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IMPROVED MODELING OF RESIDUAL STRAIN/STRESS AND CRYSTALLITE-SIZE DISTRIBUTION IN RIETVELD REFINEMENT[*]

Davor Balzar[a] and Nicolae C. Popa[b]

Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Boulder, CO 80305, U.S.A.

ABSTRACT

We propose two improvements to the microstructural modeling in Rietveld refinement. The first is the model that yields the complete texture-weighted strain and stress tensors as a function of crystallite orientations, as well as the average values of macroscopic strain and stress tensors for all Laue classes. Implementation in the Rietveld refinement program can be made through the set of refinable parameters that allow the calculation of strain and stress values. Another topic discussed is the problem of determination of coherently diffracting domain size and domain-size distributions. We present an approach where the exact size-broadened profile is obtained by averaging the interference function with a lognormal size distribution of spherical crystallites. We show that obtained size-broadened profile can be successfully modeled by a combination of Gaussian and Lorentzian functions, which permits for an analytical convolution with strain and instrumental profiles in Rietveld programs. This model can successfully fit "super-Lorentzian" line profiles that originate from a large dispersion of crystallite sizes.

INTRODUCTION

Nowadays, Rietveld refinement is a very mature set of procedures to refine complete structural information about crystalline materials. Since recently, there is an effort to include the determination of a variety of microstructural information. Notably, the inclusion of texture-determination methods through the generalized spherical harmonics, anisotropic line-broadening modeling for arbitrary crystal symmetry, and residual strain/stress determination were very important extensions of the traditional Rietveld method into new areas. Especially the problem of residual strain/stress determination has recently been the focus of new developments. Instead of traditional Voigt and Reuss approximations, recent efforts were directed toward representation of strain and stress tensors in terms of generalized spherical harmonics [1,2], that is, similar to the treatment of texture. Here, we present a modified approach that is based on a development of the texture-weighted strain tensor in a series of generalized spherical harmonics, which is in accord with the fact that a diffraction experiment yields the texture-weighted strain measure and is also used to calculate average strain and stress tensors. The approach is also extended for arbitrary crystalline symmetry and adopted specifically for implementation in Rietveld refinement programs. A more extensive description of the model can be found elsewhere [3].

Another topic of a great interest in Rietveld refinement is the determination of coherently diffracting domain size and domain-size distributions. Currently, the broadening effect of small

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[*] Contribution of the U.S. Government. Not subject to the copyright in U.S.
[a] Now at Department of Physics & Astronomy, University of Denver, Denver, CO 80208.
[b] Permanent address: National Institute for Materials Physics, P.O. Box MG-7, Bucharest, Romania.

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domain (crystallite) size is modeled phenomenologically by a pseudo-Voigt function [4]. Such models yield an average dimension of the domain size along the diffraction vector, which is only related to the real crystallite size. In principle, the size profile can be obtained by starting from a physical model for the crystallite shape and dimension distribution. Recently, Langford *et al.* [5] have considered spherical crystallites distributed according to the normal and lognormal size distributions. The model is satisfactory for a monodisperse or narrow distribution of crystallite sizes. We show that for a large dispersion of crystallite sizes, the peak breadth decreases relative to that given by the average dimension, the tails becomes longer and the pseudo-Voigt profile fails to work. Using the approximation of spherical crystallites with the lognormal distribution, we derive an analytical expression for the size profile, which is also valid for large dispersion of crystallite sizes, where the pseudo-Voigt function fails.

MODELING OF RESIDUAL STRAIN AND STRESS IN RIETVELD REFINEMENT

The diffraction method directly measures the interplanar spacing *d* along the direction of the diffraction vector, which must be parallel to a reciprocal lattice vector **H** for an (*hkl*) diffracting plane. The measured strain is then defined as an average change in the interplanar spacing from a reference value d_0:

$$< d > / d_0 - 1 = \langle \Delta d \rangle / d_0 = -\langle \Delta H \rangle / H = \langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle , \tag{1}$$

where the averaging is done by the rotation for ω around $\mathbf{h} = \mathbf{H}/H$, which is parallel to $\mathbf{y}$, the direction of the diffraction vector in the sample. If ε_i are the strain tensor elements in the crystallite coordinate system (in the condensed Voigt notation), (1) can be written as follows [6]:

$$\langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle = \sum_{i=1}^{6} E_i \int_0^{2\pi} d\omega \, f(\varphi_1', \Phi_0', \varphi_2') \varepsilon_i(\varphi_1', \Phi_0', \varphi_2') / \int_0^{2\pi} d\omega \, f(\varphi_1', \Phi_0', \varphi_2'). \tag{2}$$

The averaging is weighted by the crystallite orientation distribution function $f(\varphi_1, \Phi_0, \varphi_2)$. Here, $(\varphi_1, \Phi_0, \varphi_2)$ are the Euler's angles transforming the sample orthogonal coordinate system $(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3)$ into the crystallite orthogonal coordinate system $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$, as defined by Bunge [7]. The integration in (2) is evaluated only over values of Euler's angles $(\varphi_1', \Phi_0', \varphi_2')$ that fulfill the condition $\mathbf{h} \parallel \mathbf{y}$. They depend on values of polar and azimuthal angles of $\mathbf{h}$ in $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$, denoted as (Φ, β), of $\mathbf{y}$ in $(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3)$, denoted as (Ψ, γ), and on the rotation angle ω. In (2) the following abbreviation was used: $(E_1, \ldots, E_6) = (A_1^2, A_2^2, A_3^2, 2A_2A_3, 2A_1A_3, 2A_1A_2)$, where $(A_1, A_2, A_3) = (\cos\beta \sin\Phi, \sin\beta \sin\Phi, \cos\Phi)$ are the direction cosines of $\mathbf{h}$ in $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$.

The quantities of interest in residual strain/stress investigations are the average strain and stress tensors in the sample coordinate system, $\bar{e}_i$ and $\bar{s}_i$, $(i = 1,6)$, which are defined as follows:

$$\bar{e}_i = (1/8\pi^2) \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} d\varphi_1 d\Phi_0 d\varphi_2 \sin\Phi_0 f(\varphi_1, \Phi_0, \varphi_2) e_i(\varphi_1, \Phi_0, \varphi_2) \tag{3}$$

$$\bar{s}_i = (1/8\pi^2) \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} d\varphi_1 d\Phi_0 d\varphi_2 \sin\Phi_0 f(\varphi_1, \Phi_0, \varphi_2) s_i(\varphi_1, \Phi_0, \varphi_2). \tag{4}$$

Similar to the measurable quantity $\langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle$, these two tensors can be also expressed through the products $\varepsilon_i'(\varphi_1,\Phi_0,\varphi_2) = \varepsilon_i(\varphi_1,\Phi_0,\varphi_2)\ f(\varphi_1,\Phi_0,\varphi_2)$, if we link the strain and stress tensor components in the crystallite and sample coordinate systems:

$$s_i = \sum_{j=1}^{6} P_{ij}\sigma_j\ ,\quad e_i = \sum_{j=1}^{6} P_{ij}\varepsilon_j\ ,\quad \sigma_i = \sum_{i=1}^{6} C_{ij}\varepsilon_j\ . \qquad \text{(5a,b), (6)}$$

The third relationship presents Hooke's law with σ_i the stress tensor in the crystallite coordinate system, C_{ij} are the monocrystal elastic stiffness moduli and the elements of the matrix $\mathbf{P}$ are sums of products of two Euler's matrix elements. These matrices were given explicitly in [6].

Following the procedure used by Bunge [7] for texture, we develop the texture-weighted strain tensor elements $\varepsilon_i'(\varphi_1,\Phi_0,\varphi_2)$ into the generalized spherical harmonics:

$$\varepsilon_i'(\varphi_1,\Phi_0,\varphi_2) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{n=-l}^{l} c_{il}^{mn}\exp(im\varphi_2)P_l^{mn}(\Phi_0)\exp(in\varphi_1)\,. \qquad (7)$$

Then (2) becomes:

$$\langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle P_{\mathbf{h}}(\mathbf{y}) = \sum_{l=0}^{\infty}\frac{2}{2l+1}I_l(\mathbf{h},\mathbf{y})\,, \qquad (8)$$

where $P_{\mathbf{h}}(\mathbf{y})$ is the pole distribution function and

$$\begin{aligned} I_l(\mathbf{h},\mathbf{y}) = {} & A_1^2 t_{1l}(\mathbf{h},\mathbf{y}) + A_2^2 t_{2l}(\mathbf{h},\mathbf{y}) + A_3^2 t_{3l}(\mathbf{h},\mathbf{y}) \\ & + 2A_2A_3t_{4l}(\mathbf{h},\mathbf{y}) + 2A_1A_3t_{5l}(\mathbf{h},\mathbf{y}) + 2A_1A_2t_{6l}(\mathbf{h},\mathbf{y})\,, \end{aligned} \qquad (9)$$

$$t_{il}(\mathbf{h},\mathbf{y}) = A_{il}^0(\mathbf{y})P_l^0(\Phi) + \sum_{m=1}^{l}\left[A_{il}^m(\mathbf{y})\cos m\beta + B_{il}^m(\mathbf{y})\sin m\beta\right]P_l^m(\Phi)\,, \qquad (10)$$

$$A_{il}^m(\mathbf{y}) = \alpha_{il}^{m0}P_l^0(\Psi) + \sum_{n=1}^{l}\left(\alpha_{il}^{mn}\cos n\gamma + \beta_{il}^{mn}\sin n\gamma\right)P_l^n(\Psi)\,,\quad (m=0,l)\,, \qquad (11)$$

$$B_{il}^m(\mathbf{y}) = \gamma_{il}^{m0}P_l^0(\Psi) + \sum_{n=1}^{l}\left(\gamma_{il}^{mn}\cos n\gamma + \delta_{il}^{mn}\sin n\gamma\right)P_l^n(\Psi)\,,\quad (m=1,l)\,. \qquad (12)$$

The coefficients $\alpha_{il}^{mn},\beta_{il}^{mn},\gamma_{il}^{mn},\delta_{il}^{mn}$ obtained from c_{il}^{mn} by linear transformations can be directly refined in the Rietveld program to yield $\varepsilon_i'(\varphi_1,\Phi_0,\varphi_2)$ and the average strain and stress tensors. The number of refined coefficients required to achieve the desired precision will depend on the crystal and sample symmetries, as well on the magnitude and gradient of strain and texture. For the calculation of both average elastic strain and stress tensors, $\bar{e}_i$ and $\bar{s}_i$, only the coefficients $\alpha_{il}^{mn},\beta_{il}^{mn},\gamma_{il}^{mn},\delta_{il}^{mn}$ with $l=0$ and $l=2$ are needed because of orthogonality of the generalized spherical harmonics.

For triclinic symmetry and a given value of l, the total number of the coefficients $\alpha_{il}^{mn},\beta_{il}^{mn},\gamma_{il}^{mn},\delta_{il}^{mn}$ in (11) and (12) is $6(2l+1)^2$, where l takes only even values because of the Friedel's law. For higher crystal and sample symmetries, the number of coefficients is reduced. To find the selection rules we applied the invariance condition to the measured strain $\langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle$, for both sample and crystal symmetries. The complete selection rules for all Laue classes were given in [3].

CRYSTALLITE SIZE DISTRIBUTION AND THE DIFFRACTION-LINE PROFILE.

For the isotropic case, Langford *et al.* [5] have considered the influence of normal and lognormal size distributions of spherical crystallites on diffraction line profiles. The profile then depends on two parameters, the average crystallite radius $\overline{R}$ and the standard deviation (dispersion) of the size distribution σ_R. In [5], both parameters were refined by least-squares fitting the numerically calculated profile to the experimental pattern. They did not consider cases with a large dispersion, where the Voigt approximation for the size-broadened profile fails. Here, we demonstrate that the so-called "super-Lorentzian" line profiles may originate from size distributions with large dispersions; they can be successfully fitted with a monomodal lognormal distribution of spherical crystallites.

We consider the diffraction line profile for a single crystallite normalized to unit area in the reciprocal space, $P(s)$, in the ensemble of randomly oriented crystallites of identical shape and volume *V*. When the crystallites are not of identical size, the observed line profile is averaged over this size distribution:

$$\overline{P}(s) = \langle VP(s)\rangle / \langle V\rangle \qquad (13)$$

Here, $s = 2\sin\theta/\lambda - 1/d$, where 2θ is the scattering angle, λ is the wavelength and d is the interplanar distance. For the particular case of spherical crystallites of radius R and radius distribution function $f(R)$, we have:

$$P(s) = (3R/2)\Phi(2\pi sR), \qquad \Phi(x) = \left(x^2 + \sin^2 x - x\sin 2x\right)/x^4 \qquad (14)$$

and (13) becomes:

$$\overline{P}(s) = 3/(2\mu_3)\int_0^\infty dRf(R)R^4\Phi(2\pi sR), \qquad (15)$$

where μ_n is the $n-$th distribution moment. Taking $s = 0$ in (15) one obtains the integral breadth of the diffraction peak in reciprocal space and furthermore, the volume-weighted apparent crystallite dimension (domain size) D_V:

$$\overline{P}(0) = \beta_s^{-1} = 3\mu_4/(2\mu_3), \qquad D_V = 1/\beta_s = 3\mu_4/(2\mu_3). \qquad (16), \quad (17)$$

For the lognormal distribution

$$f(R) = R^{-1}\left[2\pi\ln(1+c)\right]^{-1/2}\exp\left\{-\ln^2\left[R\overline{R}^{-1}(1+c)^{1/2}\right]/\left[2\ln(1+c)\right]\right\}, \qquad (18)$$

where the parameter c is defined as $c = \sigma_R^2/\overline{R}^2$, n-th moment and volume-weighted domain size can be evaluated as follows:

$$\mu_n = \overline{R}^n(1+c)^{(n^2-n)/2}, \quad D_V = (3/2)\overline{R}(1+c)^3. \qquad (19), \ (20)$$

After substitutions, we obtain for (15):

$$\overline{P}(s) = \left(3\overline{R}/2\right)(1+c)^3\,\overline{\Phi}(2\pi s\overline{R}), \quad \overline{\Phi}(x) = \pi^{-1/2}\int_{-\infty}^{\infty} dt\exp(-t^2)\Phi\left\{x(1+c)^{7/2}\exp\left[t\sqrt{2\ln(1+c)}\right]\right\}. \quad (21a,b)$$

Eq. (21b) cannot be evaluated analytically. However, the fact that the size profile expressed in the reduced variable $x = 2\pi s\overline{R}$ depends only on the parameter c suggests that an approximation of $\overline{\Phi}(x)$ as combination of simple analytical functions (such as Gauss and Lorentz) can be found. This would greatly simplify introduction in the Rietveld-refinement programs. Therefore, the function $\overline{\Phi}(x)$ has been calculated numerically at equal steps in x in the range $1 \geq \overline{\Phi} > 10^{-2}$

by a Gauss-Hermite quadrature with 16 nodes for 53 values of c in the interval [0,6]. These exact profiles were least-squares fitted by linear combinations of Gauss and Lorentz functions. The following combination was found to be a good approximation for any c in the interval [0,6]:

$$\overline{\Phi}(x) = (8/3)(1+c)^{-3}\left\{\begin{array}{l} \eta_1 a_1^{-1}\left(1+4x^2/a_1^2\right)^{-1} + \eta_2 a_2^{-1}\left(1+4x^2/a_2^2\right)^{-1} \\ +\left(1-\eta_1-\eta_2\right)a_3^{-1}\begin{cases} \exp\left(-4x^2/\pi a_3^2\right) & \text{for } c \le 1 \\ \left(1+4x^2/a_3^2\right)^{-1} & \text{for } c > 1 \end{cases} \end{array}\right\} \qquad (22a)$$

Here, a_i and η_i ($i = 1,2,3$) denote integral breadths and mixing parameters ($0 \le \eta_i \le 1$), respectively. The a_3 was constrained during the fit to conserve the integral breadth of the exact profile:

$$a_3 = \left(1-\eta_1-\eta_2\right)/\left[3(1+c)^3/8 - \eta_1/a_1 - \eta_2/a_2\right] \qquad (22b)$$

The parameters η_1, a_1, η_2, a_2 were fitted by empirical analytical functions:

$$\eta_1(c) = 0.25631 + 0.018638c + 0.001155c^2 + 3.5671c\exp(-2.0467c^{0.93346}) \qquad (23a)$$

$$\begin{aligned} a_1(c) &= 4.02326\exp(-44.643c) + 3.1398\exp(-7.0113c) \\ &\quad + 0.58074\exp(-0.41396c) + 0.38125\exp(-1.1083c) \end{aligned} \qquad (23b)$$

$$\eta_2(c) = \begin{cases} 0 & \text{for } c \le 0.4 \\ 0.59951 - 0.020058(c-0.4) - 0.45347/\left[1+3.3933(c-0.4)^2\right] & \\ -0.14604\exp\left[-0.49272(c-0.4)^2\right] & \text{for } c \ge 0.4 \end{cases} \qquad (23c)$$

$$a_2(c) = 0.32781\left[1+1.5399(c-0.4) - 0.21223(c-0.4)^2 + 0.18158(c-0.4)^3\right]^{-1} \qquad (23d)$$

As can be seen from (23), the pseudo-Voigt function is a satisfactory approximation for the size profile only for $c < 0.4$. For higher values of c, a second Lorentz function must be added. Its weight increases with increasing c and the weight of the Gauss component decreases. For $c \sim 1$, the profile is well approximated by a sum of two Lorentz functions. A third Lorentz function must be added for $c > 1$. For $c > 6$, even three Lorentz functions are not sufficient for a satisfactory fit, but it is highly unlikely to find samples with such a large dispersion of crystallite sizes.

This model was tested on a commercially available CeO_2 powder (Nanophase*). The line profiles were "super-Lorentzians", that is, the profiles had longer tails that a Lorentzian limit of a Voigt (pseudo-Voigt) function, and therefore cannot be treated by most Rietveld-refinement programs (see Fig. 1a, where the fit with a Lorentzian function is shown). Fig. 1b shows the fit assuming a monomodal lognormal size distribution of spherical crystallites, following (22)-(23), convoluted with an instrumental function and a Gaussian to account for strain (estimated at 0.02 %), gives a very good fit to the observed "super-Lorentzian" line profiles. Table 1 gives refined values of the size parameters $\overline{R}$, c and corresponding volume-weighted domain size D_V, as obtained by the refinement of two diffraction patterns with 11 CeO_2 diffraction lines. The large value of c indicates a large dispersion of crystallite sizes, where a Voigt (pseudo-Voigt) approximation for a size-broadened line profile fails (compare with (22) and (23)). Although the fit with a single profile is very good, the "super-Lorentzian" line profiles can be alternatively explained by a

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multimodal size distribution. Therefore, additional information, preferably by an unrelated method such as TEM, is necessary to give an unequivocal determination of the size distribution, although this is not easy to achieve by any experimental method in case of a broad distribution with large percentage of small crystallites, such as this sample.

Table 1. The refined parameters of the lognormal size distribution, $\overline{R}$, c, and the corresponding volume-weighted domain size D_V.

$\overline{R}$ (nm)	c	D_V (nm)
1.68(2)	2.820(2)	141(1)

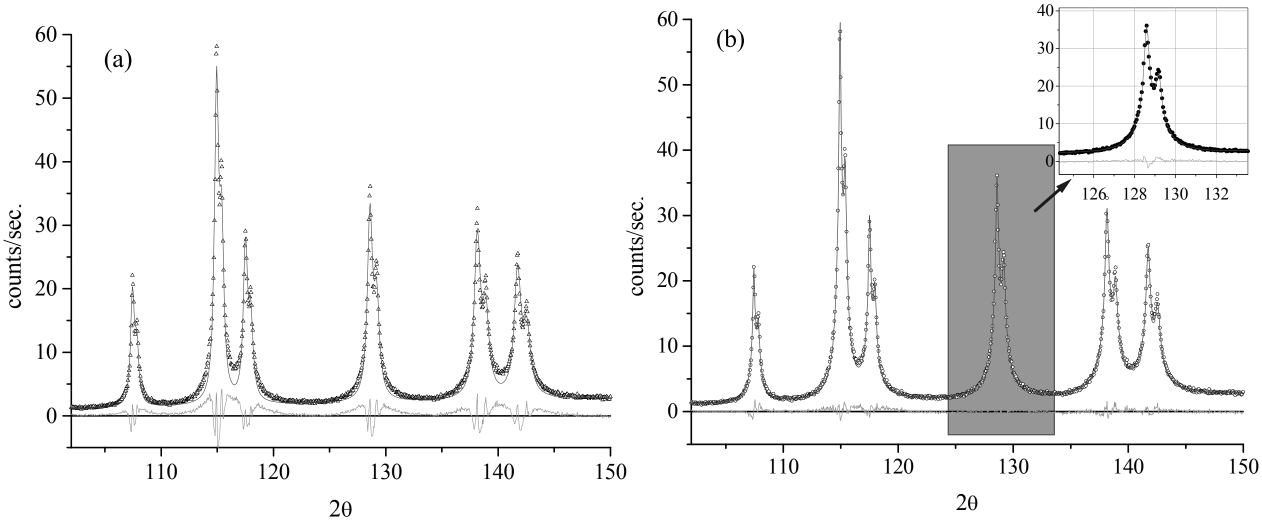

Figure 1. Fit of “super-Lorentzian” line profiles of a commercial CeO_2 powder: (a) Size broadened profile approximated with a Lorentz function; (b) Size-broadened profile approximated with a lognormal size distribution of spherical crystallites, according to (22)-(23).

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