Modeling of diffraction patterns based on microstructural properties

Gábor Ribárik

ribarik@elte.hu

Department of Materials Physics, Institute of Physics and Astronomy, Eötvös University,

Budapest, P.O.Box 32, H-1518, Hungary

Introduction:

- modeling size and strain broadening
- modeling planar faults
- the Momentum Method
- the Scherrer equation
- the MWH method
- the CMWP method

The theoretical Fourier transform

The patterns are measured in function of 2θ, which should be converted to the coordinate of the reciprocal space using the transformation $K = 2\frac{\sin\theta}{\lambda}$. The Fourier transform of a $I(K)$ intensity profile is denoted by $A(L)$.

According to Warren and Averbach (1952), the theoretical Fourier transform is expressed as:

$$A(L) = A^S(L)A^D(L),$$

where S stands for size and D stands for strain effect.

This convolutional equation can be further extended including all other sources of broadening, e.g.:

- planar faults
- instrumental broadening

The size effect

- the peak-profile of a real crystal is broadened due to its finite size.
- a policrystalline or fine powder sample consists of many crystallites
- the crystallites are defined as crystalline regions from which the X-rays are scattered coherently
- the crystallite size obtained from X-ray measurements can be equal to the grain or particle size, but it is usually (much) smaller
- a correlation between the crystallite size and grain size can be supposed

The size effect

- in the X-ray experiments usually a large number of crystallites are irradiated and the broadened intensity profiles are summed up
- the profile function can be determined for arbitrary shaped and sized crystallites
- by assuming a crystallite shape and crystallite size distribution function, the model based size profile can be calculated
- by applying the model based function to the measurements, the parameters of the size distribution can be obtained
- average size parameters can also be calculated

The size effect

If we suppose:

- spherical crystallites
- lognormal f(x) size distribution density function:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma}\frac{1}{x}\exp\left[-\frac{\left(\log\left(\frac{x}{m}\right)\right)^2}{2\sigma^2}\right],$$

(σ: variance, m: median).

The lognormal size distribution function

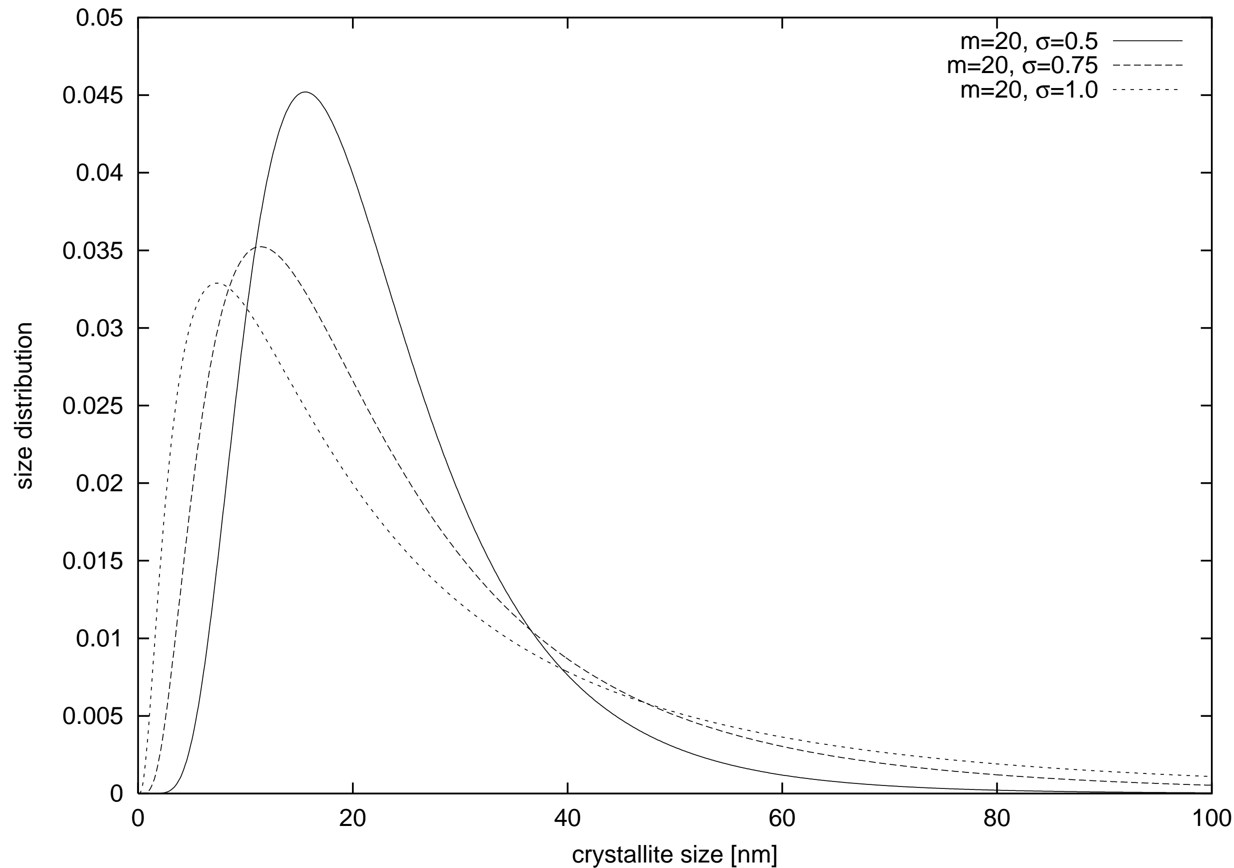


Figure 1: The $f(x)$ lognormal size distribution function for fix m and varying σ values.

The lognormal size distribution function

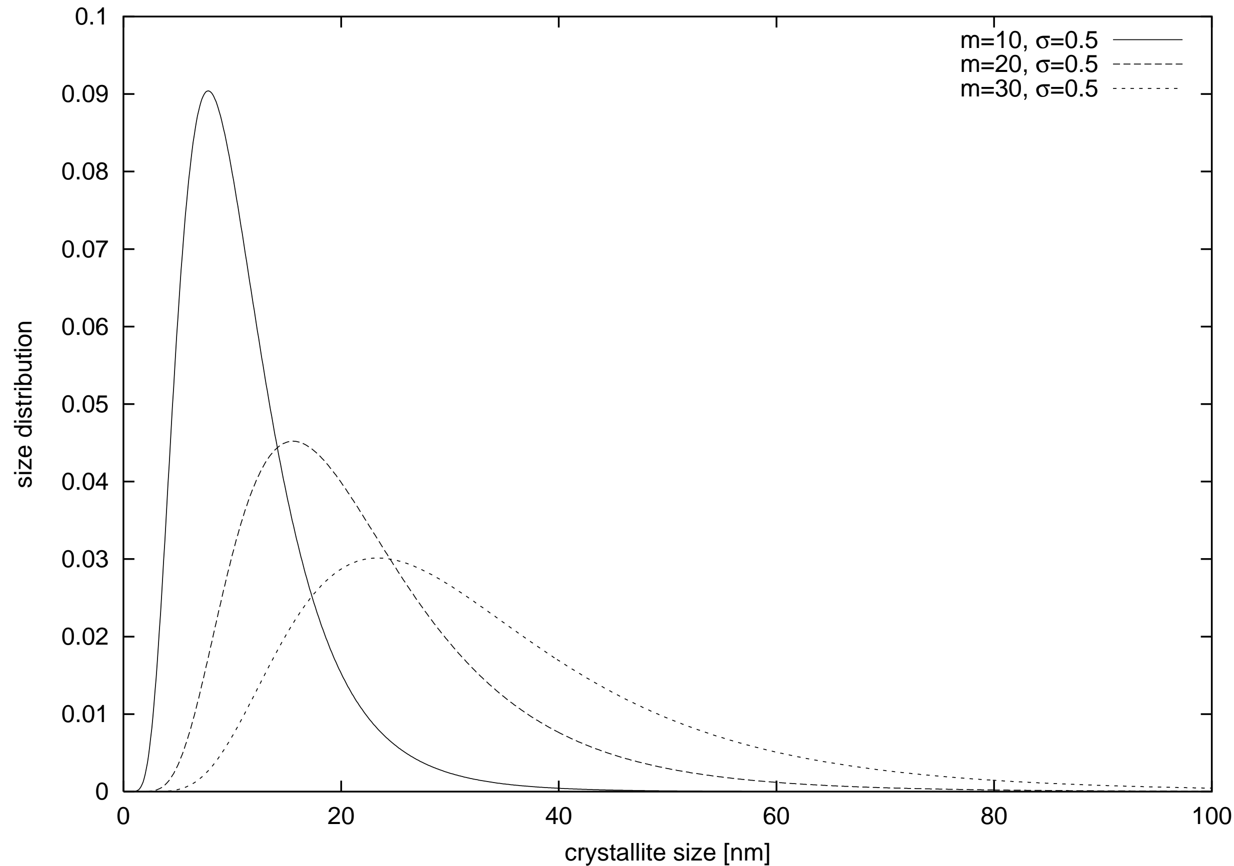


Figure 2: The $f(x)$ lognormal size distribution function for fix σ and varying m values.

Determining the size profile

Determining the size profile (Bertaut; 1949 and Guinier; 1963):

i) the crystallites are divided into columns parallel to the diffraction vector **g**,

ii) the size intensity profile is obtained as the volume-weighted sum of the intensity profiles normalized by their integral intensties corresponding to each column.

The Size Function

The intensity profile of an infinite plane crystallite with the thickness of N atoms:

$$I(\mathbf{\Delta k}) = |A|^2 = AA^* = F_{hkl}^2 \sum_i e^{-i\,2\pi\,\mathbf{\Delta k}\,\mathbf{r_i}} \sum_i e^{i\,2\pi\,\mathbf{\Delta k}\,\mathbf{r_i}}.$$

Using $\mathbf{r_i} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$, where $n_1, n_2, n_3 \in \mathbb{N}$ and $\sum_{i \in N} q^i = \frac{q^N - 1}{q - 1}$:

$$I(s) = F_{hkl}^2 \left(\frac{e^{-i\,N\,2\pi\,s} - 1}{e^{-i\,2\pi\,s} - 1} \right) \left(\frac{e^{i\,N\,2\pi\,s} - 1}{e^{i\,2\pi\,s} - 1} \right),$$

where $s = \mathbf{\Delta k a_1}$. Let's assume that the summation is finite *only* for n_1 and the crystal's width in the $\mathbf{a_1}$ direction is: Na_1.

The Size Function

Using
$(e^{-i\,x}-1)(e^{i\,x}-1)=2-e^{-i\,x}-e^{i\,x}=2-2\cos x=4\sin^2\left(\frac{x}{2}\right)$:

$$I(s)=F_{hkl}^2\frac{\sin^2(N\,\pi s)}{\sin^2(\pi s)}.$$

For large N values, the result is:

$$I(s)=F_{hkl}^2\frac{\sin^2(N\,\pi s)}{(\pi s)^2}=F_{hkl}^2N^2\frac{\sin^2(N\,\pi s)}{(N\pi s)^2}. \qquad (1)$$

The Size Function

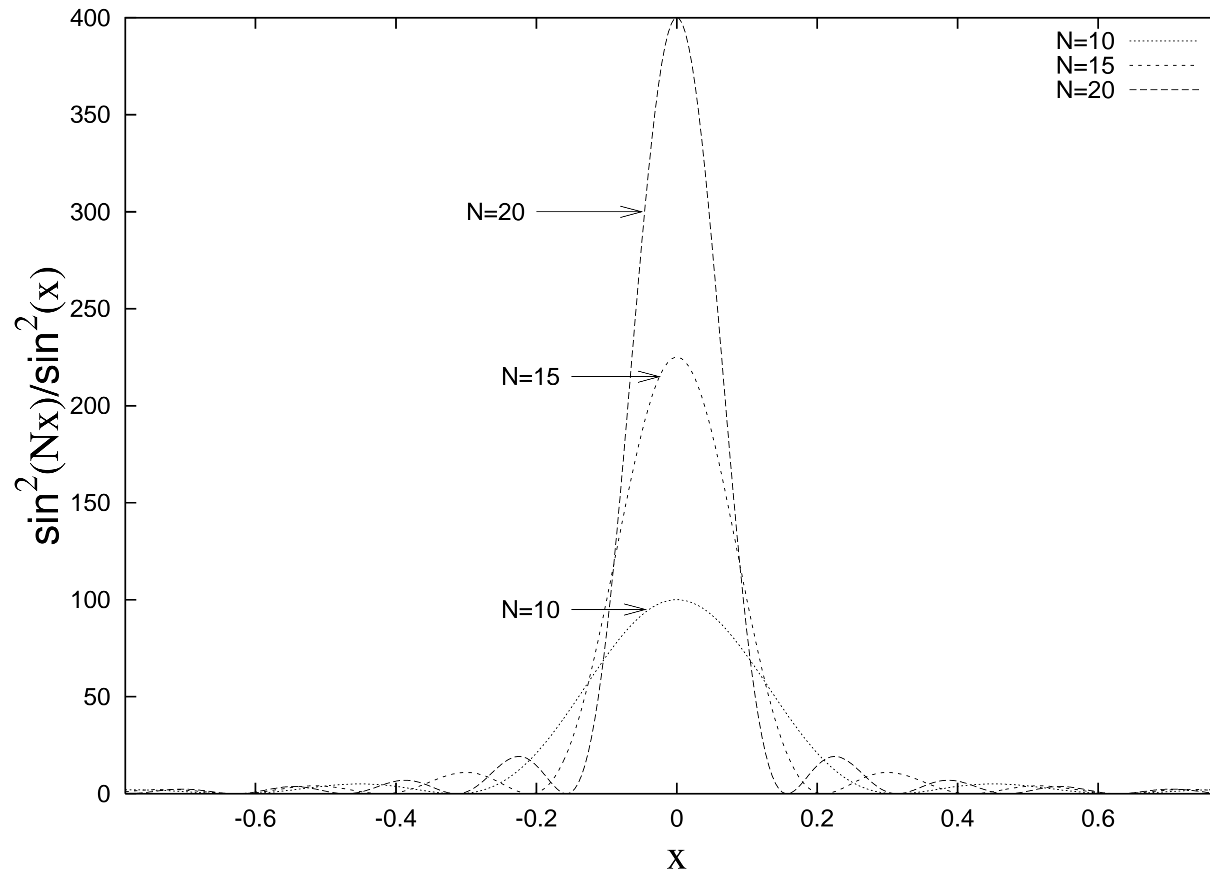


Figure 3: The function $\dfrac{\sin^2(Nx)}{\sin^2(x)}$ plotted close to its first maximum for different values of N. As N tends to infinity, the curve becomes a delta function.

The Size Function

The area normalized intensity profile of a column with area A_i and height M_i:

$$\frac{\sin^2(M_i\,\pi s)}{M_i\,(\pi s)^2}. \tag{2}$$

By summing up the contributions from all columns of all crystallites:

$$I(s) \sim \sum_i \frac{\sin^2(M_i\,\pi s)}{M_i\,(\pi s)^2}\,A_i M_i. \tag{3}$$

The Size Function

If we assume spherical crystallite shape and lognormal size distribution we obtain the following size intensity profile:

$$I^S(s) = \int_0^\infty \mu \frac{\sin^2(\mu \pi s)}{(\pi s)^2} \operatorname{erfc}\left[\frac{\log\left(\frac{\mu}{m}\right)}{\sqrt{2}\sigma}\right] \mathrm{d}\mu,$$

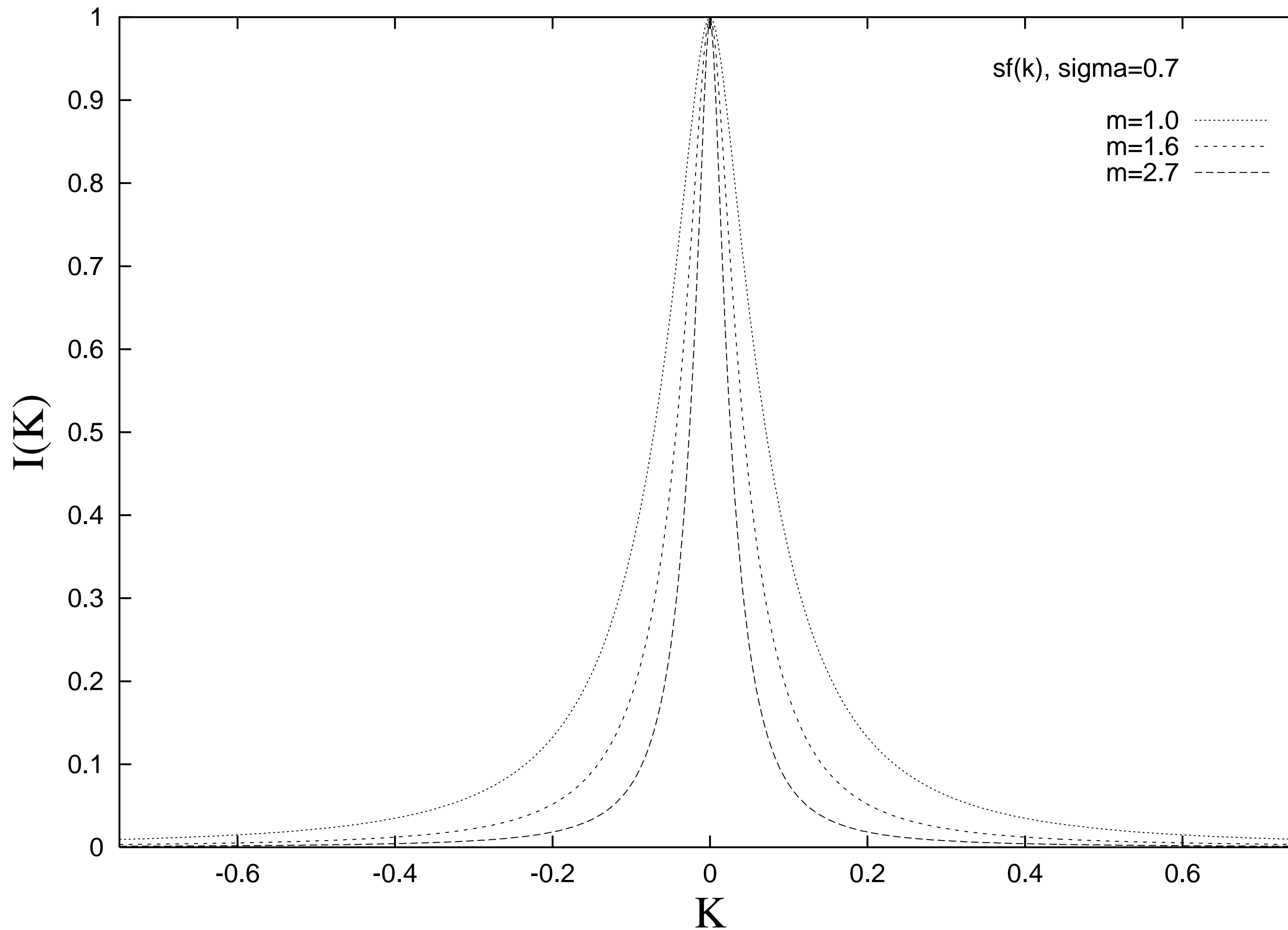
where erfc is the complementary error function, defined as:

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} \, \mathrm{d}t. \tag{4}$$

It depends on two independent parameters: m, the median of the lognormal size distribution and σ, the variance of the distribution.

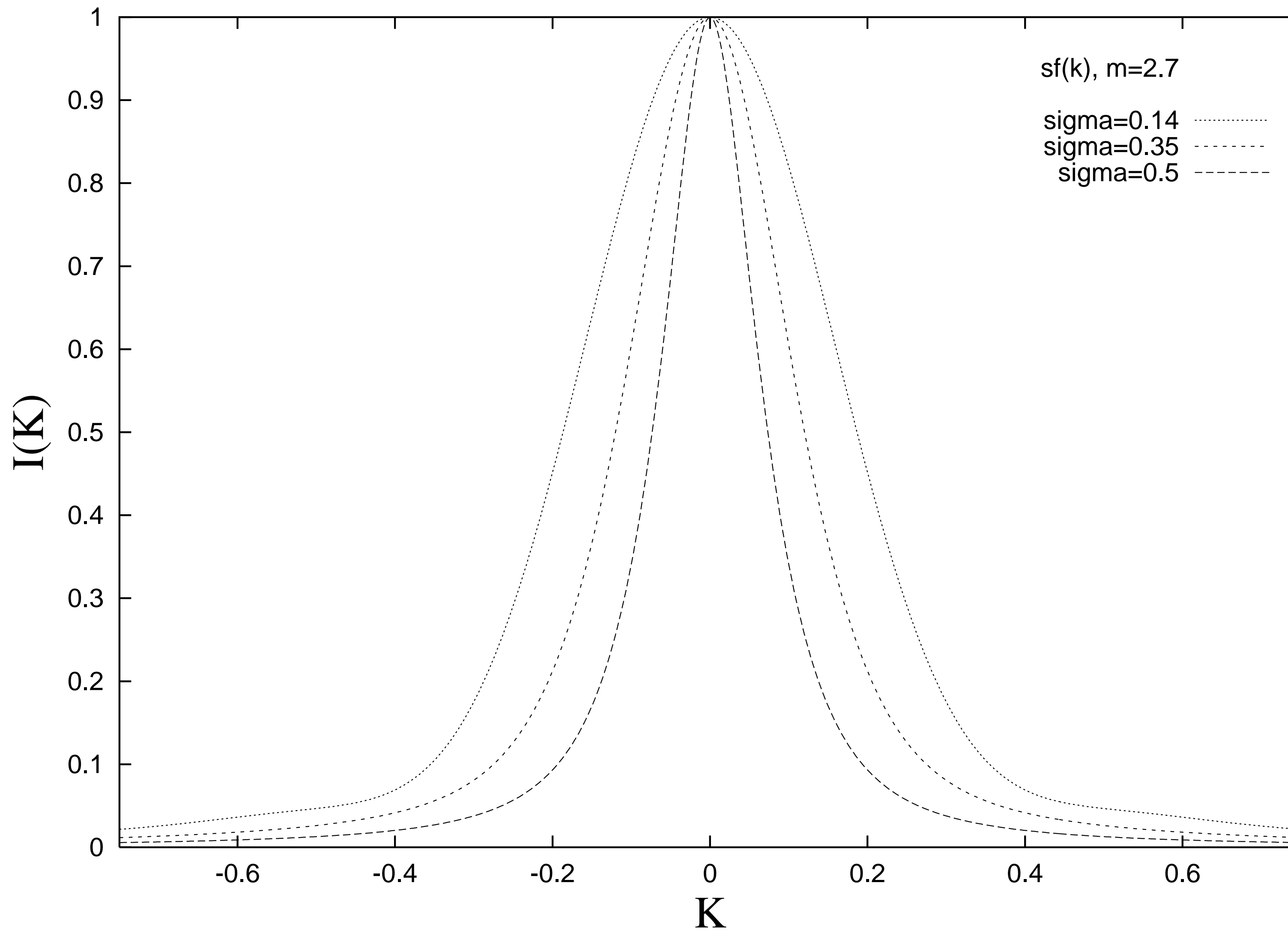
The Size Function

For fixed σ values:



The Size Function

For fixed m values:



The Size Fourier Transform

The Fourier transform of the function $\dfrac{\sin^2(M\,\pi s)}{(\pi s)^2}$ is:

$$\begin{cases} M - |L|, & \text{if } |L| \le M \\ \\ 0, & \text{if } |L| > M. \end{cases} \tag{5}$$

The Size Fourier Transform

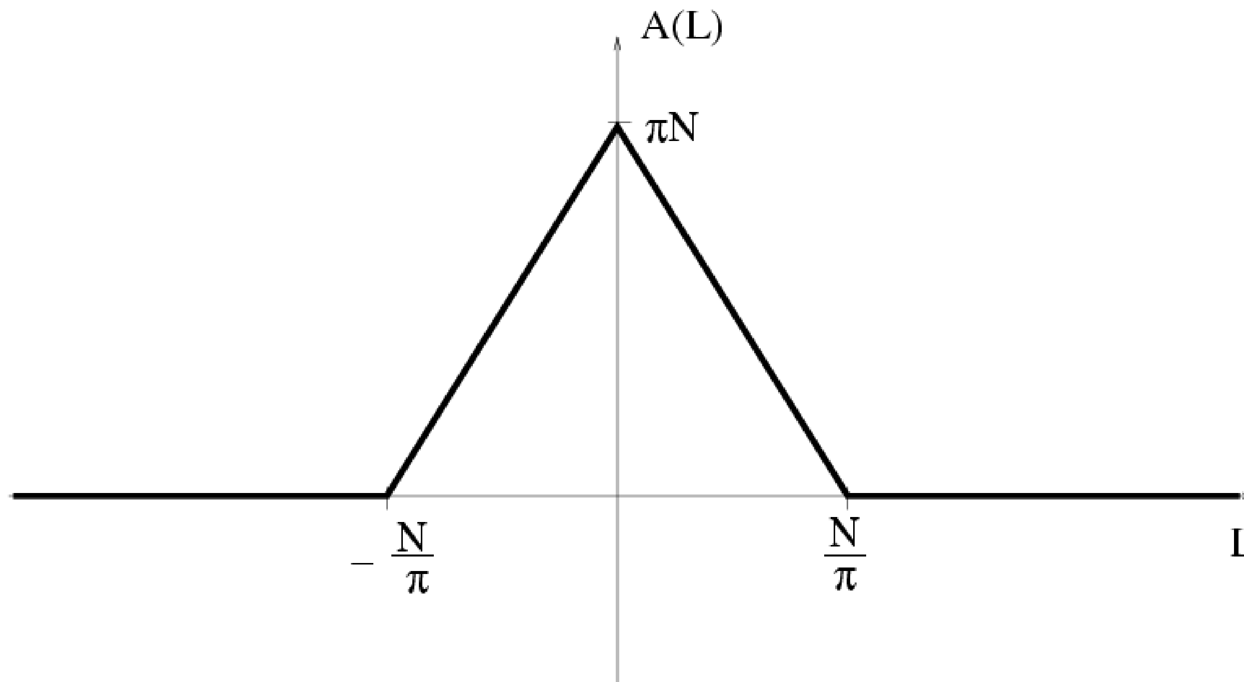


Figure 4: The Fourier transform of the function $\frac{\sin^2(Nx)}{x^2}$.

The Size Fourier Transform

$$
\begin{aligned}
A^S(L) &= 2\int_0^\infty I^S(s)\cos(2\pi sL)\,\mathrm{d}s = \\
&= 2\int_0^\infty \left(\int_0^\infty M\,\frac{\sin^2(M\,\pi s)}{(\pi s)^2}\,\mathrm{erfc}\left[\frac{\log\left(\frac{M}{m}\right)}{\sqrt{2}\sigma}\right]\,\mathrm{d}M \right) \cos(2\pi sL)\,\mathrm{d}s = \\
&= \int_0^\infty M \left(2\int_0^\infty \frac{\sin^2(M\,\pi s)}{(\pi s)^2}\,\cos(2\pi sL)\,\mathrm{d}s \right) \mathrm{erfc}\left[\frac{\log\left(\frac{M}{m}\right)}{\sqrt{2}\sigma}\right]\,\mathrm{d}M = \\
&= \int_{|L|}^\infty \left(M^2 - |L|M\right)\,\mathrm{erfc}\left[\frac{\log\left(\frac{M}{m}\right)}{\sqrt{2}\sigma}\right]\,\mathrm{d}M.
\end{aligned}
\tag{6}
$$

The Size Fourier Transform

By using substitutions and partial integration this integral can be further simplified:

$$A^S(L,m,\sigma) = \frac{m^3 \exp\left(\frac{9}{4}(\sqrt{2}\sigma)^2\right)}{3} \operatorname{erfc}\left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \frac{3}{2}\sqrt{2}\sigma\right] -$$

$$\frac{m^2 \exp(\sqrt{2}\sigma)^2}{2} |L| \operatorname{erfc}\left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \sqrt{2}\sigma\right] +$$

$$\frac{|L|^3}{6} \operatorname{erfc}\left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma}\right].$$

Average Crystallite Sizes

The volume weighted averaged crystallite size:

$$< x >_{vol} = m \exp\left(3.5\sigma^2\right) \tag{7}$$

The area weighted averaged crystallite size:

$$< x >_{area} = m \exp\left(2.5\sigma^2\right) \tag{8}$$

XRD and TEM Size

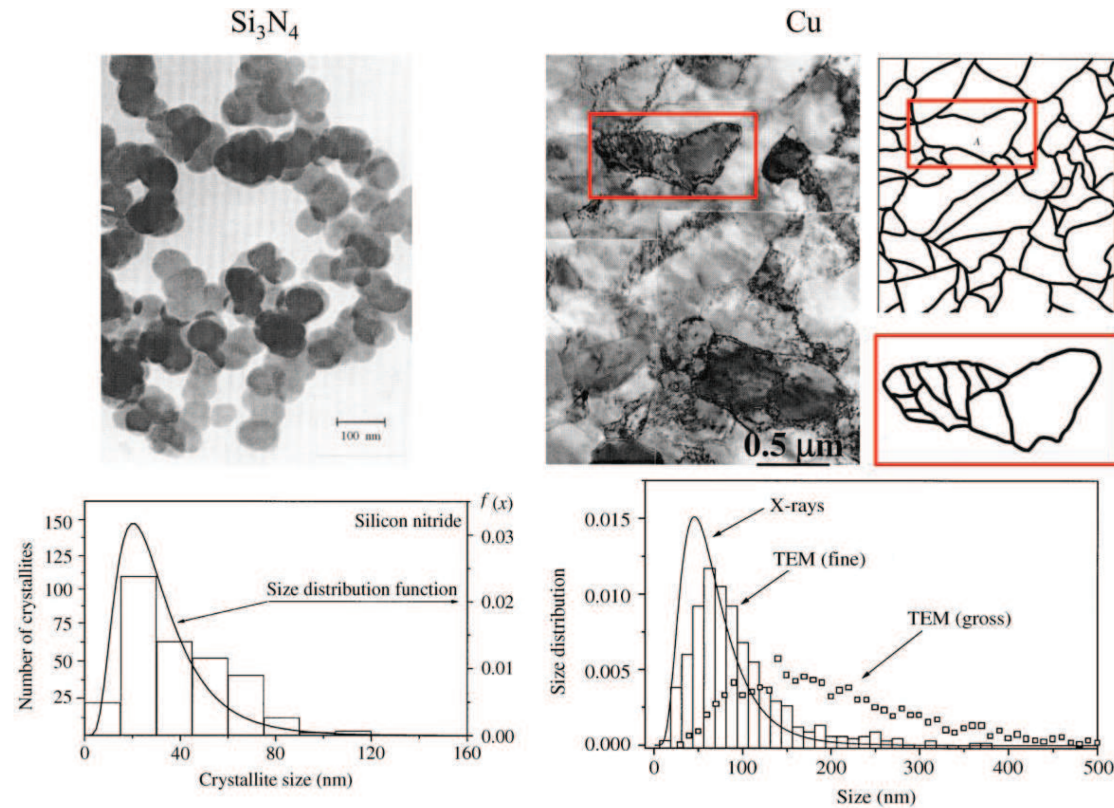


Figure 5: Comparing size distributions obtained by XRD and TEM.

XRD and TEM Size

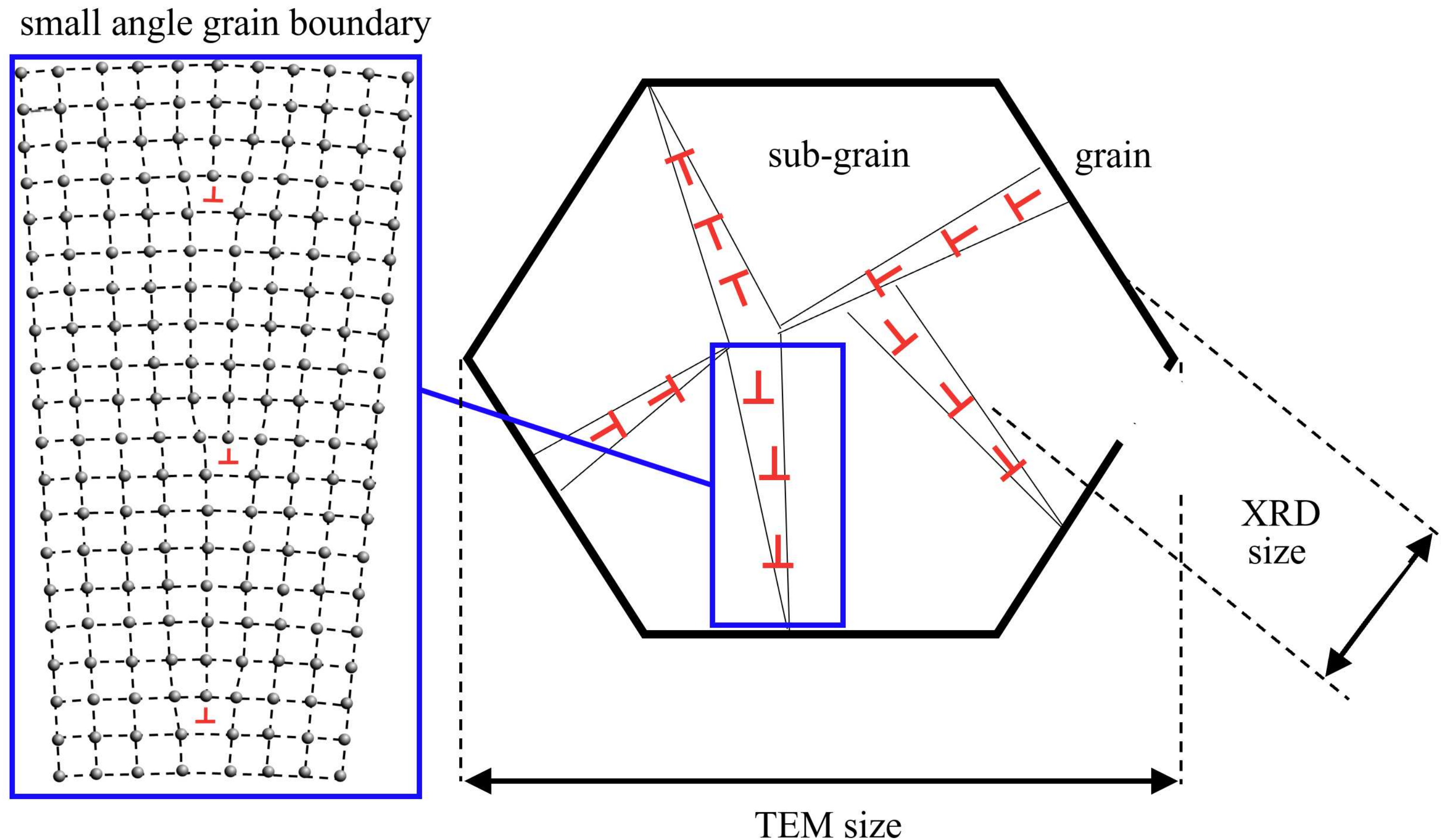


Figure 6: The size of the different structures in the sample. XRD always provides the coherent domain size. Source: PhD thesis of E. Odor (2023).

The strain effect

According to Warren and Averbach (1952), the Fourier transform of the line profile:

$$\log A(L) = \log A_S(L) - 2\pi^2 g^2 L^2 \langle \varepsilon_L^2 \rangle$$

The distortion Fourier coefficients:

$$A^D(L) = \exp\left(-2\pi^2 g^2 L^2 \langle \varepsilon_L^2 \rangle\right),$$

where

- g is the absolute value of the diffraction vector,
- $\langle \varepsilon_L^2 \rangle$ is the *mean square strain*.

The strain effect

The scattered intensity is:

$$I = f^2 \sum_{j,j'} e^{i2\pi \Delta\mathbf{k}\,(\mathbf{r_j} - \mathbf{r_{j'}})}.$$

The effect of distortion:

- let's denote the atomic position vectors in an ideal lattice with $\mathbf{r_j^0}$ and $\mathbf{r_{j'}^0}$
- in the imperfect crystal it is shifted: $\mathbf{r_j} = \mathbf{r_j^0} + \delta\mathbf{r_j}$, $\mathbf{r_{j'}} = \mathbf{r_{j'}^0} + \delta\mathbf{r_{j'}}$
- the reciprocal space is also distorted: **g** is an ideal reciprocal space vector, it is shifted by a small **s** vector: $\Delta\mathbf{k} = \mathbf{g} + \mathbf{s}$

The strain effect

According to the Laue equations, $\mathbf{g}(\mathbf{r_j^0} - \mathbf{r_{j'}^0}) \in \mathbb{Z}$ and $\mathbf{s}(\delta\mathbf{r_j} - \delta\mathbf{r_{j'}})$ is negligible, so:

$$I(\mathbf{s}) = f^2 \sum_{j,j'} e^{i2\pi\mathbf{s}(\mathbf{r_j^0} - \mathbf{r_{j'}^0})} e^{i2\pi\mathbf{g}(\delta\mathbf{r_j} - \delta\mathbf{r_{j'}})}.$$

This expression can be transformed in a form of Fourier series and leads to the equation:

$$\log A(L) = \log A_S(L) - 2\pi^2 g^2 L^2 \langle \varepsilon_L^2 \rangle,$$

where the strain, ε_n is defined as:

$$\varepsilon_n = \frac{\delta\mathbf{r_j} - \delta\mathbf{r_{j'}}}{n},$$

where $n = j - j^{'}$ is the distance of the atoms j and $j^{'}$.

The strain effect

The most important models for $\langle \varepsilon_L^2 \rangle$:

- Warren & Averbach (1952) has shown that if the displacement of the atoms is random, $\langle \varepsilon_L^2 \rangle$ is constant.
- Krivoglaz & Ryaboshapka (1963) supposed that strain is caused by dislocations with random spatial distribution. For small L values $\langle \varepsilon_L^2 \rangle$ is expressed as:

$$\langle \varepsilon_L^2 \rangle = \left(\frac{b}{2\pi} \right)^2 \pi \rho C \log \left(\frac{D}{L} \right),$$

  where D is the crystallite size.
- Wilkens (1970) supposed a restrictedly random distribution of dislocations and calculated a strain function which is valid for the entire L range.

The Wilkens dislocation theory

Wilkens introduced the effective outer cut off radius of dislocations, R_e^*, instead of the crystal diameter. Assuming infinitely long parallel *screw* dislocations with *restrictedly random* distribution (Wilkens, 1970):

$$\langle \varepsilon_L^2 \rangle = \left(\frac{b}{2\pi} \right)^2 \pi \rho \, C f^* \left(\frac{L}{R_e^*} \right),$$

where b is the absolute value of the Burgers-vector, ρ is the dislocation density, C is the contrast factor of the dislocations and $f^*(\eta)$ is the Wilkens strain function, where: $\eta = \frac{1}{2} \exp \left(-\frac{1}{4} \right) \frac{L}{R_e^*}$. The f^* function is given in (Wilkens, 1970) in equations A6-A8 in Appendix A. Kamminga and Delhez (2000) has shown using numerical simulations that the line profile calculated by the Wilkens model is also valid for edge and curved type dislocations.

The Wilkens function

$$f^*(\eta) = -\log\eta + \left(\frac{7}{4} - \log 2\right) + \frac{512}{90\pi}\frac{1}{\eta} +$$

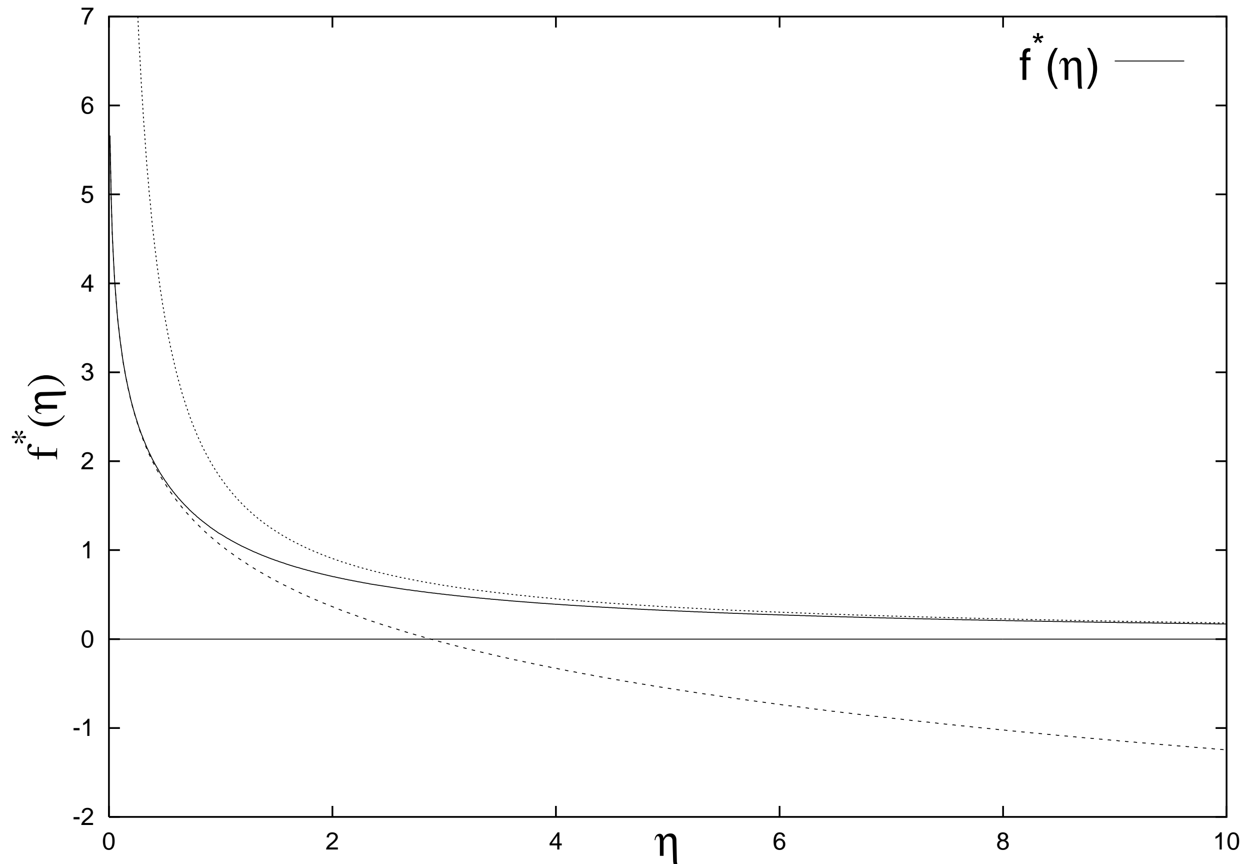
$$\frac{2}{\pi}\left[1 - \frac{1}{4\eta^2}\right]\int_0^\eta \frac{\arcsin V}{V}\mathrm{d}V -$$

$$\frac{1}{\pi}\left[\frac{769}{180}\frac{1}{\eta} + \frac{41}{90}\eta + \frac{2}{90}\eta^3\right]\sqrt{1-\eta^2} -$$

$$\frac{1}{\pi}\left[\frac{11}{12}\frac{1}{\eta^2} + \frac{7}{2} + \frac{1}{3}\eta^2\right]\arcsin\eta + \frac{1}{6}\eta^2, \quad \text{if } \eta \leq 1,$$

$$f^*(\eta) = \frac{512}{90\pi}\frac{1}{\eta} - \left[\frac{11}{24} + \frac{1}{4}\log 2\eta\right]\frac{1}{\eta^2}, \quad \text{if } \eta \geq 1,$$

The Wilkens function



The Wilkens function and its approximations: $-\log \eta + \left(\frac{7}{4} - \log 2\right)$ and $\frac{512}{90\pi}\frac{1}{\eta}$.

The Wilkens dislocation theory

The meaning of the restrictedly random distribution of the Wilkens model:

- Wilkens supposed tubes with radius of R_e. The dislocations are located parallelly and inside the tubes,
- the dislocations are distributed randomly in each tube and the dislocation density in the tubes is exactly ρ.

The distortion Fourier–transform in the Wilkens model:

$$A^D(L) = \exp\left[-\frac{\pi b^2}{2}(g^2 C)\rho L^2 f^*\left(\frac{L}{R_e^*}\right)\right].$$

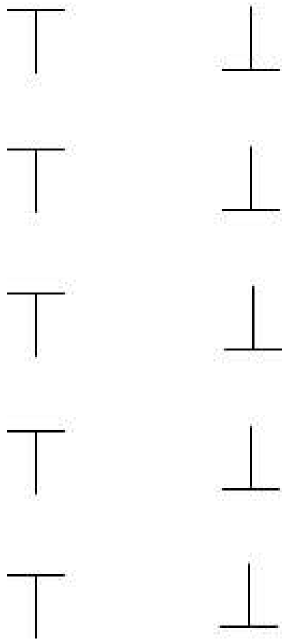
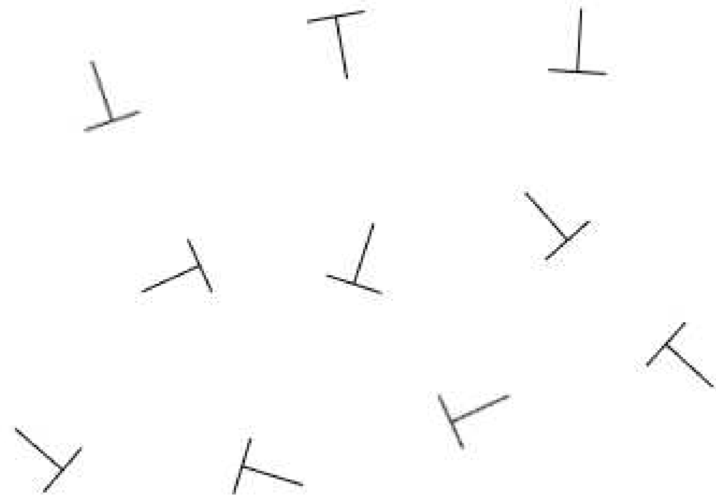
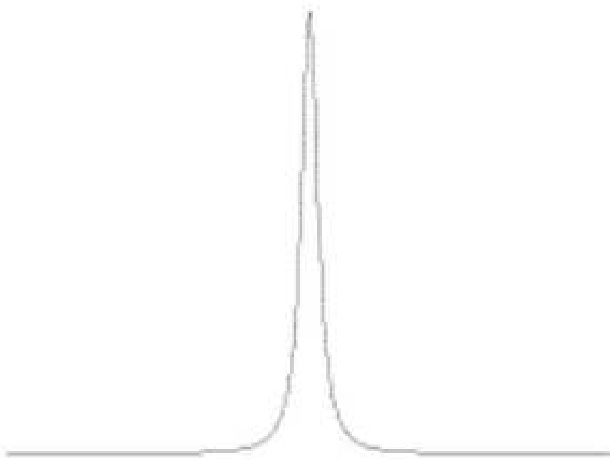
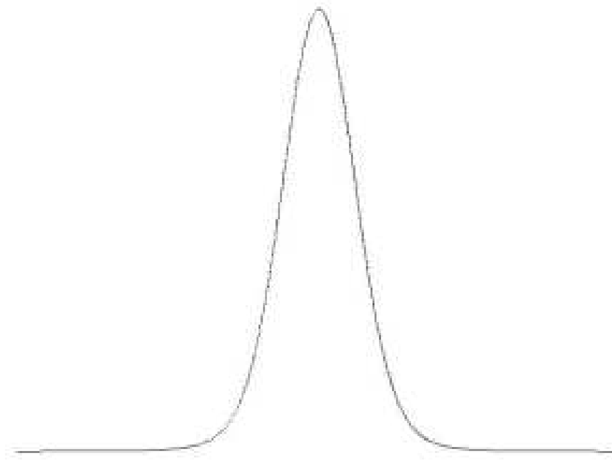
The dislocation arrangement parameter

Wilkens introduced M^*, a dimensionless parameter:

$$M^* = R_e^* \sqrt{\rho} = \frac{R_e^*}{< d_{\text{disl.}} >},$$

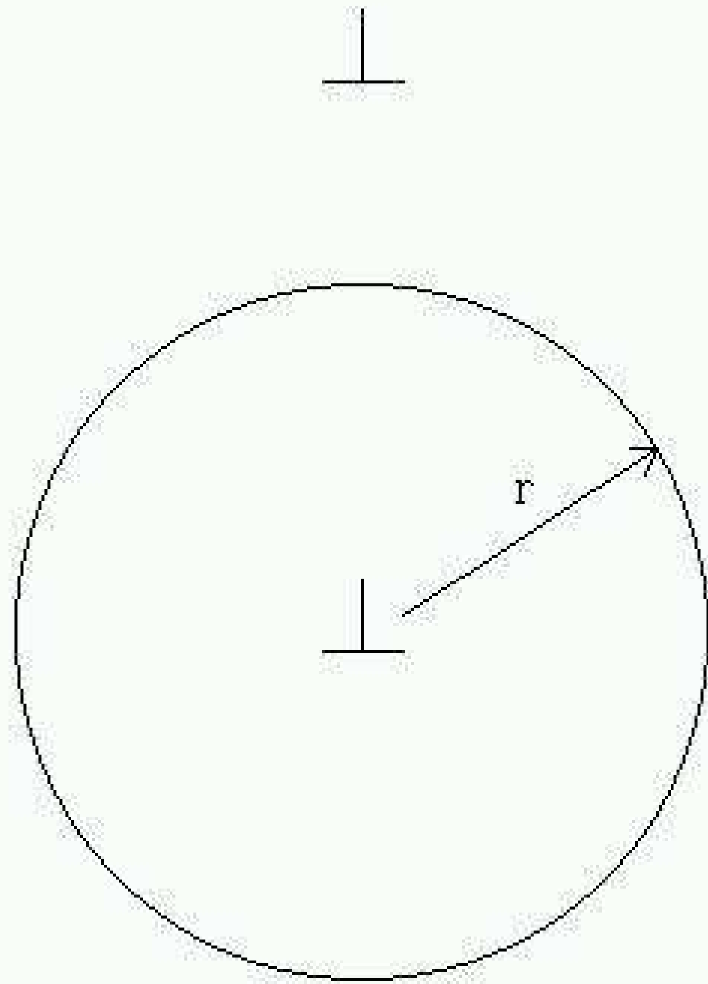
where $< d_{\text{disl.}} >$ is the average dislocation distance. The M^* parameter characterizes the dislocation arrangement:

- if the value of M^* is small, the correlation between the dislocations is strong
- if the value of M^* is large, the dislocations are distributed randomly in the crystallite

$$R_e^* << \frac{1}{\sqrt{\rho}}$$
$$M^* << 1$$

$$R_e^* >> \frac{1}{\sqrt{\rho}}$$
$$M^* >> 1$$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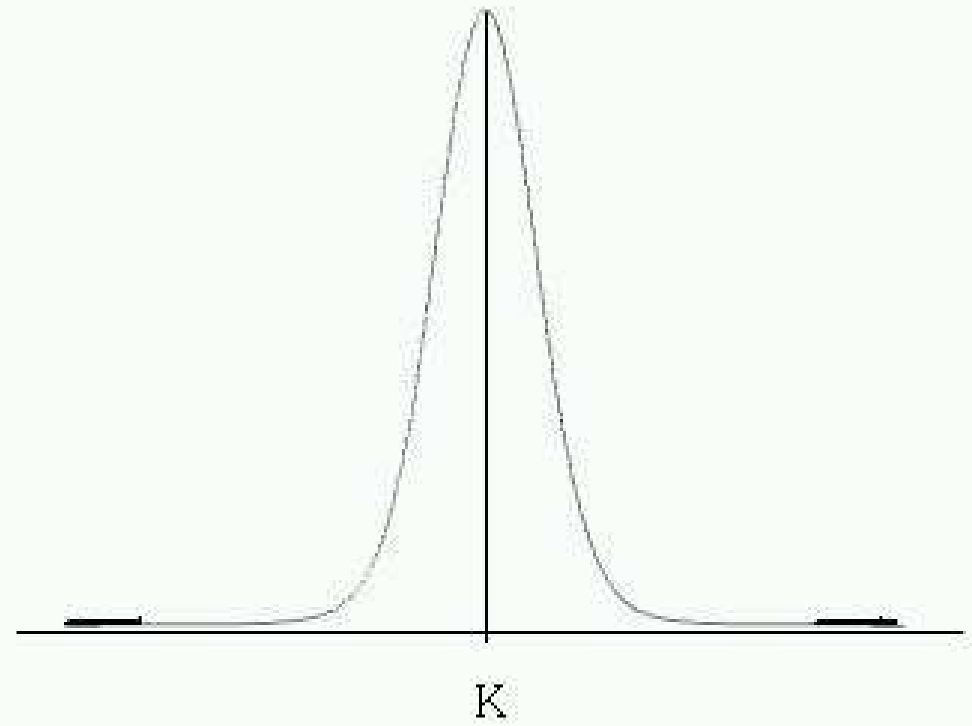
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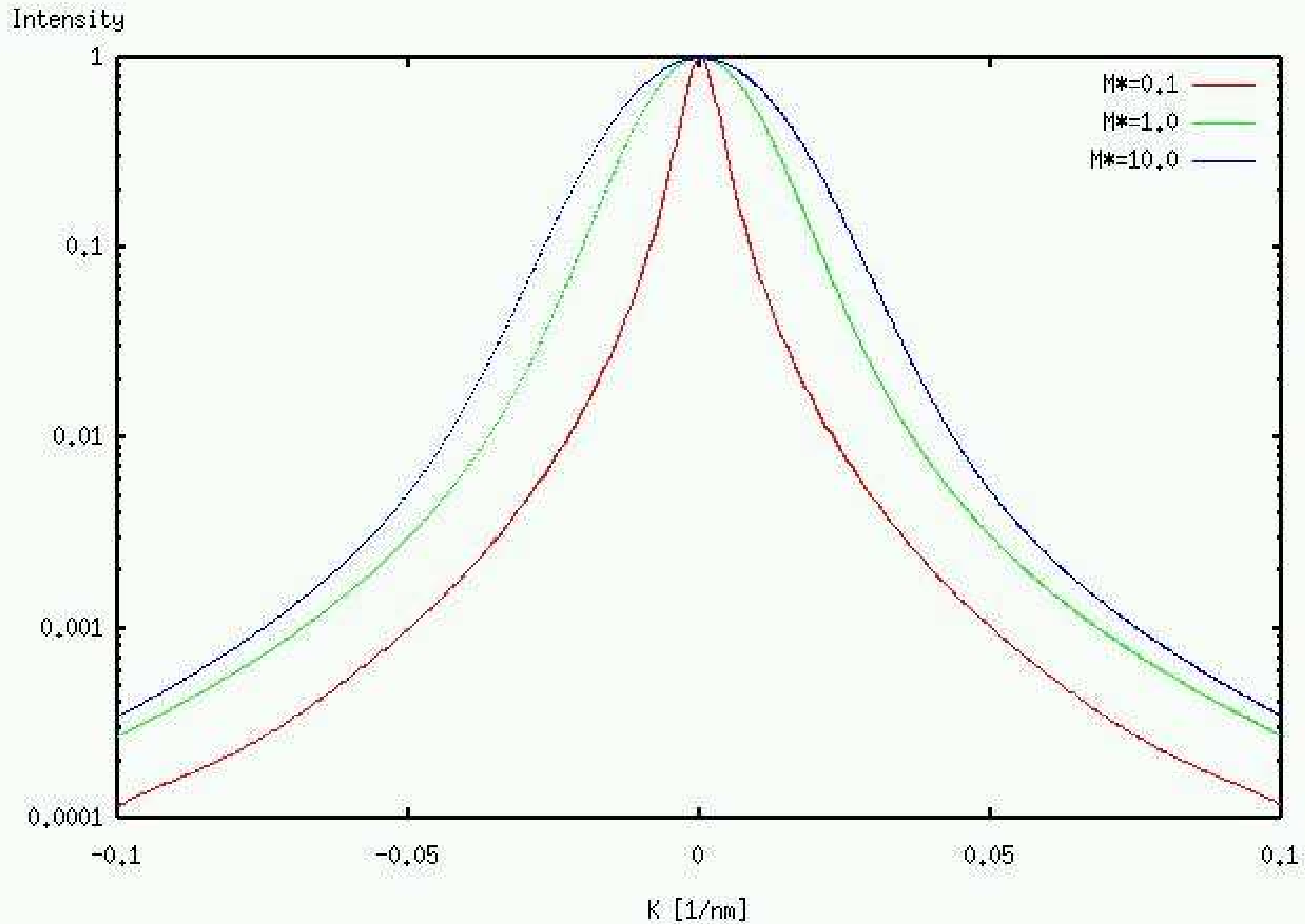
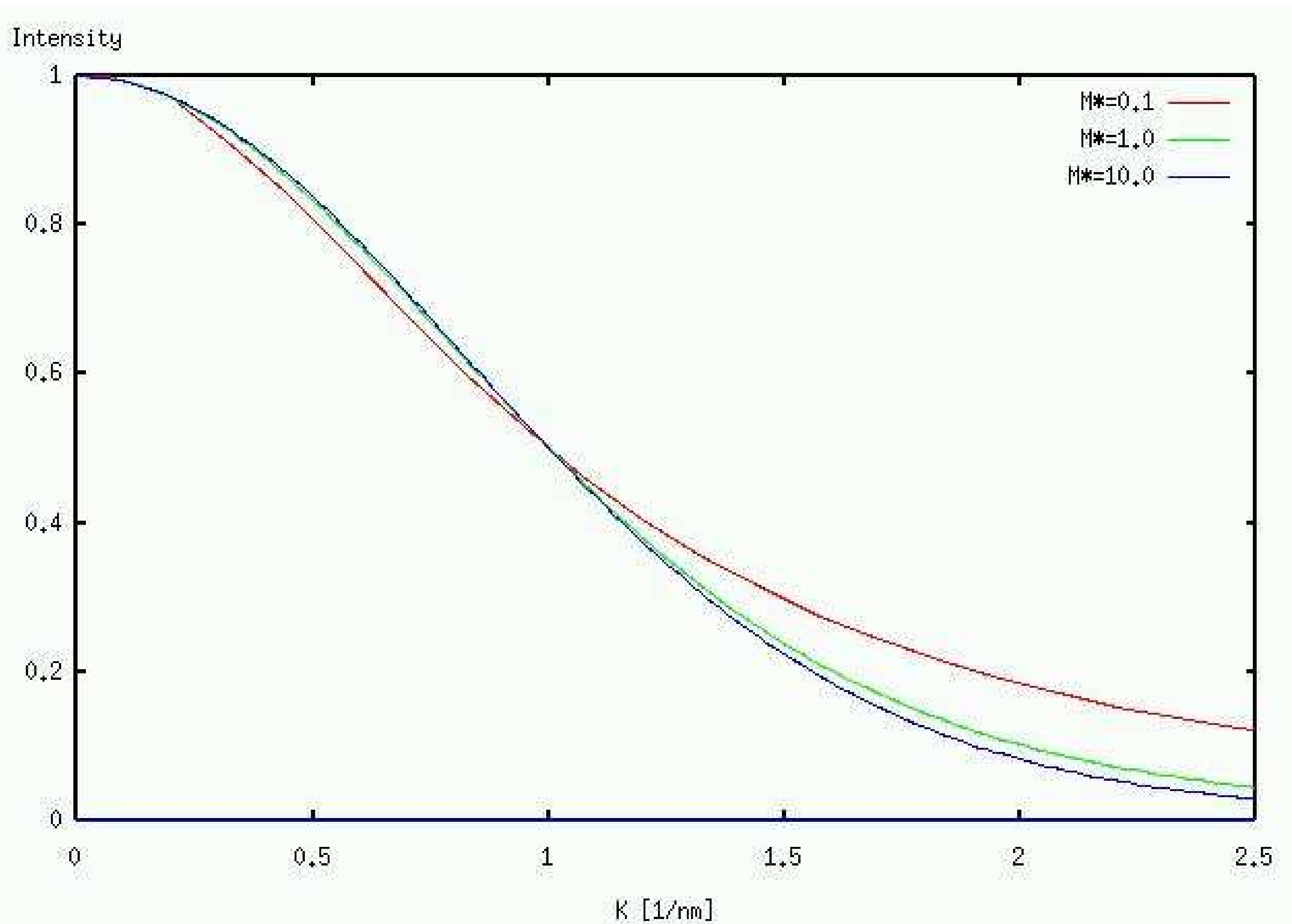
The strain profile for fixed ρ and variable M^* values:

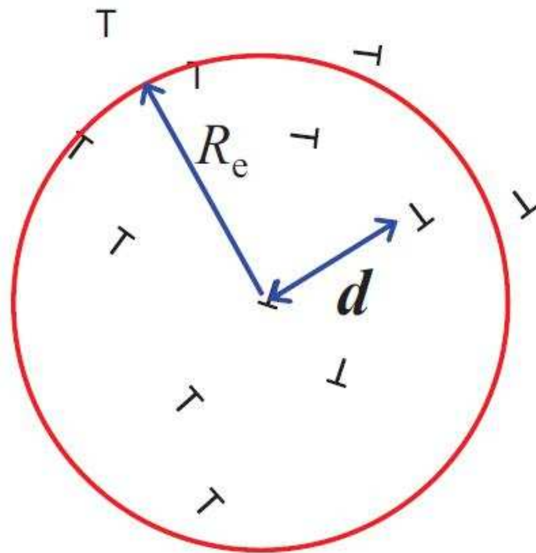


The shape of the strain profile for fixed ρ and variable M^* values:



Dislocation **arrangement** parameter

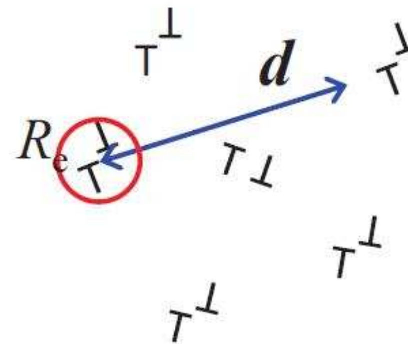
random



$R_e > d$ $\rho^{1/2} = 1/d$

$\boldsymbol{M} = R_e/d = R_e\rho^{1/2}$ **> 1**

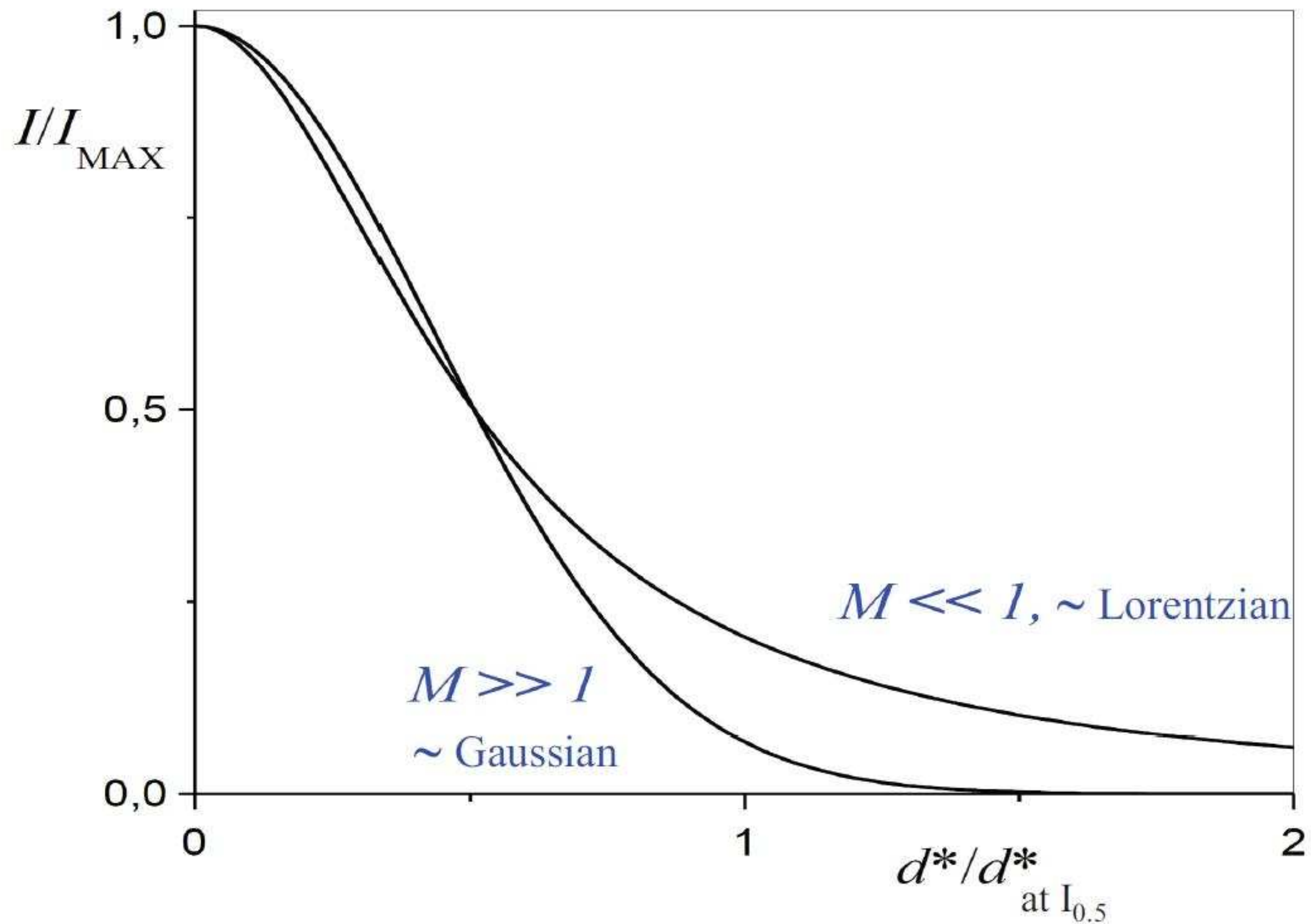
highly correlated



$R_e << d$ $\rho^{1/2} = 1/d$

$\boldsymbol{M} = R_e\rho^{1/2}$ **<< 1**

shape of strain-profiles



Dislocation contrast

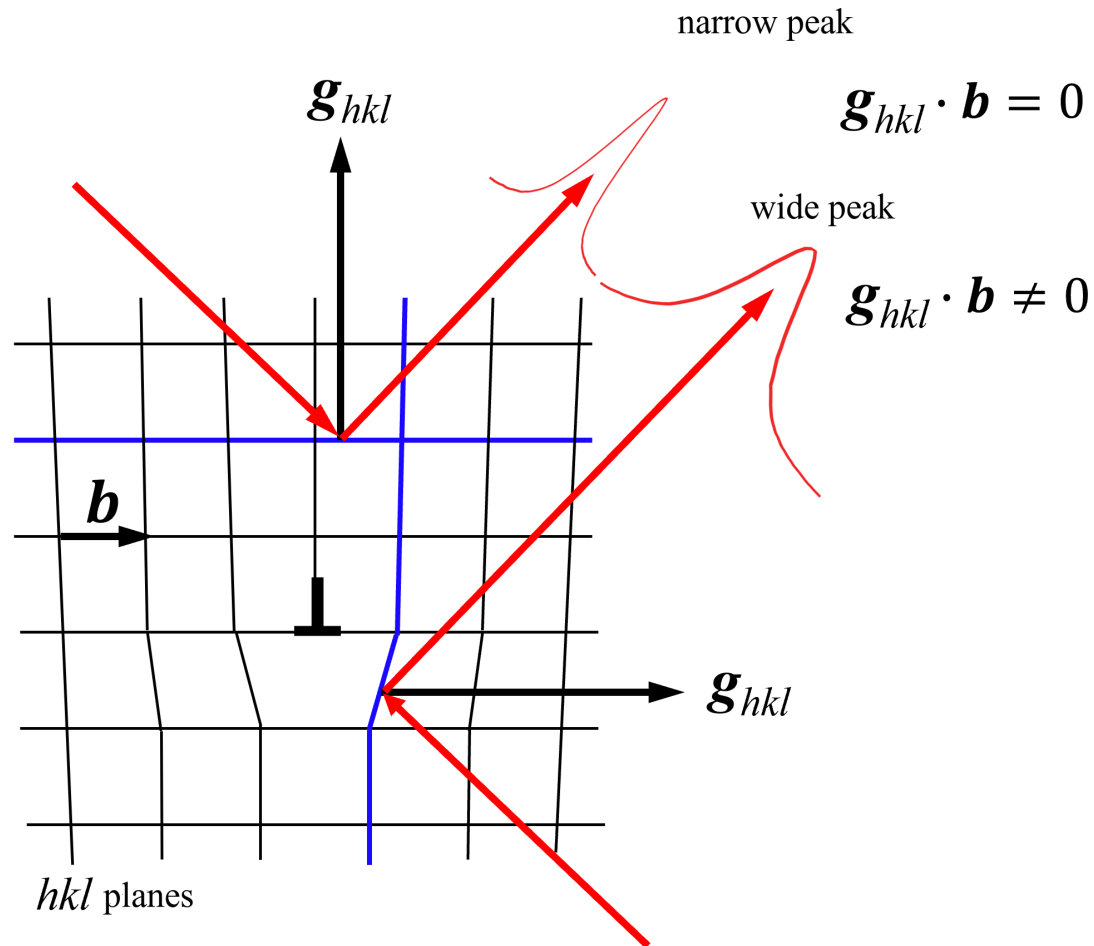


Figure 7: The effect of dislocation contrast: the same dislocation has different broadening effect on different planes. Source: PhD thesis of E. Odor (2023).

Strain anisotropy

According to (Ungár & Tichy, 1999), the average contrast factors of dislocations can be expressed in the following form for cubic crystals:

$$C = C_{h00}(1 - qH^2),$$

where

$$H^2 = \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}.$$

For hexagonal crystals:

$$C = C_{hk0}(1 + a_1 H_1^2 + a_2 H_2^2),$$

where

$$H_1^2 = \frac{[h^2 + k^2 + (h+k)^2]\, l^2}{[h^2 + k^2 + (h+k)^2 + \frac{3}{2}(\frac{a}{c})^2 l^2]^2},$$

$$H_2^2 = \frac{l^4}{[h^2 + k^2 + (h+k)^2 + \frac{3}{2}(\frac{a}{c})^2 l^2]^2},$$

and $\frac{a}{c}$ is the ratio of the two lattice constants.
The constants C_{h00} and C_{hk0} are calculated from the elastic constants of the crystal (Ungár et al, 1999).

Planar faults

The profile is the sum of a δ-function and shifted and broadened Lorentzian profile functions

$$I^{st}(s) = p_0^{hkl}\delta(s) + \frac{p_1^{hkl}}{1+\left(\frac{s-s_1^{hkl}}{w_1^{hkl}}\right)^2} + \frac{p_2^{hkl}}{1+\left(\frac{s-s_2^{hkl}}{w_2^{hkl}}\right)^2} + \frac{p_3^{hkl}}{1+\left(\frac{s-s_3^{hkl}}{w_3^{hkl}}\right)^2}$$

- FWHM $\sim$ density of faults
- hkl-dependence: DIFFaX-software (Treacy et al., Proc. Roy. Soc., 1991)
- implementation into CMWP is based on the work of Dr. Levente Balogh (PhD thesis, 2009).

Planar faults

The w_i^{hkl} and s_i^{hkl} can be expressed as fifth order polynomials of the α_j probability of planar faults:

$$w_1^{hkl} = W_{1,1}^{hkl}\alpha_j + W_{1,2}^{hkl}\alpha_j^2 + W_{1,3}^{hkl}\alpha_j^3 + W_{1,4}^{hkl}\alpha_j^4 + W_{1,5}^{hkl}\alpha_j^5$$

$$w_2^{hkl} = W_{2,1}^{hkl}\alpha_j + W_{2,2}^{hkl}\alpha_j^2 + W_{2,3}^{hkl}\alpha_j^3 + W_{2,4}^{hkl}\alpha_j^4 + W_{2,5}^{hkl}\alpha_j^5$$

$$w_3^{hkl} = W_{3,1}^{hkl}\alpha_j + W_{3,2}^{hkl}\alpha_j^2 + W_{3,3}^{hkl}\alpha_j^3 + W_{3,4}^{hkl}\alpha_j^4 + W_{3,5}^{hkl}\alpha_j^5$$

$$s_1^{hkl} = S_{1,1}^{hkl}\alpha_j + S_{1,2}^{hkl}\alpha_j^2 + S_{1,3}^{hkl}\alpha_j^3 + S_{1,4}^{hkl}\alpha_j^4 + S_{1,5}^{hkl}\alpha_j^5$$

$$s_2^{hkl} = S_{2,1}^{hkl}\alpha_j + S_{2,2}^{hkl}\alpha_j^2 + S_{2,3}^{hkl}\alpha_j^3 + S_{2,4}^{hkl}\alpha_j^4 + S_{2,5}^{hkl}\alpha_j^5$$

$$s_3^{hkl} = S_{3,1}^{hkl}\alpha_j + S_{3,2}^{hkl}\alpha_j^2 + S_{3,3}^{hkl}\alpha_j^3 + S_{3,4}^{hkl}\alpha_j^4 + S_{3,5}^{hkl}\alpha_j^5$$

Planar faults

The real and imaginary parts of the $A^{st}(L)$ Fourier transform of $I^{st}(s)$ can be expressed as:

$$\Re A^{st}(L) = p_0^{hkl} + p_1^{hkl}\cos(2\pi s_1^{hkl} L)\exp(-\pi w_1^{hkl} L) +$$

$$p_2^{hkl}\cos(2\pi s_2^{hkl} L)\exp(-\pi w_2^{hkl} L) +$$

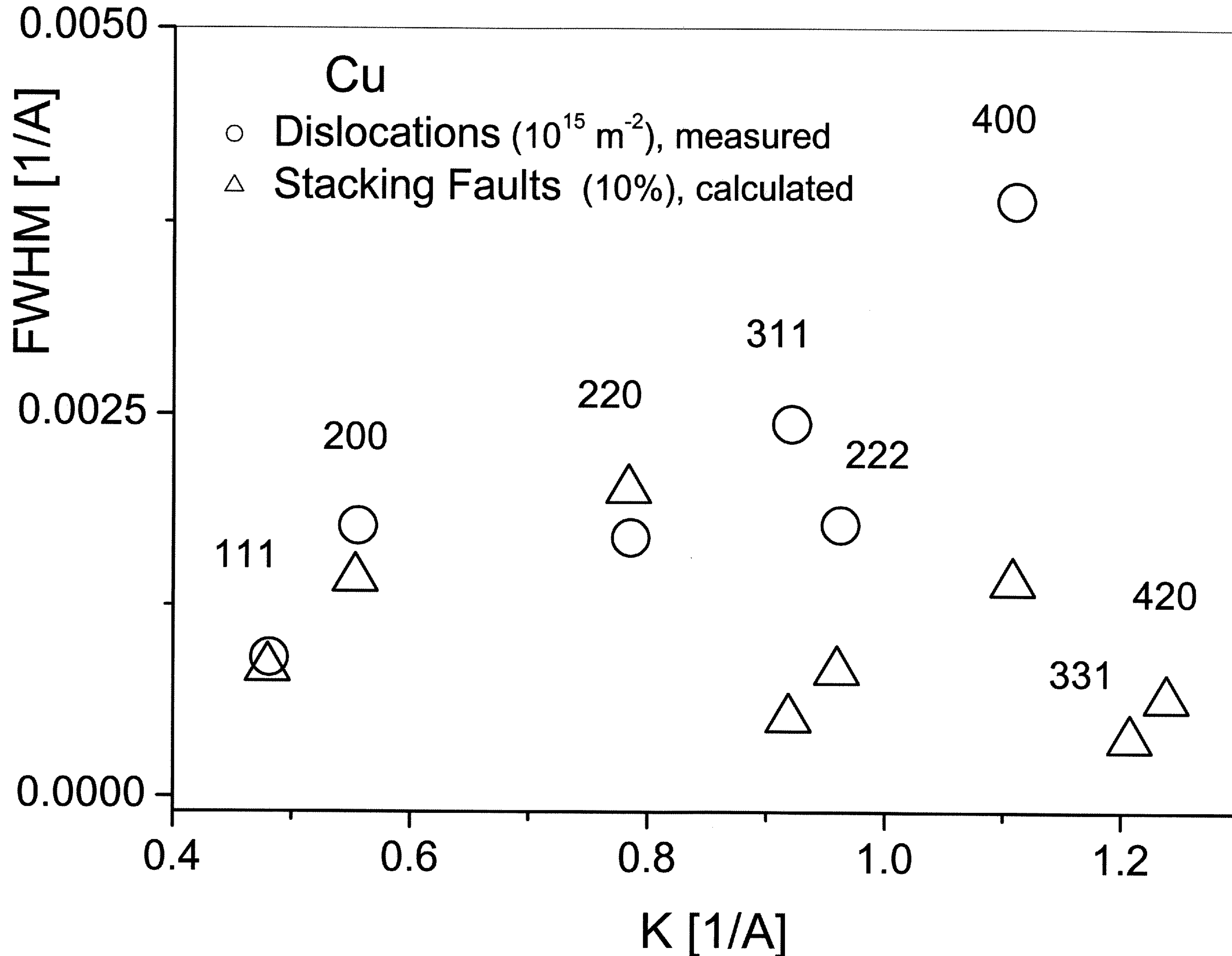
$$+ p_3^{hkl}\cos(2\pi s_3^{hkl} L)\exp(-\pi w_3^{hkl} L)$$

$$\Im A^{st}(L) = p_1^{hkl}\sin(2\pi s_1^{hkl} L)\exp(-\pi w_1^{hkl} L) +$$

$$p_2^{hkl}\sin(2\pi s_2^{hkl} L)\exp(-\pi w_2^{hkl} L) +$$

$$+ p_3^{hkl}\sin(2\pi s_3^{hkl} L)\exp(-\pi w_3^{hkl} L).$$

Anisotropy: Dislocations/Planar Faults



Microstructure Determination Methods

- Single Profile method based on profile width: Scherrer Equation
- Single Profile method based on partial (asymptotic) profile fitting: Momentum Method
- Multi Profile method based on profile widths: (Modified) Williamson-Hall Method
- Multi Profile method based on partial Fourier profile fitting: (Modified) Warren-Averbach Method
- Multi Profile method based on full Fourier profile fitting: Multiple Whole Profile fitting (MWP) method
- Multi Profile method based on full Intensity pattern fitting: Convolutional Multiple Whole Profile fitting (CMWP) method

Separation of microstructural effects

In case of single profile (momentum) method:

- Crystallite size effect: $1/q^2$ decaying
- Strain effect: $1/q^3$ decaying

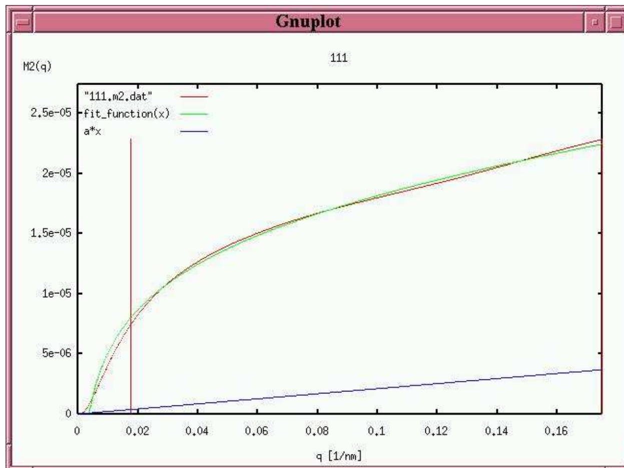
In case of multi profile methods:

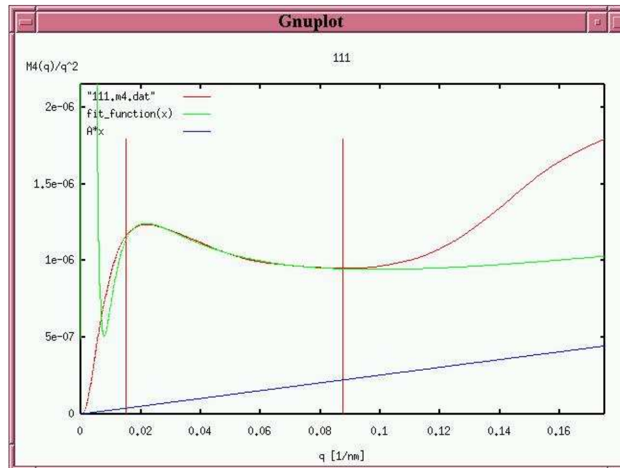
- Crystallite size effect: the broadening is independent of K ($K = \frac{2\sin(\theta)}{\lambda}$)
- Strain effect:
  - the broadening globally increases with K
  - typical anisotropy
- Planar defects: (different) anisotropy, no increasing tendency, asymmetric broadening

Momentum Method

- single profile method developed by I. Groma
- it's based on the "restricted moments" of the profiles:

$$M_k(q) = \frac{\int\limits_{-q}^{q} x^k I(x)\mathrm{d}x}{\int\limits_{-\infty}^{\infty} I(x)\mathrm{d}x}$$





- it's based on general properties of dislocations

Momentum Method

Theoretical background:

- Size profile: Lorentz-function, asymptotic form:

$$I(q) = \frac{1}{\pi^2 d} \frac{1}{q^2}$$

- Asymptotic decaying of dislocation profile (Groma, 1998):

$$I(q) = \frac{\Lambda}{4\pi^2} \langle\rho\rangle \frac{1}{q^3}$$

- Asymptotic decaying if both effects are present:

$$I(q) = \frac{1}{\pi^2 d} \frac{1}{q^2} + \frac{\Lambda}{4\pi^2} \langle\rho\rangle \frac{1}{q^3}$$

Momentum Method

$$M_k(q) = \frac{\int_{-q}^{q} x^k I(x) \mathrm{d}x}{\int_{-\infty}^{\infty} I(x) \mathrm{d}x}$$

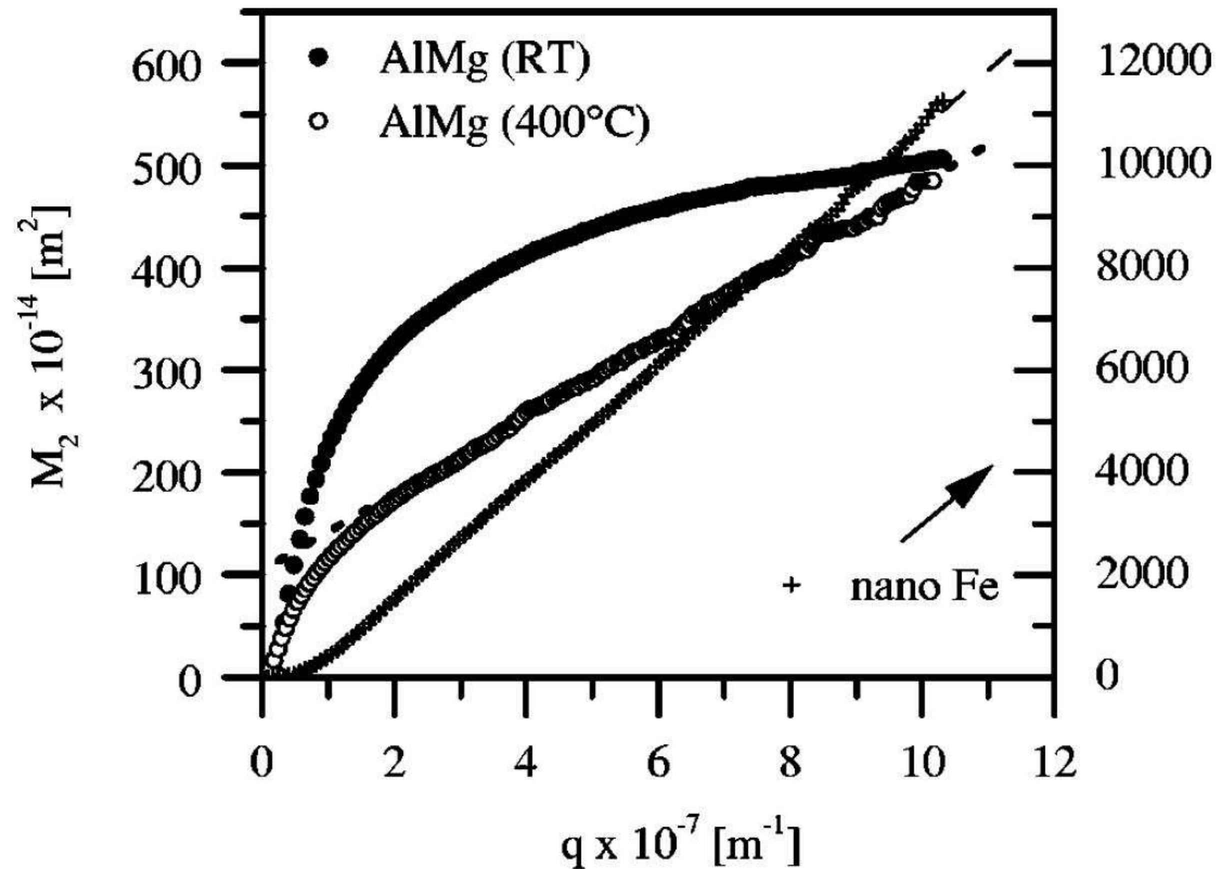
- Asymptotic form of second moment ($\Lambda = \frac{\pi}{2} g^2 b^2 C$):

$$M_2(q) = \frac{2}{\pi^2 d} q + \frac{\Lambda < \rho >}{2\pi^2} \log\left(\frac{q}{q_0}\right),$$

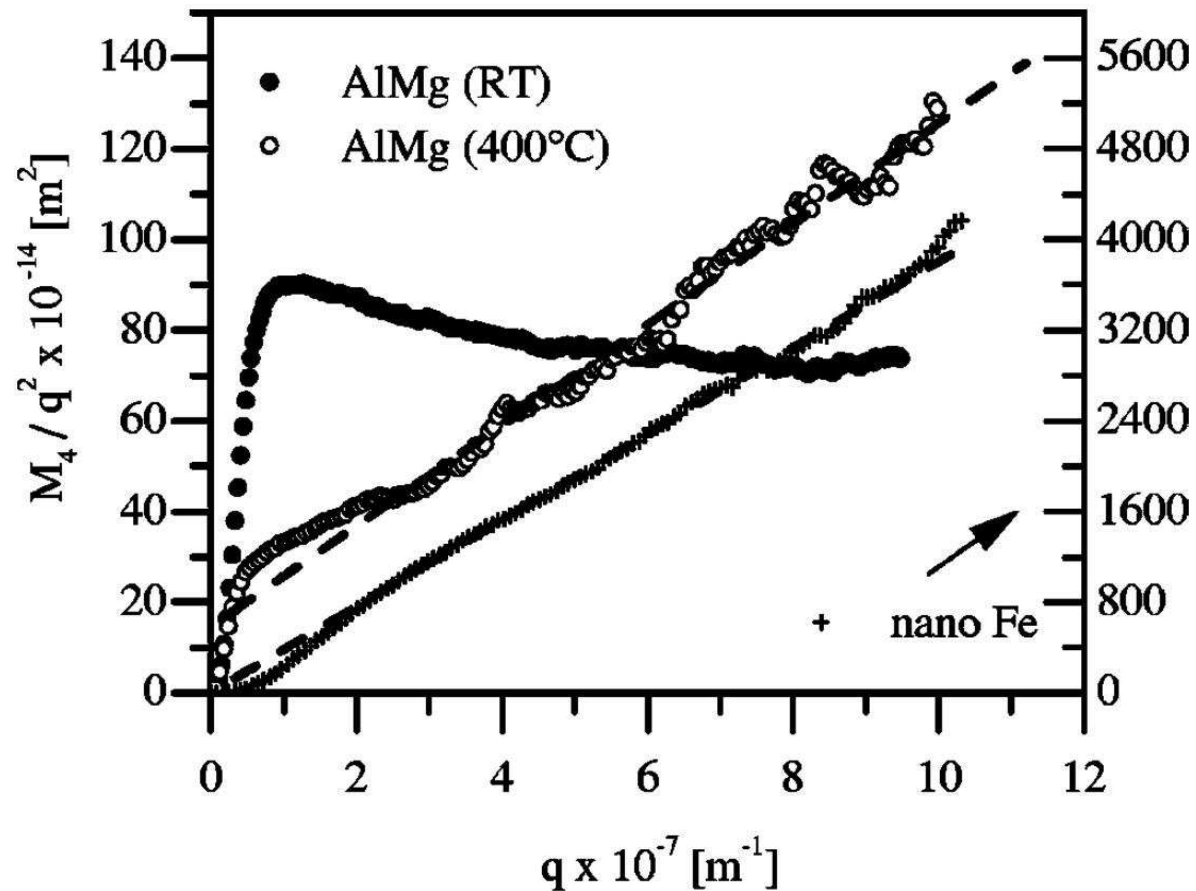
- Asymptotic form of fourth moment (divided by q^2):

$$\frac{M_4(q)}{q^2} = \frac{2}{3\pi^2 d} q + \frac{\Lambda < \rho >}{4\pi^2}$$

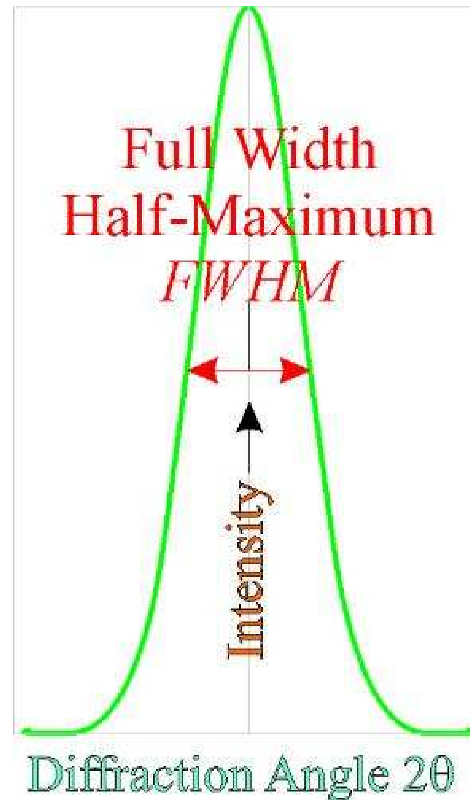
Moments (Borbély & Groma, 2001)



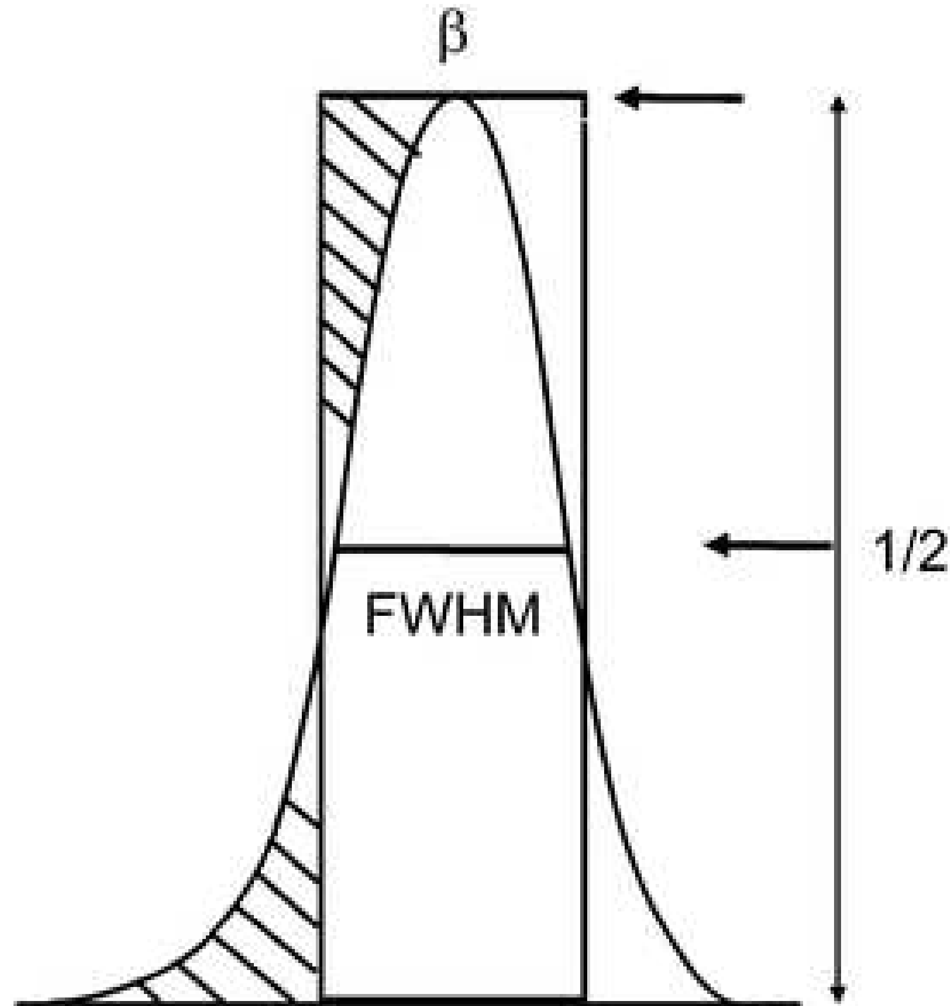
Moments (Borbély & Groma, 2001)



FWHM: definition



Integral breadth: definition



Scherrer Equation

The Scherrer Equation: $L = \dfrac{A\lambda}{\beta \cos\theta}$, was developed in 1918.

In this equation λ is the wavelength, β is the FWHM value of the $I(2\theta)$ profile (2θ and β should be in radians). Shape factor of A can be 0.62 - 2.08 and is usually taken as about 0.89. This works only if there are no dislocations and purely size broadening is present.

The Williamson-Hall procedure

The widths (FWHMs or Integral breadths), ΔK, are plotted as a function of K

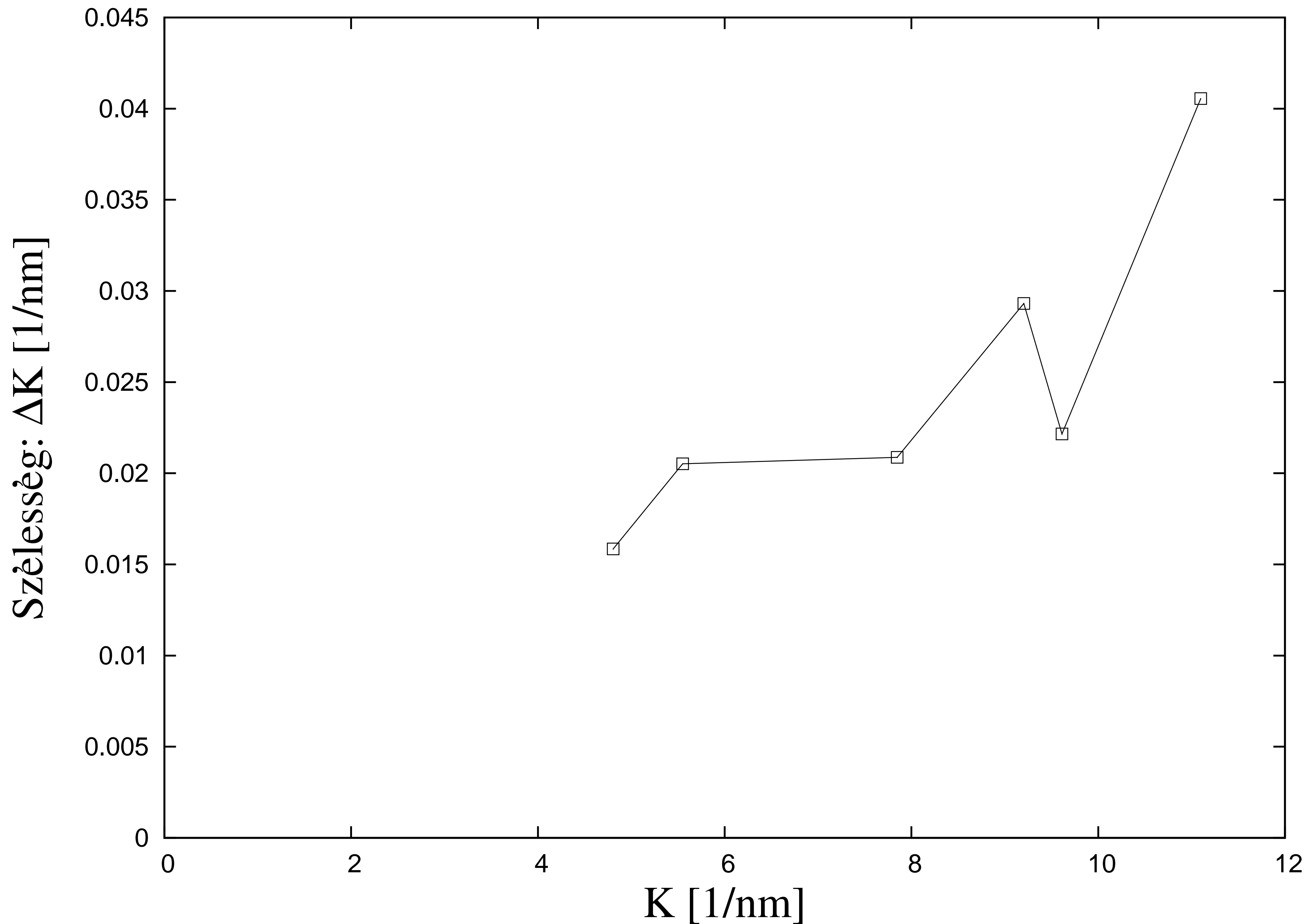
- size effect: independent of K
- strain effect: increasing with K
- from extrapolation to $K = 0$ the crystallite size can be determined (inversely proportional to $\Delta K(0)$)

The Modified Williamson-Hall procedure

For dislocated material, the broadening is anisotropic.

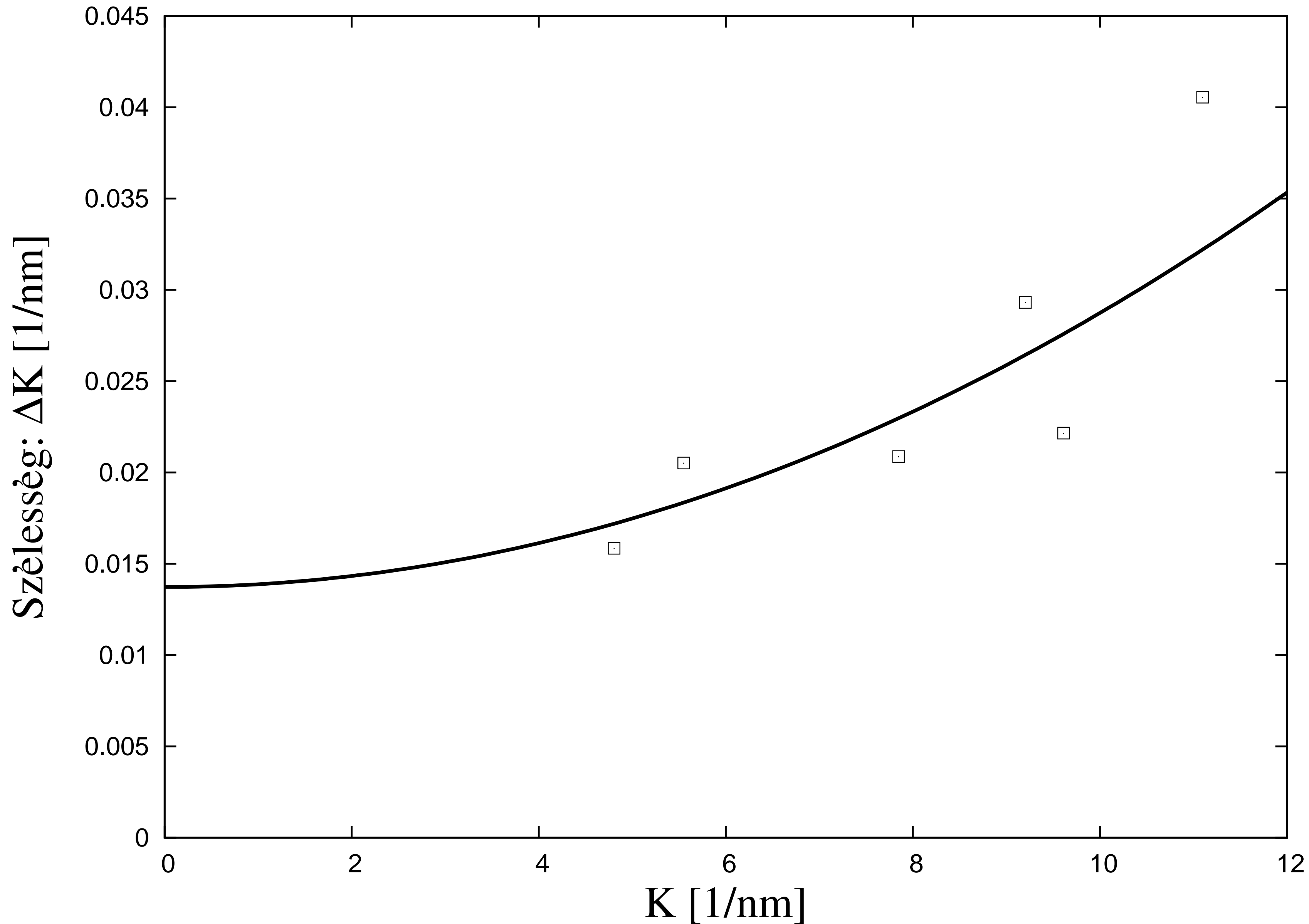
- K is scaled by the C contrast factors, $K\sqrt{C}$ or K^2C is used for the plot
- size effect: independent of K
- strain effect: increasing with K
- from extrapolation to $K = 0$ the crystallite size can be determined (inversely proportional to $\Delta K(0)$)

Williamson-Hall plot



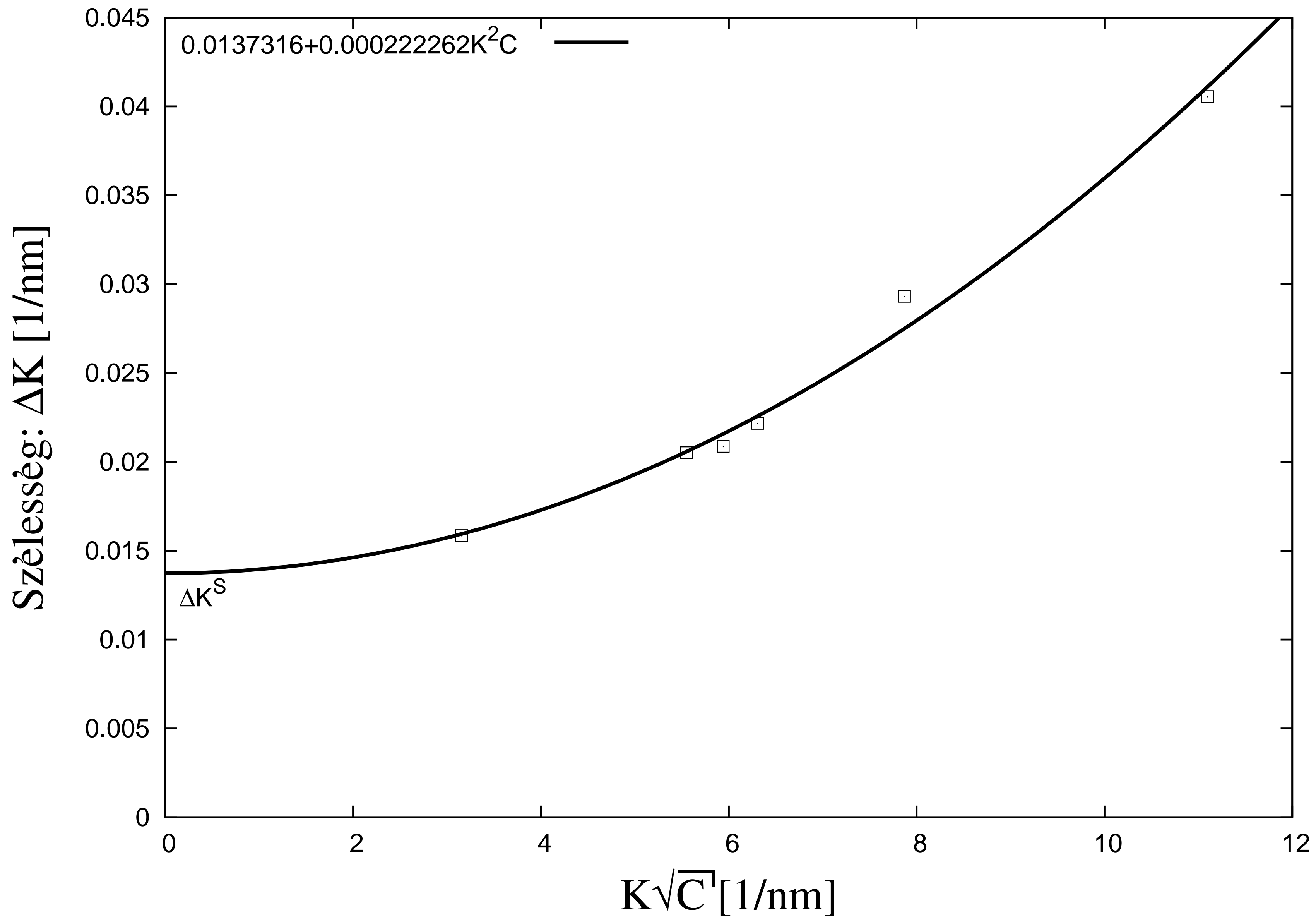
Williamson-Hall plot of the FWHM values (copper sample).

Williamson-Hall plot



Williamson-Hall plot of the FWHM values (copper sample).

Modified Williamson-Hall plot



Modified Williamson-Hall plot of the FWHM values (copper sample).

Convolutional MWP (CMWP) fitting

The CMWP method (Ribárik et al, 2004) is a full pattern fitting method for microstructure determination:

- the whole measured powder diffraction pattern is fitted by the sum of a background function (given by a polynomial function or spline) and profile functions.
- the profile functions are calculated as the convolution of the theoretical functions for physical broadening and the instrumental profiles.

CMWP-fit

This method is

- in fact: a Whole Powder Pattern fitting method
- it's a microstructural method: the unit cell is NOT refined

The aim is microstructure in terms of:

- size
- strain

Microstructural parameters

CMWP-fit provides:

- size: m, σ
- dislocations: ρ, M, q (or a_1, a_2)
- planar faults: α

The theoretical intensity pattern

$$I_{theoretical} = BG(2\Theta) + \sum_{hkl} I_{MAX}^{hkl} I^{hkl}\left(2\Theta - 2\Theta_0^{hkl}\right),$$

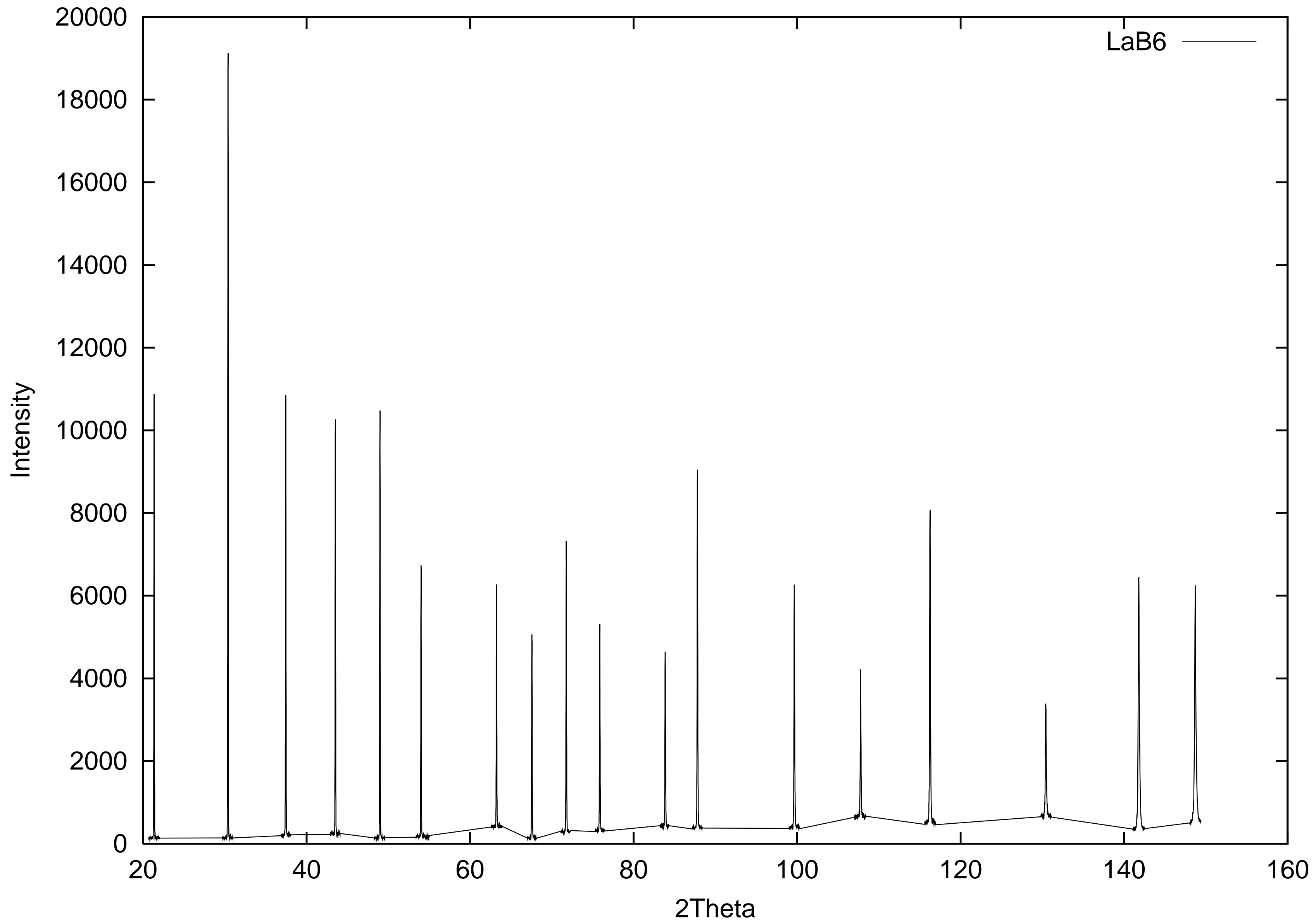
where:

$$I^{hkl} = I_{instr.}^{hkl} * \quad I_{size}^{hkl} * \quad I_{disl.}^{hkl} * \quad I_{pl.faults}^{hkl},$$

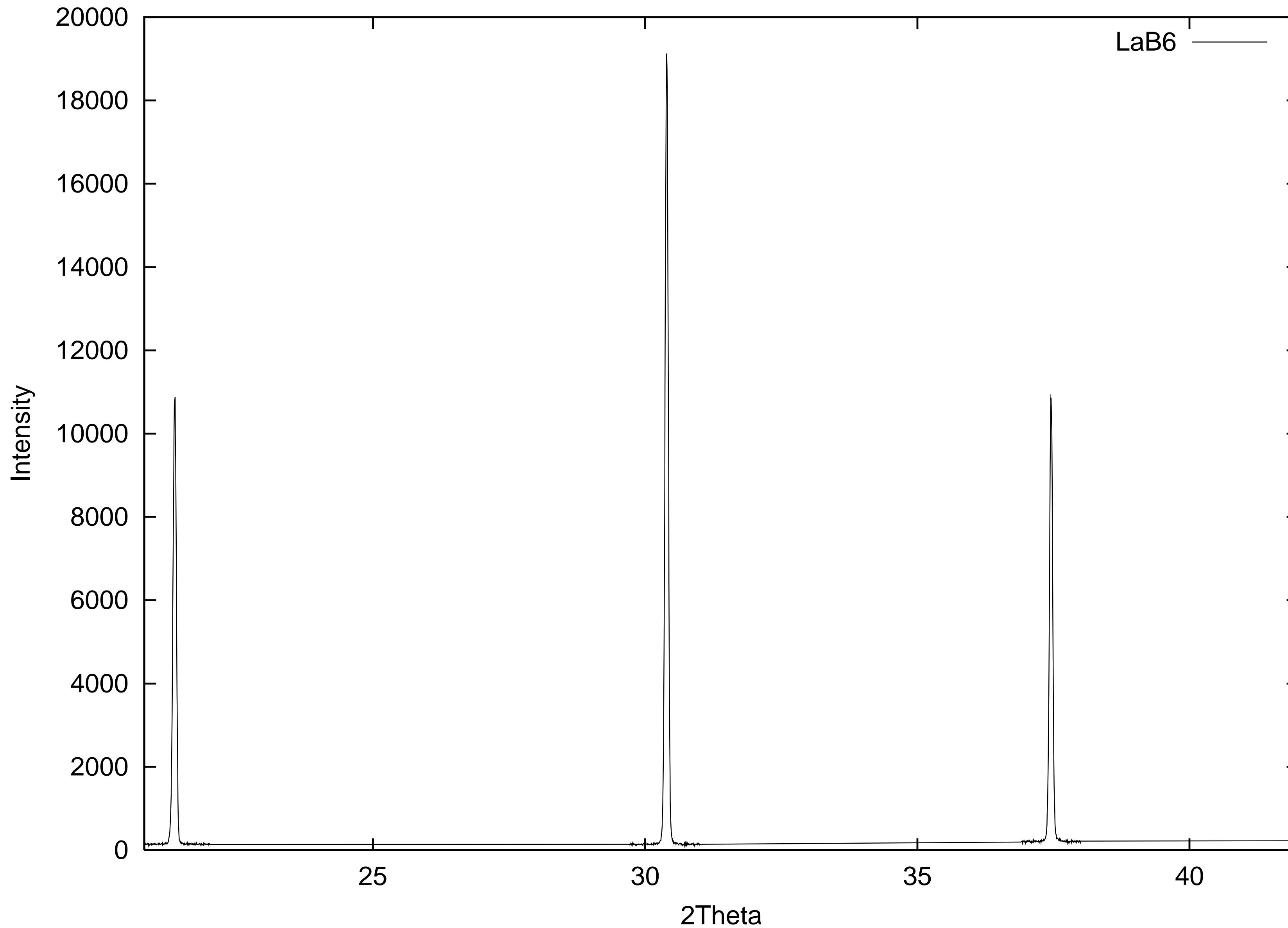
$I_{instr.}^{hkl}$: *measured* instumental profile which is directly used

The measured and theoretical patterns are compared using a nonlinear least-squares algorithm, the fitted parameters are the microstructural parameters (no individual profile parameters are used).

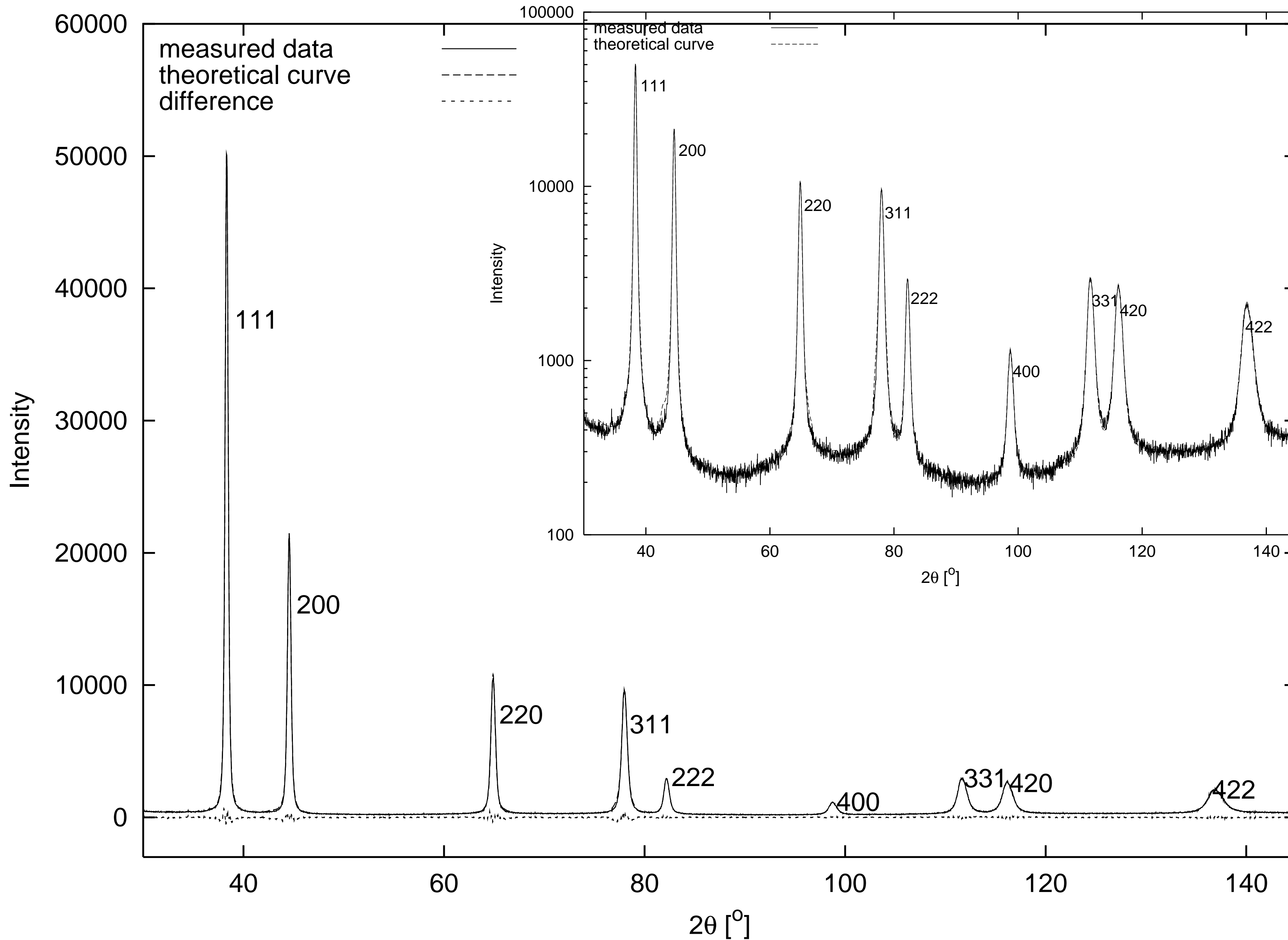
Instrumental pattern of LaB_6



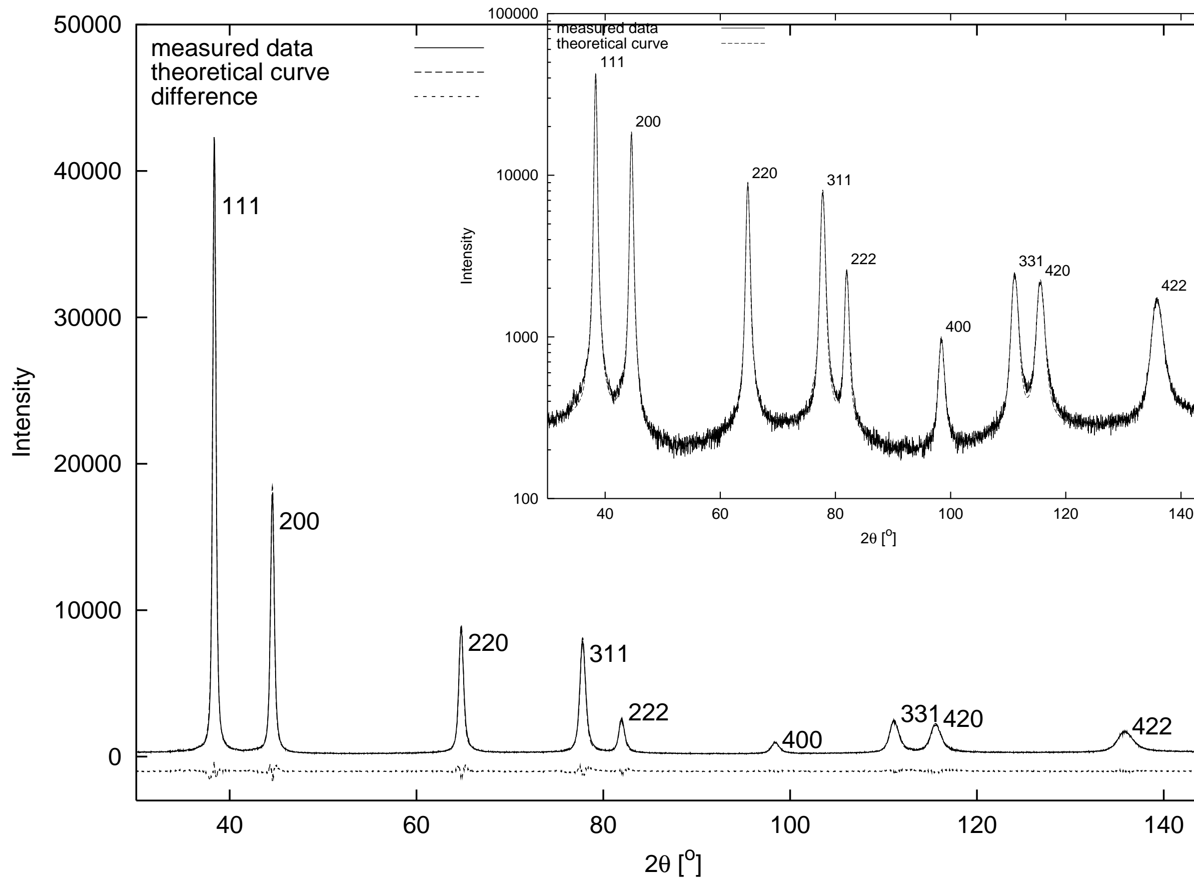
Instrumental pattern of LaB_6



Al-3Mg ball milled 3 h.



Al-6Mg ball milled 6 h.



Results of the CMWP fit:

m $= 21$nm

$\sigma = 0.36$

$\rho = 10^{16}$ m^{-2}

M $=$ R$_e\sqrt{\rho} = 1.3$

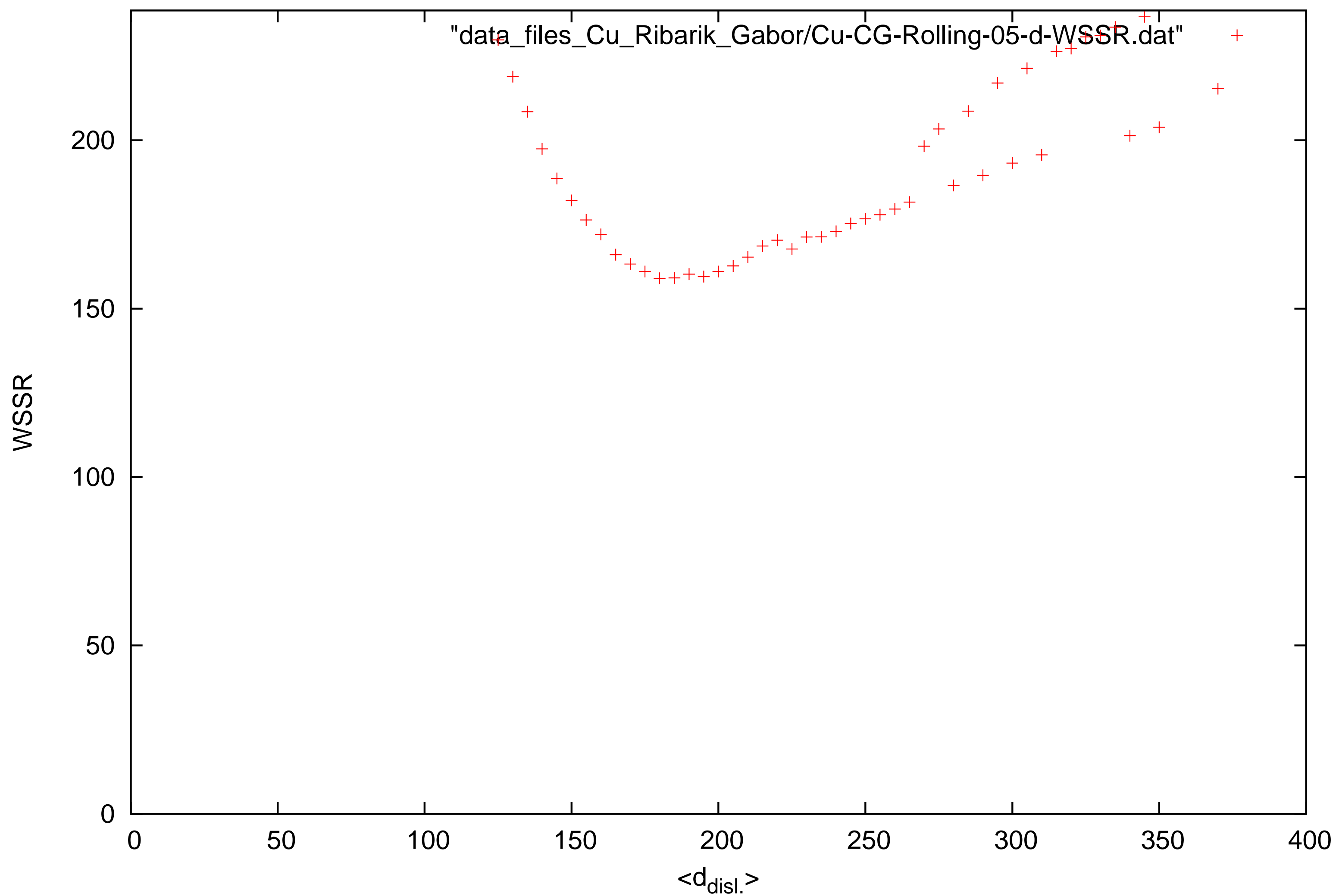
q $= 1.3$

WSSR

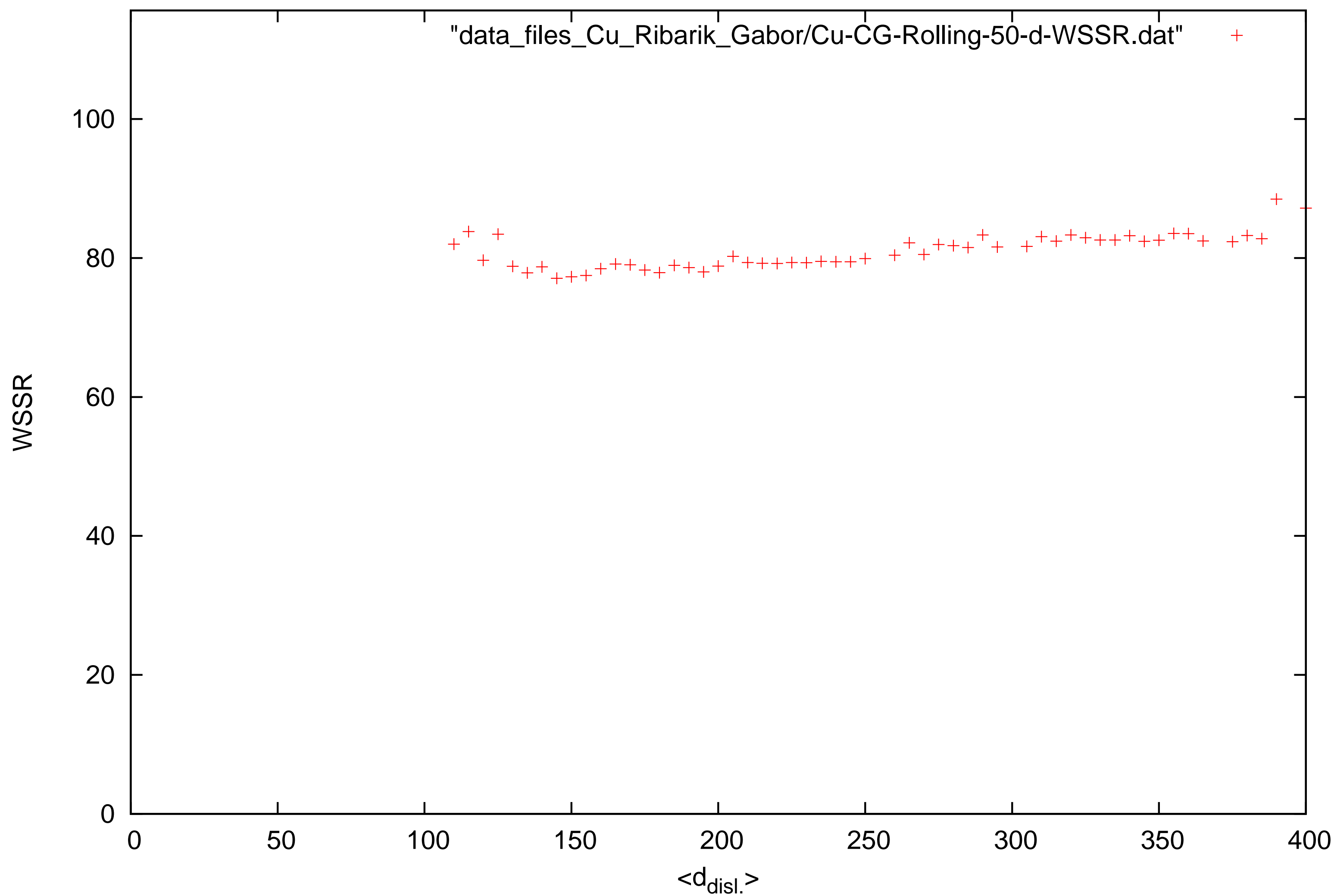
The definition of the WSSR (Weighted Sum of Squared Residuals) in the case of uniform weights:

$$WSSR = \sum_{i=1}^{i=N_{\mathrm{data}}} \left(I_{(K)}^{\mathrm{measured}} - I_{(K)}^{\mathrm{theoretical}} \right)^2$$

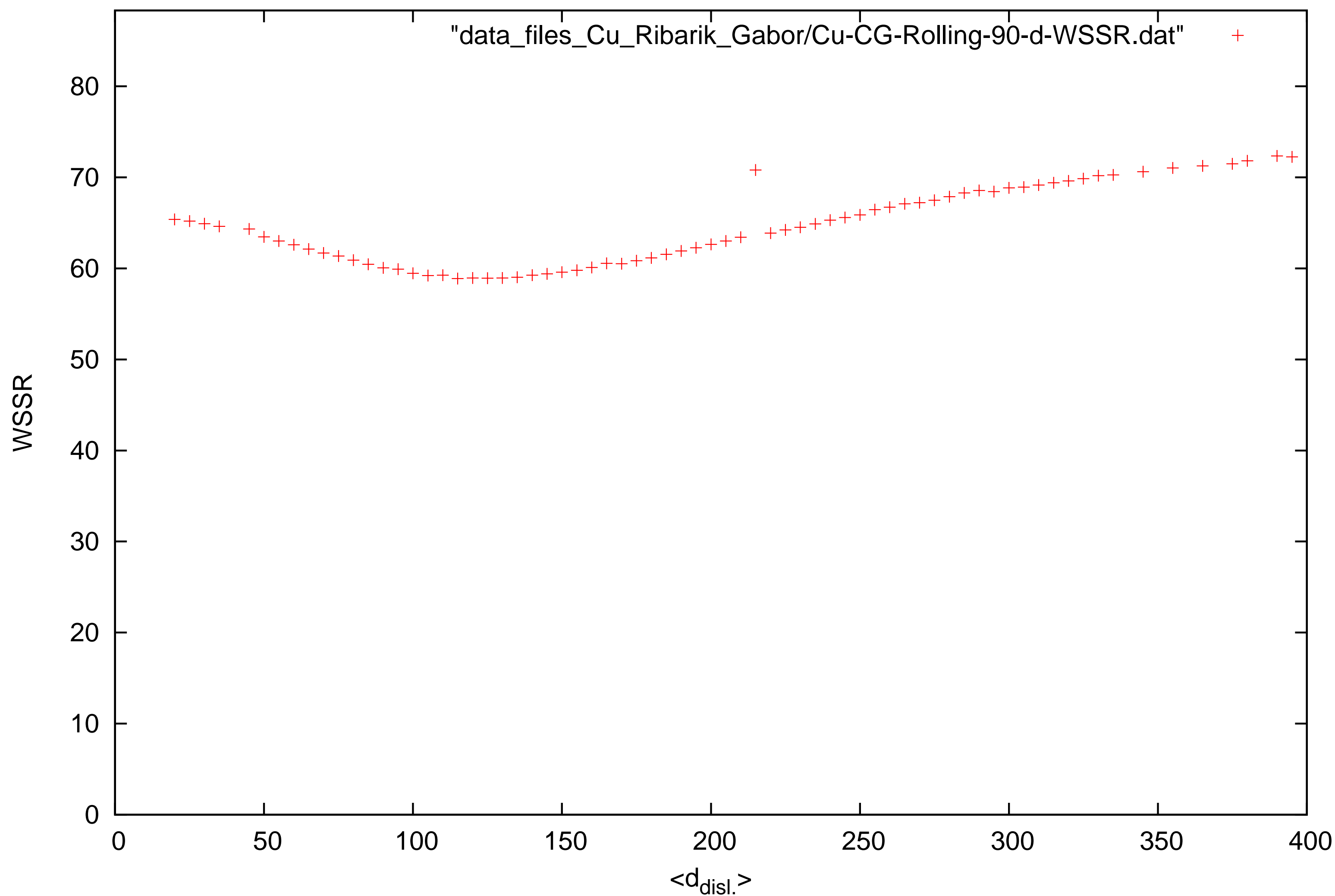
$< d_{\textbf{disl.}} >$-WSSR plots: Cu-CG-Rolled 5%



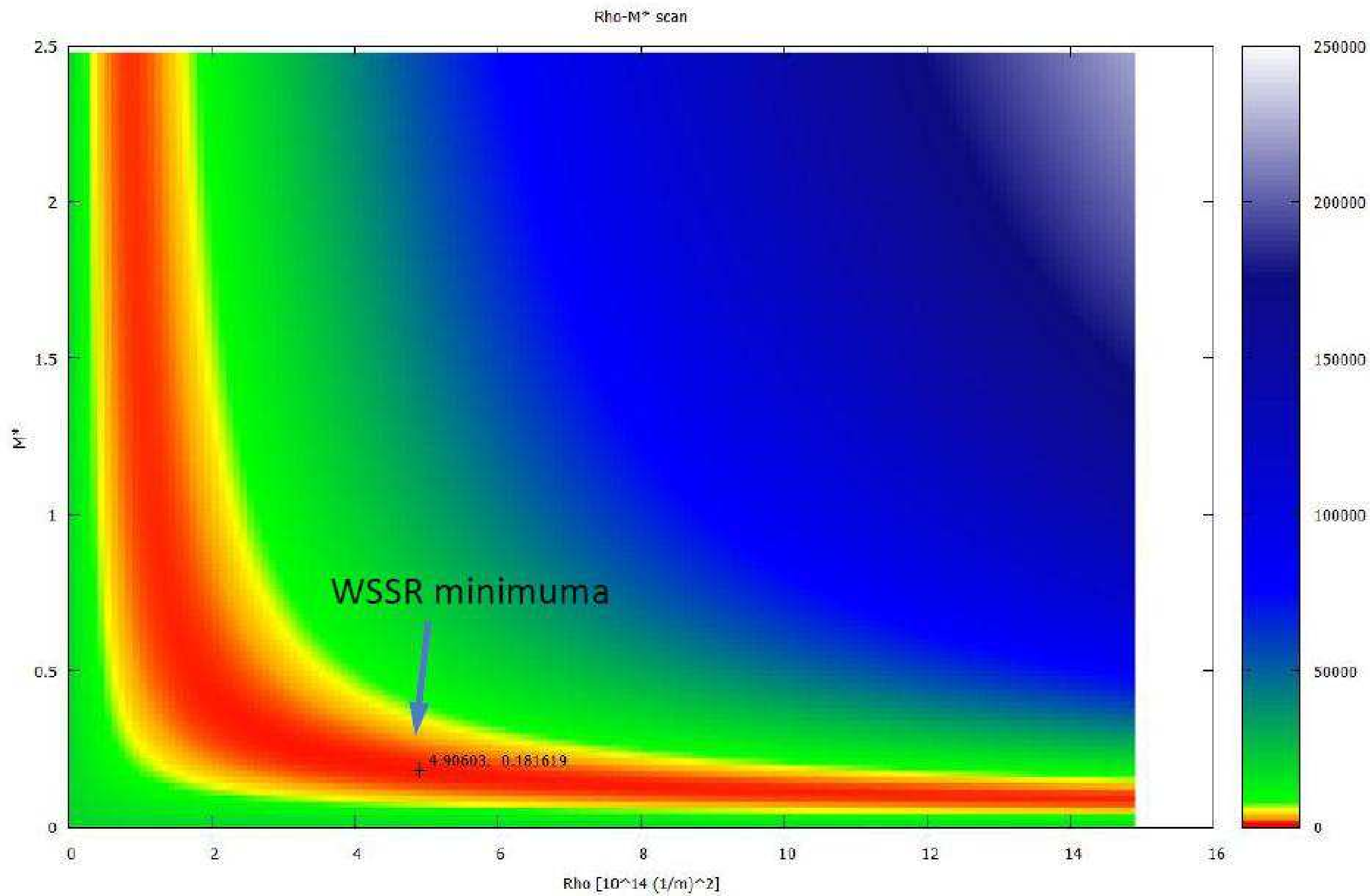
$< d_{\text{disl.}} >$-WSSR plots: Cu-CG-Rolled 50%



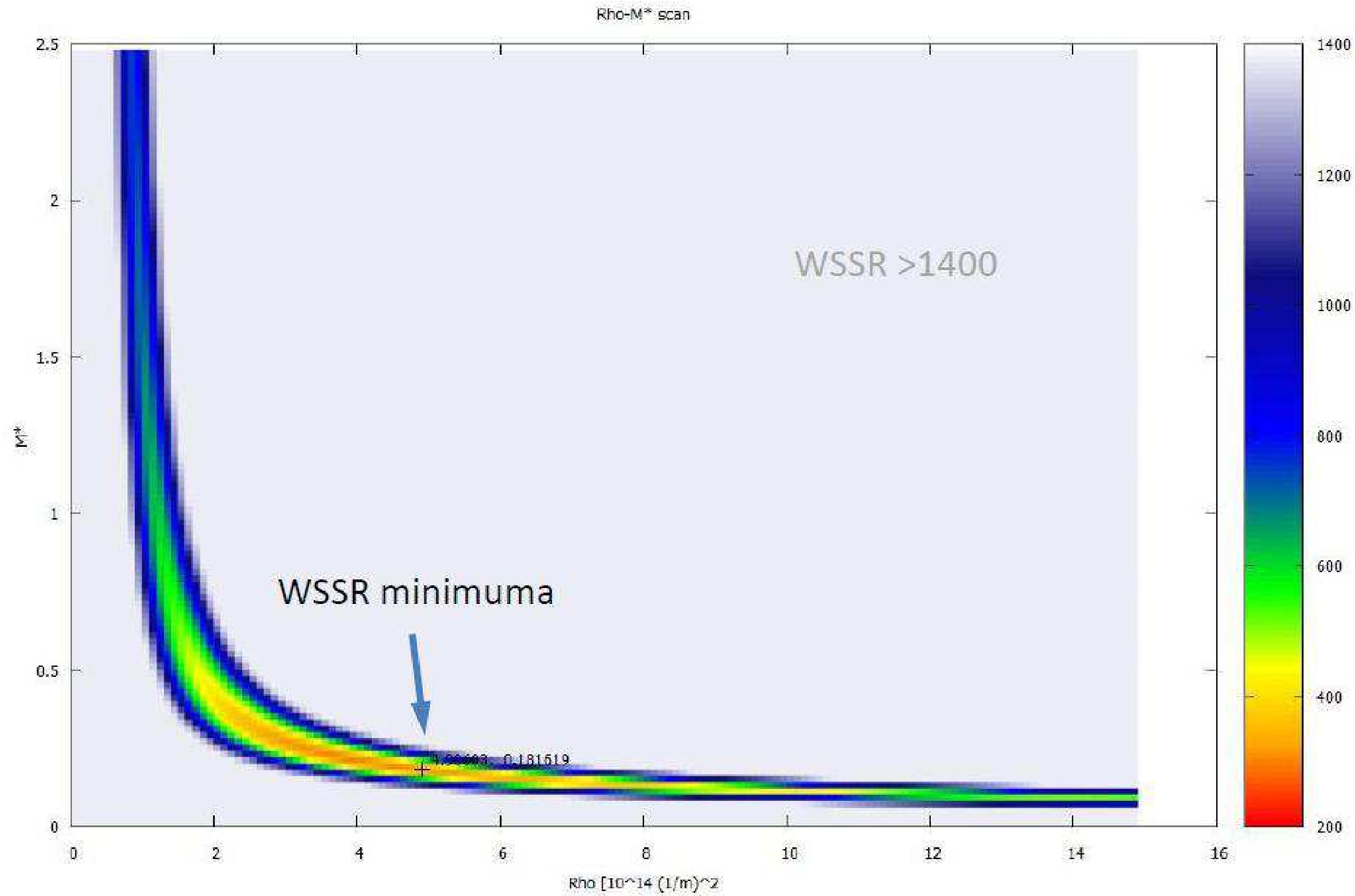
$< d_{\text{disl.}} >$-WSSR plots: Cu-CG-Rolled 90%



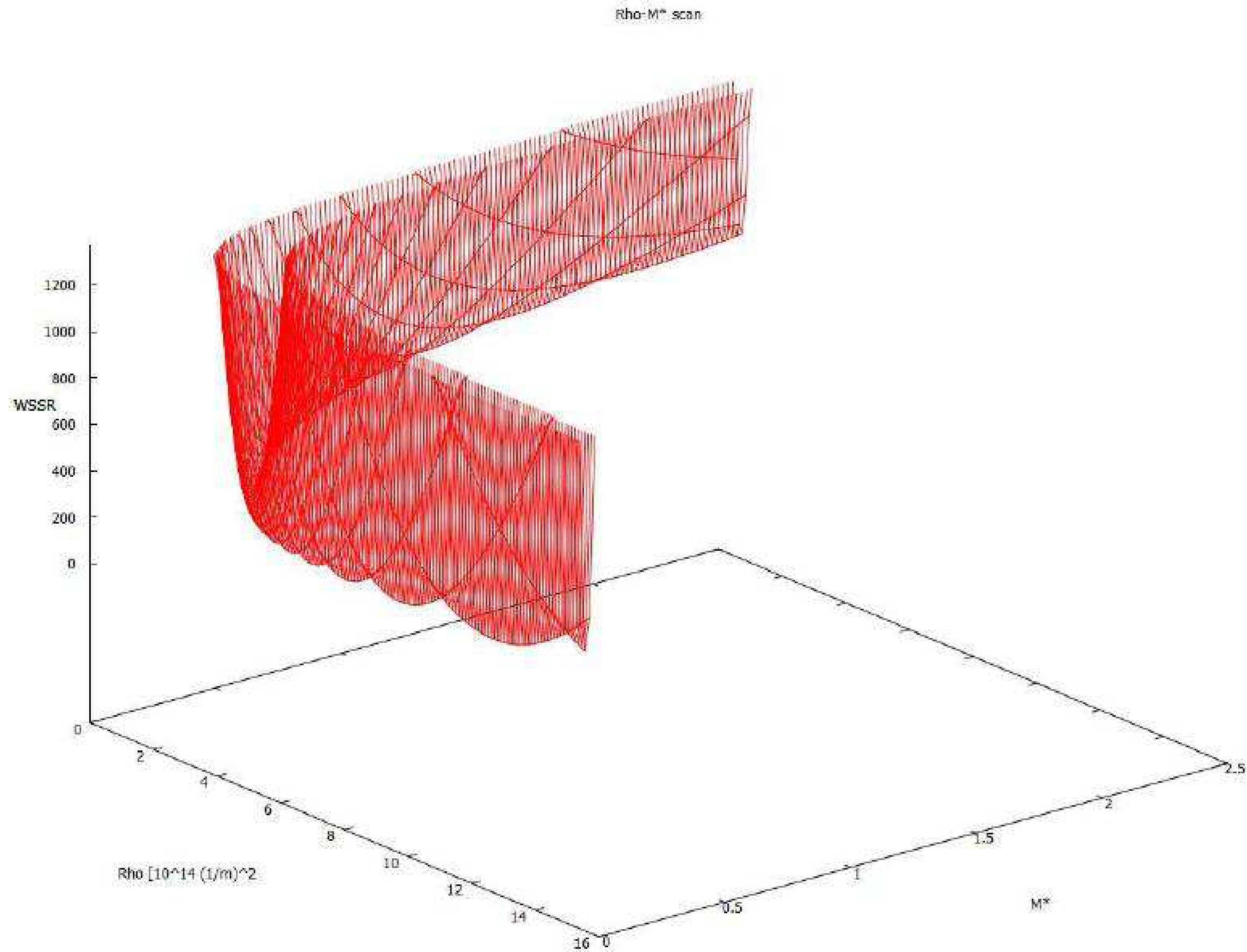
ρ-M^* scan of Cu sample



ρ-M^* scan of Cu sample



ρ-M^* scan of Cu sample



Non-linear least-squares algorithms

- Gauss-Newton, conjugate gradient algorithms (iterative methods based on Taylor-expansion)
- Marquardt-Levenberg algorithm: a scalable step is used

These methods can find only the local minimum. Some of the global optimization algorithms:

- Simulated annealing method
- Monte-Carlo methods

Monte-Carlo methods

A random generator number is used for probing the parameters. Compared to the brute force method (systematic scanning) it requires much less calculations to obtain a (less detailed) map the parameter space. It can be used iteratively, e.g. the new parameters are searched in the proximity of the previous ones.

The Monte-Carlo method of CMWP

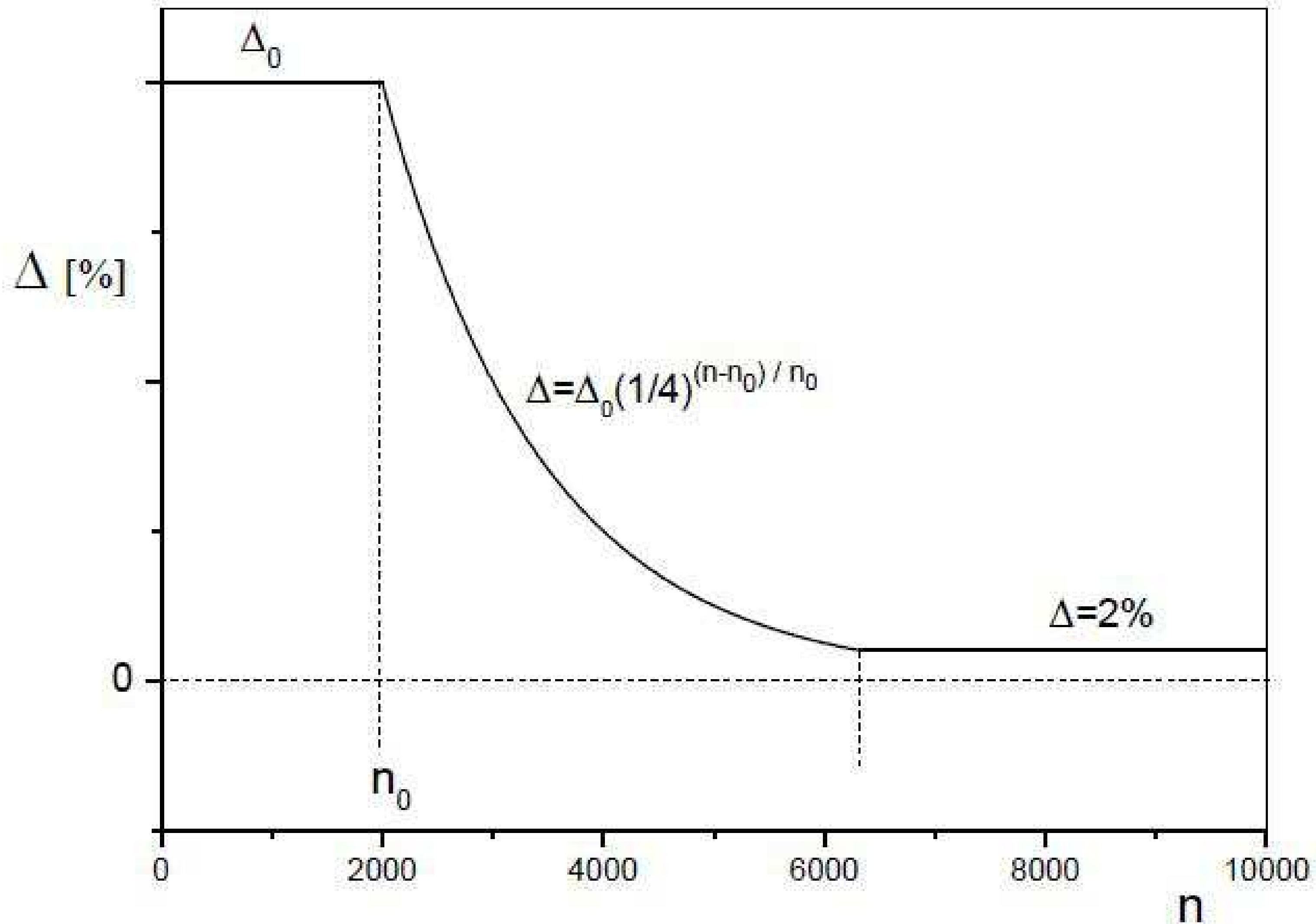
The fitting parameters are the following physical parameters: m, σ, q (or a_1, a_2), ρ and M^*. Fitting ρ and M^* provides better results (less scattering) than fitting $< d_{\text{disl.}} >$ and R_e^*. Each parameter has a minimum and maximum value which cannot be bypassed. The new parameter values are searched in the proximity of the previous ones:

$$a_n^i \in \left[a_m^i + \Delta^i \,;\; a_m^i - \Delta^i\right]$$

The Δ parameter's definition:

$$\Delta_n^i = \begin{cases} \Delta_0^i & \text{, if } n \leq n_0 \\ \Delta_0^i \cdot (1/4)^{\frac{n-n_0}{n_0}} & \text{, if } n > n_0 \\ 2\% & \text{, if } \Delta_n^i < 2\%. \end{cases}$$

The evolution of the Δ parameter



The Monte-Carlo method of CMWP

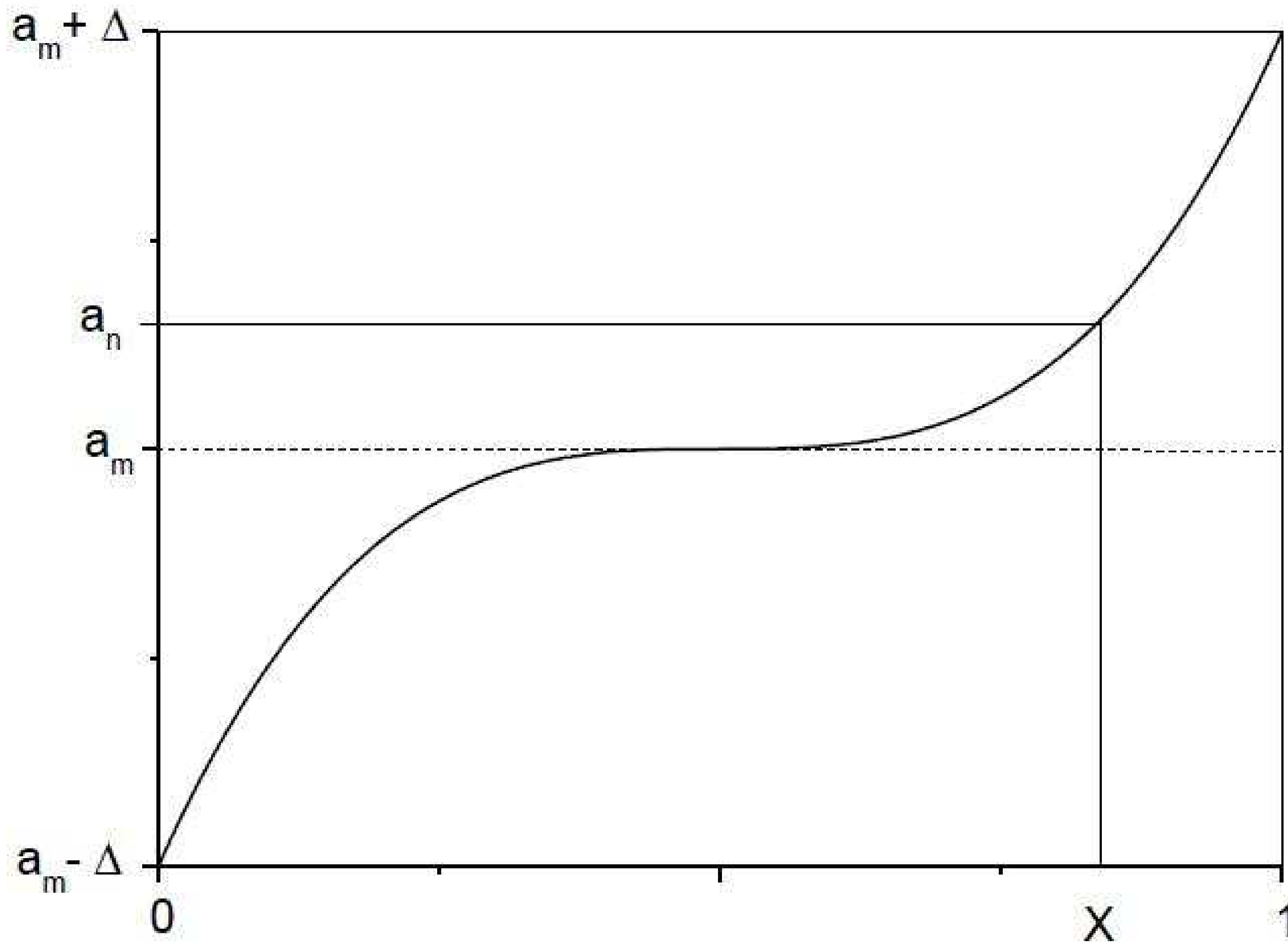
The new parameters are deviated to the previous ones using a cubic probability function:

$$a_n^i = \Delta_n^i \cdot \left(2x_n^i - 1\right)^3 + a_m^i$$

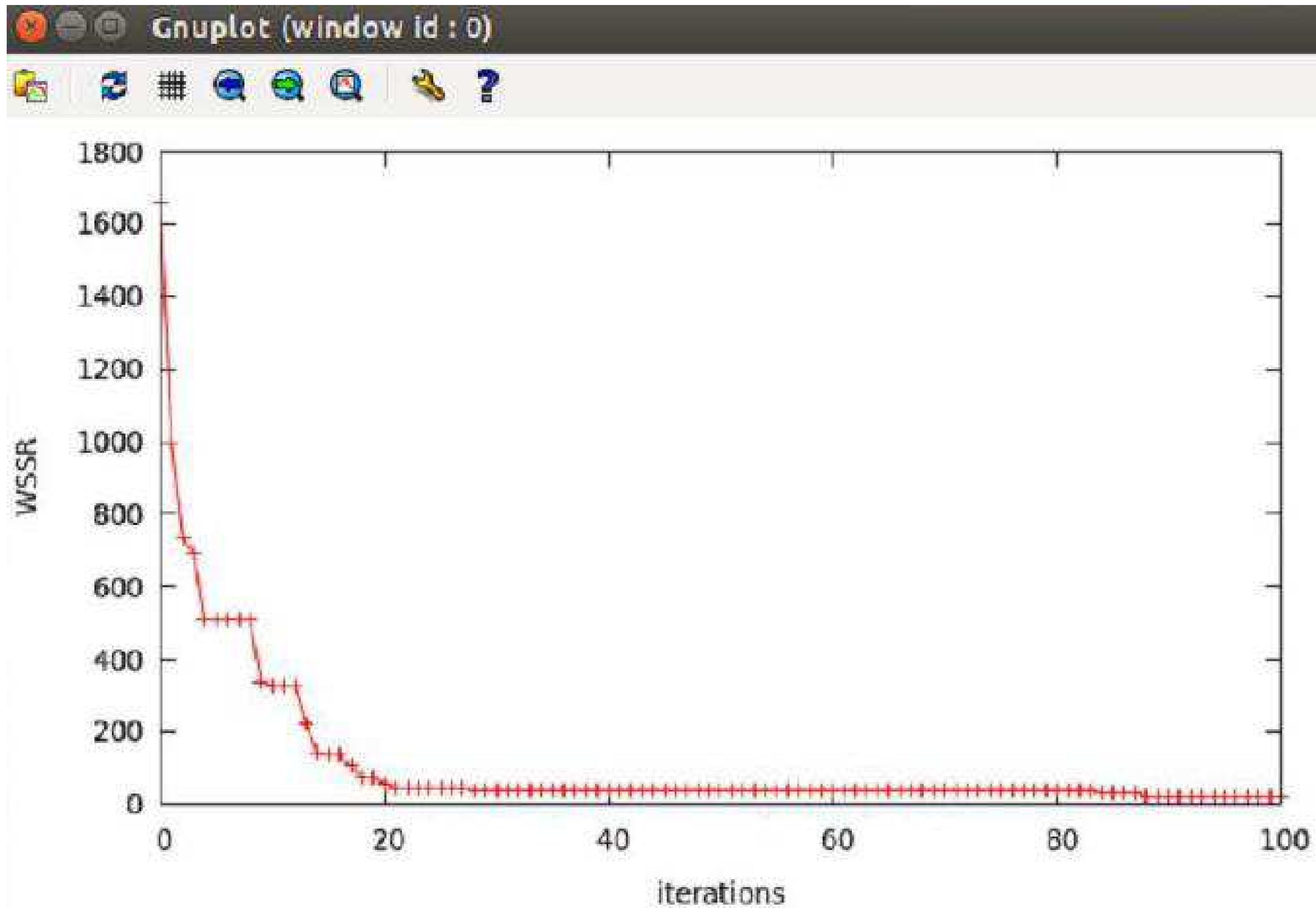
where $x_n^i \in [0, 1]$ is a random number. The condition for accepting the new parameters:

$$a_{m+1}^i = \begin{cases} a_n^i \text{, if } WSSR^n < WSSR^m \\ a_m^i \text{, if } WSSR^n \geq WSSR^m \end{cases}$$

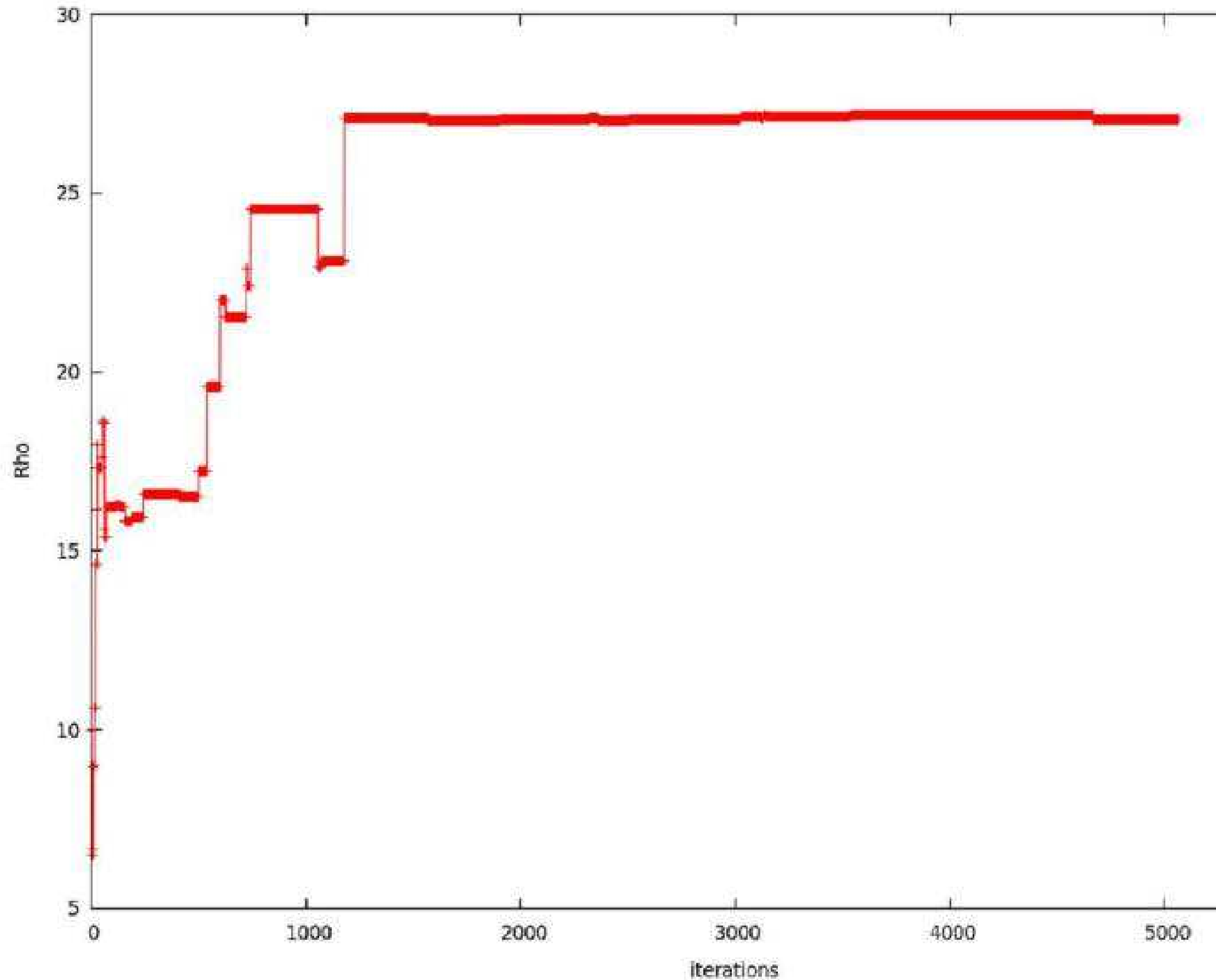
The cubic probability function



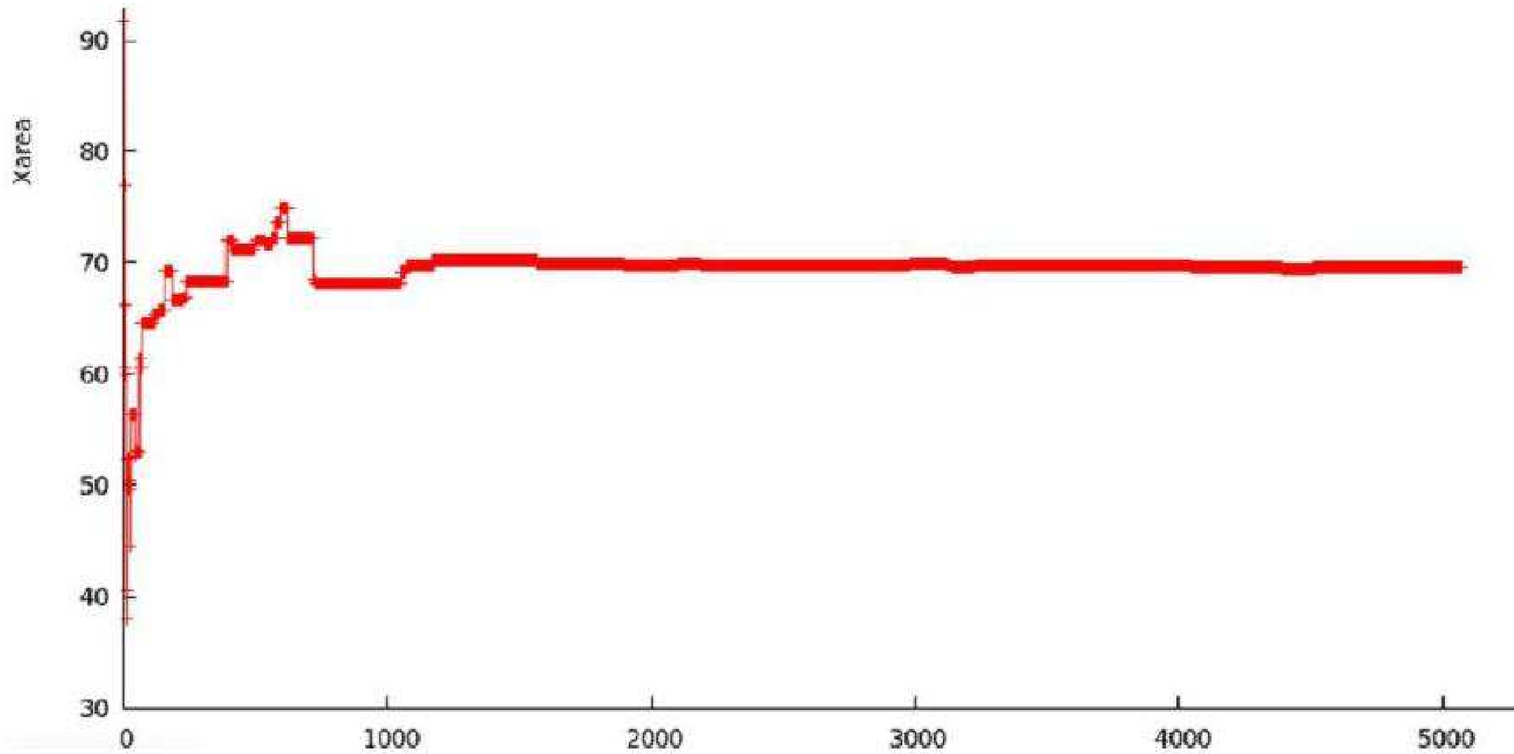
MC method: WSSR evolution



MC method: ρ evolution



MC method: $< x >_a$ evolution



Stability of the MC scan

```
1.sol:Final (best) WSSR value from MC scan: 11347
2.sol:Final (best) WSSR value from MC scan: 11340
3.sol:Final (best) WSSR value from MC scan: 11404
4.sol:Final (best) WSSR value from MC scan: 11374
5.sol:Final (best) WSSR value from MC scan: 11355
6.sol:Final (best) WSSR value from MC scan: 11340
7.sol:Final (best) WSSR value from MC scan: 11347
8.sol:Final (best) WSSR value from MC scan: 11354
9.sol:Final (best) WSSR value from MC scan: 11335
10.sol:Final (best) WSSR value from MC scan: 11337
```

Stability of the final results

```
1.sol:final sum of squares of residuals : 11333.9
2.sol:final sum of squares of residuals : 11333.9
3.sol:final sum of squares of residuals : 11333.9
4.sol:final sum of squares of residuals : 11333.9
5.sol:final sum of squares of residuals : 11332.9
6.sol:final sum of squares of residuals : 11332.9
7.sol:final sum of squares of residuals : 11333.9
8.sol:final sum of squares of residuals : 11333.9
9.sol:final sum of squares of residuals : 11333.9
10.sol:final sum of squares of residuals : 11333.9
```

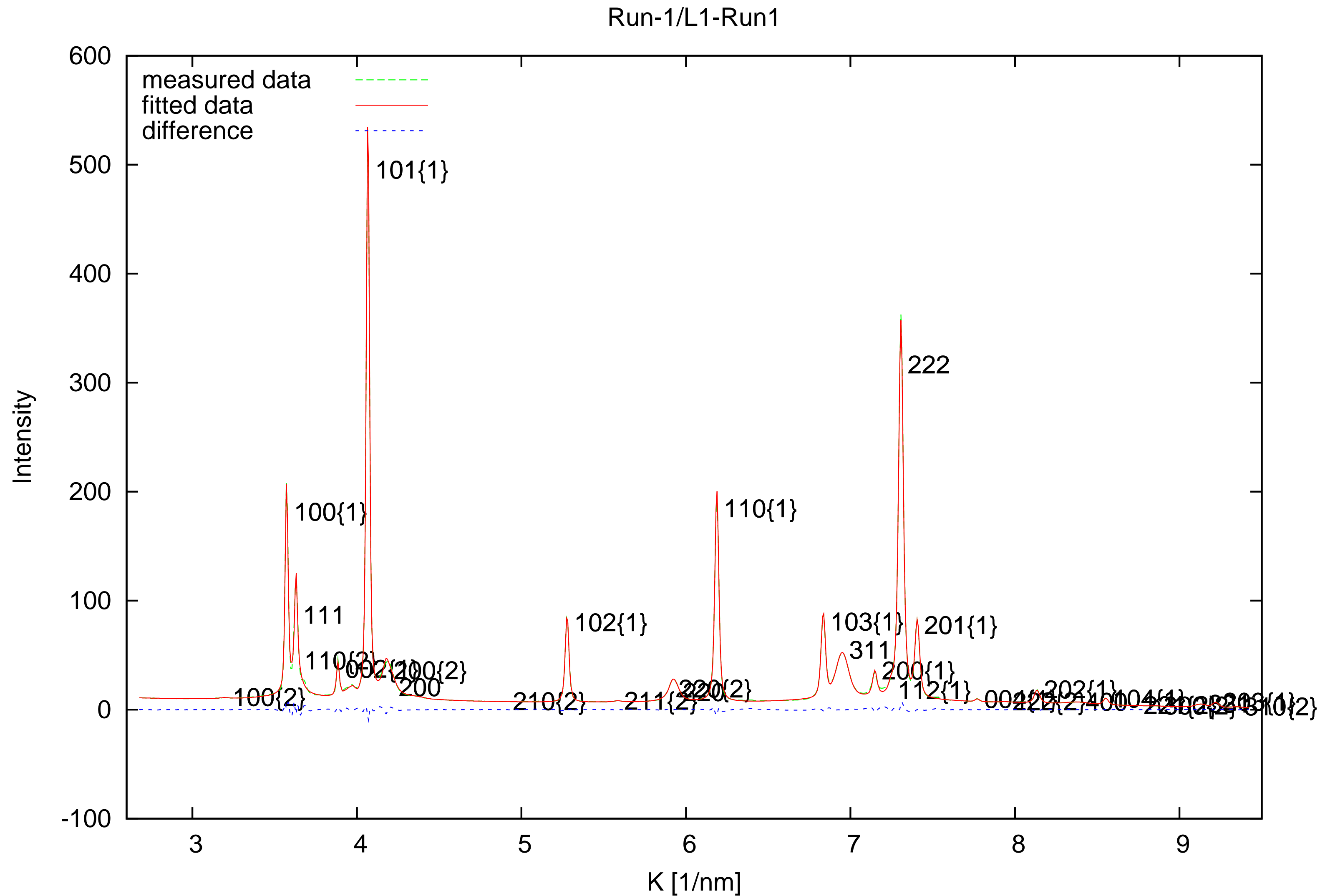
Stability of ρ from MC scan

```
1.sol:d              = 67.357 (60.83-87.647)
2.sol:d              = 66.718 (54.784-72.845)
3.sol:d              = 58.621 (46.825-60.909)
4.sol:d              = 61.071 (53.869-64.286)
5.sol:d              = 71.738 (66.664-80.551)
6.sol:d              = 72.085 (65.768-87.398)
7.sol:d              = 63.617 (48.022-67.695)
8.sol:d              = 65.589 (59.505-72.337)
9.sol:d              = 66.94 (56.841-82.475)
10.sol:d             = 66.312 (60.552-85.871)
```

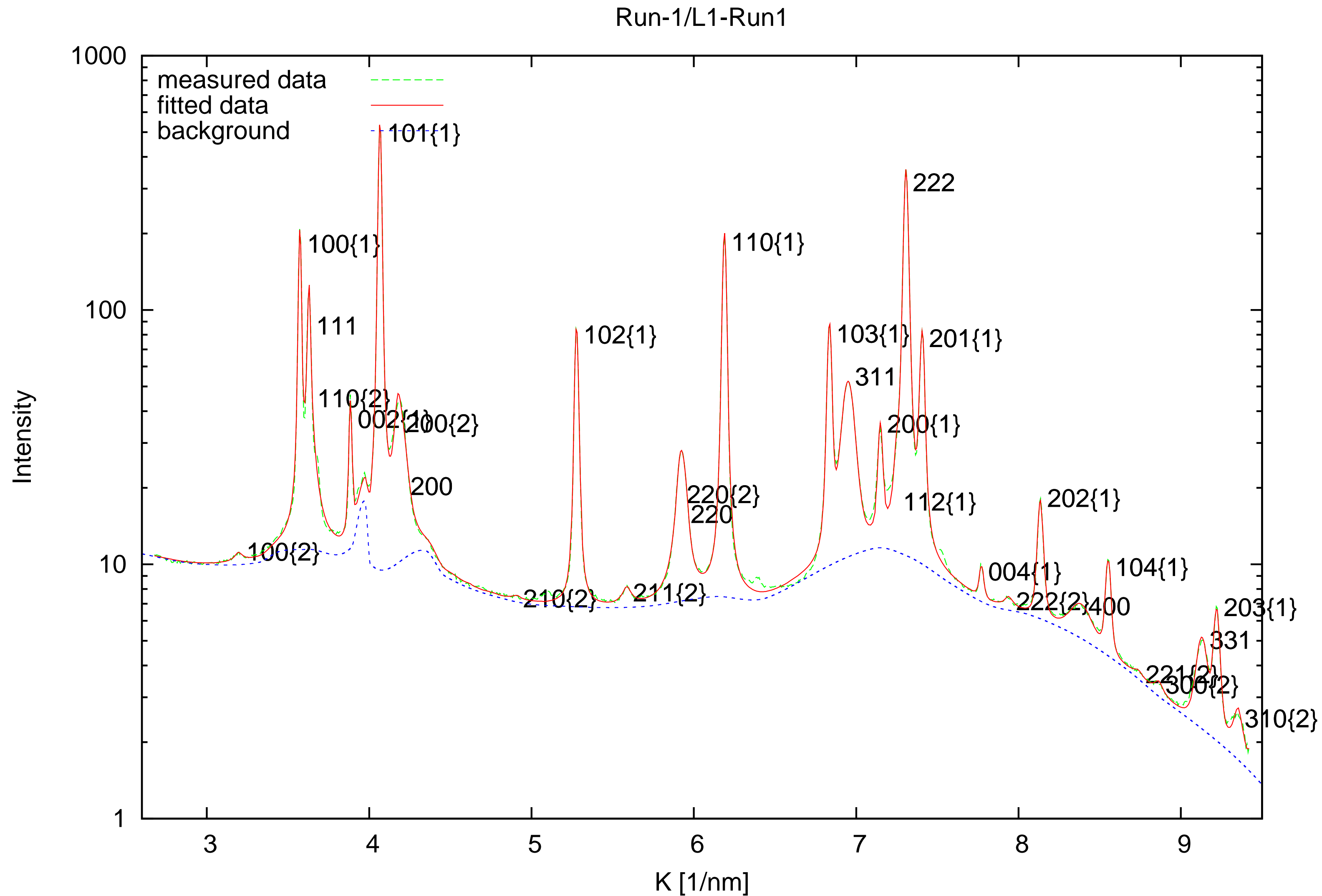
Stability of the final ρ value

```
1.sol:rho=d/1e4=0.0067762(1/nm)^2
2.sol:rho=d/1e4=0.00677642(1/nm)^2
3.sol:rho=d/1e4=0.00677669(1/nm)^2
4.sol:rho=d/1e4=0.00677671(1/nm)^2
5.sol:rho=d/1e4=0.00685561(1/nm)^2
6.sol:rho=d/1e4=0.0068558(1/nm)^2
7.sol:rho=d/1e4=0.0067759(1/nm)^2
8.sol:rho=d/1e4=0.00677664(1/nm)^2
9.sol:rho=d/1e4=0.00677638(1/nm)^2
10.sol:rho=d/1e4=0.00677656(1/nm)^2
```

MC fitting of ZrH samples



MC fitting of ZrH samples



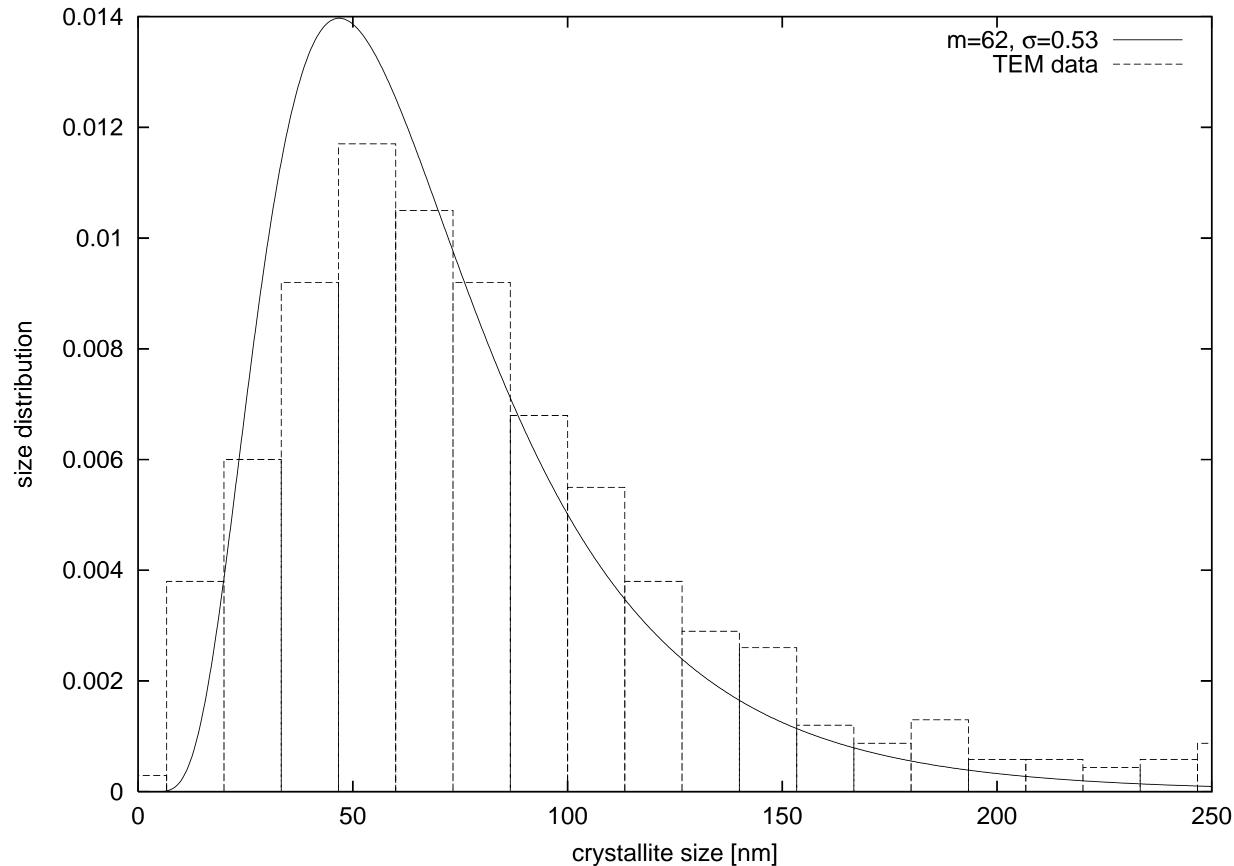
The combined fitting method

We also run Marquardt-Levenberg (ML) fitting with different parameter lists after the Monte-Carlo (MC) method finished. The steps of the combined evaluation procedure:

- MC fitting of the physical parameters
- ML fitting of the background spline parameters (optional)
- ML fitting the peak positon parameters (optional)
- ML fitting the peak intensity parameters (optional)
- ML fitting of the physical parameters
- ML fitting of all (physical, peak position, peak intensity) parameters (optional)

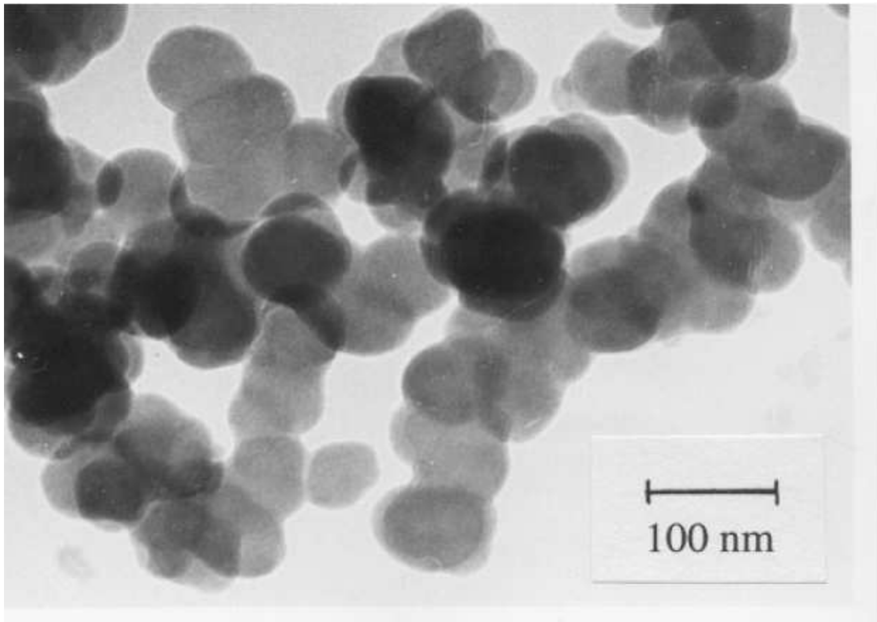
The steps of the combined evaluation procedure can be repated several times (by setting the `"MC cycle num."` parameter).

Comparison with TEM

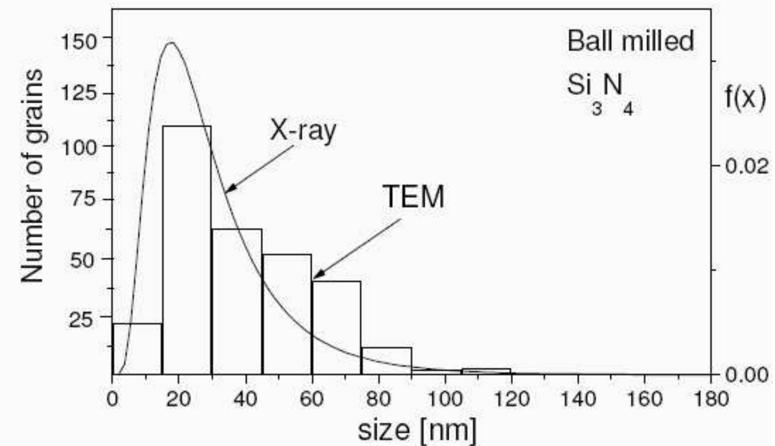


The size distribution density function corresponding to the parameters of the MWP fit and the size distribution obtained by TEM for an ECA pressed copper sample.

Comparison with TEM



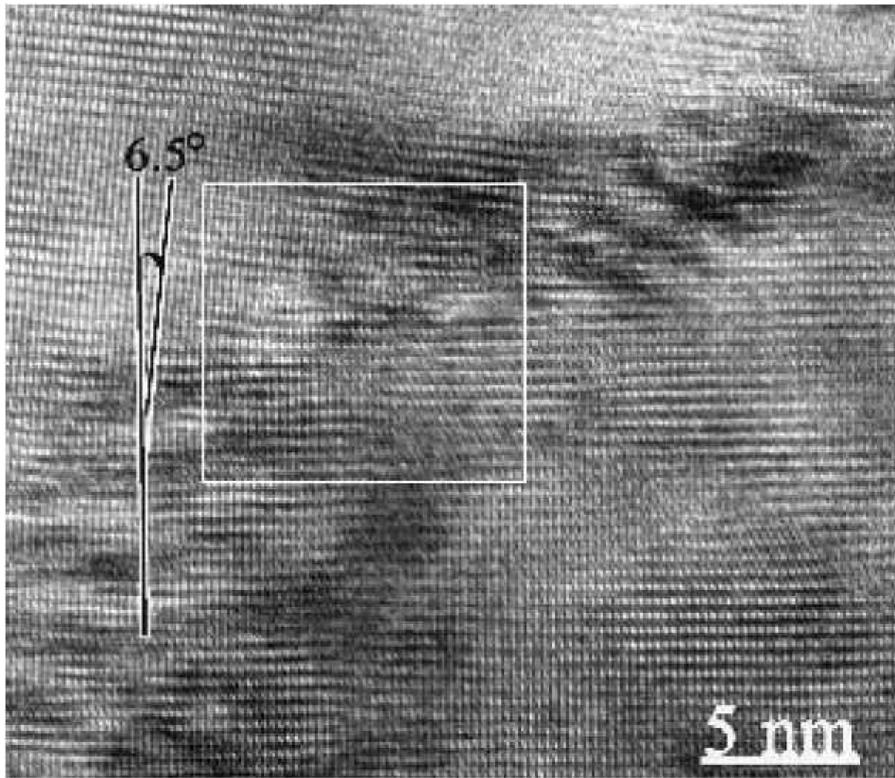
a)

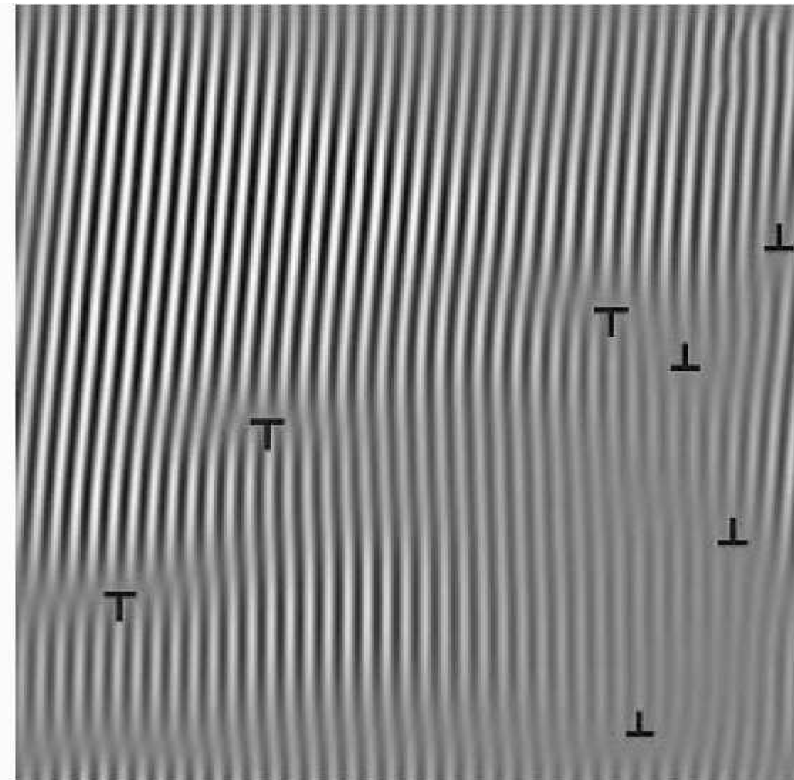


b)

The TEM micrograph (a) and the size distribution functions (b) measured by TEM and X-ray line profile analysis for nanoncrystalline Si_3N_4 particles.

Comparison with TEM





(a) High resolution TEM image of nanocrystalline titanium sample (b) Fourier-filtered image from the white frame in (a), showing the dislocation arrangement in the grain boundary.