X-ray line profile analysis based on microstructural properties

Gábor Ribárik

gabor.ribarik@univ-lorraine.fr

Institut Jean Lamour, UMR 7198, Département SI2M,

équipe 304 - Physique et plasticité, Nancy, France

Introduction:

- information in X-ray measurements
- extracting microstructure using X-ray line profile analysis
- modeling size and strain broadening
- the MWH and MWA methods
- the MWP method
- the CMWP method

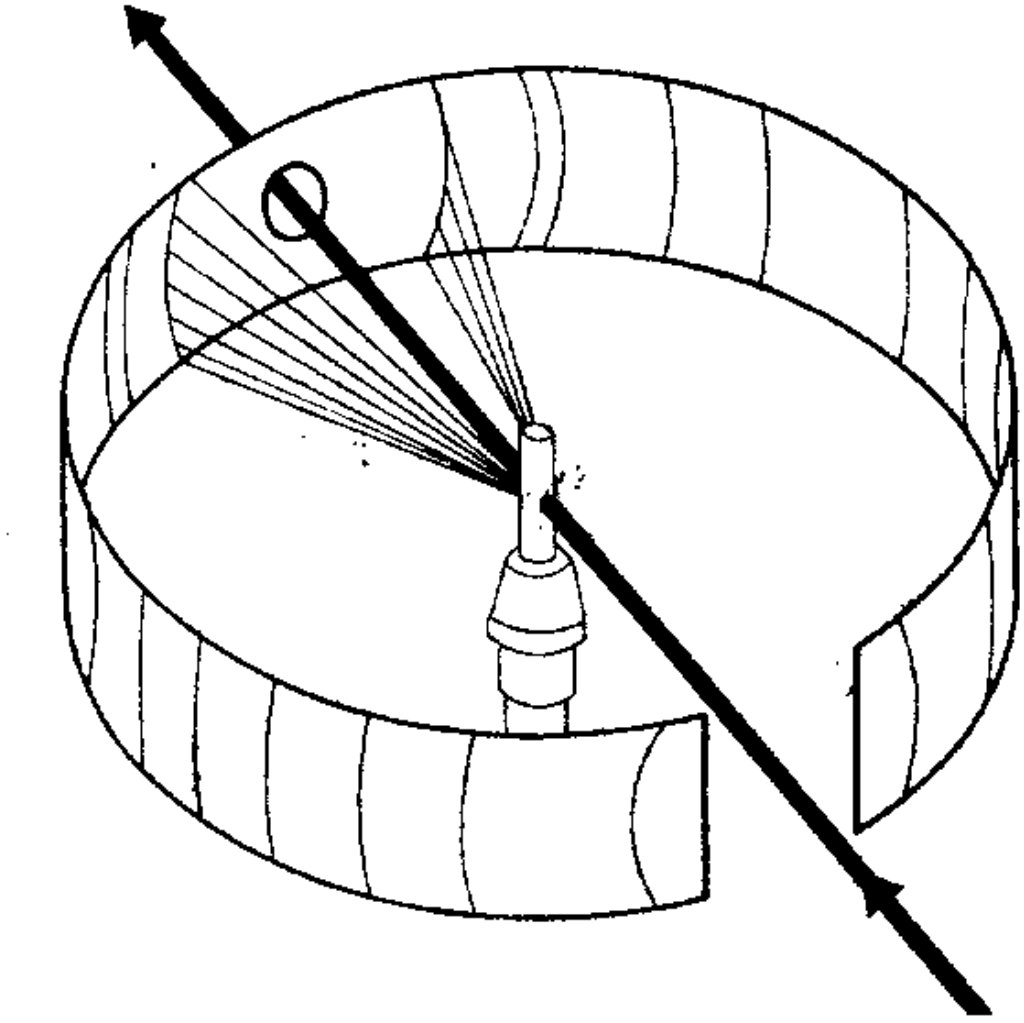
Experimental techniques

The Bragg equation $\lambda = 2d_{hkl} \sin \theta_{hkl}$ should be satisfied.

- Laue's method: the single crystal is fixed and it is irradiated by X-rays with continous wavelength distribution
- rotated crystal method: a fix wavelength is used and the single crystal is rotated
- Debye-Scherrer's method: a fix wavelength is used and a fine powder or policrystalline material is used. For some of the crystallites the Bragg equations are satisfied and the diffracted intensity is recorded either on
  - a 2 dimensional detector (can be spherical)
  - using a θ-2θ diffractometer (the sample rotated by an angular speed of ω and the detector is rotated by an angular speed of 2ω).

Experimental techniques

The Debye-Scherrer geometry



Materials

The following type of materials can be studied by X-ray diffraction:

- amorphous materials, SAXS
- crystalline materials, WAXS
  - single crystals (e.g. Superalloys)
  - policrystalline materials (e.g. bulk metals, like copper or alloys)
  - fine powder materials (e.g. carbon black powder)

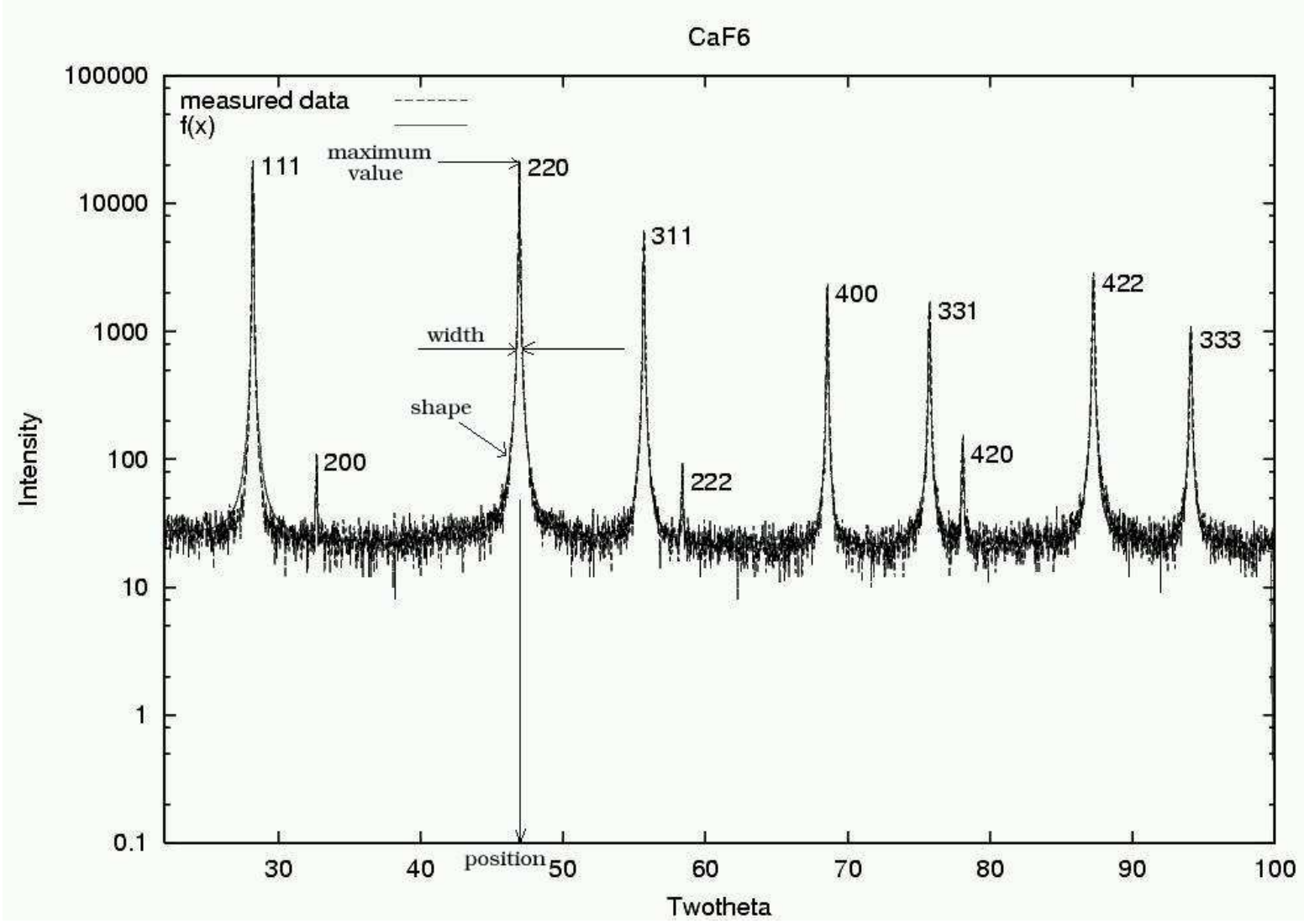
Materials

Preparation of materials:

- applying stress: press or tension
- using large deformation: rolling, HPT, ECAP
- applying heat treatment
- applying cyclic deformation
- using ball milling

These methods can also be combined, or in-situ measurements can be done (e.g. examining plastic deformation and measuring X-ray patterns simultaneously).

X-ray patterns



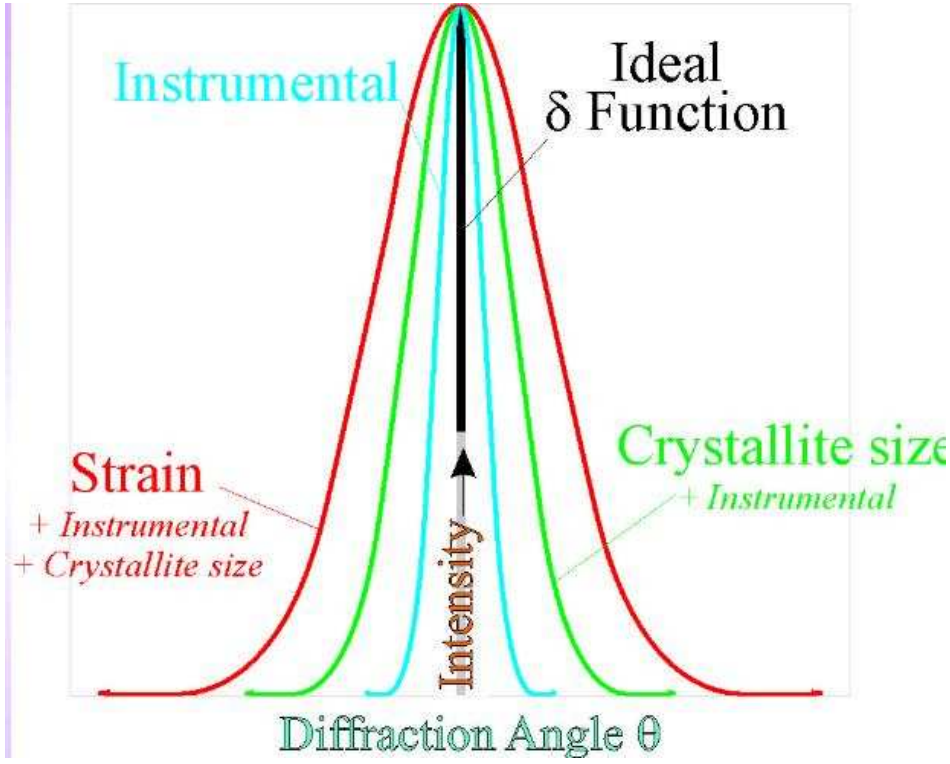
X-ray patterns

The ideal X-ray pattern of an infinite single crystal is a set of $\delta(2\theta - 2\theta_{hkl})$ functions at the exact $2\theta_{hkl}$ Bragg positions. However in a real crystal, the maximal intensity has a finite value ($N^2 F_{hkl}^2$) and the peaks are broadened.

Information in X-ray patterns:

- the information about the crystal structure (e.g. the lattice type and the lattice parameters) is in the position and maximal intensity values of the profiles. The most commonly used procedure is the Rietveld method.
- the information about the microstructure (e.g. crystallite size, crystallite shape, crystallite size distribution and lattice defects: dislocation density, type of dislocations, dislocation arrangement, planar faults) is in the width and shape of the profiles.

X-ray broadening sources



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 simplest case is the scattering of an infinite plane crystallite with the thickness of N atoms. In the book of Warren (1969) it is given as:

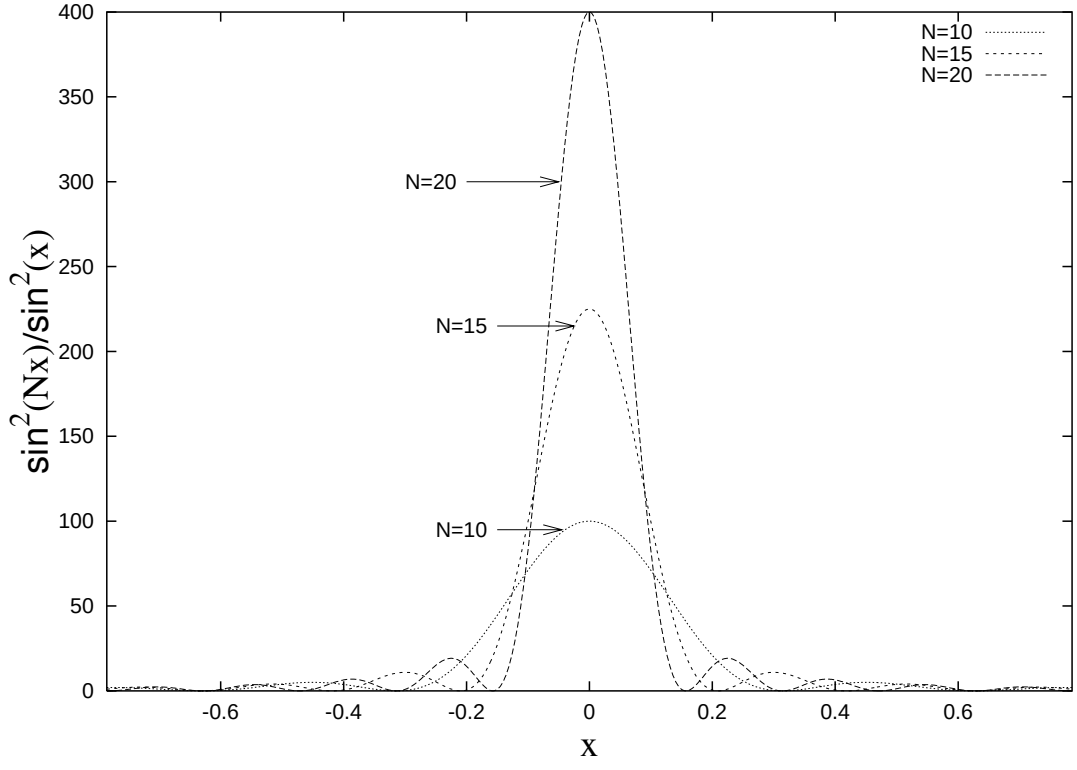
$$I(s) \sim \frac{\sin^2(N\,x)}{\sin^2(x)}, \tag{1}$$

where $x = \pi \mathbf{G}\mathbf{a}$, $\mathbf{G} = \mathbf{g} + \Delta\mathbf{g}$, $\mathbf{g}$ is the diffraction vector, $\Delta\mathbf{g}$ is a small vector, and $\mathbf{a}$ is the unit cell vector chosen to be perpendicular to the plane of the crystallite.

The size effect

For large values of N it can be approximated by:

$$\frac{\sin^2(Nx)}{\sin^2 x} = N^2\left(\frac{\sin(Nx)}{Nx}\right)^2 = N^2\mathrm{sinc}^2(Nx). \qquad (2)$$



The size effect

A more general and more realistic will be described here. If we suppose:

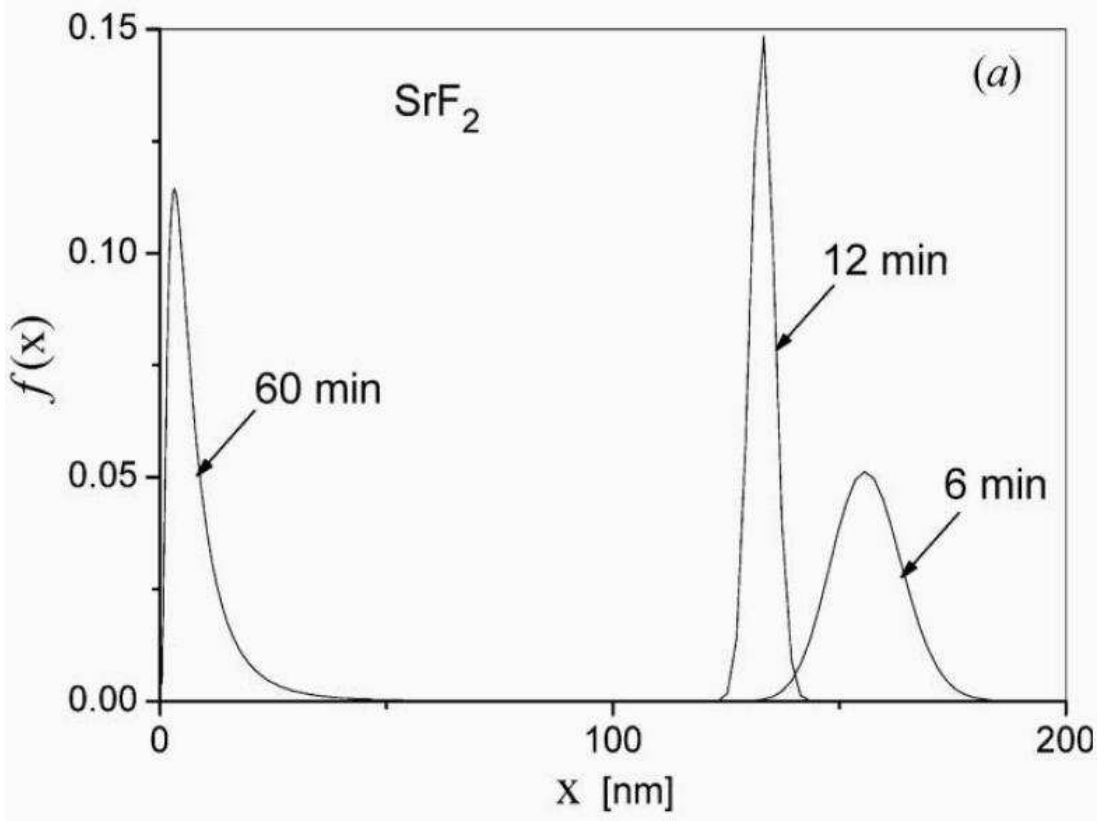
- spherical crystallites
- lognormal f(x) size distribution density function:

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

(σ: variance, m: median).

The size effect

Example for the lognormal distribution function:



Determining the size profile

According to (Bertaut; 1949 and Guinier; 1963) it can be calculated exactly. The final form of the size intensity profile:

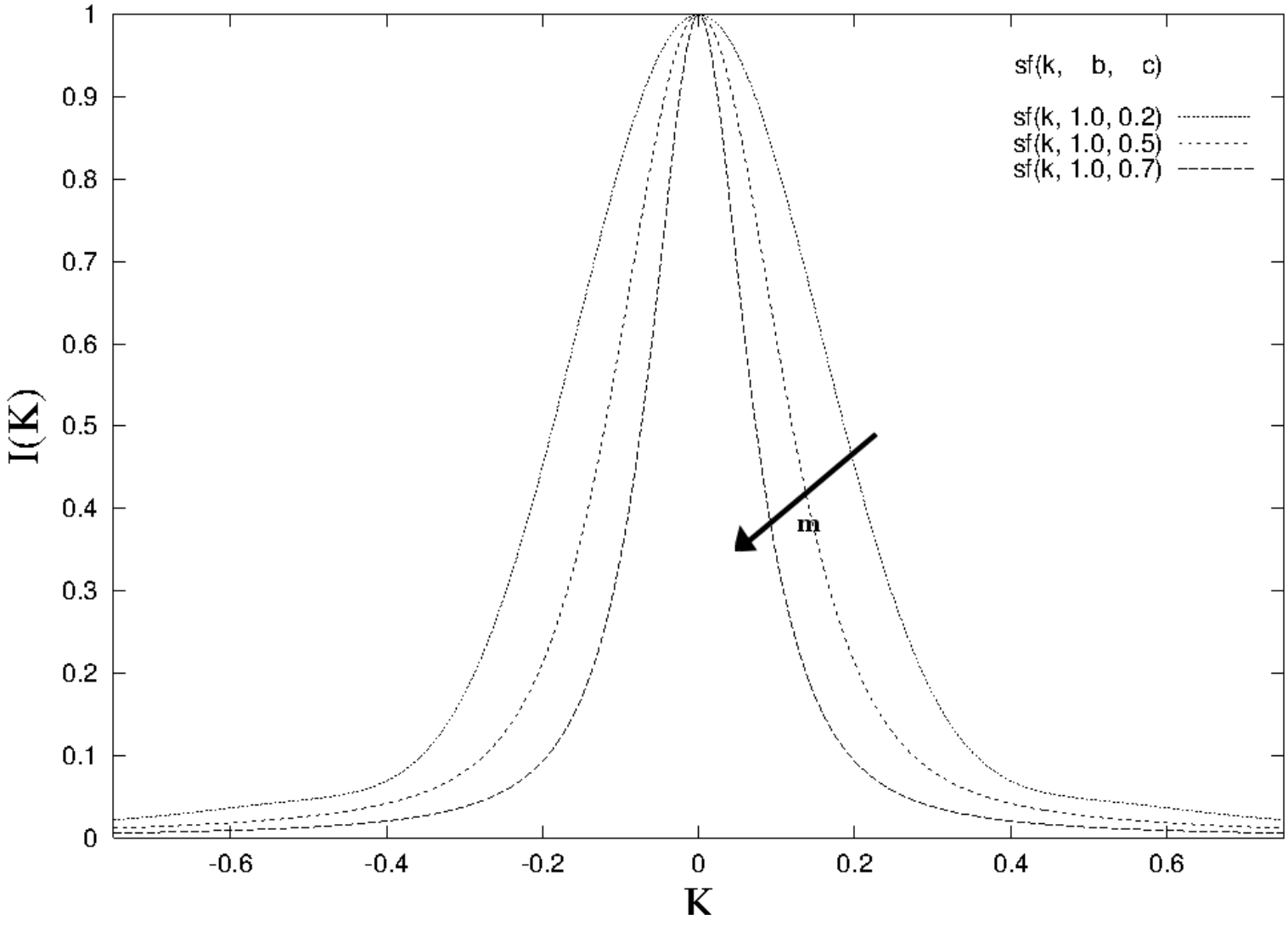
$$I^S(s) = \int_0^\infty \mu \, \frac{\sin^2(\mu \, \pi s)}{(\pi s)^2} \, \mathrm{erfc} \left[\frac{\log\left(\frac{\mu}{m}\right)}{\sqrt{2}\sigma} \right] \, \mathrm{d}\mu,$$

where erfc is the complementary error function, defined as:

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} \, \mathrm{d}t. \qquad (3)$$

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

The Size Function



The Size Fourier Transform

$A(L)$ can be determined in an almost closed form:

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

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

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

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 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^* is the Wilkens strain function. f^* 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.

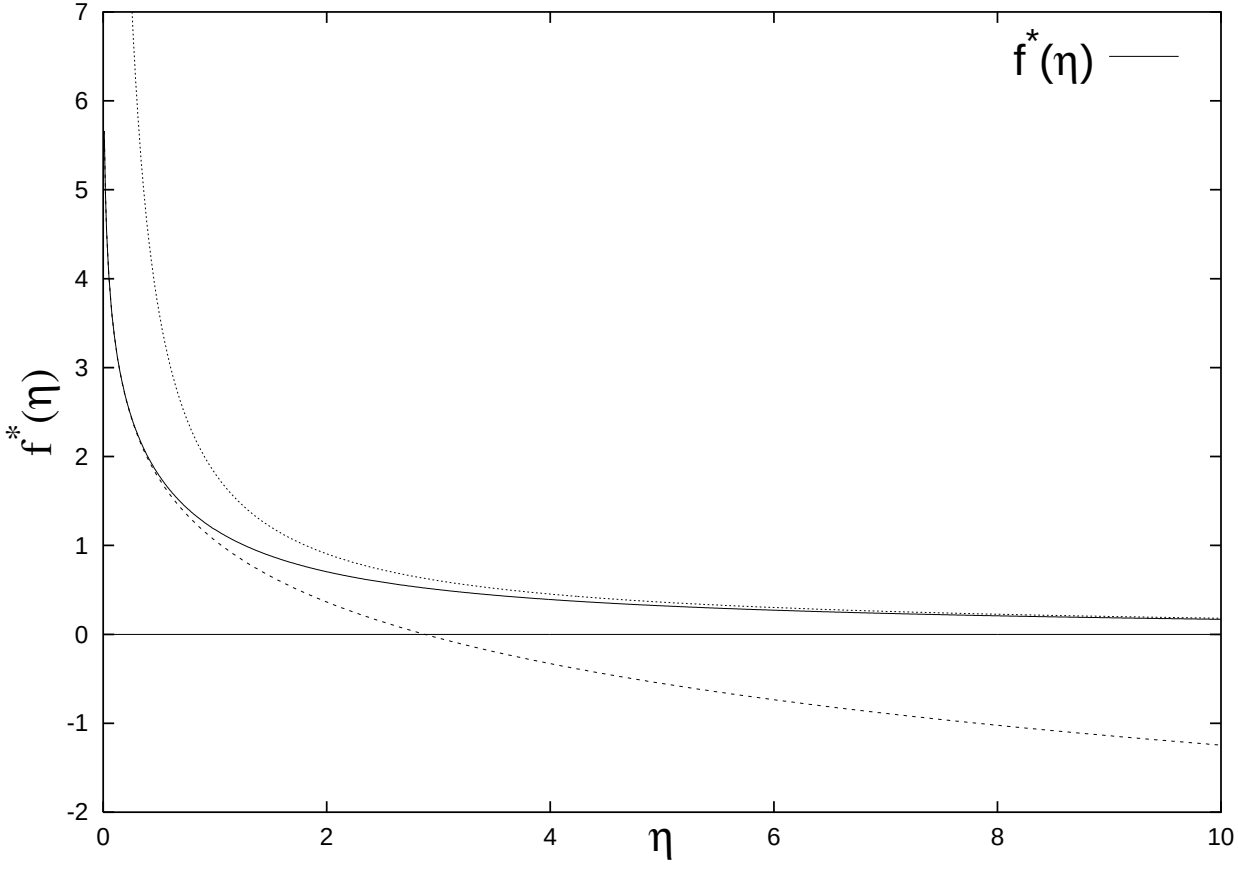
The meaning of the restrictedly random distribution of the Wilkens model:

- 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:

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

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 dislocation arrangement parameter

Wilkens introduced M^*, a dimensionless parameter:

$$M^* = R_e^* \sqrt{\rho}$$

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

Strain anisotropy

A dislocation with $\mathbf{gb} = 0$ has no broadening effect in isotropic material.

For a single dislocation the contrast factor C can be calculated numerically depending on the relative orientation of the **b**, **n**, **l** and **g** vectors and the C_{ij} the elastic constants.

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

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

For hexagonal crystals:

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

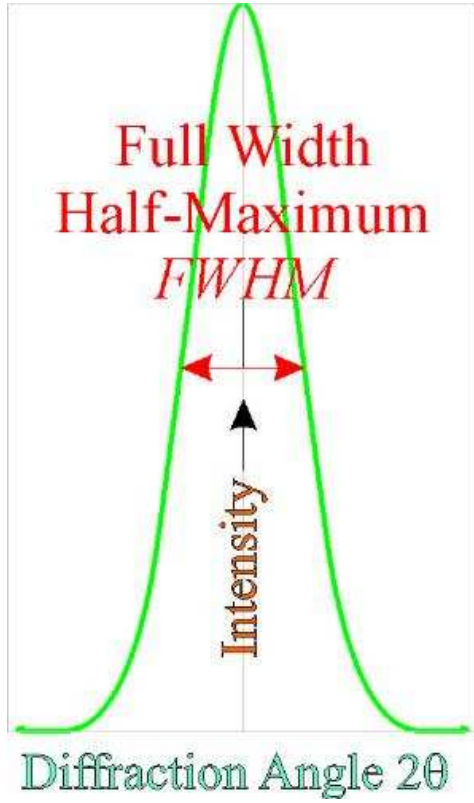
where

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

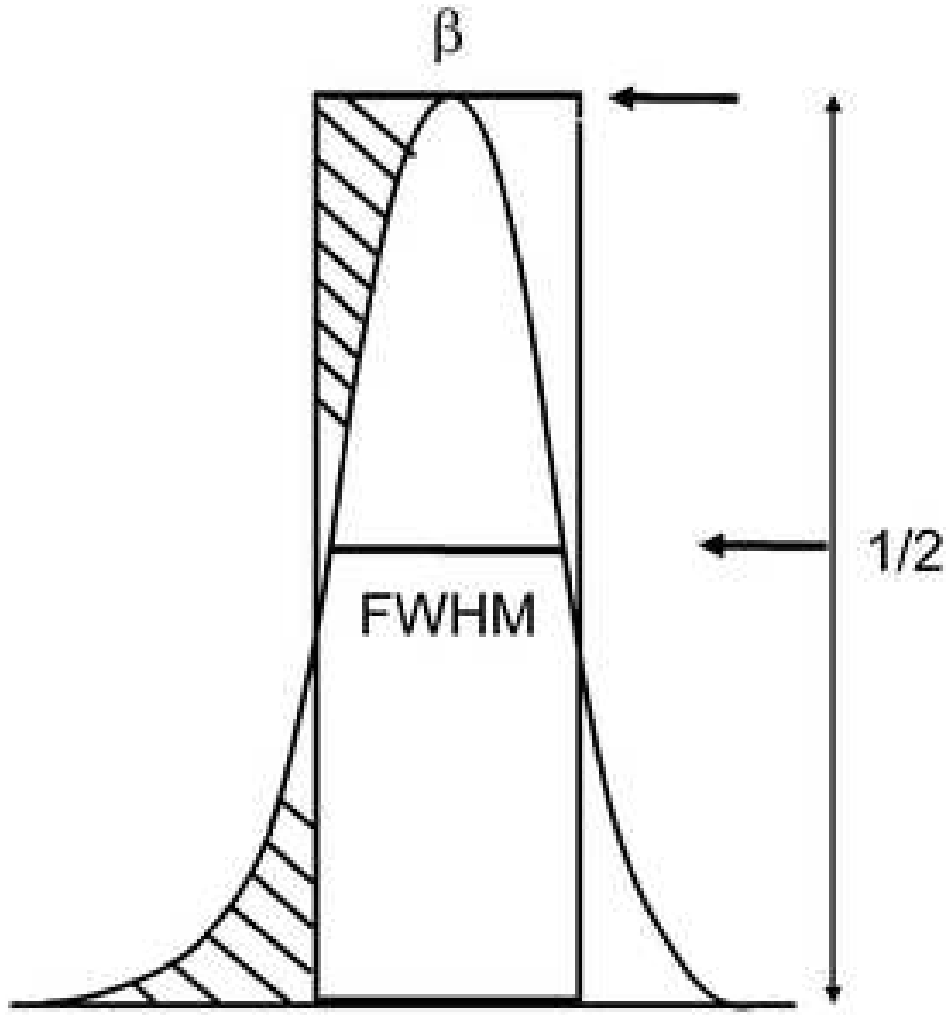
$$H_2^2 = \frac{l^4}{\left[h^2 + k^2 + (h+k)^2 + \frac{3}{2}(\frac{a}{c})^2 l^2\right]^2},$$

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).

FWHM: definition



Integral breadth: definition



The Williamson-Hall procedure

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

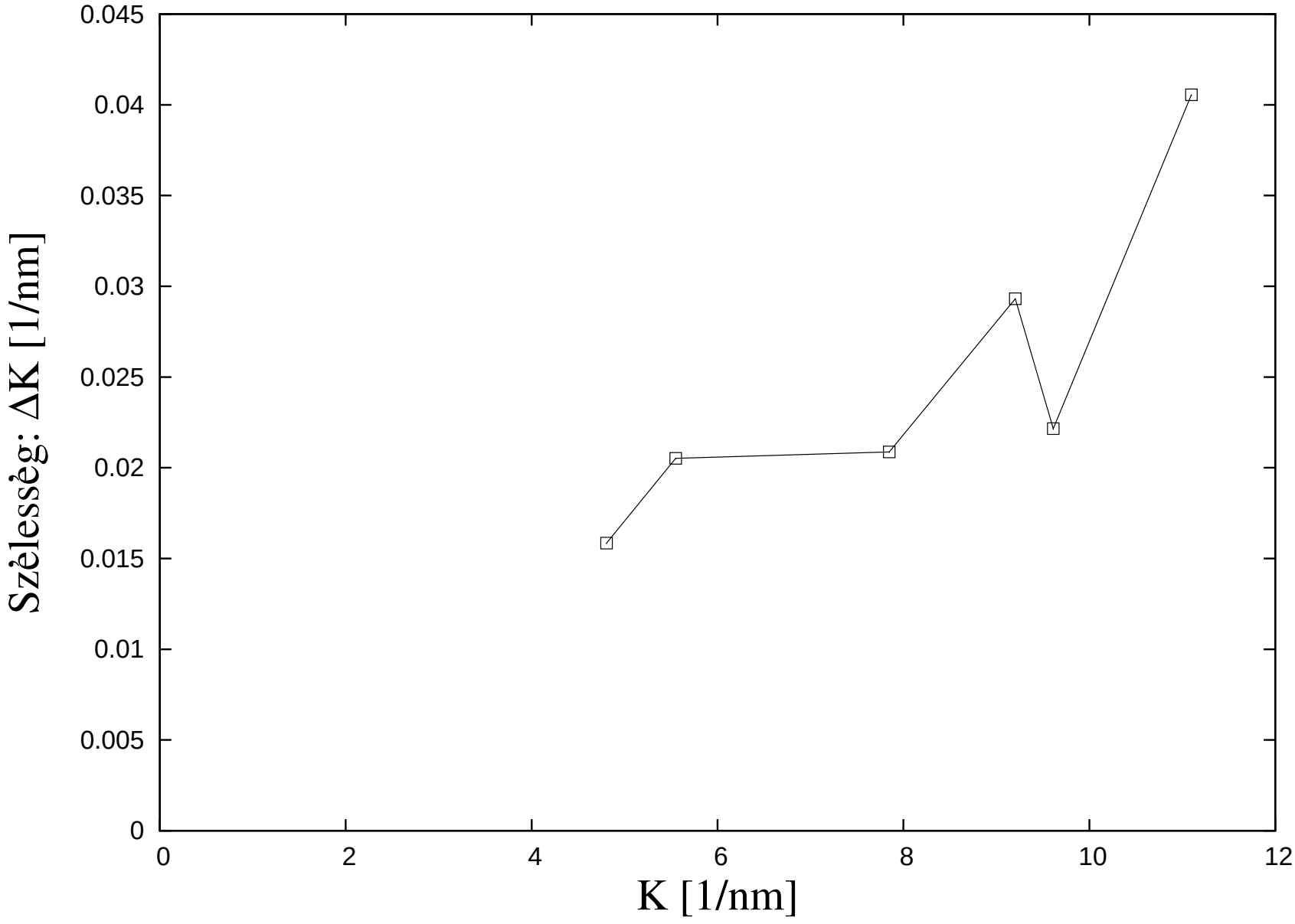
- size effect: independent of K
- strain effect: increasing with K
- from extrapolation to $K = 0$ the crystallite size can be determined (inversely proportional to $\Delta K(0)$)

The Modified Williamson-Hall procedure

For dislocated material, the broadening is anisotropic.

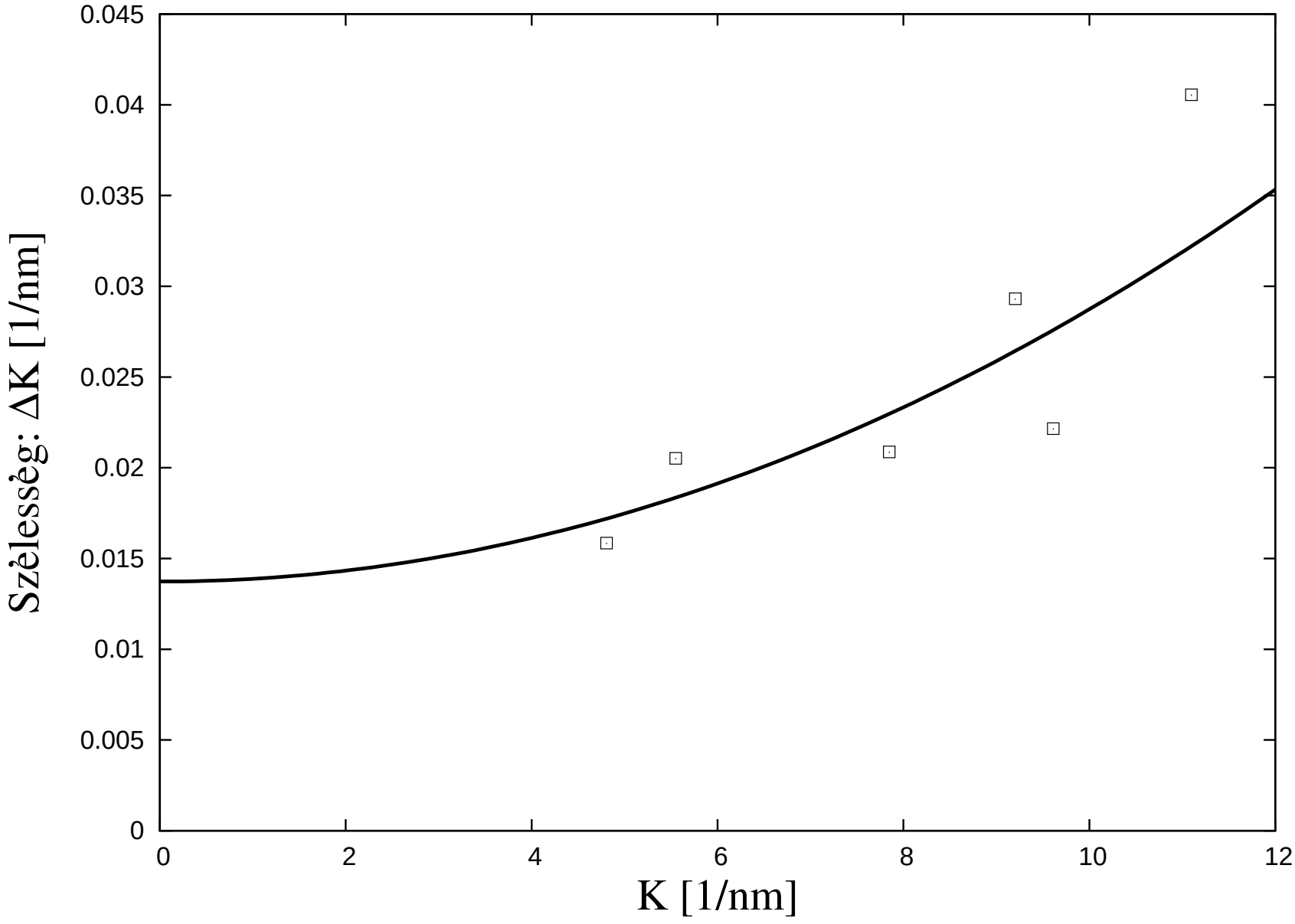
- K is scaled by the C contrast factors, $K\sqrt{C}$ or K^2C is used for the plot
- size effect: independent of K
- strain effect: increasing with K
- from extrapolation to $K = 0$ the crystallite size can be determined (inversely proportional to $\Delta K(0)$)

Williamson-Hall plot



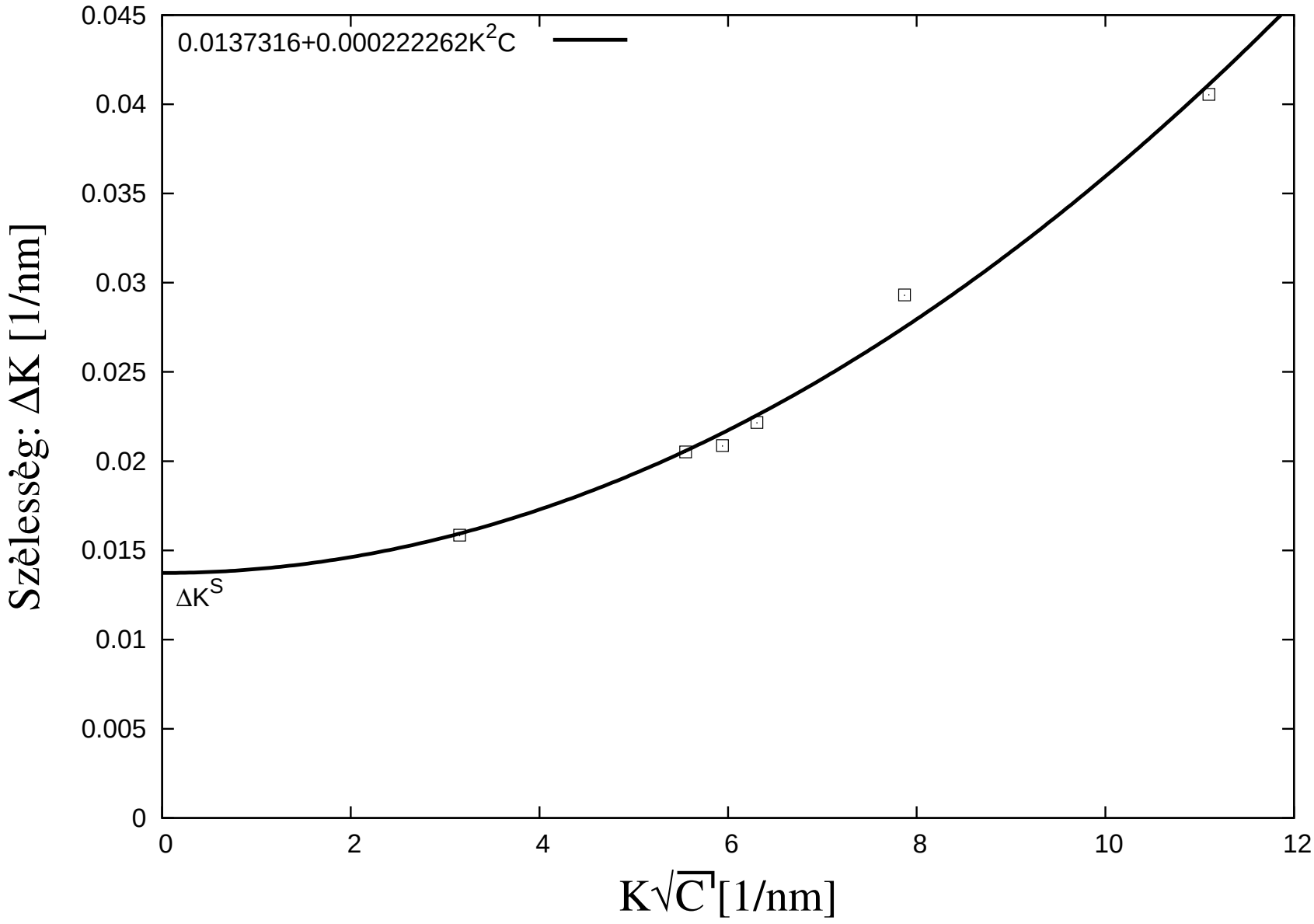
Williamson-Hall plot of the FWHM values (copper sample).

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).

(Modified) Warren Averbach procedure

Basic equation:

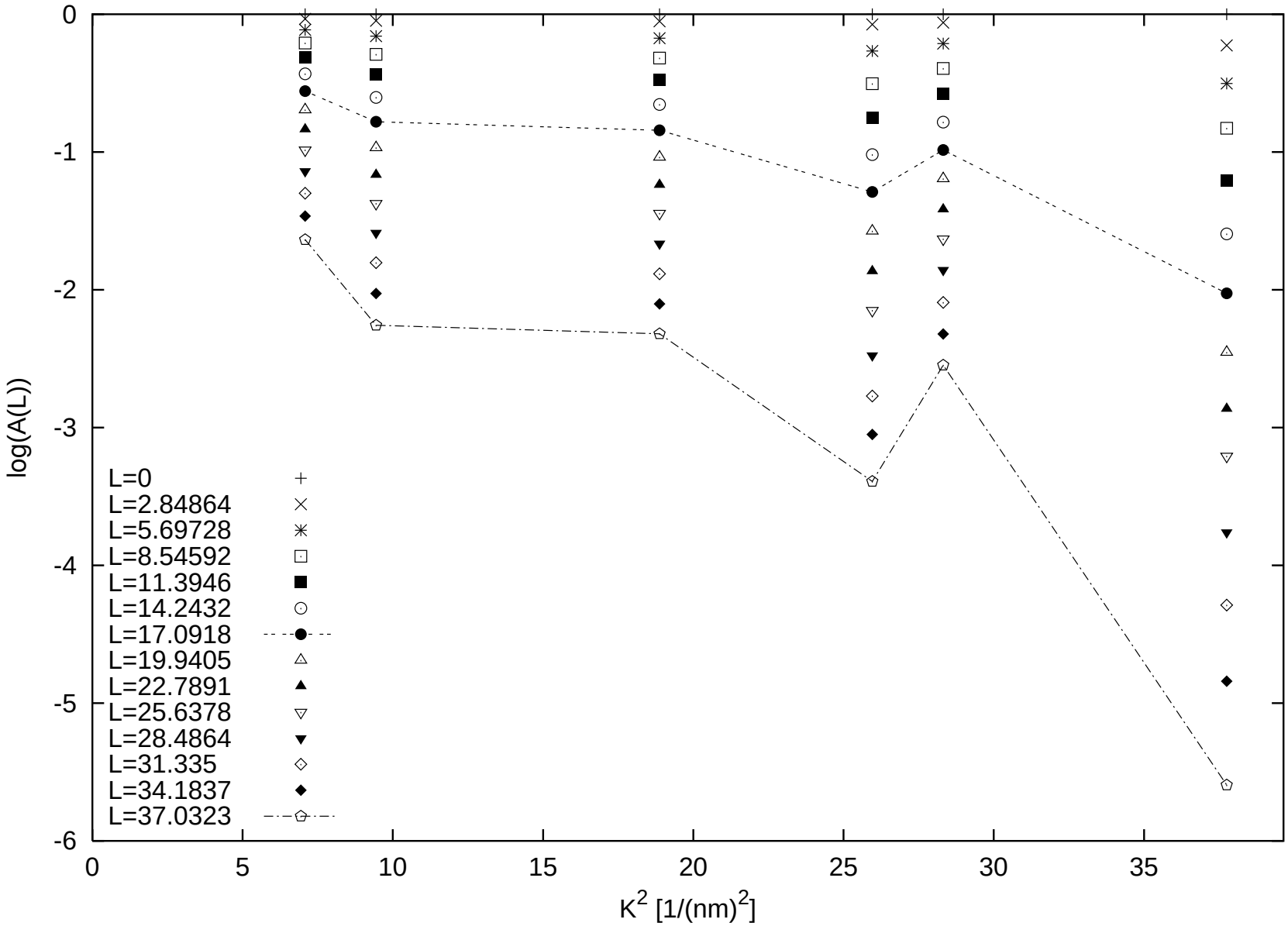
$$\log A(L) \approx \log A^S(L) - \rho B L^2 \log\left(\frac{R_e}{L}\right)(K^2C), \qquad (4)$$

$\log A(L)$ is plotted as a function of K^2 or K^2C for different L values, $A^S(L)$ is obtained by extrapolating to $K = 0$. By analysing the strain part, ρ and R_e can also be determined.

For each value of L_i, $\log A(L_i)$ is fitted by the parabolic curve $a_i + b_i K^2C + c_i K^4C^2$

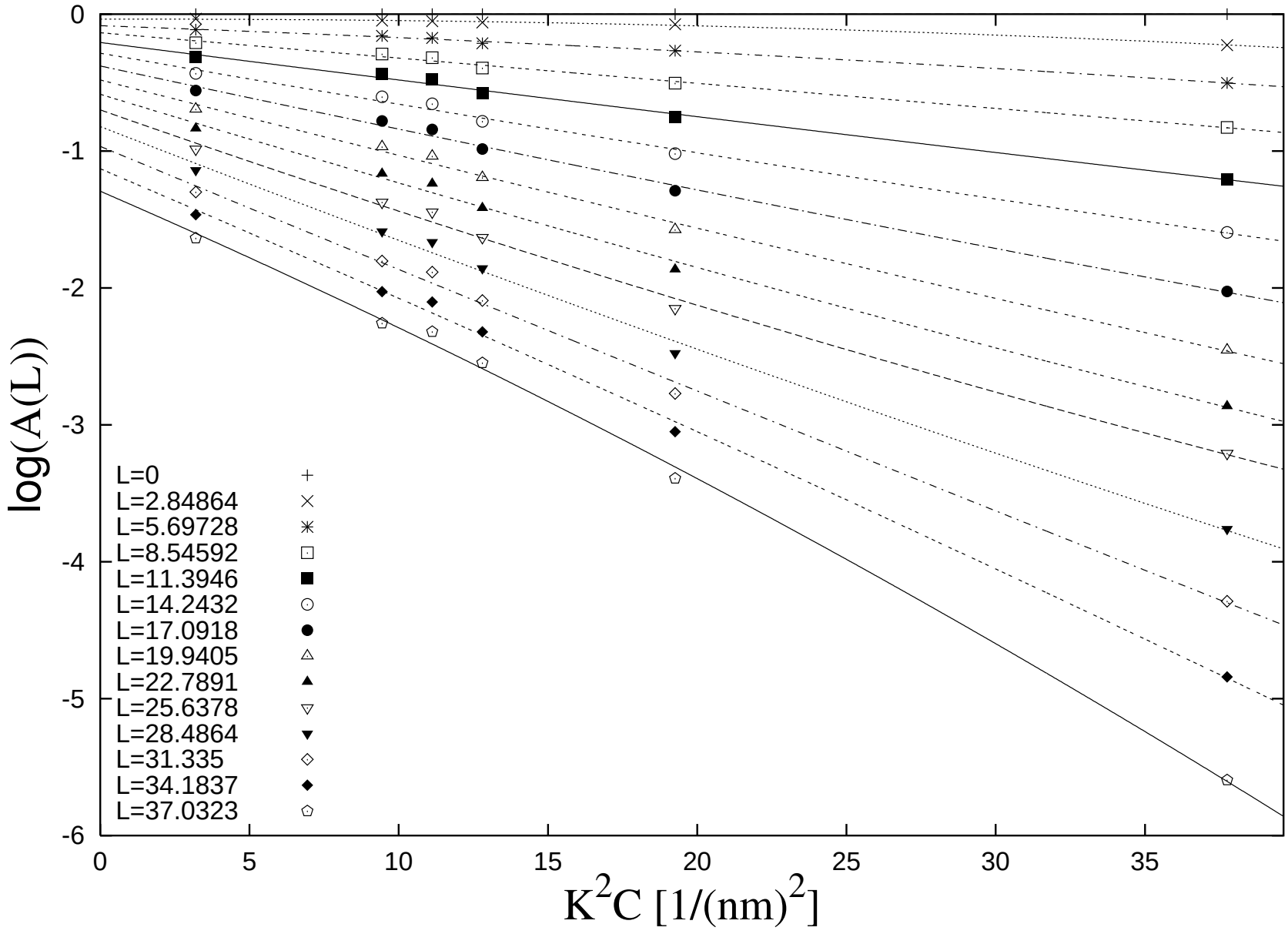
- The exponential of the a_i values gives $A^S(L)$
- Then b_i divided by L_i^2 are plotted as a function of $\log L_i$ and by using a linear fit ρ and R_e is determined

Warren-Averbach plot



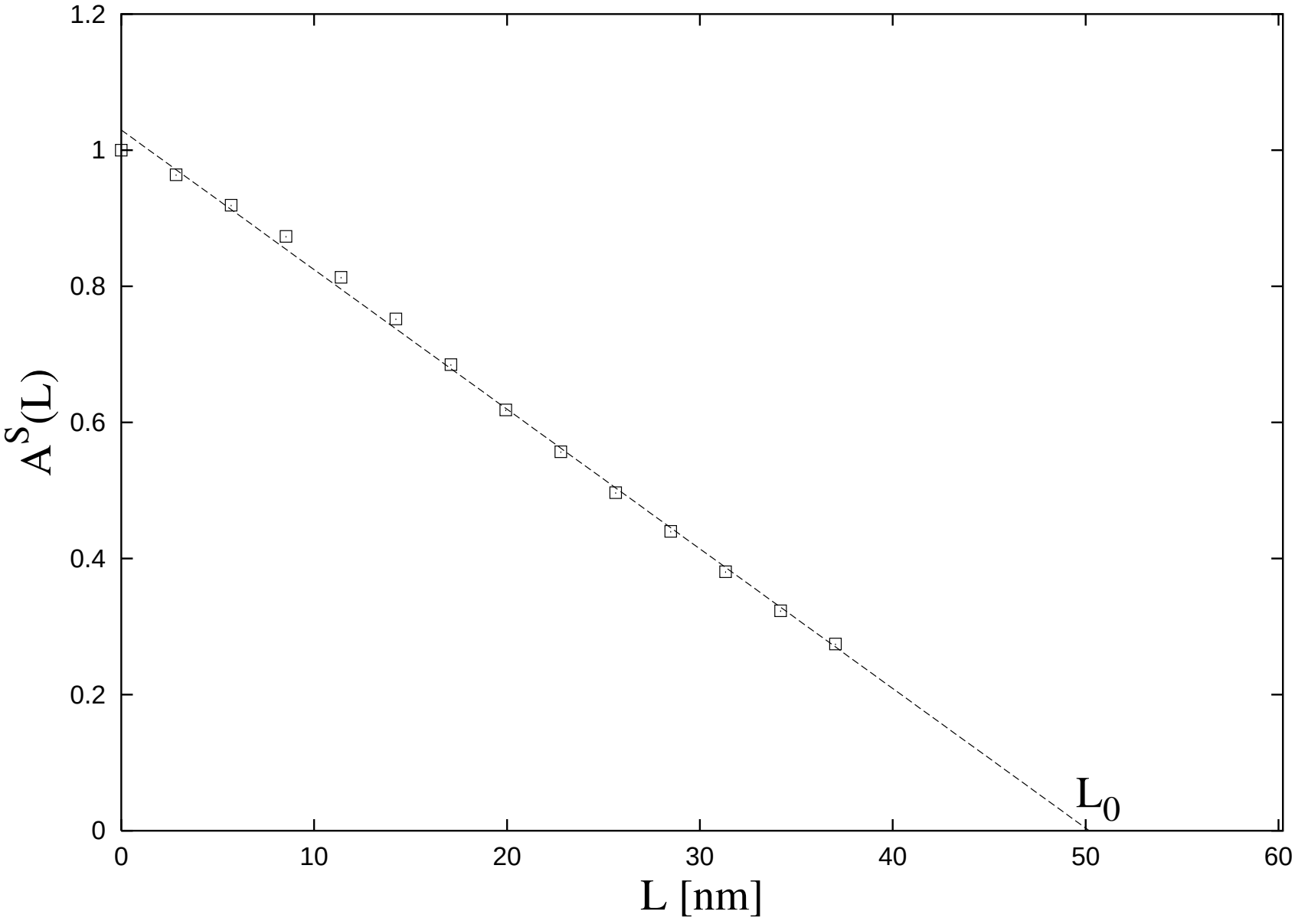
Warren-Averbach plot (copper sample).

Modified Warren-Averbach plot



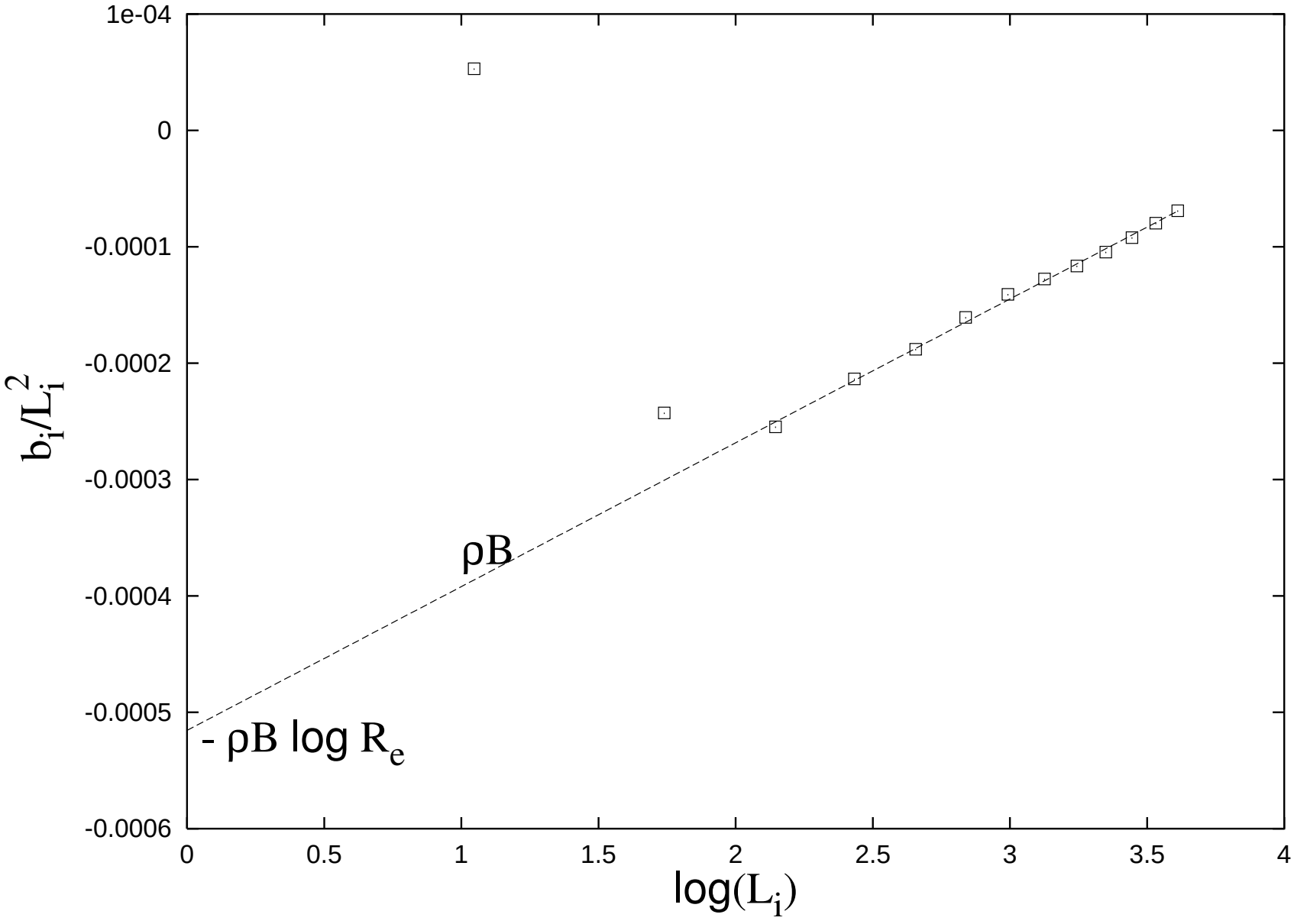
Modified Warren-Averbach plot (copper sample).

Modified Warren-Averbach plot



Size function obtained by the Modified Warren-Averbach procedure.

Modified Warren-Averbach plot



Strain function obtained by the Modified Warren-Averbach procedure.

Microstructural parameters

The theoretical functions depend on the following microstructural parameters:

- size: m, σ, ε
- dislocations: ρ, M, q
- planar faults: α

MWP-fit

The method is:

- a Whole Profile fitting method using ab-initio theoretical profile functions
- a Fourier method, which works on multiple profiles simultaneously

The data must be prepared before applying the method:

- the profiles should be separated
- the instrumental broadening is corrected for by deconvolution using the Stokes method
- the separated and instrumental-free profiles are Fourier-transformed

MWP data preparation

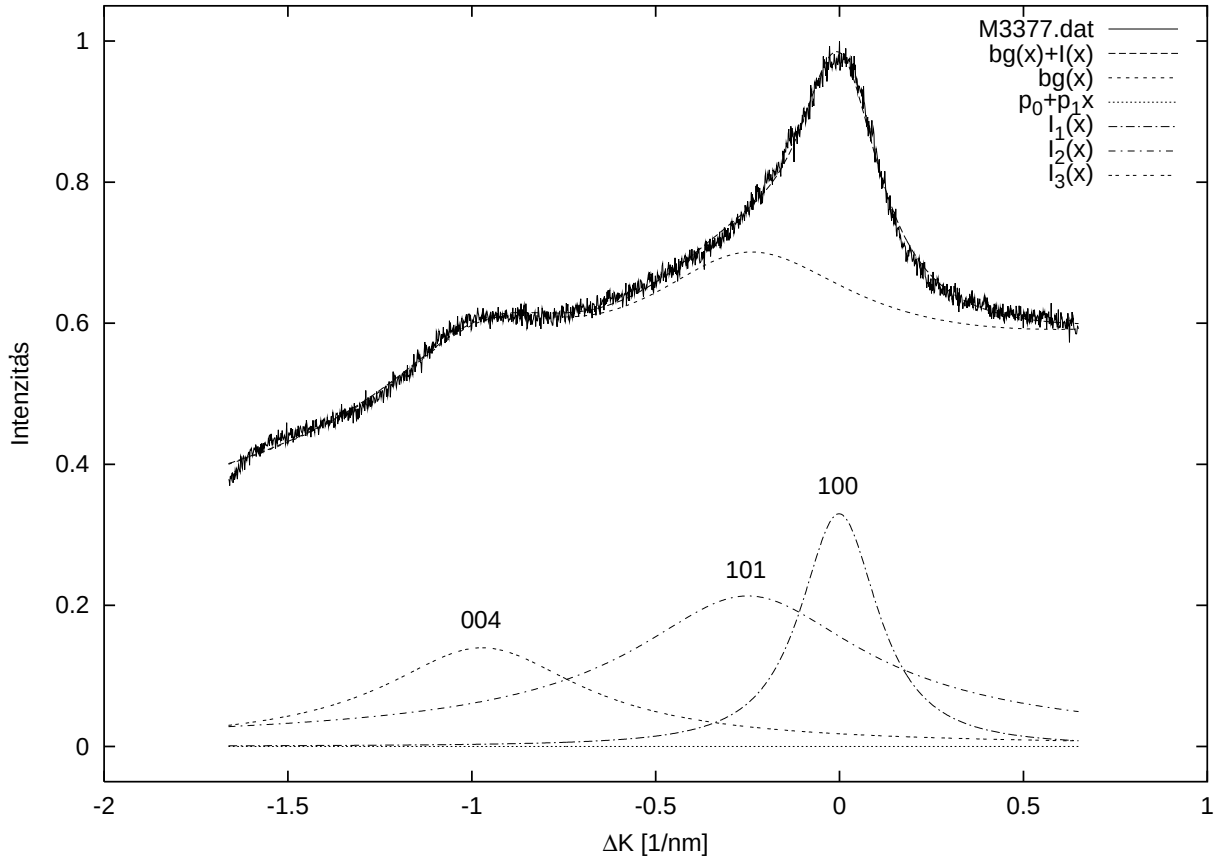


Figure 1: Example for profile separation

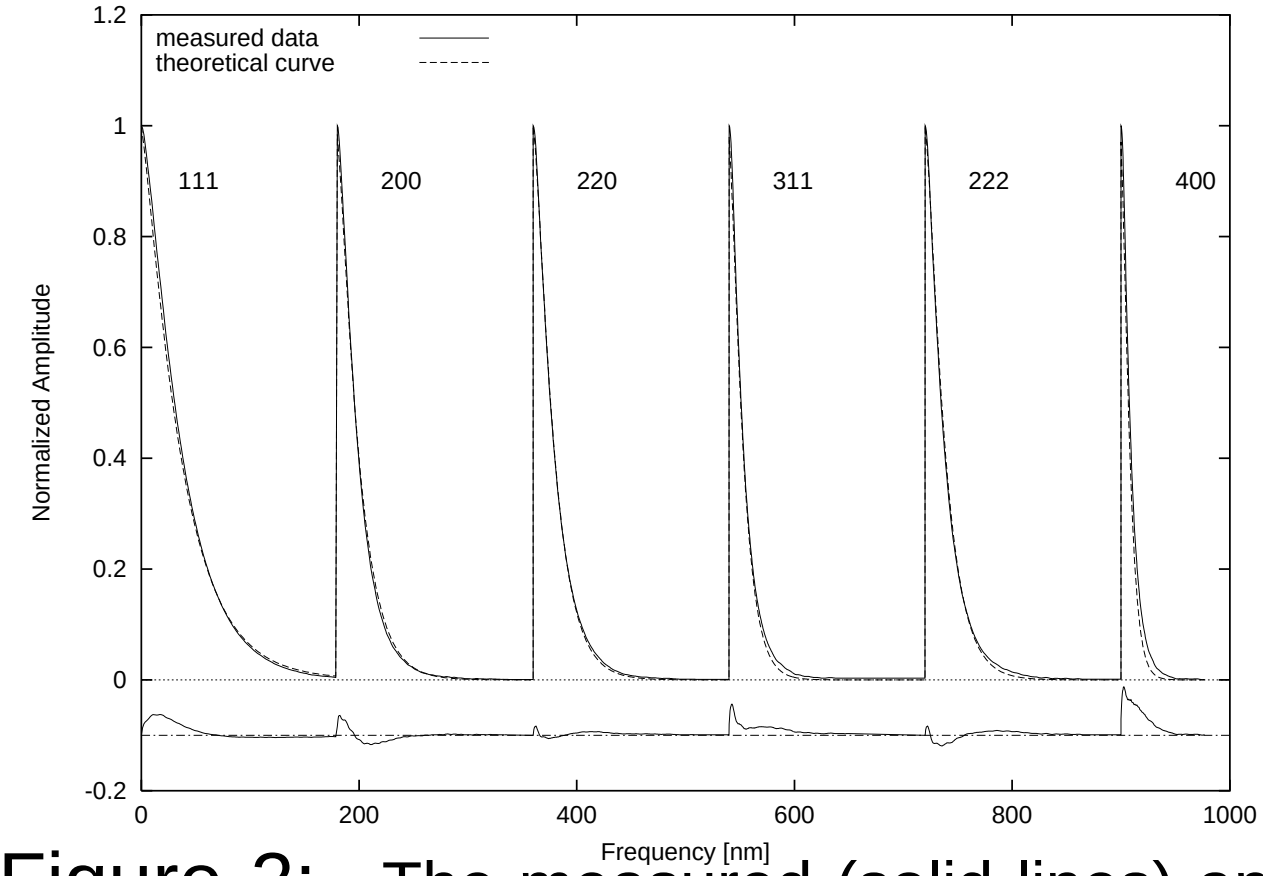
Multiple Whole Profile (MWP) fitting

Multiple Whole Profile fitting of the Fourier–transforms.

In this procedure first the measured intensity profiles are Fourier–transformed and normalized. Then all of them are fitted simultaneously by the normalized theoretical Fourier–transform:

$$A(L) = \frac{A^S(L)}{A^S(0)} \exp\left[-\frac{\pi b^2}{2}(g^2 C)\rho L^2 f\left(\frac{L}{R_e^*}\right)\right],$$

MWP application to Cu sample



Results of the MWP fit:

$m = 62\text{nm}$

$\sigma = 0.53$

$\rho = 1.7 \cdot 10^{15}\ \text{m}^{-2}$

$M = R_e\sqrt{\rho} = 1.7$

$q = 1.84$

Figure 2: The measured (solid lines) and theoretical fitted (dashed lines) Fourier transforms for copper sample deformed by ECAP (equal-channel angular pressing) as a function of the Fourier Frequency, L. The difference plot is also given.

Comparison with TEM

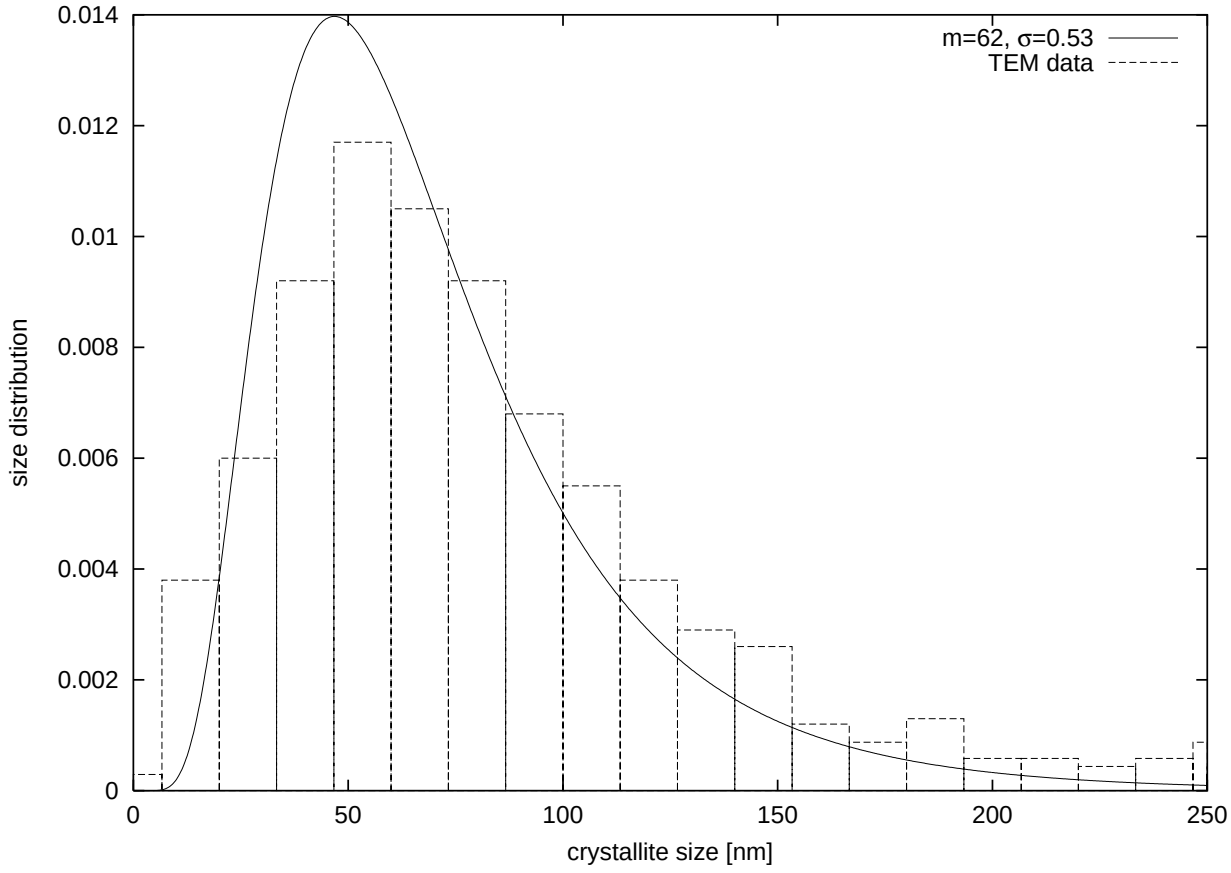


Figure 3: The size distribution density function corresponding to the parameters of the MWP fit and the size distribution obtained by TEM for the ECA pressed copper sample.

CMWP-fit means:

Convolutional

Multiple

Whole

Profile

fitting

Convolutional MWP fitting

When the MWP fitting procedure is used:

- the deconvolution of the physical and the instrumental profiles increases the noise in the corrected profile.
- the selection of the analytical function used in the peak separation influences the shape of the individual profile.

In order to avoid these uncertainties the method of Convolutional Multiple Whole Profile (CMWP) fitting was elaborated.

In this procedure the whole measured powder diffraction pattern is fitted by the sum of a background polinom and profile functions. The profile functions are calculated as the convolution of the theoretical functions for physical broadening and the instrumental profiles.

Therefore neither the separation of the peaks nor the deconvolution is needed.

CMWP-fit

The method is:

- a whole powder pattern fitting method
- a microstructural method: the unit cell is NOT refined
- it works directly on the measured pattern

The theoretical intensity pattern

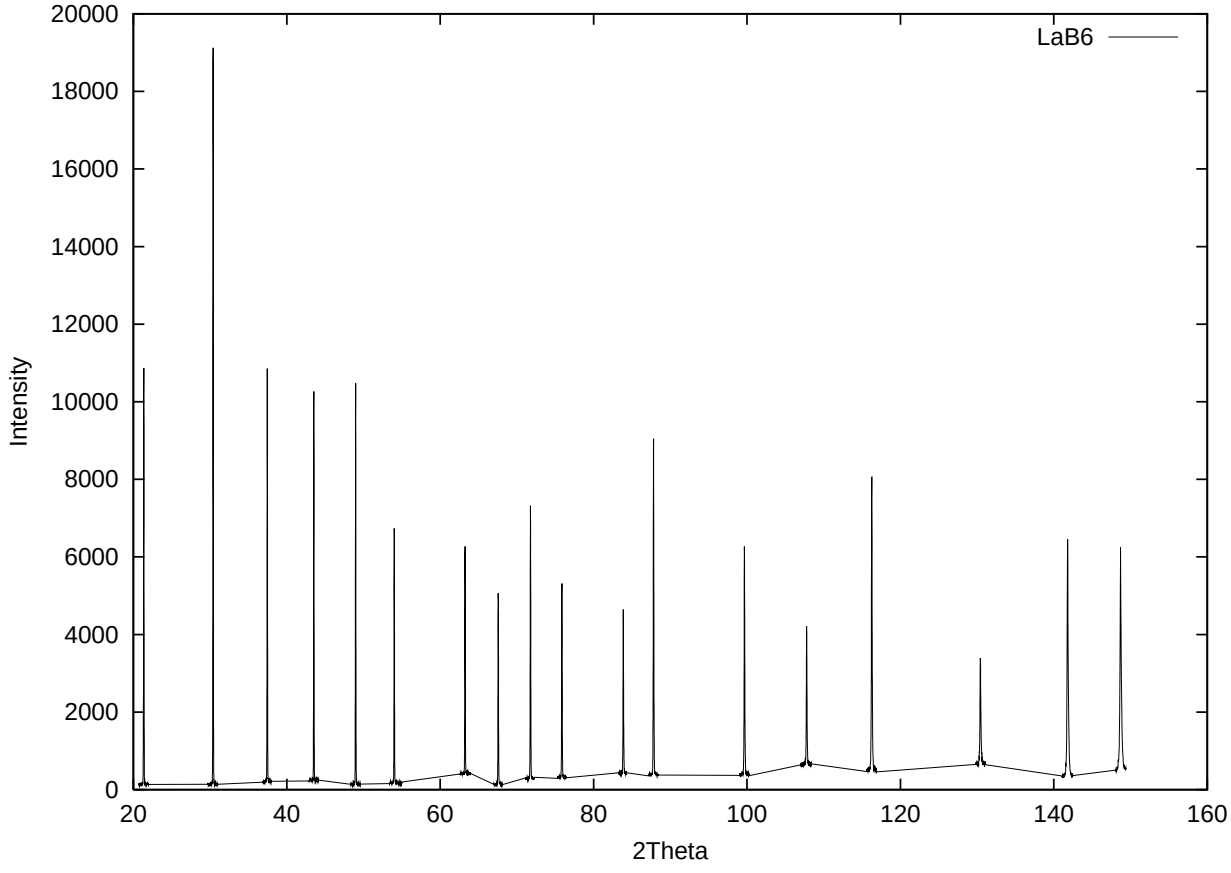
$$I_{theoretical} = BG(2\Theta) + \sum_{hkl} I^{hkl}_{MAX} I^{hkl}(2\Theta - 2\Theta^{hkl}_0),$$

where:

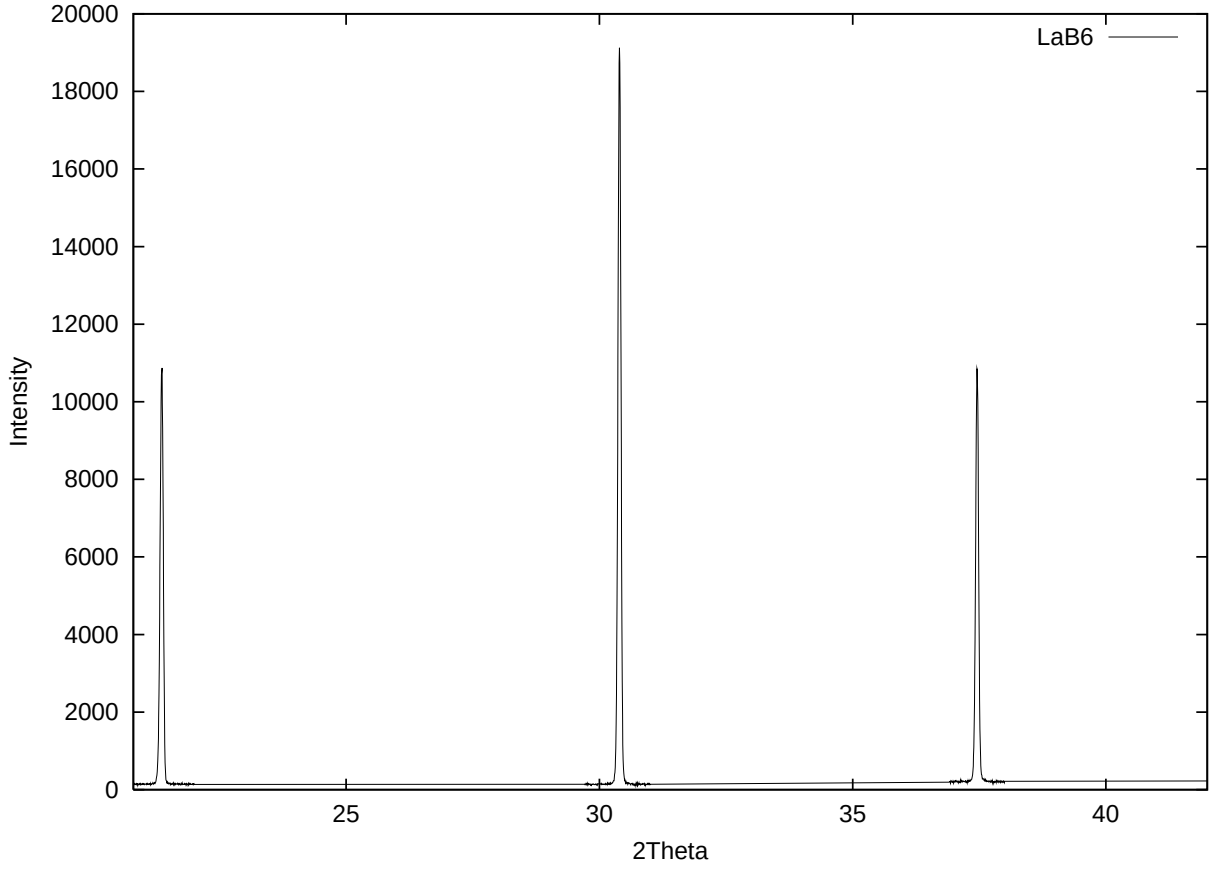
$$I^{hkl} = I^{hkl}_{instr.} * \quad I^{hkl}_{size} * \quad I^{hkl}_{disl.} * \quad I^{hkl}_{pl.faults},$$

$I^{hkl}_{instr.}$: *measured* instumental profile

Instrumental pattern of LaB_6



Instrumental pattern of LaB_6



Al-3Mg ball milled 3 h.

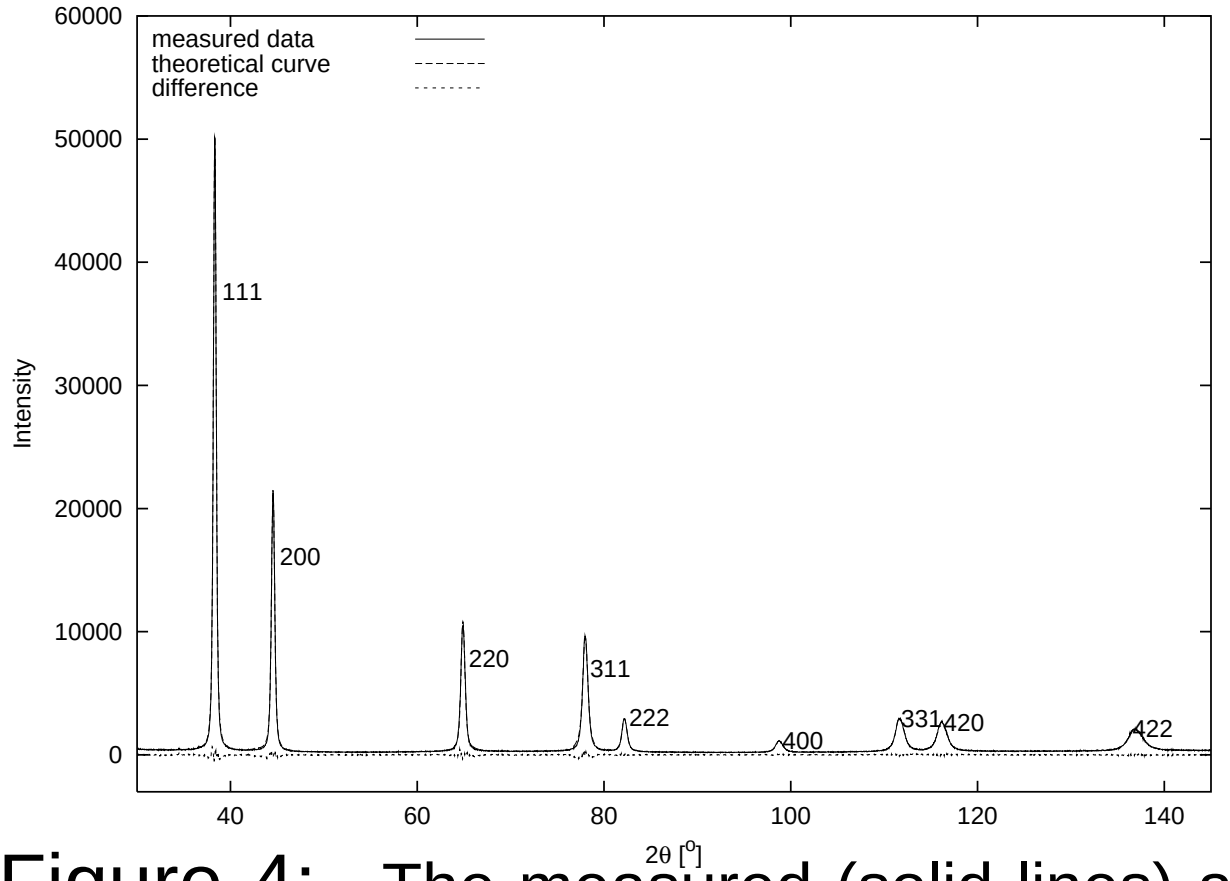
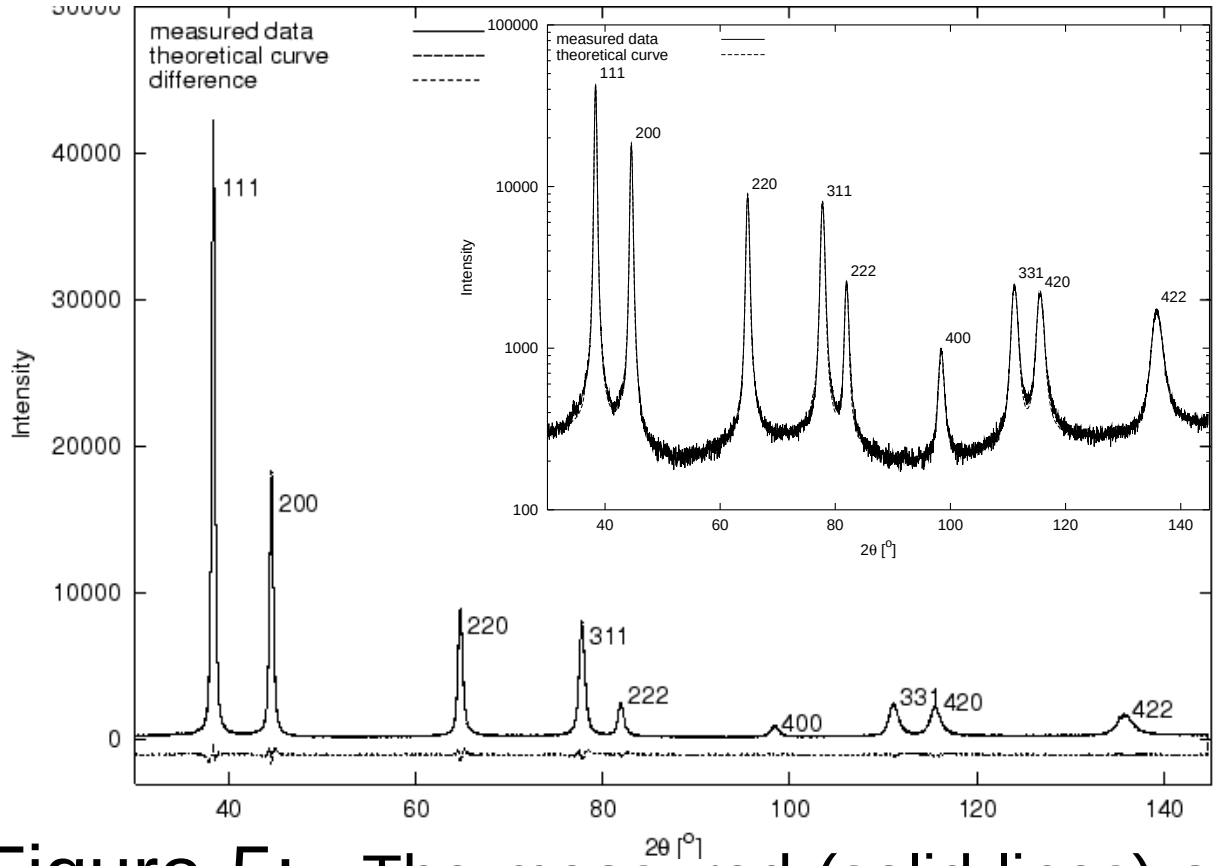


Figure 4: The measured (solid lines) and theoretical fitted (dashed lines) intensity patterns for Al-3Mg sample ball milled for 3 hours as a function of 2θ.

Al-6Mg ball milled 32 h.



Results of the CMWP fit:

$m = 21\text{nm}$

$\sigma = 0.36$

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

$M = R_e\sqrt{\rho} = 1.3$

$q = 1.3$

Figure 5: The measured (solid lines) and theoretical fitted (dashed lines) intensity patterns for Al-6Mg sample ball milled for 6 hours as a function of 2θ. The same figure is plotted in logharitmic scale in the upper-right corner.

Comparing results to TEM

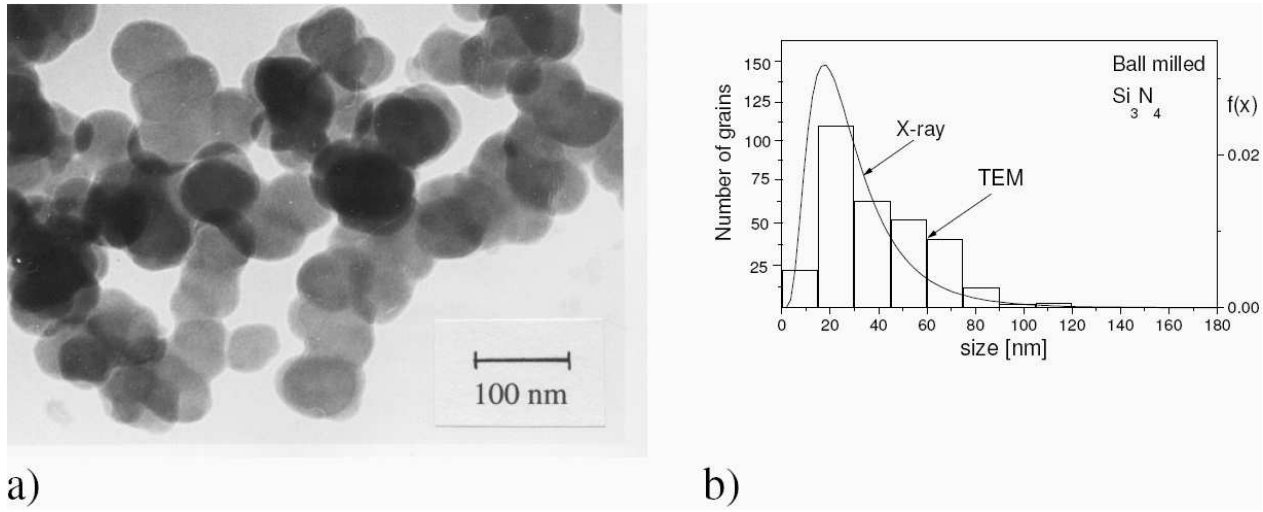


Figure 6: Example for SiN: an experimental size distribution can be obtained (with low statistics)

Comparing results to HRTEM

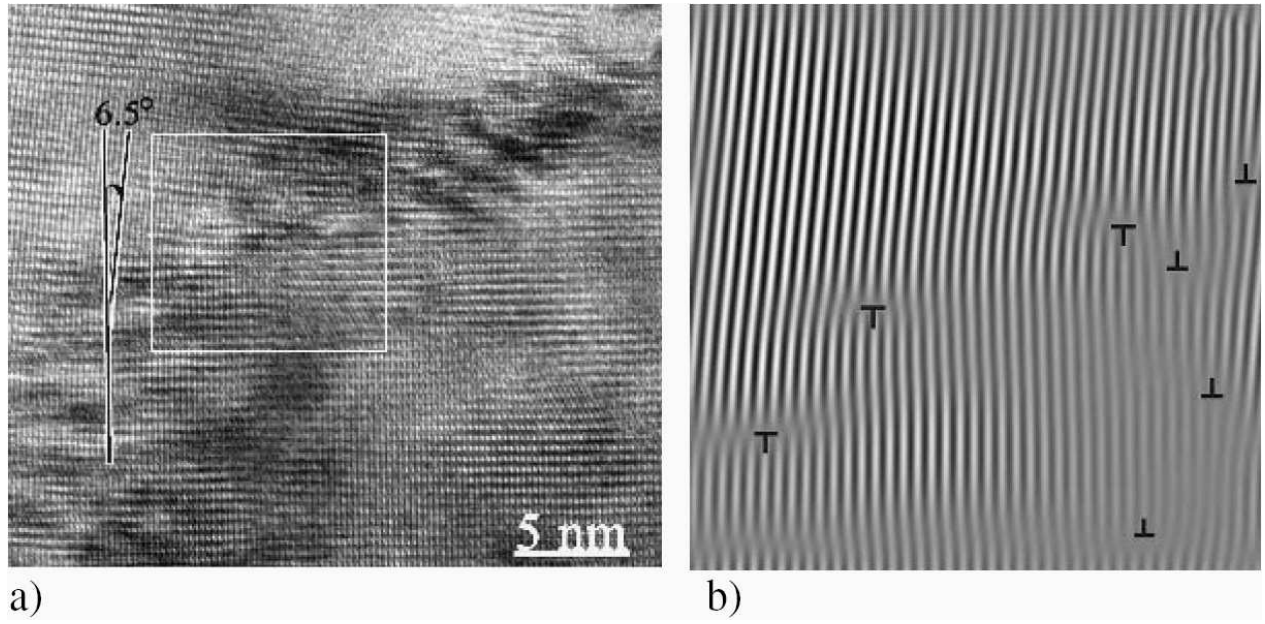


Figure 7: Example for Ti: a local dislocation density can be estimated ($\rho \approx \frac{7}{12^2 \text{nm}^2}$)

Summary

- modeling the broadening of line profiles:
  - size effect
  - strain effect
- application to X-ray line profile analysis:
  - the classical methods
  - the MWP method
  - the CMWP method