

# Study of Micro-Structural Effects by Powder Diffraction Using the Program FULLPROF

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The combination of the Rietveld method together with a modeling of the peak shape is extremely useful when the materials under study suffer from bad crystallization. The presence of structural defects like dislocations, stacking faults, anti-phase domains, micro-strains and small crystallite sizes manifests in the diffraction pattern by a broadening of the Bragg peaks. In most cases the Voigt approximation for peak broadening is sufficient to get quantitative explanation of the existing defects through the different  $hkl$  and angular dependence of the broadening. In this paper we give an introduction to the treatment of microstructural effect using the program *FullProf*.

## Introduction

The microstructural effects within *FullProf* are treated using the Voigt approximation: both instrumental and sample intrinsic profiles are supposed to be described approximately by a convolution of Lorentzian and Gaussian components. The TCH pseudo-Voigt profile function [1] is used to mimic the exact Voigt function and it includes the Finger's treatment of the axial divergence [2]. The integral breadth method to obtain volume averages of sizes and strains is used to output a microstructural file where an analysis of the size and strain contribution to each reflection is written. No physical interpretation is given by the program; only a phenomenological treatment of line broadening in terms of coherent domain size and strains due to structural defects is performed. The user should consult the existing broad literature to go further in the interpretation of the results. A recent book [3], gathering different articles, is a good introduction to microstructural problems.

## Some useful expressions for microstructural analysis

A particular peak shape will be generally denoted as  $\Omega(x)$ , the argument is  $x = T - T_h$ , ( $T$  is the scattering variable and  $T_h$  the Bragg position) and the FWHM will be called  $H$ .

Let us define explicitly the most important parameters defining the relevant peak shapes for microstructural analysis. The Voigt approximation is based on the assumption that the contribution of microstructural effects to the final peak shape can be approximated by a Voigt function: convolution of a Gaussian and a Lorentzian. The normalized Gaussian function is defined as:

$$G(x) = a_G \exp(-b_G x^2) \quad (1)$$

where:

$$a_G = \frac{2}{H} \sqrt{\frac{\ln 2}{\pi}} \quad b_G = \frac{4 \ln 2}{H^2}$$

The integral breadth of the Gaussian function is:  $\beta_G = \frac{1}{a_G} = \frac{H}{2} \sqrt{\frac{\pi}{\ln 2}}$

The normalized Lorentzian function is defined as:

$$L(x) = \frac{a_L}{1 + b_L x^2} \quad (2)$$

where:

$$a_L = \frac{2}{\pi H} \quad b_L = \frac{4}{H^2}$$

The integral breadth of the Lorentzian function is:  $\beta_L = \frac{1}{a_L} = \frac{\pi H}{2}$

It is important to realize that the requirement of normalization (i.e.  $\int_{-\infty}^{+\infty} \Omega(x) dx = 1$ ) is essential in a Rietveld program than can automatically perform quantitative phase analysis. This requirement is not common in the literature on microstructural analysis, where the parameters  $a_G$  and  $a_L$  are taken as the height of the peak. See the appendix for the relations between the parameters defining the both the normalized and non-normalized pseudo-Voigt functions.

The Voigt function defined as the convolution of a Lorentzian and a Gaussian:

$$V(x) = L(x) \otimes G(x) = \int_{-\infty}^{+\infty} L(x-u)G(u)du \quad (3)$$

where  $L(x)$  and  $G(x)$  have different FWHM ( $H_L$  and  $H_G$ , respectively). The shape of the Voigt function is determined by the relative importance of the two components ( $H_L, H_G$ ). The Voigt function can be written in a closed form in terms of the complex error function and the integral breadths of the Lorentzian ( $\beta_L$ ) and Gaussian components ( $\beta_G$ ):

$$V(x) = V(x, H_L, H_G) = V(x, \beta_L, \beta_G)$$

$$V(x) = \beta_G^{-1} \operatorname{Re} \left[ \operatorname{erf} \left( \frac{\sqrt{\pi}}{\beta_G} |x| + i \frac{\beta_L}{\beta_G \sqrt{\pi}} \right) \right] \quad (4)$$

where:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (5)$$

The pseudo-Voigt function,  $pV(x)$ , is an approximation of the Voigt function that substitutes the two shape parameters  $H_L$  and  $H_G$  by the pair  $(\eta, H)$ :

$$pV(x) = \eta L'(x) + (1 - \eta)G'(x) \quad 0 \leq \eta \leq 1 \quad (6)$$

The  $pV(x)$  function is a linear combination of a Lorentzian ( $L'$ ) and a Gaussian ( $G'$ ) of the same FWHM ( $H$ ), so there are two parameters characterizing the peak shape:  $pV(x) = pV(x, \eta, H)$ . If  $L'(x)$  and  $G'(x)$  are normalized,  $pV(x)$  is also normalized. It is easy to verify that the FWHM is the same for  $L(x)$ ,  $G(x)$  and  $pV(x)$ .

The integral breadth of a normalized pseudo-Voigt function is just the inverse of the maximum value. If the function is multiplied by a constant (integrated intensity) the integral breadth doesn't change:

$$\beta_{pV} = \frac{\int \Omega(x) dx}{\Omega(0)} = \frac{\int I_i pV(x) dx}{I_i pV(0)} = \frac{1}{pV(0)} \quad (7)$$

$$\beta_{pV} = \frac{\pi H/2}{\eta + (1-\eta)\sqrt{\pi \ln 2}}$$

Numerically it is more easy and fast to calculate the pseudo-Voigt approximation (6) instead of directly using the expression (4). The mapping between the pairs  $(H_L, H_G)$  and  $(\eta, H)$  can easily be obtained using the numerical approximation provided by TCH expressions[1]:

$$(H, \eta) = F(H_G, H_L) \quad (8)$$

$$H^5 = (H_G^5 + 2.69269H_G^4 H_L + 2.42843H_G^3 H_L^2 + 4.47163H_G^2 H_L^3 + 0.07842H_G H_L^4 + H_L^5) \quad (9)$$

$$\eta = 1.36603 \frac{H_L}{H} - 0.47719 \left( \frac{H_L}{H} \right)^2 + 0.11116 \left( \frac{H_L}{H} \right)^3 \quad (10)$$

The inversion of the above two expressions leads to the relations:

$$(H_G, H_L) = F^{-1}(H, \eta) \quad (11)$$

$$\frac{H_L}{H} = 0.72928\eta + 0.19289\eta^2 + 0.07783\eta^3 \quad (12)$$

$$\frac{H_G}{H} = (1 - 0.74417\eta - 0.24781\eta^2 - 0.00810\eta^3)^{1/2} \quad (13)$$

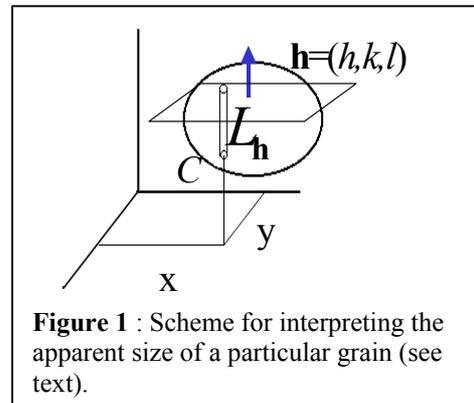
The integral breadth of the Voigt function is then calculated using the expression (7) of the pseudo-Voigt approximation, through the previous calculation of  $(H, \eta) = F(H_G, H_L)$  using the expressions (9) and (10).

The intrinsic profile of a particular reflection due to size effect has an integral breadth  $\beta_s$ , the Scherrer formula:

$$\langle D \rangle_V = \frac{\lambda}{\beta_s \cos \theta} = \frac{1}{\beta_s^*} \quad (14)$$

gives the volume-averaged apparent size of the crystallites in the direction normal to the scattering planes. This apparent size has a perfectly defined physical interpretation:

$$\langle D \rangle_V = \frac{1}{N} \sum_{i=1, \dots, N} \frac{1}{V_i} \iiint_{C_i} L_h(x, y) d^3 \mathbf{r} \quad (15)$$



or in terms of the normalized column-length distribution  $p_V(L)$ :

$$\langle D \rangle_V = \int_0^{\infty} L p_V(L) dL \quad (16)$$

The integrals (15) give the average for all crystallites of the sample in reflection position ( $N$ ) of the volume average of the length of the cords (column-length) normal to the scattering planes for each crystallite. It is clear that the relation of the apparent size with physical dimensions of the coherent domains is not direct. We should normally assume a particular average shape of the crystallite (e.g. spheres) in order to relate the apparent sizes obtained for different Bragg reflections with characteristics dimensions (e.g. diameter).

The intrinsic profile of a particular reflection due to a strain effect has an integral breadth  $\beta_D$ , the apparent strain is defined as  $\eta = \beta_D \cot \theta$  [4]. We shall use the so-called maximum strain, which is derived from the apparent strain as:

$$e = \frac{\Delta d}{d} = \frac{\eta}{4} = \frac{1}{2} \beta_D d \quad (17)$$

The relation of this definition of strain with the root-mean-square (RMS) strain can be found in the literature [3]. In the Voigt approximation the mean-square strain can be written in terms of the Gaussian and Lorentzian components and the distance  $L$  separating two cells along the normal to the scattering planes. If  $L$  is the undistorted distance and  $\Delta L$  is the distortion, the local strain is  $\varepsilon(L) = \Delta L/L$ , so the mean-square strain is:

$$\langle \varepsilon^2(L) \rangle = \left( \frac{\beta_{GD}^2}{2\pi} + \frac{\beta_{LD}}{\pi^2 L} \right) d^2 \quad (18)$$

### The treatment of microstructural effects within FullProf

There is a new file containing information about the microstructure (extension “.mic”) that is output only if the user provides an input file containing the instrumental resolution function (IRF, see manual for the different ways of giving resolution parameters). At present, this option works only for constant wavelength mode.

The FWHM of the Gaussian ( $H_G$ ) and Lorentzian ( $H_L$ ) components of the peak profile have an angular dependence given by:

$$H_G^2 = (U + (1 - \xi)^2 D_{ST}^2(\mathbf{a}_D)) \tan^2 \theta + V \tan \theta + W + \frac{I_G}{\cos^2 \theta} \quad (19)$$

$$H_L = (X + \xi D_{ST}(\mathbf{a}_D)) \tan \theta + \frac{[Y + F(\mathbf{a}_Z)]}{\cos \theta}$$

If the user provides a file with the IRF, the user should fix  $V$  and  $W$  to zero, then the rest of parameters in the above formula have a meaning in terms of strains ( $U, \mathbf{a}_D, X$ ) or size ( $Y, I_G, \mathbf{a}_Z$ ). The functions  $D_{ST}(\mathbf{a}_D)$  and  $F(\mathbf{a}_Z)$  have different expressions depending on the particular model used of strain and size contribution to broadening. The parameter  $\xi$  is a mixing coefficient to mimic Lorentzian contribution to strains.

The anisotropic strain broadening is modeled using a quartic form in reciprocal space. This corresponds to an interpretation of the strains as due to static fluctuations and correlations between metric parameters [5].

$$M_{hkl} = \frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk = M(\alpha_i; hkl) \quad (20)$$

The metric parameters  $\alpha_i$  (direct, reciprocal or any combination) are considered as stochastic variables with a Gaussian distribution characterized by the mean  $\langle \alpha_i \rangle$  and the variance-covariance matrix  $C_{ij}$ . Here we consider the set:  $\{\alpha_i\} = \{A, B, C, D, E, F\}$ . The position of the peaks is obtained from the average value of  $M_{hkl}$  given by:  $\langle M_{hkl} \rangle = M(\langle \alpha_i \rangle; hkl)$ . The broadening of the reflections is governed by the variance of  $M_{hkl}$ :

$$\sigma^2(M_{hkl}) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j} = \begin{pmatrix} h^2 & k^2 & l^2 & kl & hl & hk \end{pmatrix} \begin{pmatrix} S_A^2 & C_{AB} & C_{AC} & C_{AD} & C_{AE} & C_{AF} \\ C_{AB} & S_B^2 & C_{BC} & C_{BD} & C_{BE} & C_{BF} \\ C_{AC} & C_{BC} & S_C^2 & C_{CD} & C_{CE} & C_{CF} \\ C_{AD} & C_{BD} & C_{CD} & S_D^2 & C_{DE} & C_{DF} \\ C_{AE} & C_{BE} & C_{CE} & C_{DE} & S_E^2 & C_{EF} \\ C_{AF} & C_{BF} & C_{CF} & C_{DF} & C_{EF} & S_F^2 \end{pmatrix} \begin{pmatrix} h^2 \\ k^2 \\ l^2 \\ kl \\ hl \\ hk \end{pmatrix} \quad (21)$$

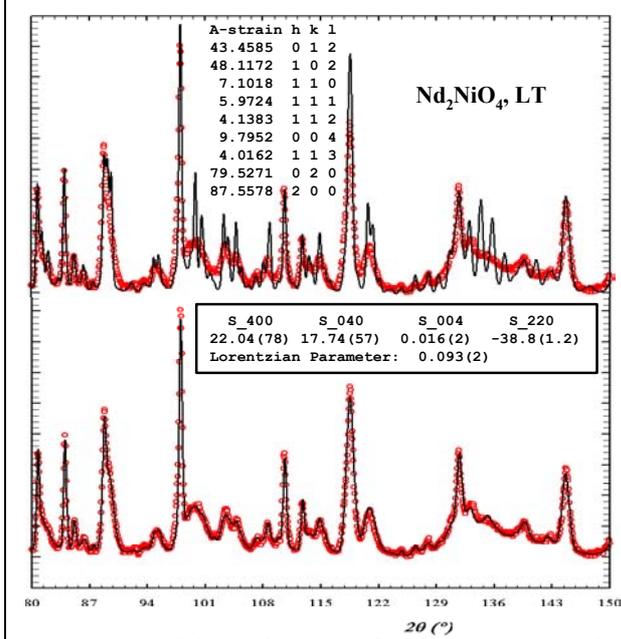
Where the non-diagonal terms may be written as product of standard deviations multiplied by correlation terms:  $C_{ij} = S_i S_j \text{corr}(i, j)$ . This original formulation can be used with a total control of the correlation terms that must belong to the interval  $[-1, 1]$ . When using this formulation the user cannot refine all parameters (up to 21) because some of them contribute to the same term in the quartic form in reciprocal space, however this allows a better interpretation of the final results. Taking the appropriate caution one can test different degrees of correlation between metric parameters. There are several special formulations, within *FullProf*, for working with direct cell parameters instead of using reciprocal parameters.

A useful notation corresponding to a grouping of terms was proposed by Stephens [6] who also included a phenomenological Lorentzian contribution to the microstrains (the parameter  $\xi$  in the equation 19). The final grouping of terms simplifies to:

$$\sigma^2(M_{hkl}) = \begin{pmatrix} h^2 & k^2 & l^2 & kl & hl & hk \end{pmatrix} [C] \begin{pmatrix} h^2 \\ k^2 \\ l^2 \\ kl \\ hl \\ hk \end{pmatrix} = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L \quad (22)$$

The Stephens' notation can also be used within *FullProf*. A maximum of 15 parameters can be refined for the triclinic case. Whatever the model used for microstrains the mixing Lorentzian parameter,  $\xi$ , may be used. In *FullProf* the function  $D_{ST}^2(\mathbf{a}_D)$ , being  $\mathbf{a}_D$  the set of parameters  $C_{ij}$  or  $S_{HKL}$ , is given by:

$$D_{ST}^2(\mathbf{a}_D) = 10^{-8} 8 \text{Ln}2 \left( \frac{180}{\pi} \right)^2 \frac{\sigma^2 (M_{hkl})}{M_{hkl}^2} \quad (23)$$



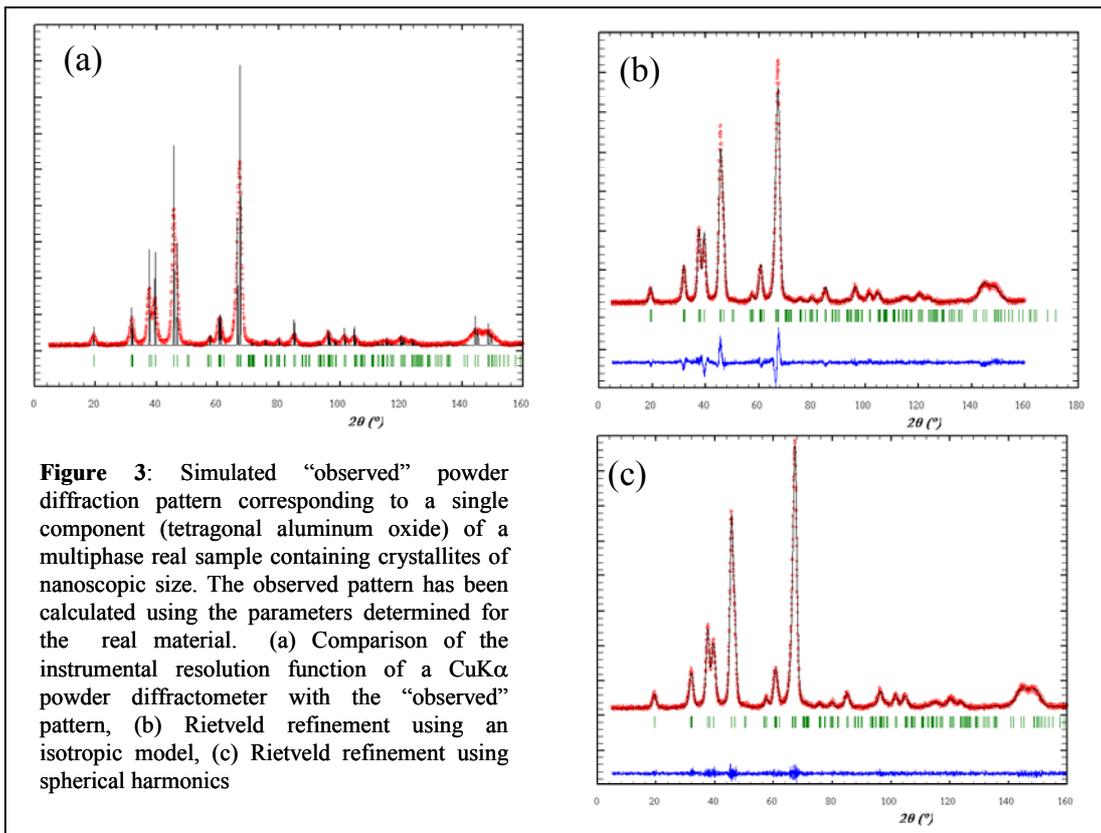
**Figure 2:** High angle part of the neutron powder diffraction pattern (D2B, ILL) of the low temperature phase of  $\text{Nd}_2\text{NiO}_4$  [11]. (top) Comparison of the observed pattern with the calculated pattern using the resolution function of the diffractometer. (bottom) Observed and calculated pattern using an anisotropic model of strains with non-null values given in the panel. A list of apparent strains ( $\times 10^{-4}$ ), extracted from the microstructure file, for a selected number of reflections is also given.

An example of anisotropic strain refined using this formulation is shown in Figure 2, where the neutron diffraction pattern of the low temperature phase of  $\text{Nd}_2\text{NiO}_4$  is refined using the diffractometer D2B at ILL [7].

Concerning anisotropic size broadening it is possible to use a very general phenomenological model, using the Scherrer formula, that considers the size broadening can be written as a linear combination of spherical harmonics (SPH). At present the anisotropic size is supposed to contribute to the Lorentzian component of the total Voigt function. A Gaussian contribution will be introduced using a mixing parameter similar to that used for anisotropic strain. The explicit formula for the SPH treatment of size broadening is the following:

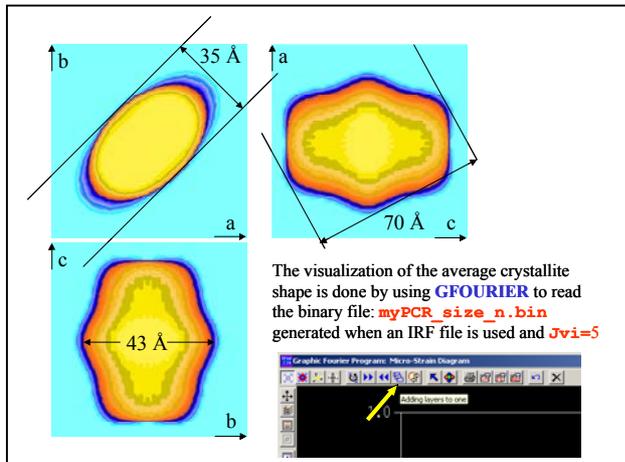
$$\beta_h = \frac{\lambda}{D_h \cos \theta} = \frac{\lambda}{\cos \theta} \sum_{imp} a_{imp} y_{imp} (\Theta_h, \Phi_h)$$

Where  $\beta_h$  is the size contribution to the

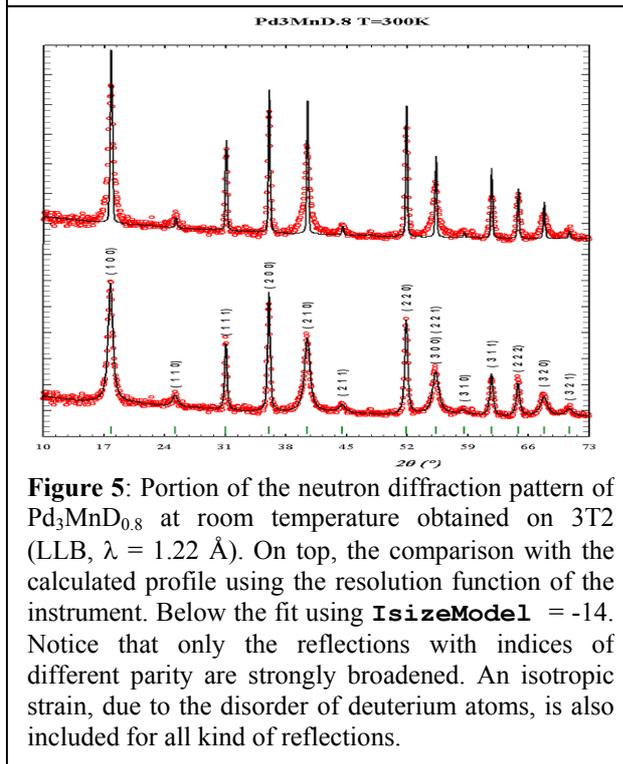


**Figure 3:** Simulated “observed” powder diffraction pattern corresponding to a single component (tetragonal aluminum oxide) of a multiphase real sample containing crystallites of nanoscopic size. The observed pattern has been calculated using the parameters determined for the real material. (a) Comparison of the instrumental resolution function of a  $\text{CuK}\alpha$  powder diffractometer with the “observed” pattern, (b) Rietveld refinement using an isotropic model, (c) Rietveld refinement using spherical harmonics

integral breadth of reflection  $\mathbf{h}$ , and  $y_{imp}(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}})$  are the real spherical harmonics with normalization as in [8]. The arguments are the polar angles of the vector  $\mathbf{h}$  with respect to the Cartesian crystallographic frame. After refinement of the coefficients  $a_{imp}$  the program calculates the apparent size (in angstroms) along each reciprocal lattice vectors if the IRF is provided in a separate file.



**Figure 4:** Visualisation of the average crystallite shape obtained from refinement of spherical harmonics coefficients in a tetragonal material.



In Figure 3 we can see the aspect of the refinement of a diffraction pattern corresponding to a tetragonal material (aluminum oxide) and, in Figure 4, the visualizing of the results obtained by reading with *GFourier* [12] the output binary file generated with *FullProf* when **Jvi=5**

An important type of defects that give rise to size-like peak broadening is the presence of anti-phase domains and stacking faults. These defects produce selective peak broadening that cannot be accounted using a small number of coefficients in a SPH expansion. In fact only a family of reflections verifying particular rules suffers from broadening. For such cases there are a number of size models built into *FullProf* corresponding to particular sets of reflections that are affected from broadening. In Figure 5 it is represented the case of  $\text{Pd}_3\text{MnD}_{0.8}$  [9] of structure similar to  $\text{Au}_3\text{Mn}$  and showing the same kind of defects: anti-phase domains [10]. In Figure 6 a portion of the final microstructural file is shown.

Other models for size broadening in *FullProf* following particular rules for each  $(hkl)$  are available. Moreover an anisotropic size broadening modeled with a quadratic form in reciprocal space is also available. The expression presently used in *FullProf* is the following:

$$F(\mathbf{a}_z) = k_s d^2 \left( \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk \right)$$

Where  $k_s$  is defined as  $k_s=360/\pi^2 \times \lambda 10^{-3}$  for the  $2\theta$  space and  $k_s=2/\pi \times \mathbf{Dtt1} 10^{-3}$  for TOF and

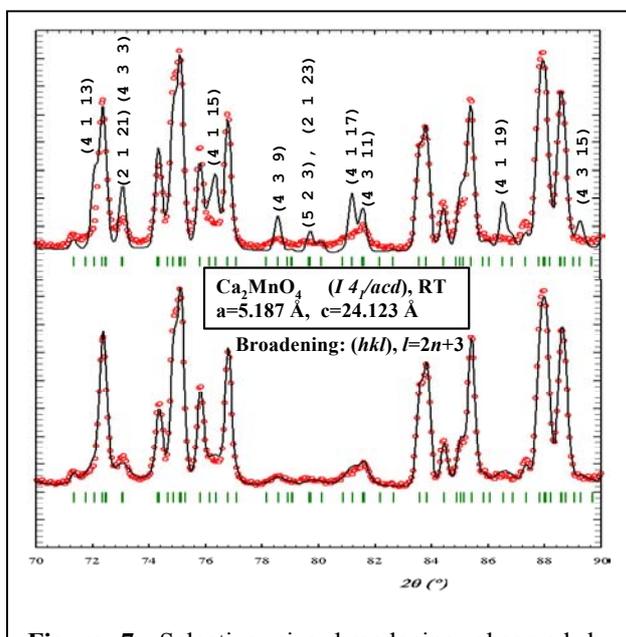
```

! MICRO-STRUCTURAL ANALYSIS FROM FULLPROF (still under development!)
! =====
! Pattern No: 1 Phase No: 1 Pd3MnD.8 - CFC
! .....
! Integral breadths are given in reciprocal lattice units (1/angstroms)x 1000
! Apparent sizes are given in the same units as lambda (angstroms) ...
! Apparent strains are given in %% (x 10000) (Strain= 1/2 * beta * d)
! An apparent size equal to 99999 means no size broadening
! .....
!
! The standard deviations appearing in the global average apparent size and
! strain is calculated using the different reciprocal lattice directions.
! It is a measure of the degree of anisotropy, not of the estimated error
! .....
...   betaG   betaL   ...   App-size App-strain   h   k   l   twtet   ...
...  1.4817  11.5859 ...   93.58  41.6395   1   0   0   17.7931 ...
...  2.0954  11.9584 ...   93.58  41.6395   1   1   0   25.2665 ...
...  2.5664   1.5573 ...  99999.00  41.6395   1   1   1   31.0743 ...
! .....
...  4.6855  13.5301 ...   93.58  41.6395   3   1   0   58.5562 ...
...  4.9142   2.9820 ...  99999.00  41.6395   3   1   1   61.7169 ...
...  5.1327   3.1146 ...  99999.00  41.6395   2   2   2   64.7864 ...
...  5.3423  13.9286 ...   93.58  41.6395   3   2   0   67.7802 ...
...  5.5440  14.0510 ...   93.58  41.6395   3   2   1   70.7114 ...
! .....

```

**Figure 6:** Portion of the microstructural file (extension *mic*) corresponding to the fitting of the neutron diffraction pattern in Figure 5.

Energy space. Simple crystallite shapes as infinite platelets and needles (**IsizeModel** = 1 and -1, respectively) are also available.



**Figure 7:** Selective size broadening observed by neutron diffraction at room temperature (3T2, LLB) for superstructure reflections in  $\text{Ca}_2\text{MnO}_4$ [11]. (top) Size parameter fixed to zero. (bottom) Single size parameter according to the rule  $(hkl), l=2n+3$ . The indices of the most intense Bragg reflections affected by size broadening are also given.

Together with the size broadening models built into *FullProf* and described above, there is another way of fitting independent size-like parameters for different sets of reflections. The user may introduce his(her) own rule to be satisfied by the indices of reflections provided the rule can be written as a linear equality of the form:  $n_1h + n_2k + n_3l = n_4n + n_5$ . Where  $n$  is an arbitrary integer and  $n_i (i=1,2,\dots,5)$  are integers given by the user. A size parameter is associated to each rule (a maximum of nine rules may be given per phase) that may be refined freely or constrained using the codewords appropriately.

To access this option in *FullProf* the value of **IsizeModel** should be in the interval [-2,-9]. The absolute value of **IsizeModel** corresponds to the number of rules (independent parameters) to be given. If all  $n_i=0$  the rule is not used. To

give a single rule one must put **IsizeModel** = -2 and put zeros for the last condition. This is needed in order to avoid the confusion with the case of an infinite needle. In Figure 7 we give an example using **IsizeModel** = -2 and in Figure 9 the relevant part of the PCR file is written.

```

. . . . .
! Selective Size-Broadening:
! hkl cond.      (n1.h + n2.k + n3.l=n n4 +/- n5)      Size-par      Code
0 0 0           0      0      1      2      3      9.61440      661.000
0 0 0           0      0      0      0      0      0.00000      0.000

```

**Figure 8:** Portion of the PCR file for **IsizeModel** = -2 corresponding to the refinement in Figure 7. The first set of zeros below the text 'hkl cond.' is not used at present.

Finally, a general formulation for peak shifts, due to defects or to residual stresses, has also been implemented. For **JSOL≠0**, the lines corresponding to shift parameters are read in the PCR file. Selective shifts can be selected when **IShif** < -1. For this option a set of up to **ABS(IShif)** (≤10) lines can be given. The lines define rules to be satisfied by reflections undergoing shifts with respect to the theoretical Bragg position due to some kind of defects (stacking and twin faults for instance). The rules are similar to those of selective size broadening discussed above. The position of the reflections satisfying the rules are displaced according to the expressions:

$$\begin{aligned}
2\theta_S &= 2\theta_B + 2 \text{Shift } d^2 \tan\theta \times 10^{-2} \text{ (} 2\theta \text{ space)} \\
\text{TOF}_S &= \text{TOF}_B - \text{Shift } d^3 \text{Dtt1} \times 10^{-2} \text{ (T.O.F. space)} \\
E_S &= E_B - \text{Shift}/(2d) \text{Dtt1} \times 10^{-2} \text{ (Energy space)}
\end{aligned}$$

Where the index B stands for the theoretical Bragg position of the non-defective material and **Shift** is the shift parameter to be refined.

The shift of Bragg reflections may also be due to external stresses or residual stresses. For those cases it is more appropriate to use the following generalized model for shifts. The model is implemented for **IShif = 100+NumLaue** (with **NumLaue** the number of the Laue class according to *FullProf* manual), and a set of parameters corresponding up to quartic form in *hkl* can be refined. The position of a reflection is displaced according to the expressions:

$$\begin{aligned}
2\theta_S &= 2\theta_B + 2 S_h d^2 \tan\theta \times 10^{-2} \text{ (} 2\theta \text{ space)} \\
\text{TOF}_S &= \text{TOF}_B - S_h d^3 \text{Dtt1} \times 10^{-2} \text{ (T.O.F. space)} \\
E_S &= E_B - S_h/(2d) \text{Dtt1} \times 10^{-2} \text{ (Energy space)}
\end{aligned}$$

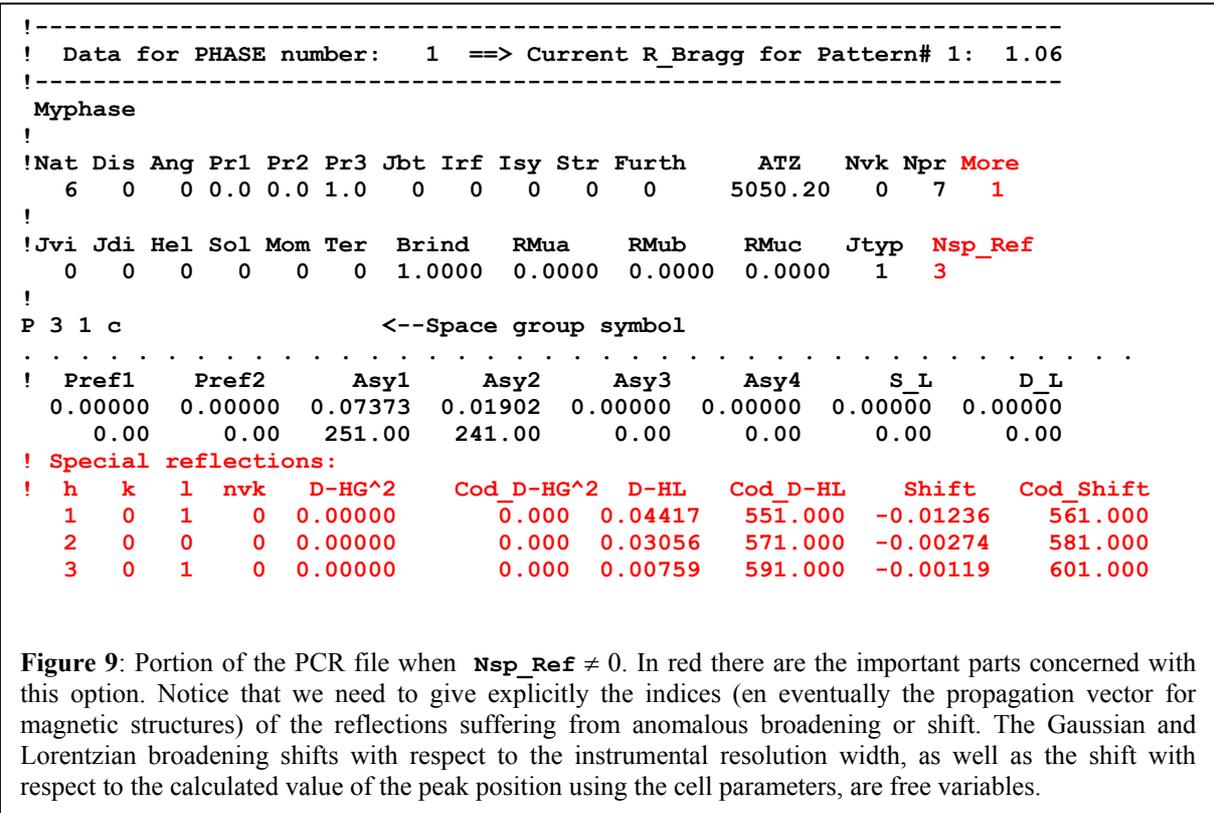
The expression used for calculating the scalar  $S_h$  for reflection **h** is given by:

$$S_h = \sum_{\{H+K+L=2\}} D2_{HKL} h^H k^K l^L + \sum_{\{H+K+L=4\}} D4_{HKL} h^H k^K l^L$$

The free parameters for this option are the sets  $D2_{HKL}$  and  $D4_{HKL}$ . To refine these parameters the average cell parameters of the non-stressed material should be fixed during the refinement.

Finally, in the desperate case where a simple rule for the *hkl* dependency of peak broadening and shifts cannot be easily obtained, there is the possibility of relaxing the peak broadening,

with respect to the resolution function, and the shifts, with respect to the Bragg positions, for individual reflections. This can help in determining *a posteriori* a physical rule governing the behavior of broadening and shifts. An example of the relevant part of a PCR file in which this last option is used is given in Figure 9.



**Note:** A non-negligible part of the present text has been previously published in [13].

## Appendix

The non-normalized pseudo-Voigt appears in many papers. Let us call the non-normalized function as:

$$pV_n(x) = \eta_n L_n(x) + (1 - \eta_n) G_n(x) \quad pV_n(0) = 1$$

where:

$$L_n(x) = \frac{1}{1 + b_L x^2} \quad L_n(0) = 1$$

$$G_n(x) = \exp(-b_G x^2) \quad G_n(0) = 1$$

The integral breadth of a non-normalized pseudo-Voigt function of peak intensity  $I_0$  and  $\text{FWHM}=H$  is given by:

$$\beta_{pVn} = \frac{\int \Omega(x) dx}{\Omega(0)} = \frac{\int I_0 pV_n(x) dx}{I_0 pV_n(0)} = \frac{\int pV_n(x) dx}{1}$$

$$\beta_{pVn} = \eta_n \int L_n(x) dx + (1 - \eta_n) \int G_n(x) dx$$

$$\beta_{pVn} = \eta_n \frac{1}{a_L} + (1 - \eta_n) \frac{1}{a_G} = \eta_n \frac{\pi H}{2} + (1 - \eta_n) \frac{H}{2} \sqrt{\frac{\pi}{\ln 2}}$$

The integral breadth of a particular peak is independent of the formulation of the pseudo-Voigt function. Both descriptions give the same FWHM and the same integral breadth, so the numerical relation between the  $\eta$  values is given by:

$$\text{Non-normalized: } \beta_{pVn} = \eta_n \frac{\pi H}{2} + (1 - \eta_n) \frac{H}{2} \sqrt{\frac{\pi}{\ln 2}}$$

$$\text{Normalized: } \beta_{pV} = \frac{\pi H/2}{\eta + (1 - \eta) \sqrt{\pi \ln 2}}$$

$$\eta_n \frac{\pi H}{2} + (1 - \eta_n) \frac{H}{2 \sqrt{\pi \ln 2}} = \frac{\pi H/2}{\eta + (1 - \eta) \sqrt{\pi \ln 2}}$$

$$\eta_n = \frac{\eta}{\eta + (1 - \eta) \sqrt{\pi \ln 2}}$$

$$\eta = \frac{\eta_n}{\eta_n + (1 - \eta_n) \frac{1}{\sqrt{\pi \ln 2}}}$$

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