

LINE BROADENING ANALYSIS USING FULLPROF*: DETERMINATION OF MICROSTRUCTURAL PROPERTIES

Rodríguez-Carvajal J.^{1,2} and Roisnel T.³

¹ LLB (CEA/CNRS), C.E. Saclay, 91191 Gif sur Yvette Cedex, France

² SPSMS/MDN, CEA/Grenoble, 17 Av. des Martyrs, 38054 Grenoble Cedex 9, France

³ LCSIM, UMR 6511 CNRS-Université de Rennes I, 35042 Rennes Cedex, France

Keywords: line broadening, micro-structural properties, Voigt function, Instrumental Resolution Function

Abstract. A short account of the methodology used within *FullProf* to extract average micro-structural properties from the analysis of broadened lines of constant wavelength diffraction patterns is presented. The approach is based on the Voigt approximation and can be combined with the Rietveld method as well as with the profile matching (Le Bail fit) procedure. Both the instrumental and sample profiles are supposed to be well described by Voigt functions. To get reliable sample parameters a good knowledge of the Instrumental Resolution Function (IRF) is needed. Only a phenomenological treatment, in terms of coherent size domains and strains due to structural defects, is performed.

Introduction

The recent development of high resolution powder diffractometers (conventional X-rays, synchrotron radiation and neutrons) has lead powder diffraction patterns of real polycrystalline materials to frequently display additional Bragg reflection broadening with respect to the expected instrumental full width at half maximum (FWHM) of the particular diffractometer. A de-convolution procedure has then to be performed in order to extract the intrinsic profile from the observed one and get micro-structural features as micro-strains, particle size and stacking faults. The general treatment of microstructural effects using Fourier procedures or *ab initio* modelling are complex and not adapted to fast primary evaluation. The Voigt approximation has proven to be suitable for many cases (see [1] and references therein). The Voigt function is the convolution of a Gaussian and a Lorentzian with different FWHM. We present in this paper the way it is implemented in the program *FullProf*, to model the sample line broadening (isotropic or anisotropic, i.e. *hkl*-dependent) through a whole profile fitting approach (Rietveld or profile matching refinement).

The Voigt approximation

The treatment of micro-structural effects within *FullProf* takes advantage of the convolution properties of Voigt functions. If both instrumental and sample intrinsic profiles are supposed to be described by Voigt functions, the sample contribution can be easily determined using the well known relations:

$$H_{Gh}^2 = H_{Gf}^2 + H_{Gg}^2 \quad (1)$$

$$H_{Lh} = H_{Lf} + H_{Lg} \quad (2)$$

* FullProf is available at <http://www-llb.cea.fr/fullweb/fp2k/fp2k.htm>

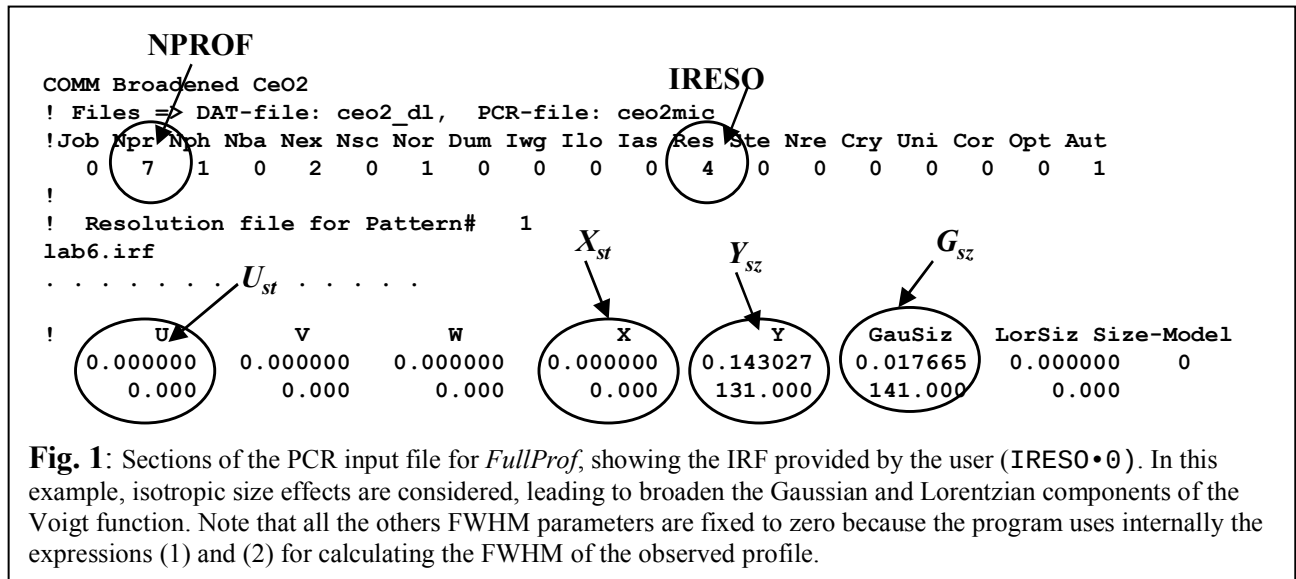
where H_G and H_L denoted the FWHM of the Gaussian and Lorentzian profile components of the Voigt function, respectively, and the h, f, g indices are relative to the observed, intrinsic and instrumental profiles, respectively. For numerical convenience the Voigt function is approximated by a pseudo-Voigt function using the Thompson-Cox-Hastings (TCH) formulae [2], so that the pair (η, H) is calculated from the pair (H_G, H_L) . This is performed within *FullProf* by using the profile parameter $NPROF=7$. This profile function includes the Finger's treatment of the axial divergence of the incident beam giving rise to asymmetry at low scattering angles [3].

Instrumental Resolution Function (IRF)

Considering the above (1) and (2) formulae, the extraction of intrinsic profiles needs a good knowledge of the instrumental resolution function (IRF), i.e. the angular dependence of the Lorentzian and Gaussian components of the Voigt function used to describe the instrumental profile. The dependence of H_{Gg} and H_{Lg} with the scattering angle should be obtained analysing the diffraction pattern of a reference sample (eg. LaB_6 , $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{11}$, Y_2O_3 or whatever strain-free “perfect powder” with large coherent diffraction domains). This can be done by the program *FullProf* itself or by any fitting program using normalised pseudo-Voigt profile functions (WinPLOTR, for instance [4]).

Line broadening treatment

Once the IRF is obtained (fig. 1) and read from a file, any increase of the FWHM in the observed diffraction profile with respect to the instrumental FWHM is considered to be intrinsic to the



sample. Size and strains effects can then be separated from their distinct angular dependence. The expressions used within *FullProf* for intrinsic H_{Gf} and H_{Lf} components are:

$$H_{Gf}^2 = \left(U_{st} + (1 - \xi) D_{st}^2(a_{st}) \right) \tan^2 \theta + \frac{G_{sz} + \gamma F_{sz}(a_{sz})}{\cos^2 \theta} = H_{Gf_st}^2 + H_{Gf_sz}^2 \quad (3)$$

$$H_{Lf} = \left(X_{st} + \xi D_{st}(a_{st}) \right) \tan \theta + \frac{Y_{sz} + (1 - \gamma) F_{sz}(a_{sz})}{\cos \theta} = H_{Lf_st} + H_{Lf_sz} \quad (4)$$

where U_{st} , X_{st} , G_{sz} , Y_{sz} , ξ and γ are refinable parameters and D_{st} and F_{sz} are analytical functions, depending on two sets of additional parameters $a_{st}=\{a_{st1}, a_{st2}, \dots\}$ and $a_{sz}=\{a_{sz1}, a_{sz2}, \dots\}$, to model the hkl -dependence broadening due to strain and size effects, respectively.

Apparent size and strains calculations

In the equations (3) and (4), size parameters are $1/\cos\theta$ dependent, while strains parameters are $\tan\theta$ dependent, in agreement with the Scherrer [5] and Stokes-Wilson [6] formulae respectively. These relationships are used to calculate apparent sizes and strains from the expression of the integral breadth of the intrinsic profile determined using the following procedure:

- Calculation of the H_{Gf} and H_{Lf} according to equations (3-4) and the relevant refined parameters.
- Mapping of the $(H_{Gf}, H_{Lf})_{sz,st}$ size and strain parameters of the Voigt function to the corresponding $(\eta_f, H_f)_{sz,st}$ pairs of the pseudo-Voigt function using the TCH formulae [2]
- Calculation of the size (β_{sz}) and strain (β_{st}) integral breadths of the normalised pseudo-Voigt function from the $(\eta_f, H_f)_{sz,st}$ parameters.

All these calculations are performed for each individual Bragg reflection and output to a detailed microstructural file of extension `mic`.

Anisotropic broadening models in *FullProf*

The analytical functions D_{st} and F_{sz} in equations (3-4) have different expressions, depending on the particular model used for the anisotropic strain and size contributions. The parameters ξ and γ are mixing coefficients to mimic Lorentzian contribution to strain and Gaussian component to size respectively. Different models can be selected through the flags `ISTR`, `IstrainModel` and `IsizeModel`.

Strain models

The hkl -dependent strain broadening is modelled using a quartic form in the reciprocal space: its corresponds to an interpretation of strains due to correlated static fluctuations between metric parameters α_i [7]. Starting from the general expression of the squared inverse of the lattice spacing:

$$M_{hkl} = \frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk = M(\alpha_i; hkl) \quad (5)$$

the metric parameters α_i (direct, reciprocal or any combination) are considered as stochastic variables with a Gaussian distribution characterised by the mean $\langle \alpha_i \rangle$ and the variance-covariance matrix C_{ij} . Position of the peaks is then obtained from the average value of M_{hkl} and the broadening of the reflections governed by the variance of M_{hkl} :

$$\sigma^2(M_{hkl}) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j} = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L \quad (6)$$

where non-diagonal terms can be written as product of standard deviations multiplied by correlations terms: $C_{ij} = S_i S_j \text{corr}(i, j)$ [8]. The right part of the expression (6) corresponds to a grouping of the C_{ij} terms as that proposed by Stephens [9]. The use of this last expression is very convenient and can be selected within *FullProf* by putting `ISTR=1` and `IstrainModel≠0` (the particular value depends on the Laue class). The set $a_{st}=\{a_{st1}, a_{st2}, \dots\}$ of strain refinable parameters

may be either C_{ij} or S_{HKL} . Several special formulations for working with direct cell parameters instead of reciprocal parameters are also implemented in *FullProf*. According to [9], distribution of α_i is not restricted to be Gaussian but is allowed to vary between Gaussian and Lorentzian using the parameter ξ .

Whatever the model or formulation used in *FullProf*, the anisotropic strain broadening function $D_{st}(a_{st})$, is given explicitly by the following expression in squared degrees:

$$D^2(a_{st}) = 10^{-8} 8 \ln 2 \left(\frac{180}{\pi} \right)^2 \frac{\sigma^2(M_{hkl})}{M_{hkl}^2}. \quad (8)$$

Size models

Several particular models for handling the anisotropic size-like broadening have been included in *FullProf*. The different models can be selected depending on the value of the `ISizeModel` parameter value and the `ISTR` flag:

- special particles shapes (infinite needles (-1), platelets (1))
- particular (hkl) indices (2, ... 14)
- particular rules, provided by the user (-2, ... -9)
- quadratic form in reciprocal space

In a very general phenomenological way, anisotropic size broadening can be written as a linear combination of spherical harmonics:

$$\beta_{hkl} = \frac{\lambda}{D_{hkl} \cos \theta} = \frac{\lambda}{\cos \theta} \sum_{lmp} a_{lmp} y_{lmp}(\Theta_{hkl}, \Phi_{hkl}) \quad (9)$$

where β_{hkl} is the integral breadth of the reflection (hkl), $y_{lmp}(\Theta_{hkl}, \Phi_{hkl})$ are the real spherical harmonics (arguments Θ_{hkl} , Φ_{hkl} are polar angles) and a_{lmp} refinable coefficients, depending on the Laue class (`ISizeModel`=15, ...22).

Besides the summary of sizes and strain values, in the appropriate units, provided in the final microstructural file, other files are output to help for plotting the polar surface giving either the apparent maximum strain or the average volume-averaged column length.

References

- [1] R. L. Snyder, H. J. Bunge and J. Fiala: *Defect and Microstructure Analysis from Diffraction* (International Union of Crystallography, Oxford Science Publications, 1999)
- [2] P. Thompson, D.E. Cox and J.B. Hastings: *J. Appl. Cryst.* 20 (1987), p. 79
- [3] L.W. Finger: *J. Appl. Cryst.* 31 (1998), p. 111; L.W. Finger, D.E. Cox and A. Jephcoat, *J. Appl. Cryst.* 27 (1997), p. 892
- [4] T. Roisnel and J. Rodríguez-Carvajal: *Mater. Sci. Forum* 378-381 (2000), p. 118
(WinPLOT on LLB Web site at: <http://www-llb.cea.fr/fullweb/winplotr/winplotr.htm>)
- [5] A. Guinier (Dunod editor, Paris 1956)
- [6] A.R. Stokes and A.J.C. Wilson: *Proc. Phys. Soc. London*, 56 (1994), p. 174
- [7] J. Rodríguez-Carvajal, M.T. Fernández-Díaz and J.L. Martínez: *J. Phys. : Condensed Matter* 3 (1991), p. 3215
- [8] J. Rodríguez-Carvajal: "Recent developments in the program *FullProf*", *Commission on Powder Diffraction Newsletter* 26 (2001), p. 12
- [9] P.W. Stephens: *J. Appl. Cryst.* 32 (1999), p. 281

European Powder Diffraction EPDIC 8

10.4028/www.scientific.net/MSF.443-444

Line Broadening Analysis Using FullProf*: Determination of Microstructural Properties

10.4028/www.scientific.net/MSF.443-444.123

DOI References

[1] R. L. Snyder, H. J. Bunge and J. Fiala: Defect and Microstructure Analysis from Diffraction International Union of Crystallography, Oxford Science Publications, 1999)

doi:10.1107/S0108767399004237

[1] R. L. Snyder, H. J. Bunge and J. Fiala: Defect and Microstructure Analysis from Diffraction (International Union of Crystallography, Oxford Science Publications, 1999)

doi:10.1107/S0108767399004237