximum, $\Gamma$, by the equation

$$\beta_L = \pi \Gamma / 2$$

and as $\Gamma$ is related to the refined parameter $t$ through (4) then, mindful that $t^{1/2}$, following convention, is expressed in degrees $\times 100$ and not radians, the apparent crystallite size, $D$, may be obtained from the equation

$$D = 36000 \lambda / (\pi^2 t^{1/2}).$$

In the particular refinement of Li$_{1-x}$Mn$_2$O$_4$ discussed in this paper $\lambda = 1.5082$ Å and $t = 456(10)$. This gives an apparent average crystallite size of 258(3) Å, which is in keeping with the anticipated substantial reduction in particle size accompanying the de-intercalation of LiMn$_2$O$_4$.

In addition to the discrepancies with the half-width parameters, differences also exist between the cell constant, zero-point and asymmetry parameter obtained in the two refinements. However, it cannot be concluded from the improvement in fit using the Voigt function that the systematic errors in the Voigt-based refinement are less than those in the Gaussian-based refinement since systematic errors probably result from the incorrect description of the asymmetry parameter used by Rietveld (1969). Recent authors (Cooper & Sayer, 1975; Howard, 1982; Thompson & Wood, 1983; Prince, 1983; van Laar & Yelon, 1984) have discussed this asymmetry and Howard (1982) has included a suitable description in a profile refinement program. Work is in progress to include this necessary correction for a rigorous description of the profile line shape into the present profile-refinement program.

deviations, are individually significant if they exceed 2.5–3. Not surprisingly, the largest discrepancies are observed between the refined half-width parameters. In particular, $u(G)$ and $w(G)$ are substantially larger than $u(V)$ and $w(V)$ ($G$ and $V$ refer respectively to Gaussian- and Voigt-based refinements) – this results from the fact that in the Gaussian-based refinement $u$, $v$ and $w$ must not only account for the Gaussian component of the peak shape but, additionally, the Lorentzian component. Furthermore, in the Gaussian-based refinement the incorrect peak description, through the high correlations (Table 3) between $u$, $v$ and $w$, lead to systematic errors in $v$ implying that the description of the angular variations of the peak half-width in Gaussian-based refinements, in the presence of substantial particle-size broadening, will involve serious discrepancies. In the analysis of the half-width parameters obtained from the Voigt-based refinement it is also worth noting that the Gaussian parameters are closer to those anticipated from the instrumental resolution – for instance the monochromator take-off angle on the D1a diffractometer is $2\theta = 120^\circ$, which corresponds to the highest instrumental position. From the Caglioti–Paoletti–Ricci relationship (1) this will occur when $2\theta_L = 2 \tan^{-1} \left( -v / 2u \right)$; for the Voigt-based refinement this is $2\theta_L = 105(5)^\circ$ [cf. for the Gaussian-based refinement $2\theta_L = 78(10)^\circ$].
Table 3. Correlation matrices (expressed as percentages)

<table>
<thead>
<tr>
<th></th>
<th>Gaussian-based refinement</th>
<th></th>
<th>Voigt-based refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$u$ $v$ $w$ $t$ asym zero $a^{*2}$ scal</td>
<td></td>
<td>$u$ $v$ $w$ $t$ asym zero $a^{*2}$ scal</td>
</tr>
<tr>
<td>$u$</td>
<td>100 -93 75 *</td>
<td></td>
<td>100 -93 78 -27 3 1 0 0 0</td>
</tr>
<tr>
<td>$v$</td>
<td>-93 100 -92 *</td>
<td></td>
<td>-93 100 -88 16 -1 0 0 0</td>
</tr>
<tr>
<td>$w$</td>
<td>78 -88 100 -45 5 2 -1 -4 3 1 -2 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>-27 16 -45 100 -16 -6 3 21 -8 0 1 -9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>asym</td>
<td>3 -1 5 -16 100 34 -22 -10 -7 -1 -4 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>zero</td>
<td>1 0 2 -6 34 100 -88 -5 -3 -3 -3 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^{*2}$</td>
<td>0 0 -1 13 -22 -88 100 3 3 3 4 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>scal</td>
<td>-8 2 -4 21 -10 -5 3 100 -6 41 -1 72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_{Li}$</td>
<td>1 0 3 -8 -7 -3 3 6 100 0 6 -3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{Mn}$</td>
<td>-3 1 1 0 -1 -3 3 41 0 100 21 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_{O}$</td>
<td>-4 4 -2 1 -1 -3 4 -1 6 21 100 -20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{O}$</td>
<td>-1 -3 8 -9 -4 0 -1 72 -3 4 -20 100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Although, from Table 3, it is clear that there is little correlation between structural and peak-shape description parameters there are, nevertheless, differences between the refined structural parameters of the Gaussian- and Voigt-based refinements. These differences are most pronounced for the Li site occupancy and the oxygen temperature factor – the manganese temperature factor and oxygen positional parameter are not significantly different between refinements. {The Li occupancy obtained in the Voigt refinement [$x = 0.087(15)$] is in closer agreement with the value of 0.02 obtained by Hunter (1981) in a similar de-intercalation.}

The results presented in this paper indicate that an improved refinement of powder neutron diffraction data of Li$_{1-x}$Mn$_2$O$_4$ may be obtained by using a Voigt function rather than a Gaussian function as a peak-shape description. As the Gaussian is a special case of the more general Voigt function this result in itself is unremarkable and it remains to be seen whether the Voigt function will provide a significant improvement over functions such as the pseudo-Voigt and Pearson VII. However, the Voigt function is the most satisfactorily from a physical viewpoint since, as a convolution of Gaussian and Lorentzian functions, it represents mathematically the correct way in which the various phenomena responsible for peak broadening combine with one another to form the final line shape. As a corollary, the half-width parameters of the Gaussian and Lorentzian components of the line shape may be coded in their separate and different ways as a function of angle. With the advent of high-resolution diffractometers such as D2B at the Institut Laue Langevin, Grenoble, this may be an important consideration.

The authors wish to thank Dr M. W. Johnson and Dr C. J. Howard for useful discussions.

Note added after submission

This paper contains much in common with the work of Ahtee, Unonius, Nurmelu & Suortti (1984). The description of the Voigt function in the present paper is, however, more straightforward and allows, in principle, the extraction of information concerned with particle-size effects.

References