$FW\frac{1}{5}/\frac{4}{5}M$ method for determination of the Grain Size Distribution from powder diffraction line profile

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Abstract

Well established Scherrer method allows for determination of the average grain size $< R >$ of a crystalline powder by measurement of Full Width at Half Maximum ($FWHM$) of the diffraction peak profile. We propose an enhancement of this classical method. Measurement of *two* widths of the same peak, allows for *two* parameters to be distinguished: the average grain size $< R >$ and dispersion of sizes σ. These parameters are sufficient to draw Grain Size Distribution (GSD) curve, that is much more informative than a single size parameter $< R >$.

We propose to measure widths at $\frac{1}{5}$ and $\frac{4}{5}$ of the peak maximum ($FW\frac{1}{5}M$ and $FW\frac{4}{5}M$, respectively). A simple algebraic formula that converts measured $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$ values into $< R >$ and σ is presented. The $FW\frac{1}{5}/\frac{4}{5}M$ method proposed in this paper is especially sensitive in case of a broad diffraction maxima, i.e. for nano-sized polycrystals.

1 Introduction

The motivation of deriving of the $FW\frac{1}{5}/\frac{4}{5}M$ method is importance of the *distribution* of crystallite sizes in nanomaterial sciences. The new functionality of nanostructured materials comes mainly from their size-dependent properties, e.g. large specific surface area (fuel retention), large fraction of atoms having different coordination than in bulk (catalysis), characteristic interaction length comparable to the grain size (mechanical, electronic, optical and magnetic properties), etc. In general, these size-dependencies are steep, having often times form of $1/R$, where R is grain size. The (usually wide) distribution of the crystallite sizes causes those unique physical properties to change tremendously from grain to grain in a polydispersive powder. Engineering of the Grain Size Distribution (GSD) is then a key point in

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design of the new materials, and consequently GSD determination is the fundamental measurement in the nanomaterials science [1, 2, 3, 4].

The method proposed is meant to be an extension of the Scherrer method for polydispersive powders. Therefore $FW\frac{1}{5}/\frac{4}{5}M$ procedure can be applied to the same classes of crystalline powders and bears same limitations as the Scherrer method does: it should be used for materials where only size broadening of the diffraction peaks appears. Other effects, e.g. lattice strain, stacking faults, $K_{\alpha 1}/K_{\alpha 2}$ doublets, overlapping peaks, etc. would artificially decrease size readings.

The method proposed has been derived from analytical expression for diffraction line profile for polydispersive crystalline powder (see below). Similar expression for monodispersive powders with cubical grains has been given by Wilson [5], then substantial effort has been made to derive peak profile formula for various crystalline shapes [6, 7]. Recently, there were published also expressions for polydispersive powders with log-normal and Gamma size distributions, however containing special functions, that disallow further analytical investigations [8, 9].

2 Line profile for polydispersive powders

It has been recently shown, that diffraction peak profile for a polydispersive powder can be expressed as [10, 11]:

$$\begin{aligned} < LP(q;R_0,m) > \quad = \quad & \frac{\left(1+q^2R_0^2\right)^{-\frac{m+1}{2}}}{\sqrt{2\pi}q^4R_0^3m(m-1)(m-2)} \cdot \\ & \Big\{3\left(1+q^2R_0^2\right)^{\frac{m+1}{2}}\left(2+q^2R_0^2(m-1)(m-2)\right) \\ & -6\left(1+q^2R_0^2\right)^{\frac{3}{2}}\cos\left[(m-2)\arctan qR_0\right] \\ & -6qR_0\left(1+q^2R_0^2\right)(m-2)\sin\left[(m-1)\arctan qR_0\right]\Big\}, \end{aligned} \tag{1}$$

where $q = \frac{4\pi\sin\theta}{\lambda}$ is scattering vector and parameters R_0 and m are related to the mean $< R >$ and dispersion σ of the GSD by:

$$R_0 = \frac{\sigma^2}{< R >} \tag{2}$$

$$m = \frac{< R >^2}{\sigma^2} - 1. \tag{3}$$

Expression (1) assumes that grain sizes obey the Gamma distribution:

$$GSD(R;R_0,m) = \frac{R_0^{-m-1}}{\Gamma(m+1)}R^m e^{-R/R_0}, \tag{4}$$

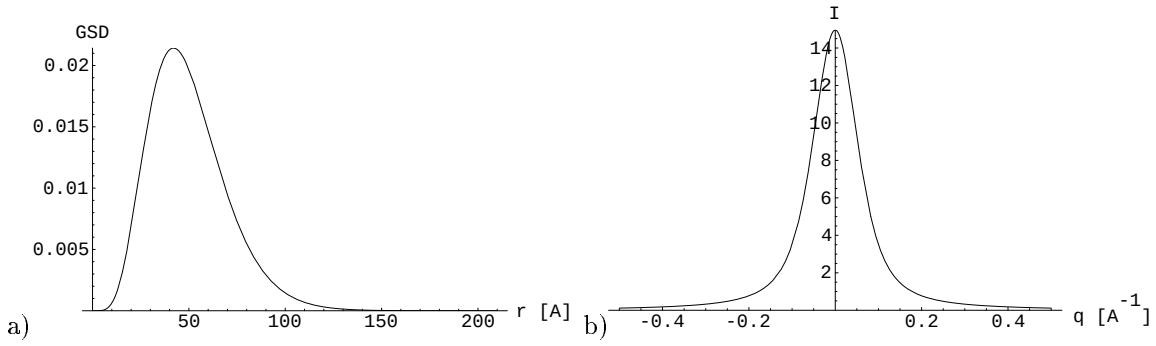

Figure 1: (a) Gamma Grain Size Distribution and (b) corresponding diffraction peak profile plotted for average grain size $< R >= 50$Å and dispersion $\sigma = 20$Å ($R_0 = 8$, $m = \frac{21}{4}$).

where $\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}dt$ is the Euler Gamma function[1]. Fig.1a shows an example of the GSD in form (4) plotted for values $R_0 = 8$ and $m = \frac{21}{4}$. The diffraction peak profile in form (1) corresponding to that distribution is plotted in the Fig.1b.

The maximum intensity of the diffraction line profile can be obtained from (1) in the limit $q \to 0$:

$$\lim_{q\to 0} < LP(q; R_0, m) >= \frac{3(m+1)R_0}{4\sqrt{2\pi}} = \frac{3}{4\sqrt{2\pi}} < R > . \tag{5}$$

Diffraction peak profile $< LP(q; R_0, m) >$ in analytical form (1) allows for direct determination of peak width at any fraction of its maximum (5). In the next section an equation for peak width at fraction h of its maximum is written, then it is solved for $h = \frac{1}{5}$ and $h = \frac{4}{5}$.

3 The $FW\frac{1}{5}/\frac{4}{5}M$ method

Widely known Scherrer equation allows to determine average crystallite size $< R >$ from $FWHM$ of the diffraction line. In order to solve *two* parameters of the GSD curve ($< R >$ and σ) from the line profile, *two* widths of the profile must be measured. It is our arbitrary choice to select widths at $\frac{1}{5}$ and $\frac{4}{5}$ of the line maximum. For numerical precision reasons, it is recommended to select widths as different as possible (i.e. closest to the top and the bottom of the peak). On the other hand, high noise level at the bottom of the peak and low number of data points at the very top of the peak, could increase errors while determining $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$ values from experimental data. It has been verified that widths measured at $\frac{1}{5}$ and $\frac{4}{5}$ of the peak maximum work fine for most data sets and will be used in further derivations.

[1] The Gamma distribution has been used because it is currently the only distribution that allows analytical line profile to be obtained for polydispersive powder. Other distributions, e.g. log-normal, lead to special functions, as it was stated in the Introduction. It is shown in this paper, that Gamma distribution can be equivalent to log-normal distribution for practical applications.

Let's equal diffraction peak profile (1) and a fraction h of its maximum (5):

$$\begin{aligned}
&\frac{\left(1+q^2R_0^2\right)^{-\frac{m+1}{2}}}{\sqrt{2\pi}q^4R_0^3m(m-1)(m-2)}\cdot \\
&\Big\{3\left(1+q^2R_0^2\right)^{\frac{m+1}{2}}\left(2+q^2R_0^2(m-1)(m-2)\right) \\
&\quad -6\left(1+q^2R_0^2\right)^{\frac{3}{2}}\cos\left[(m-2)\arctan qR_0\right] \\
&-6qR_0\left(1+q^2R_0^2\right)(m-2)\sin\left[(m-1)\arctan qR_0\right]\Big\} \quad = \quad h\frac{3(m+1)R_0}{4\sqrt{2\pi}}.
\end{aligned} \tag{6}$$

Taking advantage of the fact that quantities q and R_0 are always grouped, we can substitute dimensionless $x = qR_0$ and rewrite (6) to the form:

$$\begin{aligned}
&\frac{\left(1+x^2\right)^{-\frac{m+1}{2}}}{x^4(m+1)m(m-1)(m-2)}\cdot \\
&\Big\{\left(1+x^2\right)^{\frac{m+1}{2}}\left[8-x^2\left(hx^2m(m+1)-4\right)(m-1)(m-2)\right] \\
&\quad -8\left(1+x^2\right)^{\frac{3}{2}}\cos\left[(m-2)\arctan x\right] \\
&-8x\left(1+x^2\right)(m-2)\sin\left[(m-1)\arctan x\right]\Big\} \quad = \quad 0.
\end{aligned} \tag{7}$$

As the first term $\left(1+x^2\right)^{-\frac{m+1}{2}}$ of (7) and the denominator never vanish, we obtain equation:

$$\begin{aligned}
&\left(1+x^2\right)^{\frac{m+1}{2}}\left[8-x^2\left(hx^2m(m+1)-4\right)(m-1)(m-2)\right] \\
&\quad -8\left(1+x^2\right)^{\frac{3}{2}}\cos\left[(m-2)\arctan x\right] \\
&-8x\left(1+x^2\right)(m-2)\sin\left[(m-1)\arctan x\right] \quad = \quad 0.
\end{aligned} \tag{8}$$

Equation (8) is a transcendental equation with two unknowns: x and m (while h we can treat as known). The solution of (8) is a curve $x(m)$. However (8) cannot be solved analytically, the dependence $x(m)$ may be plotted in a wide range of values of the parameter m, that correspond to all grain size distribution widths, that may be of practical interest[2]. Series of solutions of (8) create a monotonic curves $x(m)$ showed in the Fig.2a and Fig.2b for $h = \frac{1}{5}$ and $h = \frac{4}{5}$, respectively. Those series have been fitted using *cotangent* function (red, solid lines in Fig.2). The *cotangent* function has been empirically found to best reflect curvature of $x(m)$ functions. As it is seen, the fit is perfect in the whole range of parameter m, so

[2]Parameter $(m+1) = \frac{<R>^2}{\sigma^2}$ is a measure of the relative width of the GSD. Small values of m (say, $1 < m < 2$) correspond to a wide size distributions, i.e. strongly polydispersive powders. Large values of m (say, $m > 30$) describe monodispersive powders. Hence, parameter m could be called a „monodispersity". Range $0 < m < 100$ fairly covers either polydispersive, monodispersive and intermediate cases.

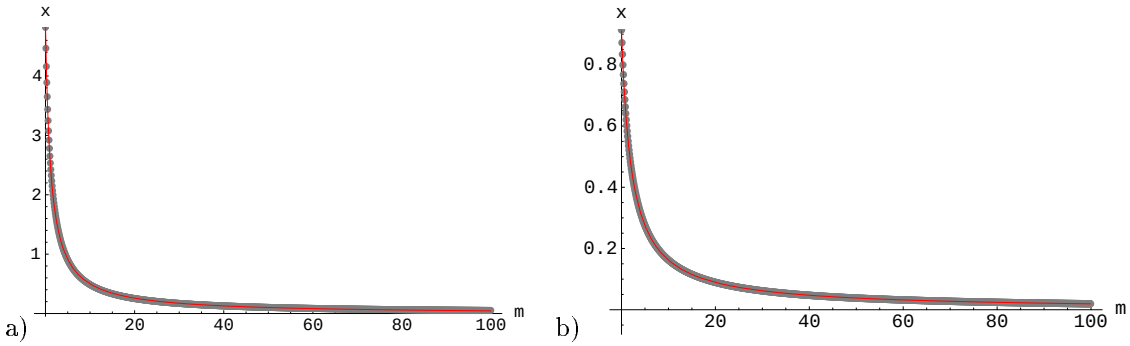

Figure 2: Numerical solutions of transcendental equation (8) for the peak width at (a) $h = \frac{1}{5}$ and (b) $h = \frac{4}{5}$ of its maximum. Series of solutions create a curve $x(m)$ (gray dots), which can be fitted by a function $x(m) = A + B \cdot ctg(C + D \cdot m)$ - (solid lines).

the curve $x(m)$ can be considered to be known and defined by:

$$x_{h=1/5}(m) \cong -0.0081 + 0.0208 \cdot ctg(0.004238 + 0.003675 \cdot m) \tag{9}$$

$$x_{h=4/5}(m) \cong 0.001555 + 0.00884 \cdot ctg(0.00972 + 0.00453 \cdot m). \tag{10}$$

As the $x = qR_0$ substitution has been made, having solutions $x_{1/5}(m)$ and $x_{4/5}(m)$ in forms of functions (9) and (10), and finally having measured widths $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$, the following system of equations can be written:

$$\begin{cases} x_{1/5}(m) = qR_0 \\ x_{4/5}(m) = qR_0 \end{cases} = \begin{cases} x_{1/5}(m) = \frac{1}{2} \cdot FW\frac{1}{5}M \cdot R_0 \\ x_{4/5}(m) = \frac{1}{2} \cdot FW\frac{4}{5}M \cdot R_0 \end{cases} . \tag{11}$$

Equations (11) can be easily solved with respect to R_0 and m. Subsequently, the solution given by pair (R_0, m) can be expressed by the physical variables $(< R >, \sigma)$ due to (2) and (3).

The formula that readily converts measured values of $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$ into physically meaningful quantities: mean $< R >$ and dispersion σ of the Grain Size Distribution takes form:

$$\begin{aligned} < R > &= \frac{2BC}{FW\frac{4}{5}M} \\ \sigma &= \frac{2B\sqrt{C}}{FW\frac{4}{5}M}, \end{aligned} \tag{12}$$

where auxiliary factors A, B and C are:

$$\begin{aligned} A &= arcctg\left(277069 - 105723\frac{FW\frac{1}{5}M}{FW\frac{4}{5}M}\right) \\ B &= 0.001555 + 0.00884 \cdot ctg\left(0.002237 - 2101 \cdot A\right) \end{aligned}$$

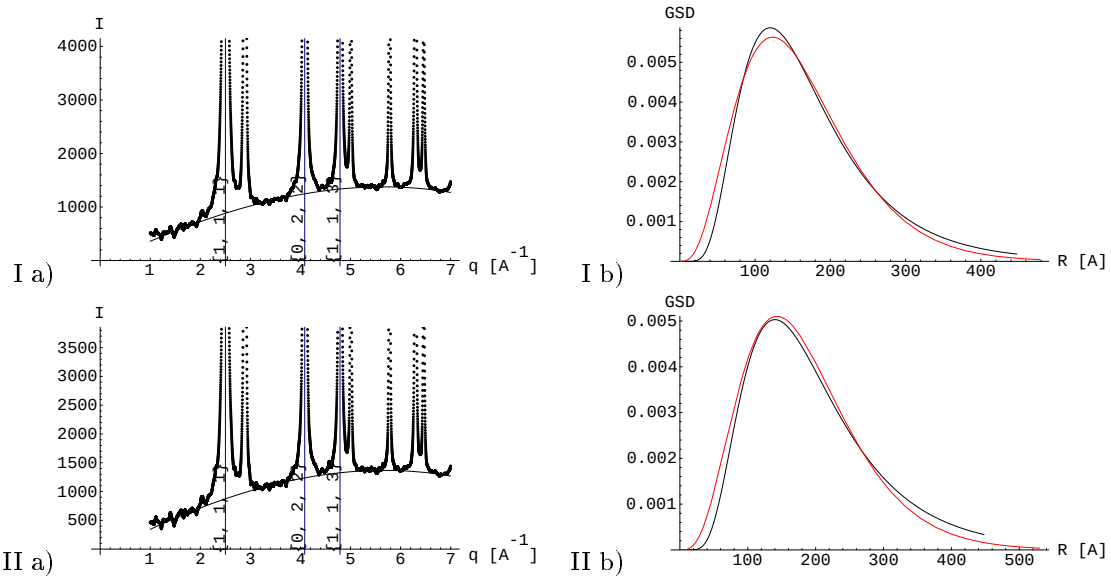

Figure 3: Examples of application of method $FW\frac{1}{5}/\frac{4}{5}M$. Powder diffraction patterns of SiC (Fig. I,II a) have been calculated *ab initio* for powder with log-normal Grain Size Distribution (discontinued curve on Fig. I,II b). After background subtraction, widths of lines (111) at $\frac{1}{5}$ and $\frac{4}{5}$ of their maxima have been measured. Expressions (12) have been used to determine the GSD (fully decaying curves on Fig. I,II b) from the measured widths. Assumed in $FW\frac{1}{5}/\frac{4}{5}M$ method gamma distribution of crystallite sizes fairly reflects shape of log-norm distribution used for patterns calculation.

$$C = -0.6515 - 463695 \cdot A$$

4 Discussion and Examples

Fig.3 shows examples of the GSD determinations performed for *ab initio* calculated diffraction patterns. Theoretical diffraction patterns were obtained with log-normal GSD assumed. After background subtraction, widths of (111) lines have been measured at $\frac{1}{5}$ and $\frac{4}{5}$ their maximum. Then expressions (12) have been used in order to obtain GSD parameters $< R >$ and σ. The GSD curve obtained has been drawn, according to (4), on the right-hand side of the Fig.3 (fully decaying curve) together with the original log-normal GSD used during *ab initio* calculations of the diffraction pattern (discontinued curve). Fig.3 shows that gamma distribution of sizes used in derivation of the $FW\frac{1}{5}/\frac{4}{5}M$ method well reflects shape of log-normal distribution and (however differs from the latter in mathematical properties) is certainly sufficient for evaluations of experimental data. One has to state, however, that every quantitative analysis of the diffraction profile, including $FW\frac{1}{5}/\frac{4}{5}M$ method, is sensitive to any deformation of line, e.g. resulting from stacking faults or lattice strains.

Another example of usage of the $FW\frac{1}{5}/\frac{4}{5}M$ is given on Fig.4. It shows standard GSD evaluation for BN nanocrystals from profile of (111), (220) and (311) diffraction lines. Numerical fitting standard

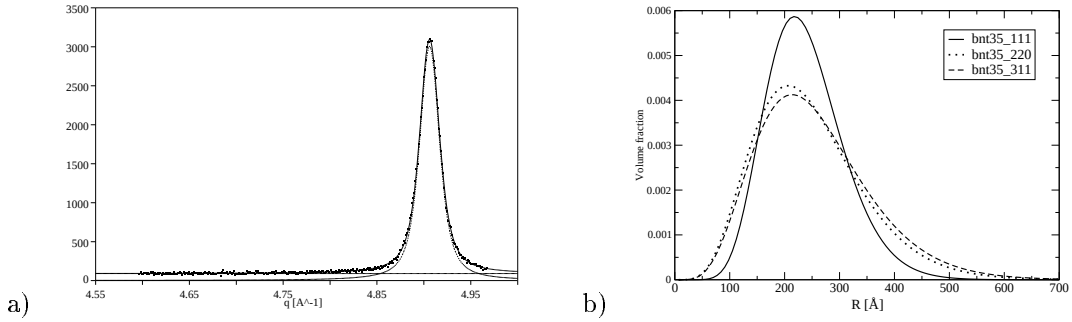

Figure 4: Examples of application of method $FW\frac{1}{5}/\frac{4}{5}M$ to the experimental data. (a) Powder diffraction pattern of nanocrystalline BN have been evaluated (peak 220 shown). (b) Resulting Grain Size Distribution functions show anisotropy of average shape of nanocrystals evaluated. Obtained values are: $< R >_{(111)}= 238 \pm 1.5$Å, $\sigma_{(111)} = 71 \pm 3$Å, $< R >_{(220)}= 246 \pm 1$Å, $\sigma_{(220)} = 99 \pm 1.5$Å, $< R >_{(311)}= 256 \pm 1.1$Å, $\sigma_{(311)} = 104 \pm 2$Å. (a) Theoretical peak profiles calculated for obtained GSD (solid curve) with constant background (solid line) fits tightly corresponding experimental data (dots + underlaying solid curve).

deviations do not exceed 1% for average sizes determined and 4% for dispersions. Such a small deviations are due to good quality of diffraction data (smooth experimental curves).

In the next section a practical supplement to the $FW\frac{1}{5}/\frac{4}{5}M$ method is presented. It allows for direct application of parameters obtained during fitting Pearson7 curve to the experimental peak profile. Curve Pearson7 is commonly used in popular crystallographic software.

5 Application of function Pearson7 to the $FW\frac{1}{5}/\frac{4}{5}M$ method

Presented $FW\frac{1}{5}/\frac{4}{5}M$ method of GSD determination is only as precise as measurements of both widths $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$. This precision can be raised by fitting an analytical curve to the experimental data being evaluated, then measurement of widths of the analytical (instead of experimental) curve. One of possible choices could be popular function Pearson7:

$$P7(q, a_0, a_1, a_2, a_3) = \frac{a_0}{\left[1 + 4\left(\frac{q-a_1}{a_2}\right)^2 \left(2^{1/a_3} - 1\right)\right]^{a_3}}, \tag{13}$$

where a_0 is line intensity, a_1 - line position, a_2 and a_3 are line widths. Putting $a_0 = 1$ and $a_1 = 0$ and comparing expression (13) to $h = \frac{1}{5}$ and $h = \frac{4}{5}$ we obtain equation for the width of Pearson7 curve at $\frac{1}{5}$ and $\frac{4}{5}$ of maximum:

$$\frac{1}{\left[1 + 4\left(\frac{\Delta q}{a_2}\right)^2 \left(2^{1/a_3} - 1\right)\right]^{a_3}} = h \tag{14}$$

Interesting solutions of above equation are:

$$FW\frac{1}{5}M(a_2,a_3) = 2\Delta q = 2\frac{a_2\sqrt{-1+5^{1/a_3}}}{\sqrt{-4+2^{2+1/a_3}}} \quad (15)$$

$$FW\frac{4}{5}M(a_2,a_3) = 2\Delta q = 2\frac{a_2\sqrt{-1+\left(\frac{5}{4}\right)^{1/a_3}}}{\sqrt{-4+2^{2+1/a_3}}} \quad (16)$$

Above expressions are functions of parameters a_2 and a_3, being immediate result of fitting in a crystallographic software (e.g. PeakFit). These values $FW\frac{1}{5}M(a_2,a_3)$ and $FW\frac{4}{5}M(a_2,a_3)$ can be placed in equations (12) and we obtain a recipe how to transform Pearson7 widths to the physical quantities of $< R >$ and σ, defining GSD.

6 Concluding remarks

The $FW\frac{1}{5}/\frac{4}{5}M$ method presented has been thought as an extension of the classical Scherrer method. It derives both: the mean and the dispersion of the Grain Size Distribution. We have to state, that quality of determination of the dispersion parameter is very sensitive to the diffraction data statistics (level of noise). Therefore, full GSD determination requires longer data acquisition times and/or stronger radiation sources that those used for „standard" powder diffraction measurements.

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References

[1] J. Karch, R.Birringer, and H. Gleiter *Nature*, vol. 330, p. 556, 1987.

[2] M.Ruhle, H.Dosch, E.J.Mittemejer, and M. van de Voorde, eds., *European White Book on Fundamental Research in Materials Science*. Stuttgart: Max-Planck Institute for Metals research, 2001.

[3] W.Lojkowski and H.J.Fecht, "The structure of Intercrystalline Interfaces," *Progress in Materials Science*, vol. 45, p. 339, 2000.

[4] M.Poliakoff *Nature*, vol. 412, p. 125, 2001.

[5] A. J. C. Wilson, *X-ray Optics (The Diffraction of X-rays by Finite and Imperfect Crystals)*. Methuen's Monographs on Physical Subjects, London: Methuen, 1949.

[6] J. I. Langford and D. Louër, "Diffraction Line Profiles and Scherrer Constants for Materials with Cylindrical Crystallites," *Journal of Applied Crystallography*, vol. 15, pp. 20–26, 1982.

[7] R. Vargas and D. Louër, "Diffraction Line Profiles and Scherrer Constants for Materials with Hexagonal Crystallites," *Journal of Applied Crystallography*, vol. 16, pp. 512–518, 1983.

[8] P. Scardi and M. Leoni, "Diffraction line profiles from polydisperse crystalline systems," *Acta Cryst.*, vol. A57, pp. 604–613, 2001.

[9] N. C. Popa and D. Balzar, "An analytical approximation for a size-broadened profile given by the lognormal and gamma distributions," *Journal of Applied Crystallography*, vol. 35, pp. 338–346, 2002.

[10] R. Pielaszek, *Dyfrakcyjne badania mikrostruktury nanokryształów poddawanych działaniu wysokiego ciśnienia (eng. Diffraction studies of microstructure of nanocrystals exposed to high pressure)*. PhD thesis, Warsaw University, Faculty of Physics, 2003.

[11] R. Pielaszek, "Analytical expression for Diffraction Line Profile for polydispersive powders," *World Scientific Publishing*, vol. in print, 2003.