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ON USE OF PSEUDO-VOIGT PROFILES IN DIFFRACTION LINE BROADENING ANALYSIS

PRABAL DASGUPTA

Department of C.S.S., Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India e-mail : prabaldasgupta@hotmail.com

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Sample-related X-ray diffraction profiles are often fitted with a pseudo-Voigt function, which is a linear combination of a Cauchy and a Gaussian function, particularly for the cases of size-strain analysis. This work reveals that Cauchy content, η, must be greater than 0.328 in case of pseudo-Voigt profile, otherwise one can not expect any meaningful accuracy in terms of data on crystallite size extracted from such profiles. η values published by several authors, who have made use of pseudo-Voigt function as profile fitting function, were thoroughly studied and it was found that their reported η values agree with the present theory.

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1. Introduction

Several microstructural parameters contribute to X-ray diffraction peak broadening. Diffraction peaks, when corrected for all non-Bragg components, i.e. background, instrumental contribution etc., bear informations about crystallite size, mean-square strain and other microstructural parameters. This corrected profile is usually termed as purely sample-related profile and is believed to be mainly a convolution of strain-related and size-related profiles. On the basis of certain experimental and theoretical evidence, Warren [1] pointed out that for Gaussian strain distribution, the Warren-Averbach (WA) analysis is exact. In other words, Gaussian function can model strain distribution reasonably well for WA analysis. However, a Gaussian alone cannot properly model size-related broadening because its first derivative approaches zero for small coherent domain size and hence area-weighted crystallite size calculated using Warren-Averbach's [2] formalism approaches infinity. This directly contradicts the very basis of Warren's theory that it holds good for small coherent domain size. It should be mentioned in this context that meaningful volume-weighted ($< D >_v$) crystallite size can be extracted from a Gaussian size-related profile [3]. For similar reasons, Pearson type VII can not model size-related broadening [4], while a Cauchy function, which is also a bell shaped function, yields non-zero first derivative and, therefore, can model size broadening reasonably well.

The Voigt function [5–6], which is a convolution of a Gaussian and a Cauchy function, has been found to be more useful in describing purely sample-related profiles. Recently, Balzar and Ledbetter [7] have made use of a two Voigt function model to describe sample-related profile. According to them, a combination of both Cauchy and Gaussian function contributes to both size- and strain-broadening separately. Therefore, both size-related and distortion-related broadening are better represented by one Voigt function each. The sample-related profile is a convolution of these two Voigt functions which in turn is another Voigt function.

Pseudo-Voigt function, which is an approximate form of Voigt function, can take different shapes according to the values of parameter η. When $\eta = 1$, it becomes a Cauchy function. On the contrary, when $\eta = 0$, it becomes a Gaussian function. It is widely believed that η can take any value between 0 to 1. Present work shows that for the most frequently used form of pseudo-Voigt function, Eq. (1) (written below), η must be greater than 0.328 (in the case of size-strain analysis), otherwise no meaningful result in terms of crystallite size can be obtained.

2. Theory

The analytical form of pseudo-Voigt function used by most of the crystallographers is written as

$$I_p(x) = I_p\{\eta C(x) + (1-\eta)G(x)\}\,, \tag{1}$$

where $C(x) = (1 + x^2)^{-1}$ and $G(x) = \exp[-(\ln 2)x^2]$, with $x = (2\theta - 2\theta_0)/w$, w is the full-width at half-maximum (FWHM), η the Cauchy content and $2\theta_0$ the position of the peak maximum.

The Fourier transform of the above mentioned form of the pseudo-Voigt function, Eq. (1), is given by

$$F(L) = (1-\eta)\sqrt{\frac{\pi}{\ln 2}}\,\exp\left(-\frac{\pi^2 w^2 L^2}{\ln 2}\right) + \eta\pi\,\exp(-2\pi w L)\,. \tag{2}$$

Therefore,

$$\left.\frac{\mathrm{d}^2 F(L)}{\mathrm{d}L^2}\right|_{L\to 0} = -\frac{1}{(\ln 2)^{3/2}} + \frac{\eta}{(\ln 2)^{3/2}} + 2\eta\sqrt{\pi}\,. \tag{3}$$

According to De Keijser, Mittemeijer and Rozendaal [8],

$$\left.\frac{\mathrm{d}^2 F(L)}{\mathrm{d}L^2}\right|_{L\to 0} = \left.\frac{\mathrm{d}^2 F^s(L)}{\mathrm{d}L^2}\right|_{L\to 0} + K' < e^2 >\,, \tag{4}$$

where $< e^2 >$ is the mean-square strain, $K' = 4\pi l^2/a_3$, l is the order of reflection, a_3 the minimum distance of correlation perpendicular to the reflecting plane and $F^s(L)$ the size-related Fourier coefficient.

Now, in Eq. (4), $\mathrm{d}^2 F^s(L)/\mathrm{d}L^2$ is area-weighted crystallite-size distribution function and $K' < e^2 >$ is K' times mean-square strain. These two quantities cannot be negative and crystallite size must be greater than zero. Therefore, the sum of these two quantities must also be greater than zero, i.e.,

$$\left.\frac{\mathrm{d}^2 F(L)}{\mathrm{d}L^2}\right|_{L\to 0} > 0\,. \tag{5}$$

So,

$$-\frac{1}{(\ln 2)^{3/2}} + \frac{\eta}{(\ln 2)^{3/2}} + 2\eta\sqrt{\pi} > 0 \tag{6}$$

and

$$\eta > \frac{1}{1 + 2\sqrt{\pi}\,(\ln 2)^{3/2}} = 0.328\,. \tag{7}$$

3. *Corroboration of the present theory by experimental results*

The fact that η can never be less than 0.328 is also evident from the work of several crystallographers like Benedetti, Fagherazzi, Enzo and Battagliarin [9], Sanchez-Bajo and Cumbrera [10] and Le Bail and Jounaneuax [11]. All of them made use of same form of pseudo-Voigt function, i.e. Eq. (1).

None of the above mentioned authors have reported a single η value smaller than 0.328 (for the sample related profile) as evident from Tables 1, 2 and 3. Moreover, in the size-strain analysis of ultrafine cubic zirconia for 222 reflection, Benedetti, Fagherazzi, Enzo and Battagliarin [8] have reported $(1 - \eta)$ as 0.31 or $\eta = 0.69$.

TABLE 1. Values of η published by Benedetti et al. [9] for milled fluorites.

Sample fluorite	Hkl	η reported
Untreated	220	0.90
	440	0.99
0.5 hour	220	0.97
milled	440	0.99
1.5 hour	220	0.99
milled	440	0.99
3 hour	220	0.99
milled	440	0.99

TABLE 2. Data from Sanchez-Bajo and Cumbrera paper [10], powder diffraction in cubic yttria-stabilized zirconia.

Reflections	2θ	η
111	30.132	0.65
002	34.843	0.66
022	50.166	0.63
113	59.610	0.66
222	62.566	0.82
004	73.685	0.50
133	81.608	0.53
024	84.147	0.48

TABLE 3. Powder diffraction data on triclinic lead chromate $PbCrO_4$ *from Le Bail and Jounaneuax's paper [11].*

hkl	$1\bar{3}1$	$\bar{2}21$	$13\bar{2}$
FWHM	0.076	0.093	0.048
η	0.818	0.743	0.328
hkl	012	$\bar{2}12$	$13\bar{2}$
FWHM	0.122	0.043	0.047
η	0.578	0.704	0.745
hkl	112	211	
FWHM	0.082	0.054	
η	0.951	0.818	

This also complies with the present theory.

η values for the diffraction profiles of tetragonal zirconia reported in Ref. [8] are also well above 0.328.

4. Concluding remark

For the present form of pseudo-Voigt function, the threshold limit of η is 0.328. If some other form of pseudo-Voigt function is used, say

$$I_p(x) = I_p[(1-\eta)G(x) + \eta C(x)] , \tag{8}$$

with $C(x) = (1+x^2)^{-1}$ and $G(x) = \exp(-x^2)$, where again $x = (2\theta - 2\theta_0)/w$, $w = \frac{1}{2}$ FWHM and η is the Cauchy content, then it is found that η must be greater than 0.34. So there remains a threshold limit for η.

Therefore, it is evident that for size-strain analysis η can not take all possible values from 0 to 1. There is always a threshold limit of η beyond which no meaningful crystallite-size data can be extracted. This threshold limit depends upon the form of the pseudo-Voigt function chosen.

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PRIMJENA PSEUDO-VOIGTOVIH PROFILA U ANALIZAMA ŠIRENJA DIFRAKCIJSKIH LINIJA

Rendgenski difrakcijski profili uzoraka često se prilagođuju pseudo-Voigtovom funkcijom koja je linearna kombinacija Cauchyeve i Gaussove funkcije, posebno u analizama veličina kristalita i naprezanja. Ovaj rad pokazuje da sadržaj Cauchyeve funkcije mora biti veći od 0.328 za pseudo-Voigtove profile, jer inače se ne može očekivati razumna točnost iz profila izvedenih podataka za veličinu kristalita. Vrijednosti koje su objavili autori o primjenama pseudo-Voigtove funkcije za prilagodbe difrakcijskih profila smo podrobno analizirali i njihovi se podaci slažu s ovom teorijom.