

Revealing the details of microstructure

by Diffraction line profile analysis

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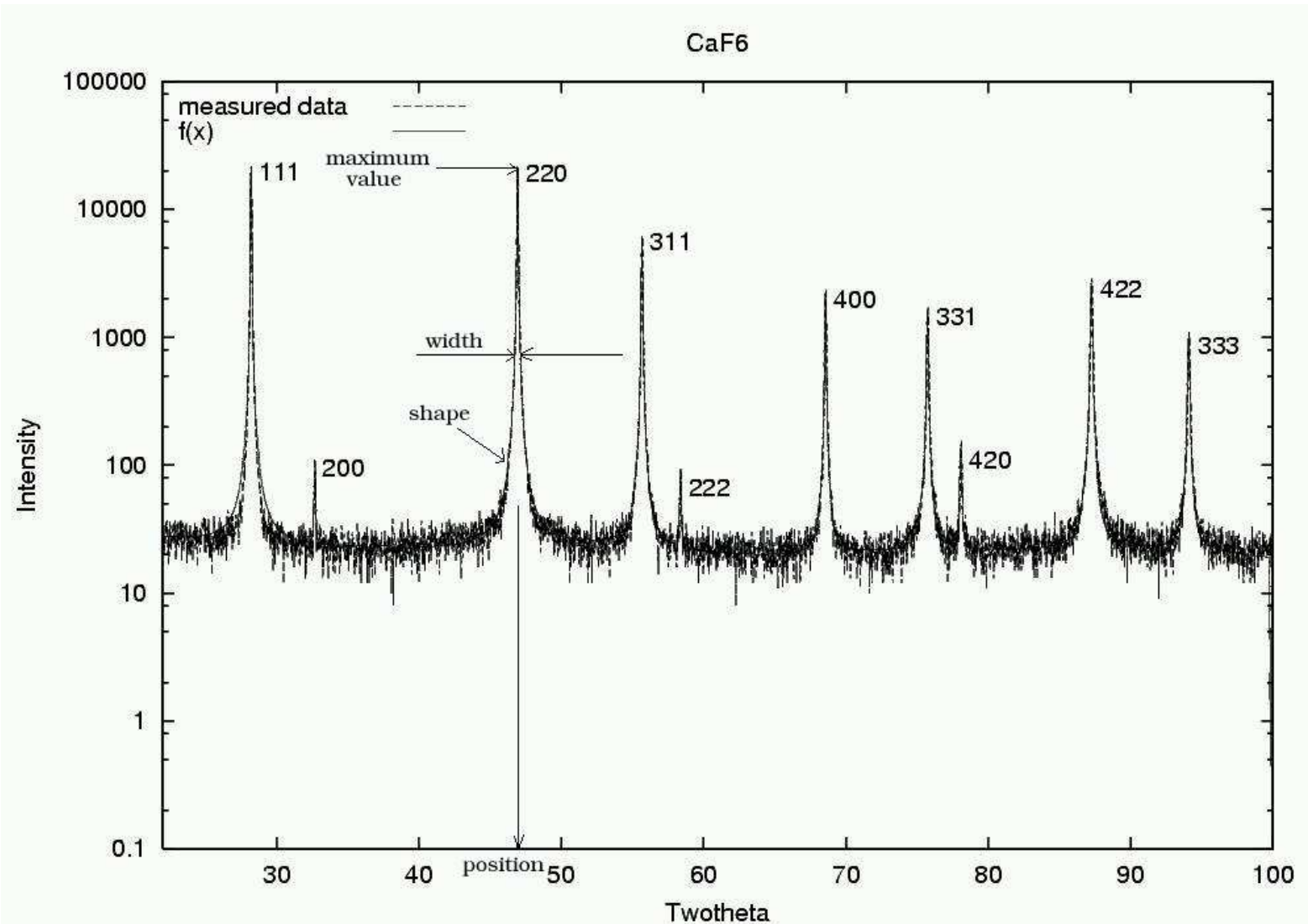
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Outline

- extracting microstructure using X-ray line profile analysis
- physical sources of broadening
- modeling size and strain broadening
- CMWP method for line profile analysis
- 3D experiments and modeling

X-ray patterns



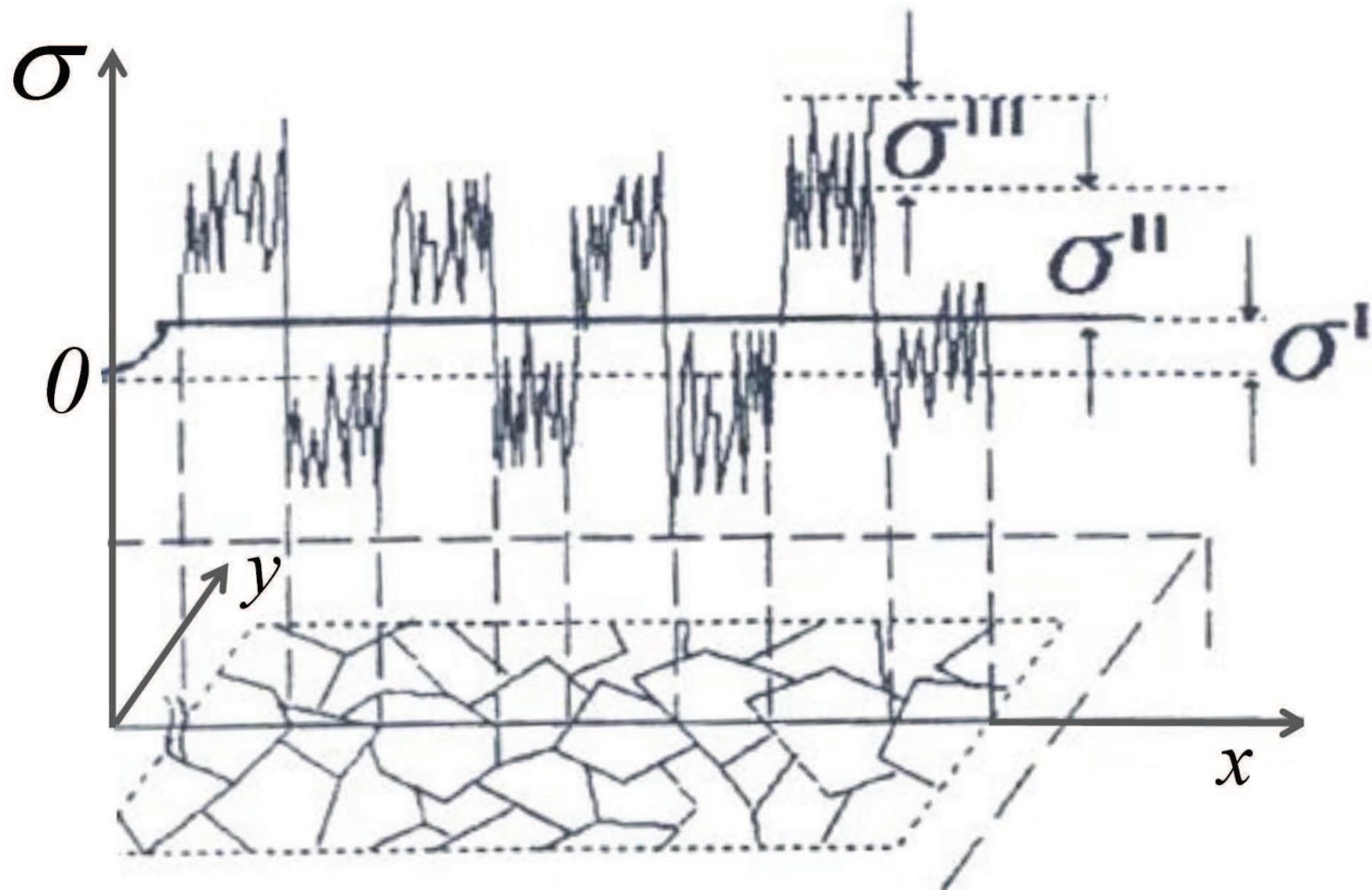
X-ray patterns

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:

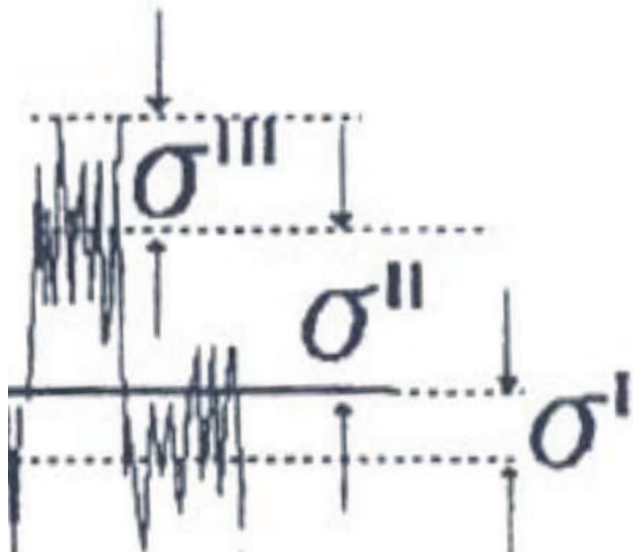
- the information about the crystal structure (e.g. the lattice type and the lattice parameters) is in the position and maximal intensity values of the profiles. The most commonly used procedure is the Rietveld method.
- the information about the microstructure (e.g. crystallite size, crystallite shape,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

Macherauch, E. (~1965)
schematic classification of internal stresses



Macherauch, E. (~1965)

schematic classification of internal stresses



σ_I : *macro-stress*

averaged over many grains

σ_{II} : *intergranular-stresses*

averaged over individual grains

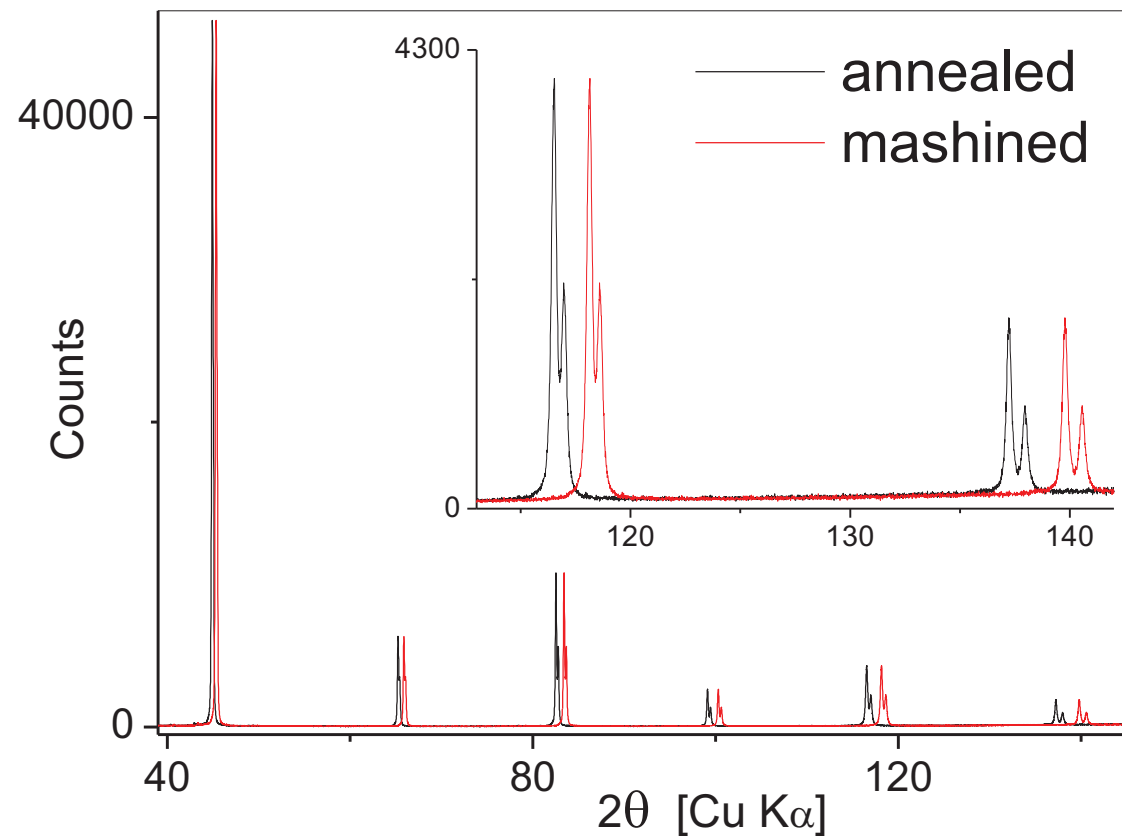
σ_{III} : *micro-strains* (or *stresses*)

produced by *dislocations*

Diffraction experiments

σ_I : *macro-stress*

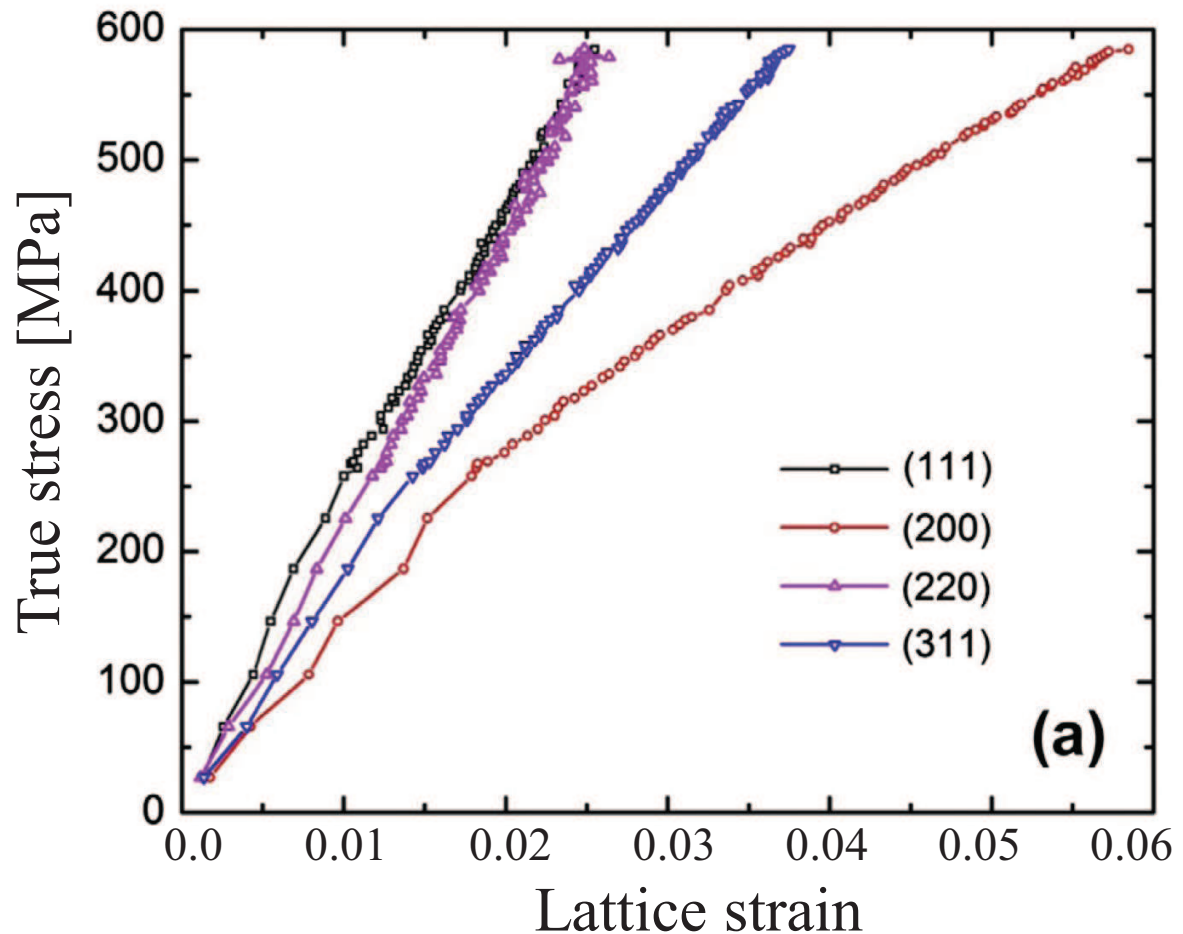
all peaks shift in the same direction



Diffraction experiments

σ_{II} : *intergranular*-strains/stresses

peak-positions corresponding to *individual grains*: **lattice-strain**

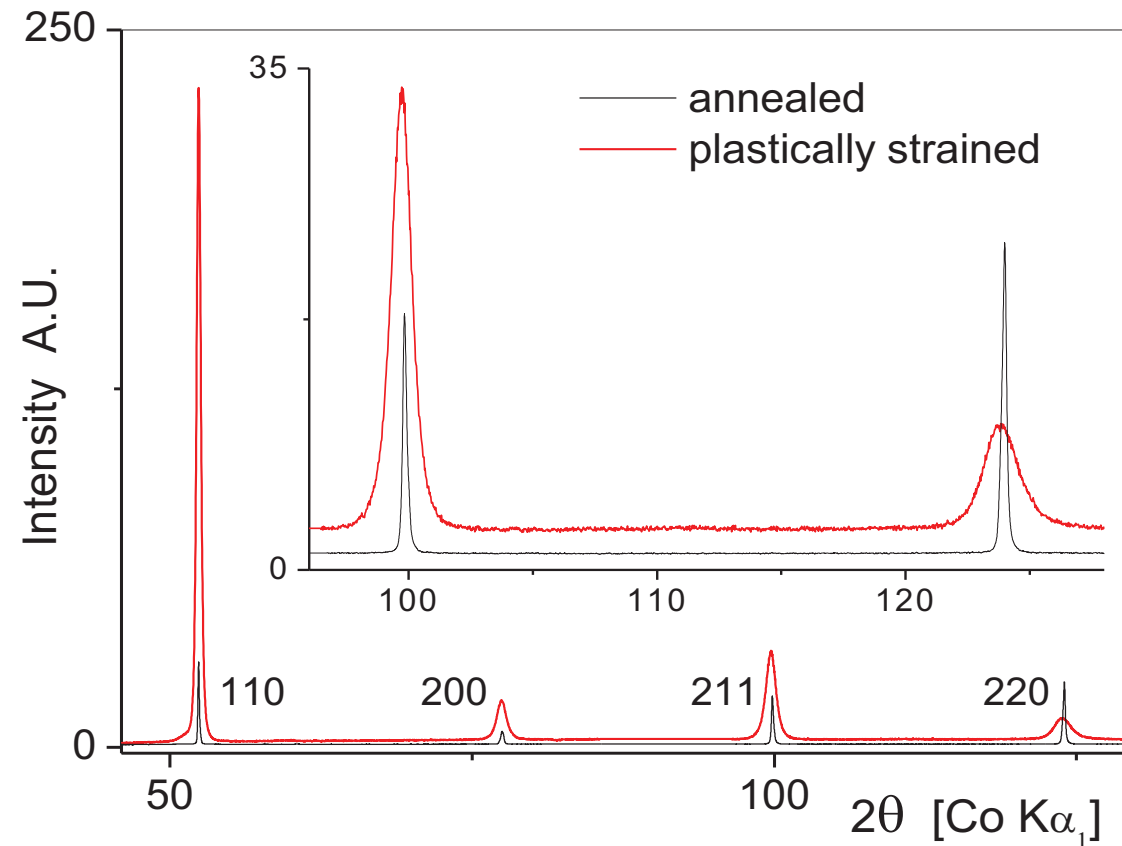


316 stainless steel

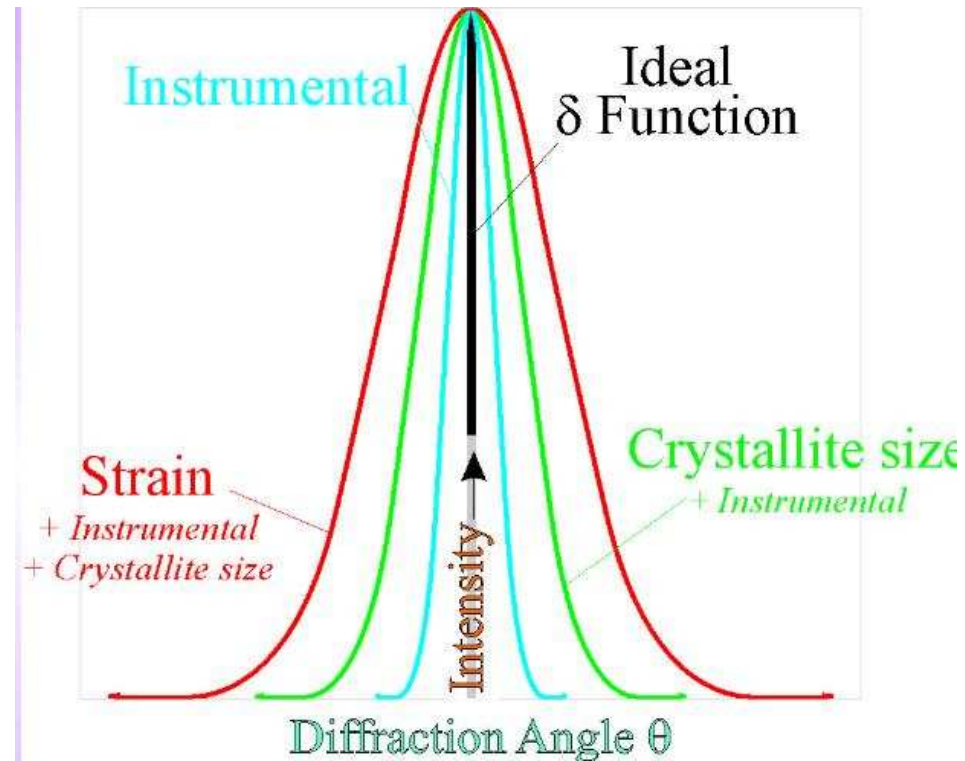
Diffraction experiments

σ_{III} : *micro-strains* (or *stresses*)

are produced by *dislocations*: peaks *broaden*



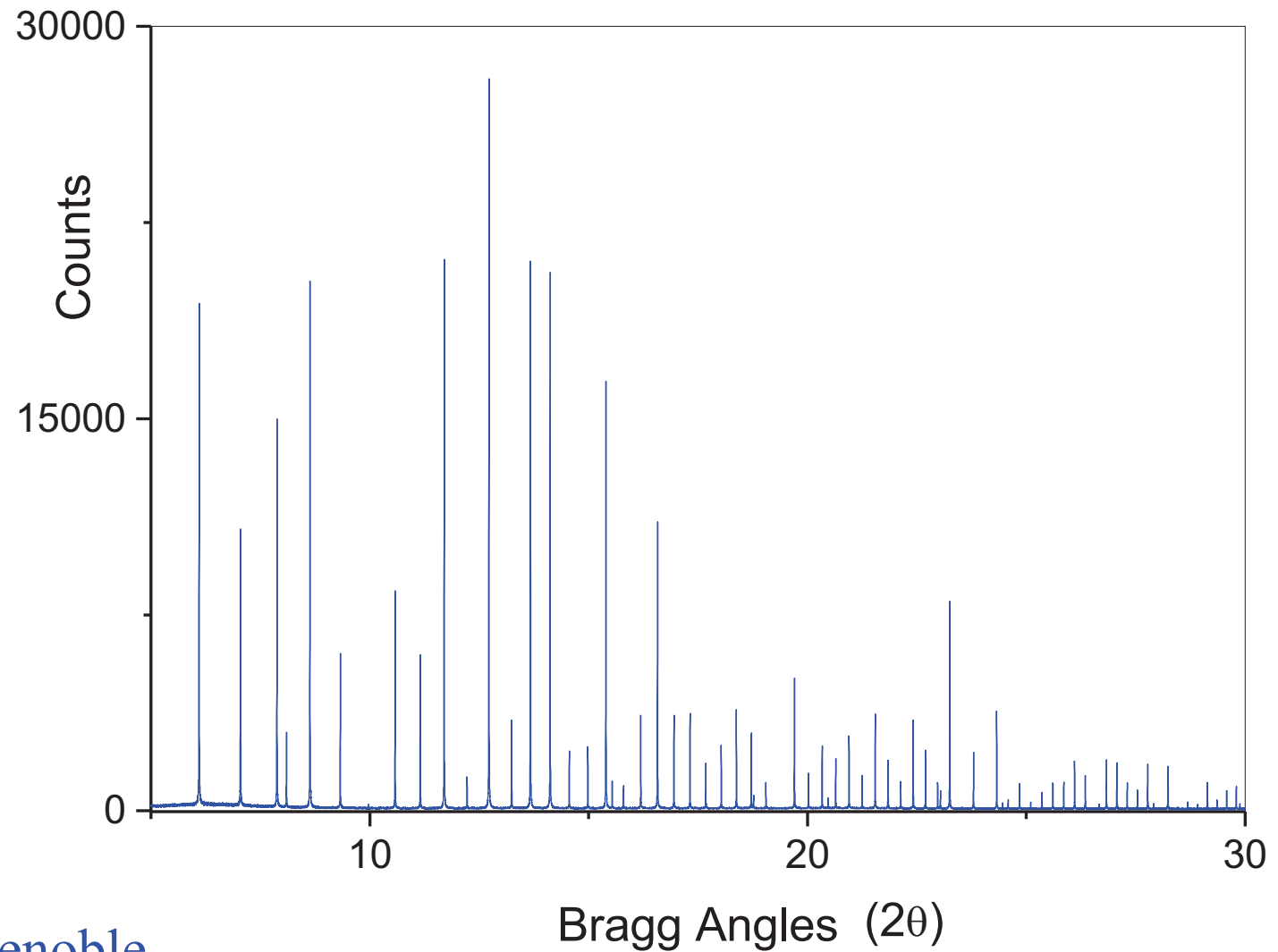
X-ray broadening sources



Fortunately the instrumental effect

- **can be small**
- **can be corrected, if necessary**

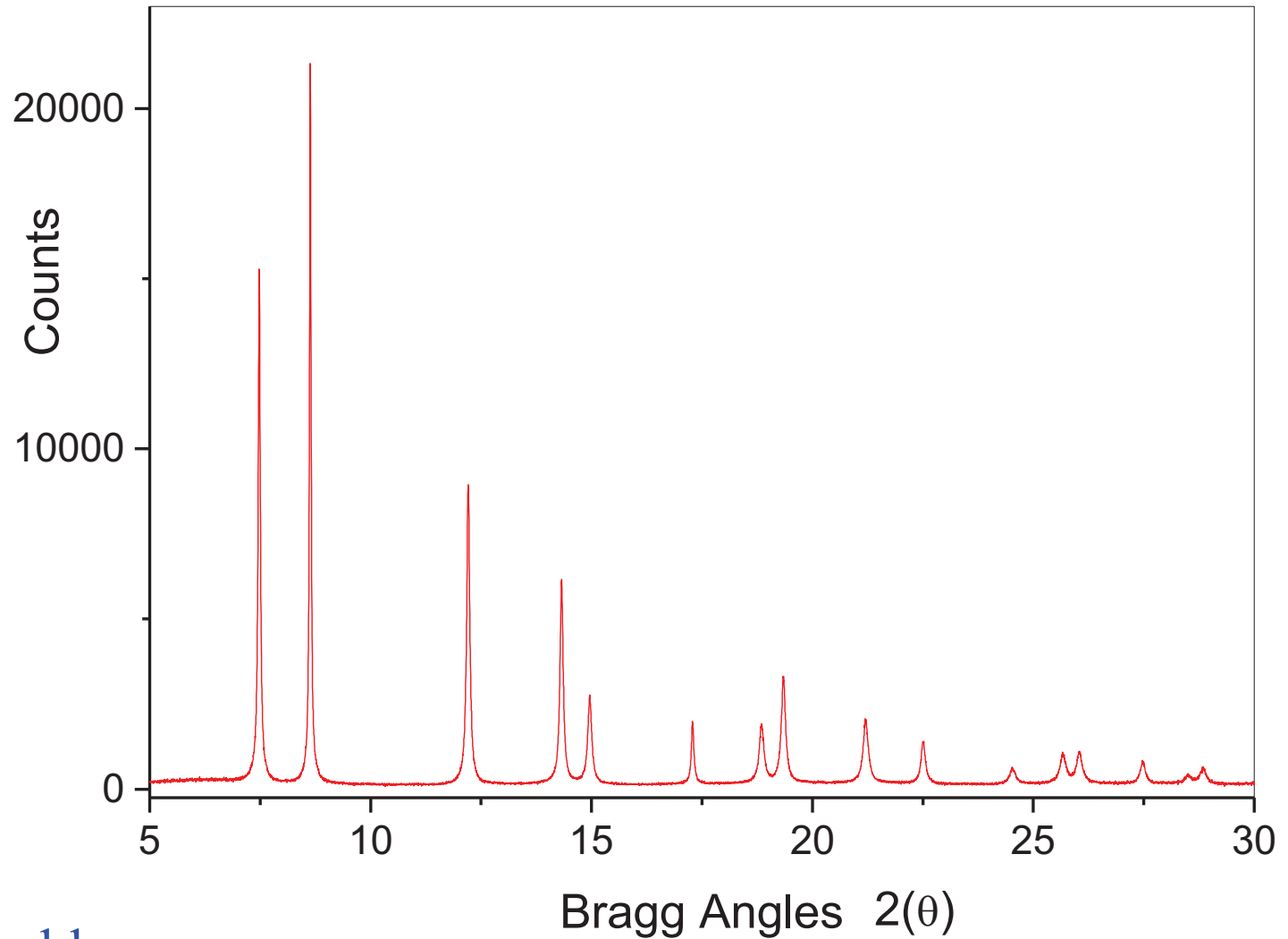
Diffraction from „perfect” crystals of LaB_6



ESRF - Grenoble

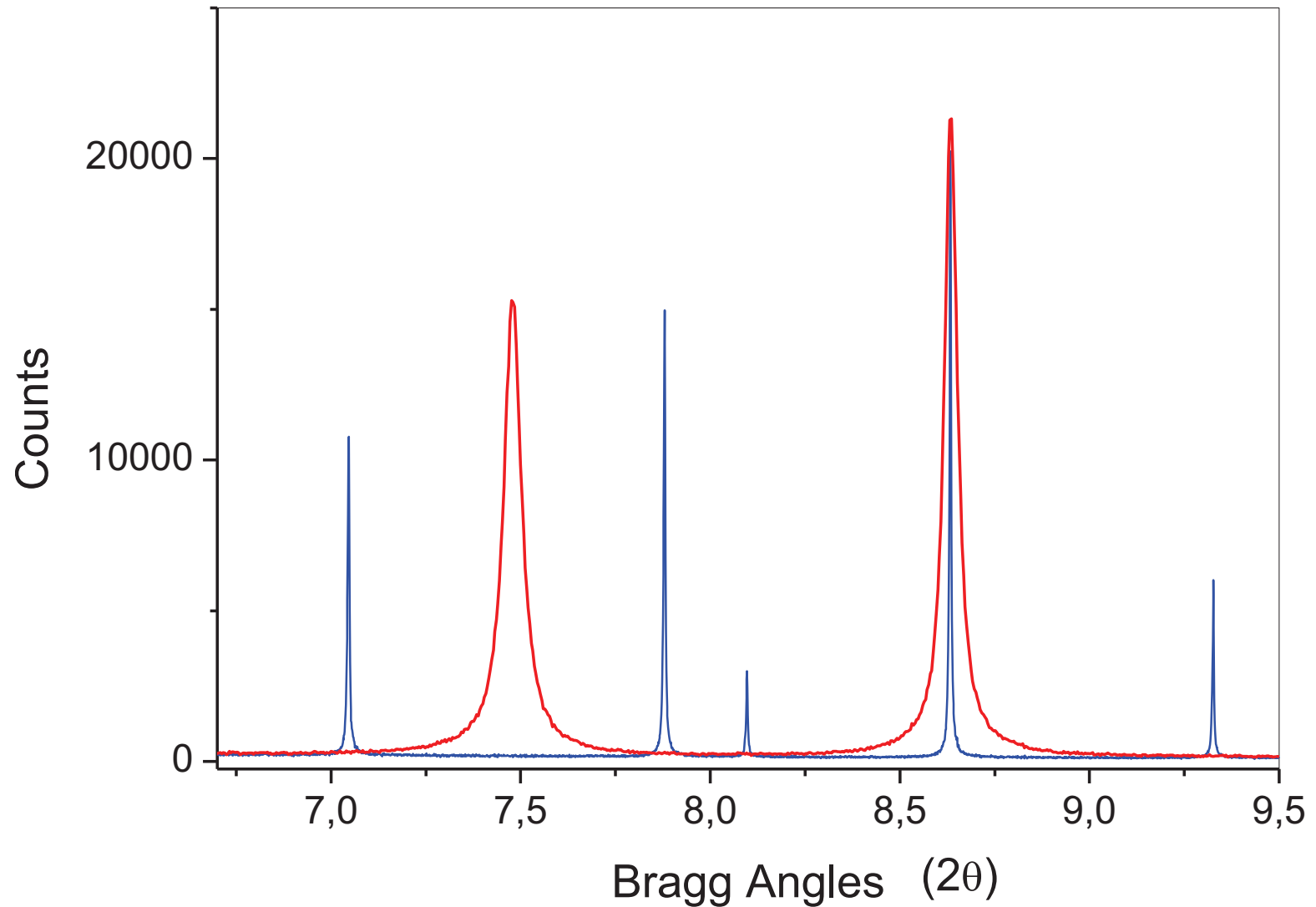
Diffraction from **PbS - Galena, grinded** for 12 hours

T. Ungár, P. Martinetto, G. Ribárik, E. Dooryhée, Ph. Walter, M. Anne, J. Appl. Phys. 91 (2002) 2455-2465.



ESRF - Grenoble

The **difference** between the **Measured** and the **Instrumental** profiles tells us the **microstructure**



The effect of crystal defects

Any combination of these:

- peak shift
- broadening
- asymmetry

[001] Cu single crystals deformed in tension

T.Ungár, H.Mughrabi, D.Roennpapel, M.Wilkens, *Acta Metall.* 32 (1984) 333.

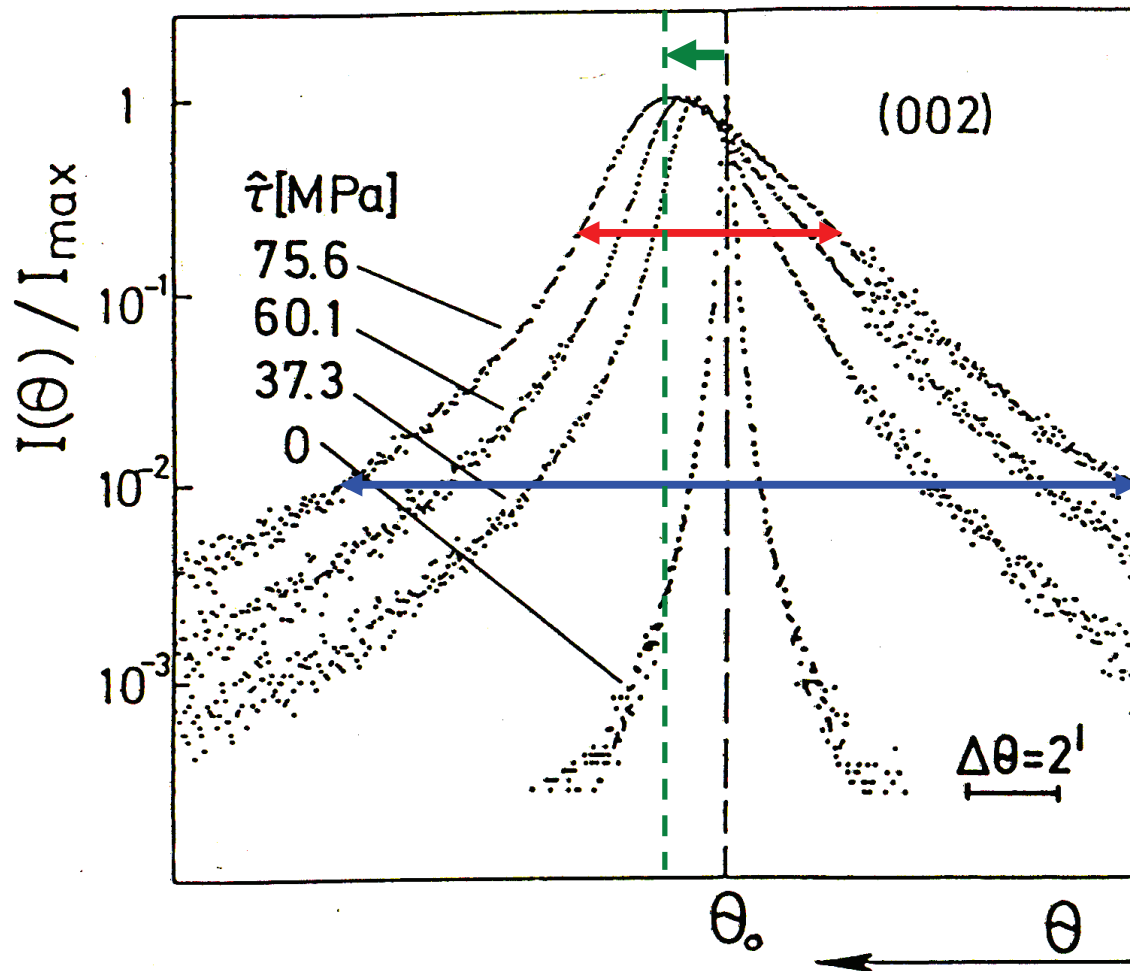
H.Mughrabi, T.Ungár, W.Kienle M.Wilkens, *Phil. Mag.* 53 (1986) 793.

(i) broadening:
dislocations

(ii) asymmetry:
internal stresses
gradient stresses

(iii) shift:
homogeneous strains
due to vacancies

(iv) background
has been subtracted



Peak shifts

internal stresses of different kinds
stacking faults,
chemical inhomogeneities

Broadening

microstrains
nanograins
subgrains
small crystallites

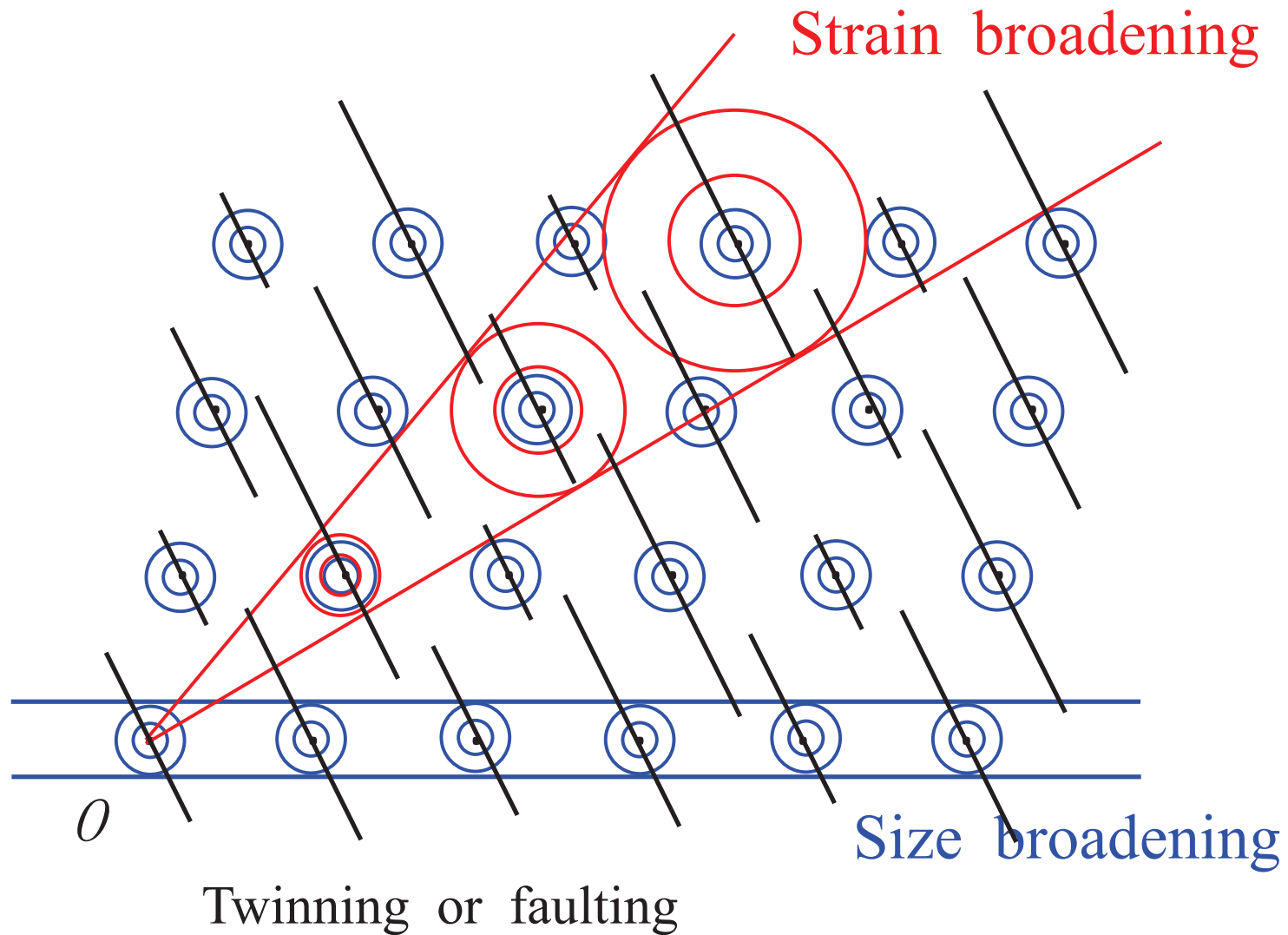
Asymmetries

internal stresses of different kinds
stacking faults,
chemical inhomogeneities

Separation of the different effects is based on

- order dependence
- *hkl* anisotropy
- profile-shape
- sub-profile displacement

Schematic picture of line broadening



Two different approaches - philosophies:

top-down

bottom-up

Top-down:

the diffraction patterns are
fitted by **analytical** profile-functions

Bottom-up:

the **profile-functions** are
created by **theoretical methods**
based on **actual lattice defects**
diffraction patterns are **fitted** by
these **defect-related profile-functions**

The $\varepsilon(\mathbf{r})$ spatial dependence of strain

0 dimensional: point defects
point-defect-type, e.g. precipitates
inclusions

$$\varepsilon(\mathbf{r}) \sim 1/r^2$$

1 dimensional: **dislocations**
non-equilibrium triple-junctions
linear-type defects

$$\varepsilon(\mathbf{r}) \sim 1/r$$

2 dimensional: planar defects, e.g. stacking faults
twin boundaries
grain boundaries
domain boundaries

$$\varepsilon(\mathbf{r}) \sim \text{constant}$$

crystal-space

versus

reciprocal-space

short distance
[m]



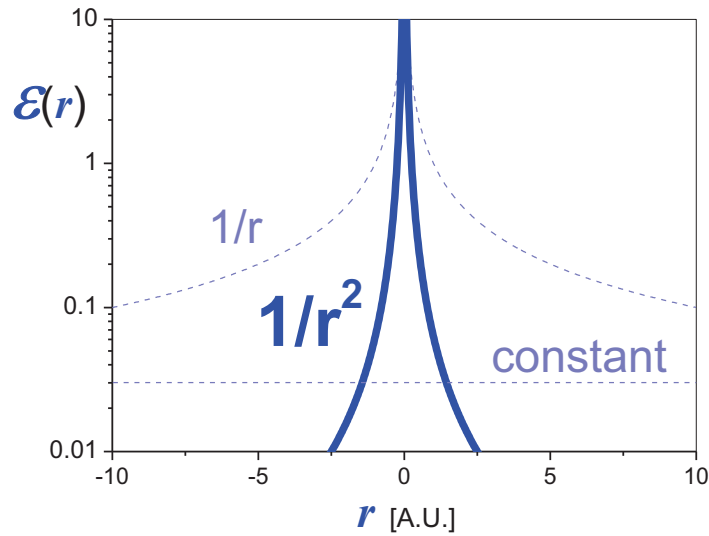
long distance
[1/m]

long distance
[m]



short distance
[1/m]

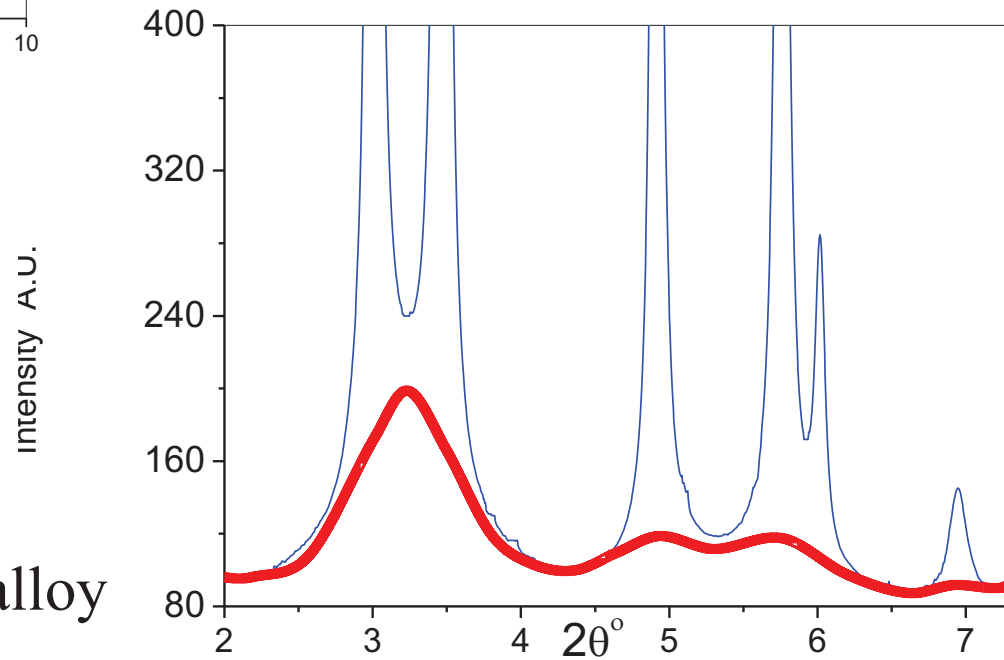
0-dimensional: point defects



crystal-space

diffraction pattern

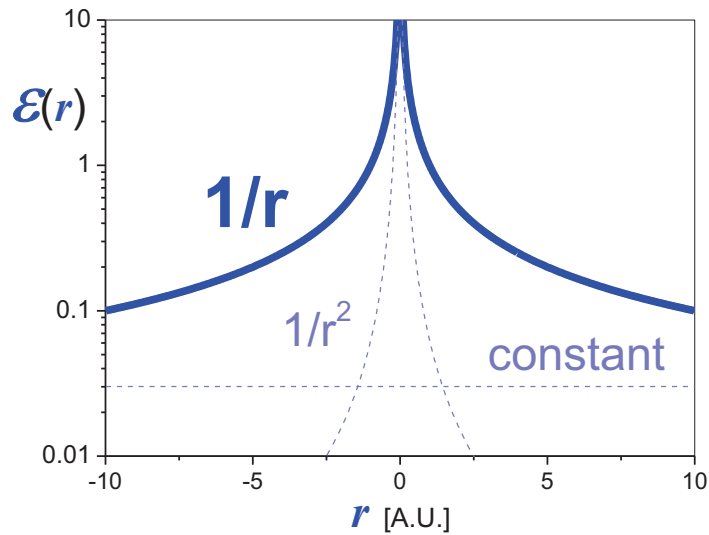
Huang-scattering



Nanocrystalline Ni-18Fe alloy
L.Li et al. ActaMater.57(2009)4988-5000

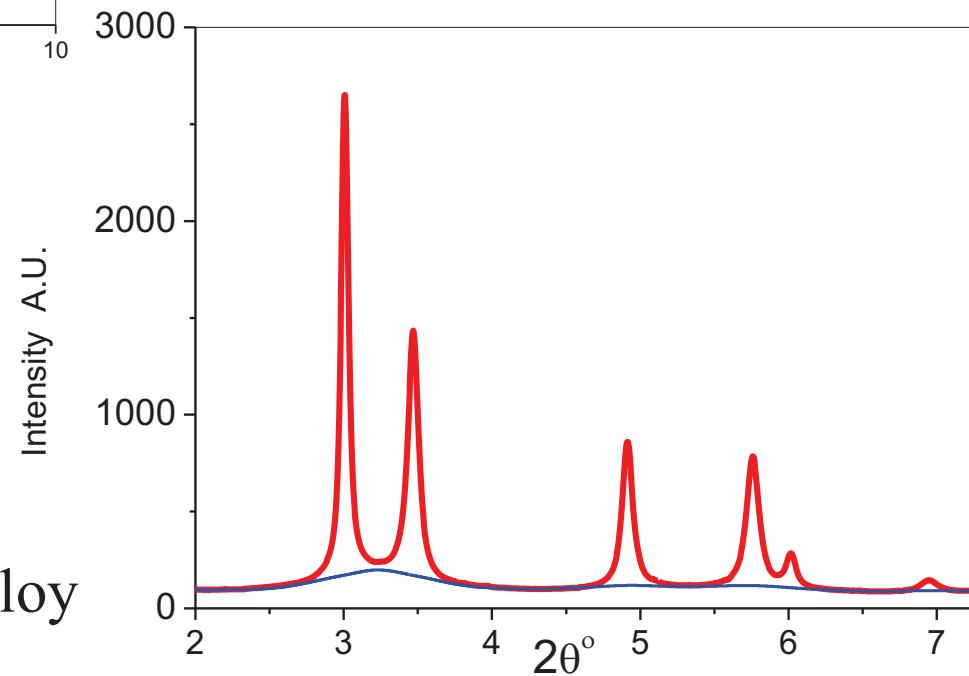
1-dimensional: linear defects: *dislocations*

line-broadening



crystal-space

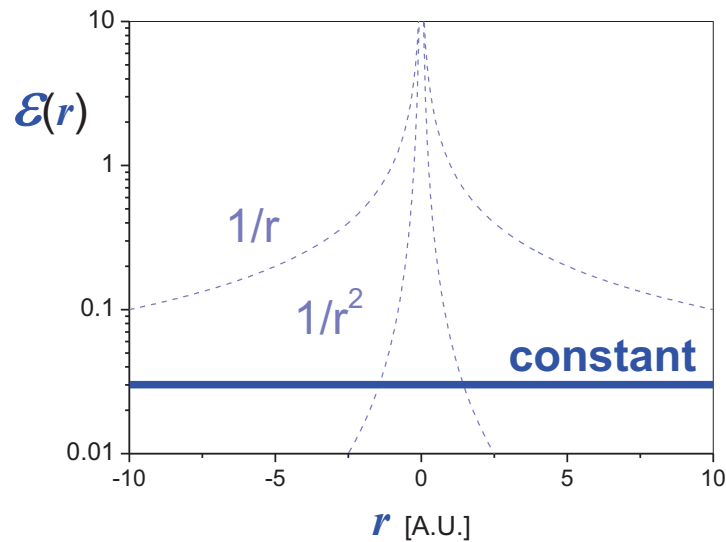
diffraction pattern



Nanocrystalline Ni-18Fe alloy
L.Li et al. ActaMater.57(2009)4988-5000

1-dimensional: planar defects: *twinning*

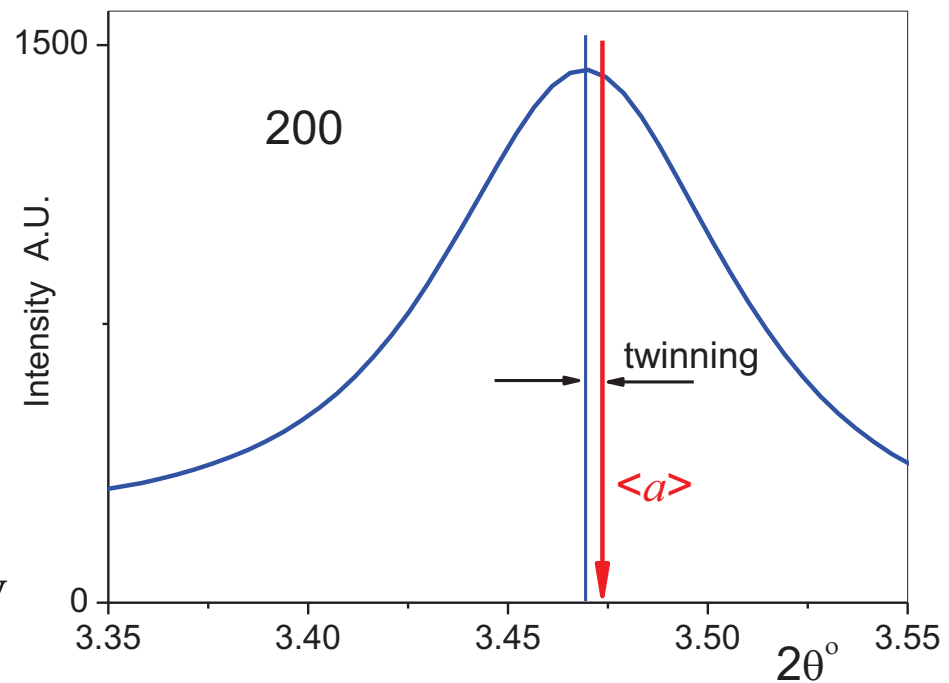
stacking faults



crystal-space

diffraction pattern

shift + *broadening*



Nanocrystalline Ni-18Fe alloy
L.Li et al. ActaMater.57(2009)4988-5000

0 dimensional: point defects
point-defect-type, e.g. precipitates
inclusions

$$\varepsilon(r) \sim 1/r^2$$

1 dimensional: **dislocations**
non-equilibrium triple-junctions
linear-type defects

$$\varepsilon(r) \sim 1/r$$

2 di

lattice defects

which cause strain broadening

domain boundaries

$$\varepsilon(r) \sim \text{constant}$$

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:

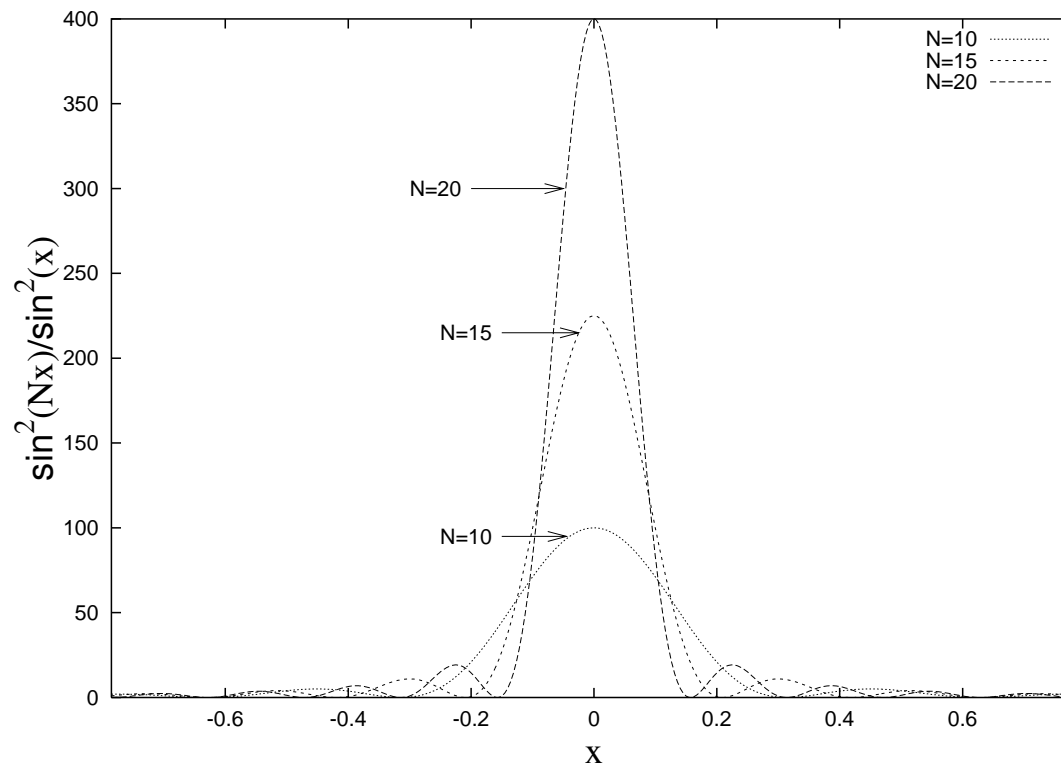
$$I(s) \sim \frac{\sin^2(Nx)}{\sin^2(x)}, \quad (1)$$

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:

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



The size effect

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

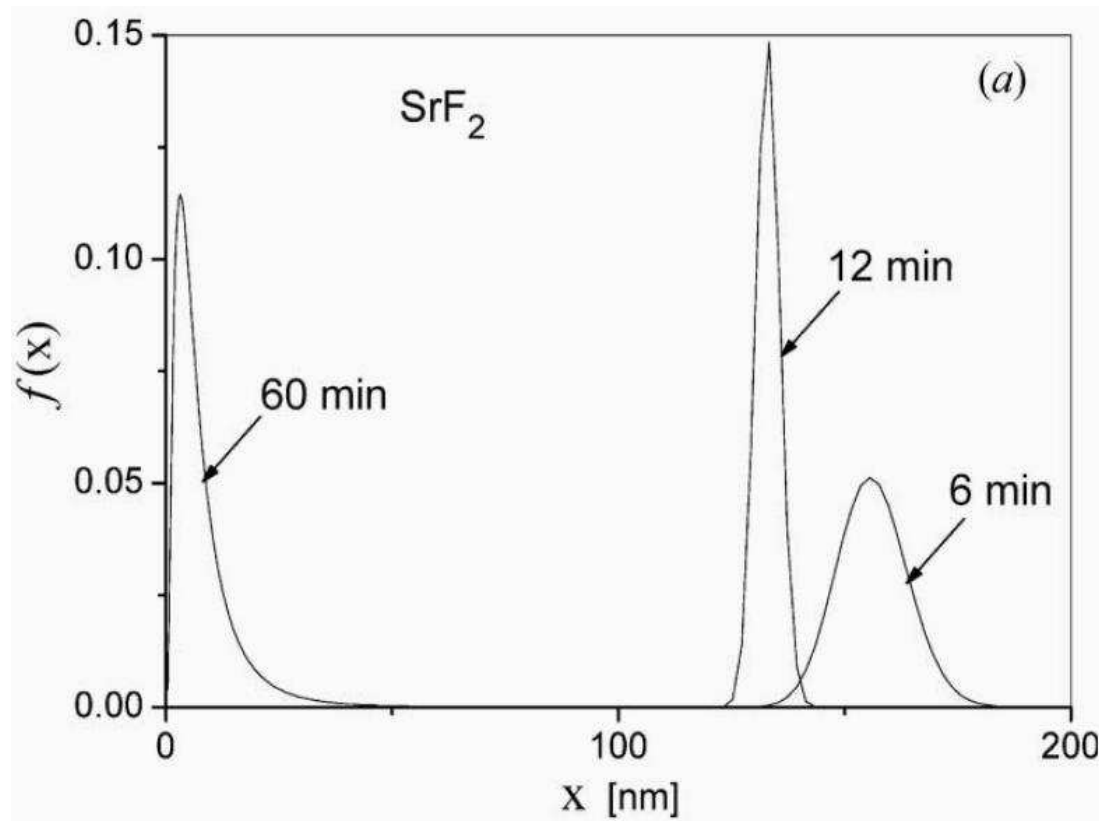
- spherical crystallites
- lognormal $f(x)$ size distribution density function:

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

(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:

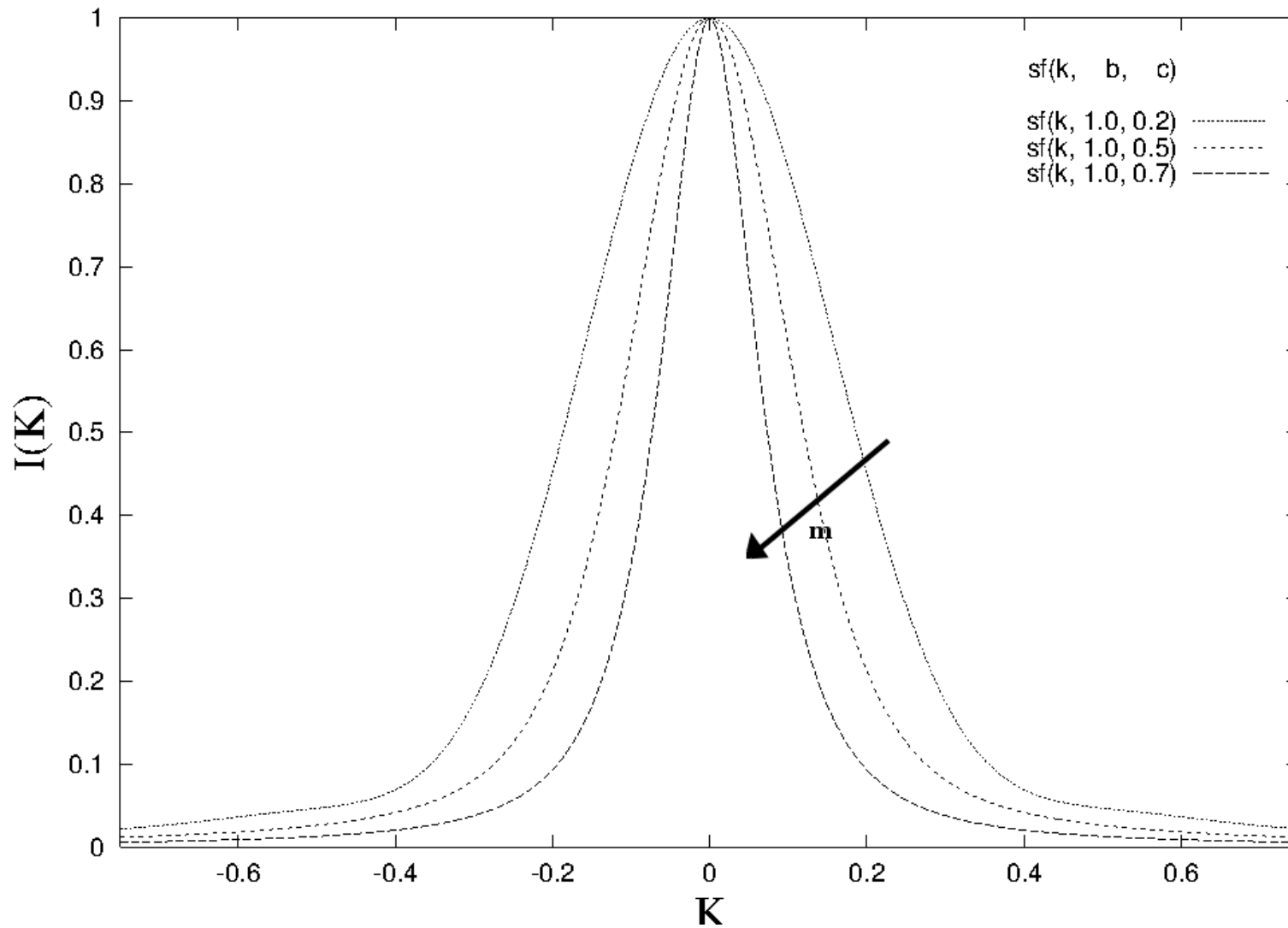
$$I^S(s) = \int_0^{\infty} \mu \frac{\sin^2(\mu \pi s)}{(\pi s)^2} \operatorname{erfc} \left[\frac{\log \left(\frac{\mu}{m} \right)}{\sqrt{2}\sigma} \right] d\mu,$$

where erfc is the complementary error function, defined as:

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt. \quad (3)$$

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:

$$A^S(L, m, \sigma) = \frac{m^3 \exp\left(\frac{9}{4}(\sqrt{2}\sigma)^2\right)}{3} \operatorname{erfc}\left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \frac{3}{2}\sqrt{2}\sigma\right] -$$
$$\frac{m^2 \exp(\sqrt{2}\sigma)^2}{2} |L| \operatorname{erfc}\left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \sqrt{2}\sigma\right] +$$
$$\frac{|L|^3}{6} \operatorname{erfc}\left[\frac{\log\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma}\right].$$

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.

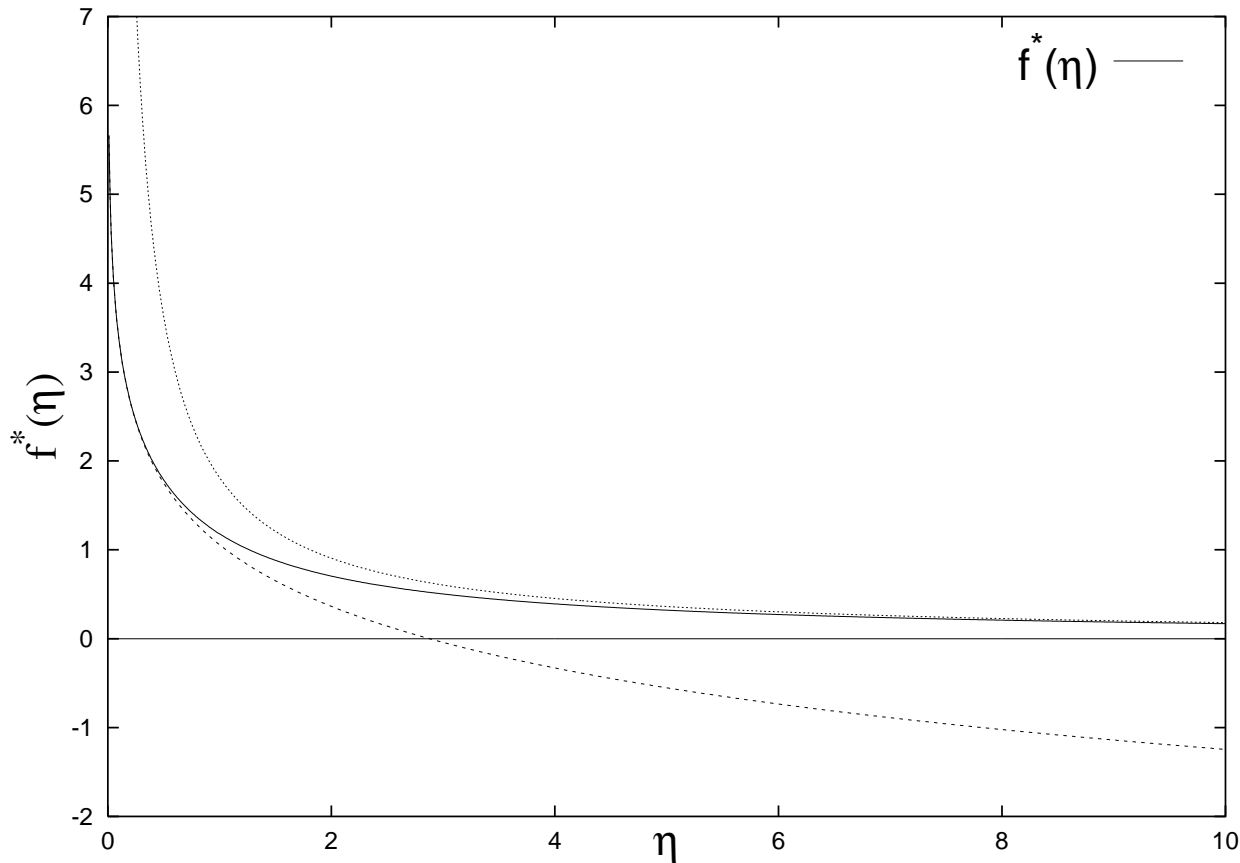
The meaning of the restrictedly random distribution of the Wilkens model:

- 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:

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

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

Wilkins introduced M^* , a dimensionless parameter:

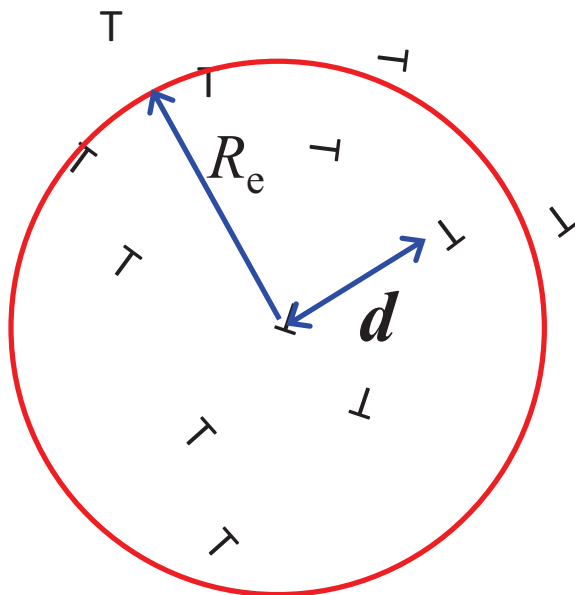
$$M^* = R_e^* \sqrt{\rho}$$

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

Dislocation arrangement parameter

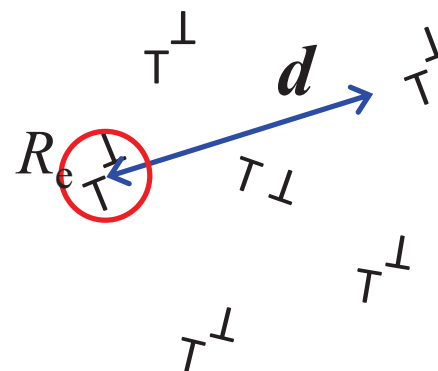
random



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

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

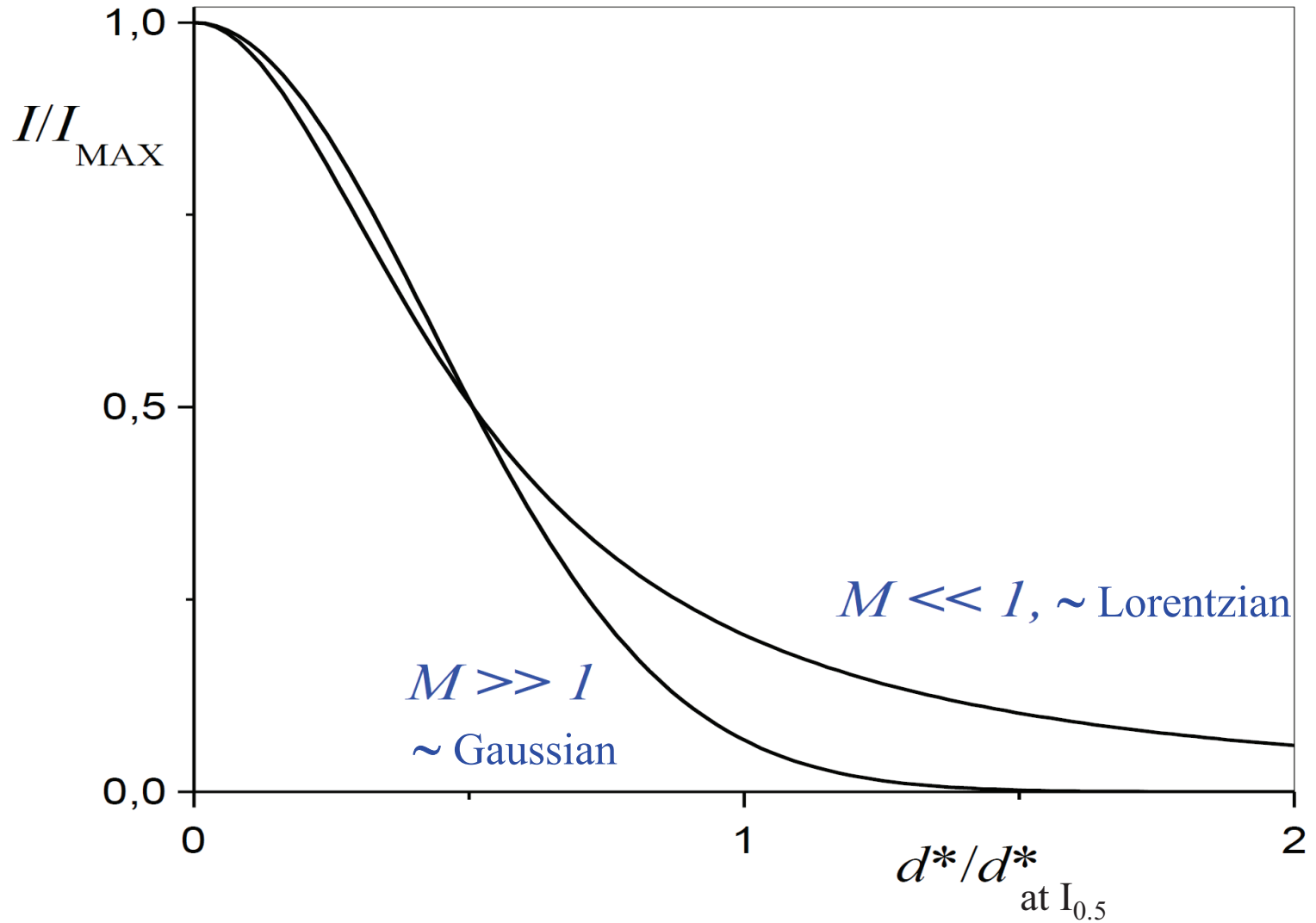
highly correlated



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

$$\mathbf{M} = R_e \rho^{1/2} \ll \mathbf{1}$$

shape of strain-profiles



Strain anisotropy

A dislocation with $\mathbf{g}\mathbf{b} = 0$ 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 \mathbf{b} , \mathbf{n} , \mathbf{l} and \mathbf{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

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

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).

CMWP method for LPA

Microstructural parameters for size and strain effect:

- size: m, σ
- dislocations: ρ, M, q (or q_1, q_2)
- planar faults: α

The measured and theoretical patterns are compared using a nonlinear least-squares algorithm.

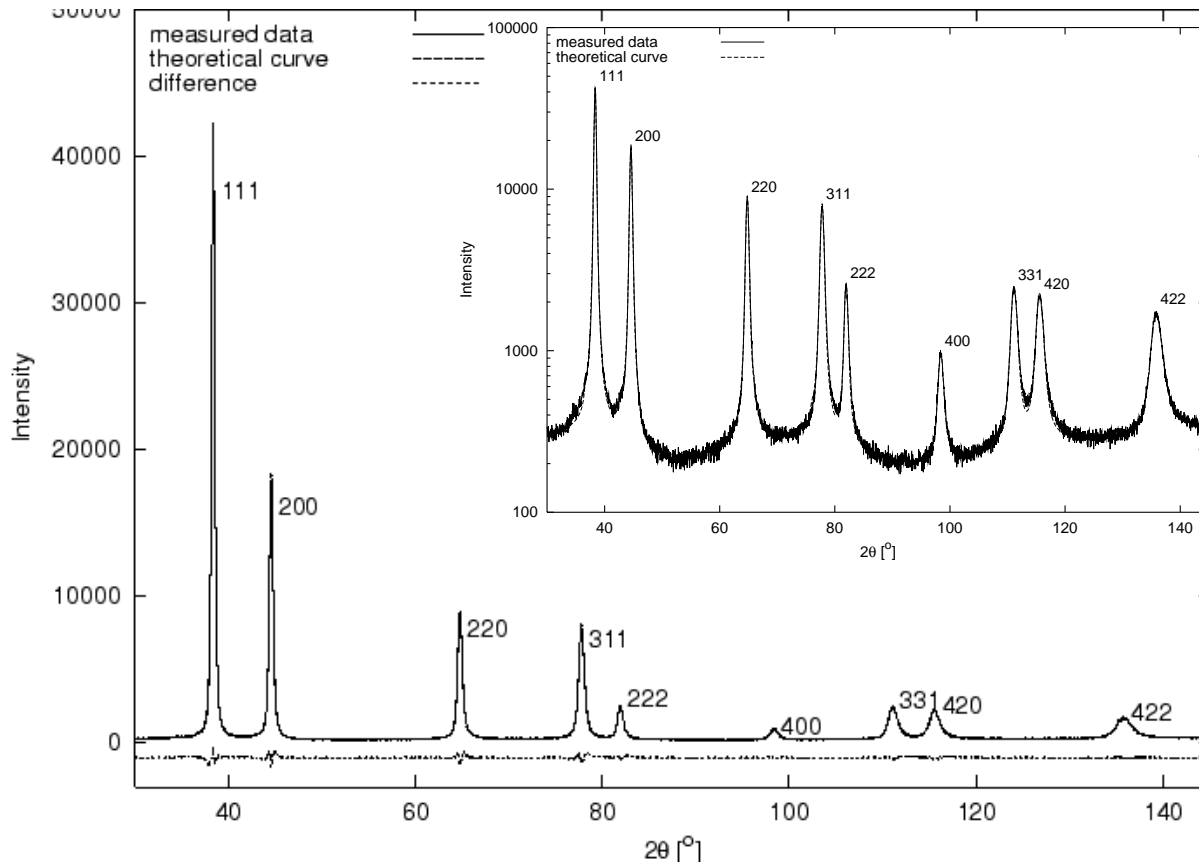
$$I_{theoretical} = BG(2\Theta) + \sum_{hkl} I_{MAX}^{hkl} I^{hkl} (2\Theta - 2\Theta_0^{hkl}),$$

where:

$$I^{hkl} = I_{instr.}^{hkl} * I_{size}^{hkl}(m, \sigma) * I_{disl.}^{hkl}(\rho, q, R_e) * I_{pl.faults}^{hkl}(\alpha),$$

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

CMWPF fit example



Results of the
CMWPF fit:

$$m = 21\text{nm}$$

$$\sigma = 0.36$$

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

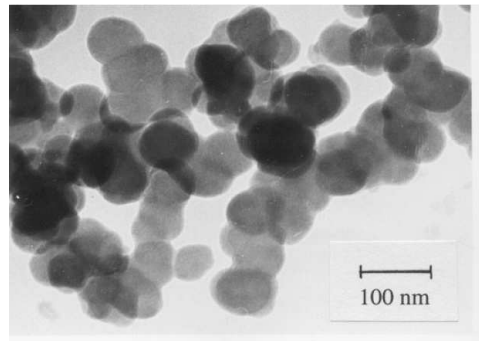
$$M = R_e \sqrt{\rho} = 1.3$$

$$q = 1.3$$

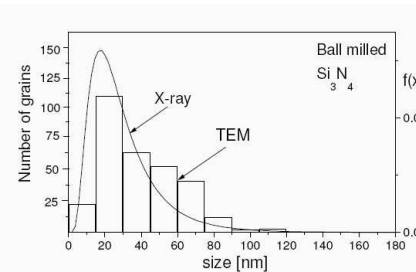
The measured (solid lines) and theoretical fitted (dashed lines) intensity patterns for Al-6Mg sample ball milled for 6 hours as a function of 2θ . The same figure is plotted in logarithmic scale in the upper-right corner.

Comparing CMWP results to TEM

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



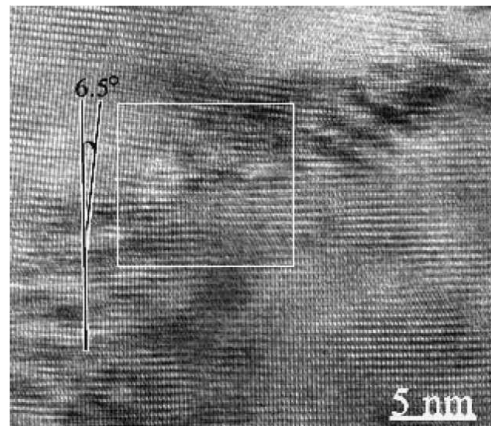
a)



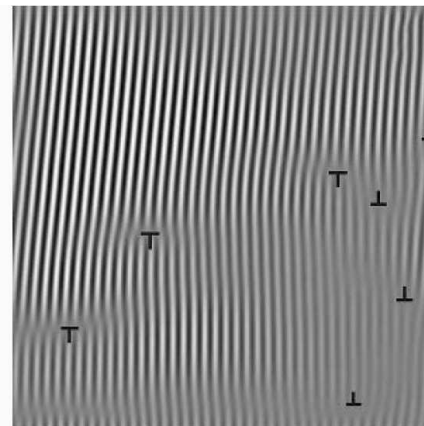
b)

Example for Ti: a local dislocation density can be estimated

$$\left(\rho \approx \frac{7}{12^2 \text{nm}^2}\right)$$



a)

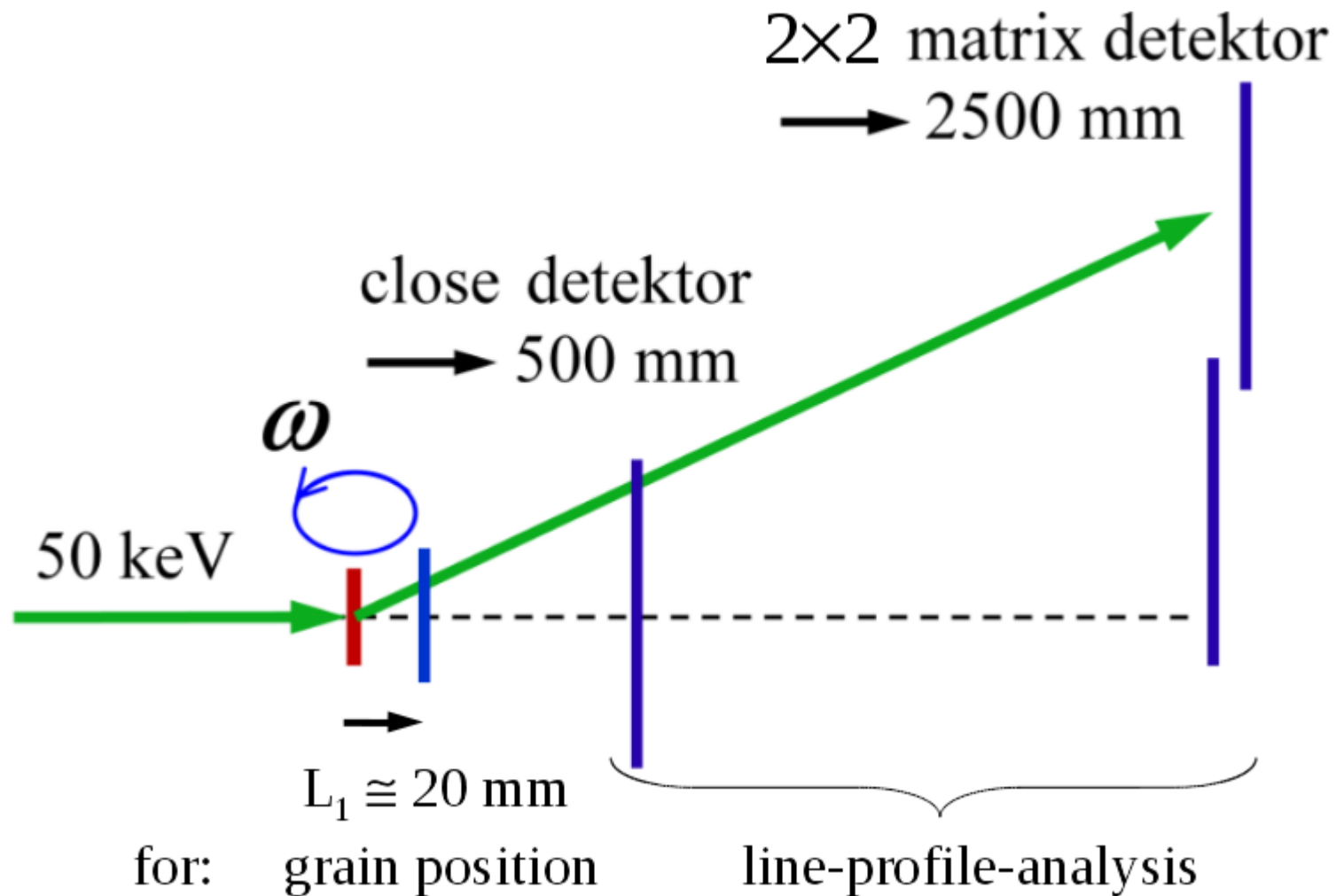


b)

3D experiments

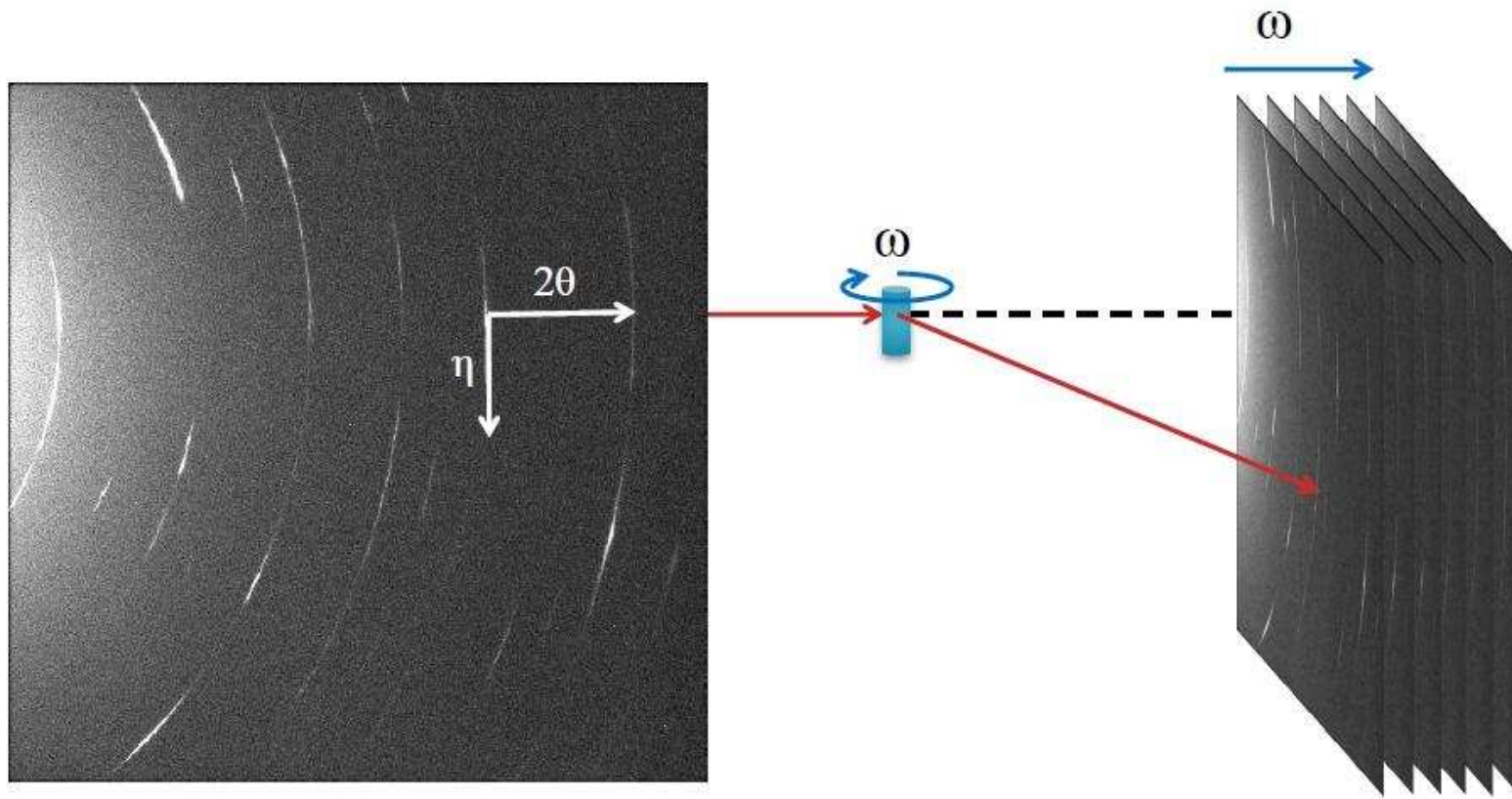
- XLPA (X-ray Line Profile Analysis): connection between microstructure and line profiles
 - determining average size and strain based on line broadening (modified Williamson-Hall method)
 - bottom-up procedure based on analytical models: CMWP method based on microstructural parameters and ab-initio profiles
 - some cases the microstructure is more complex, a special model is needed
- 3D synchrotron experiments provide 3D profiles: extract more information from the measurements

3DXRD setup for LPA



3D profiles

3D intensity profile ($2\theta, \eta, \omega$) $\xrightarrow{\text{Integration}}$ 1D line profile (2θ)



FFT based method for LPA

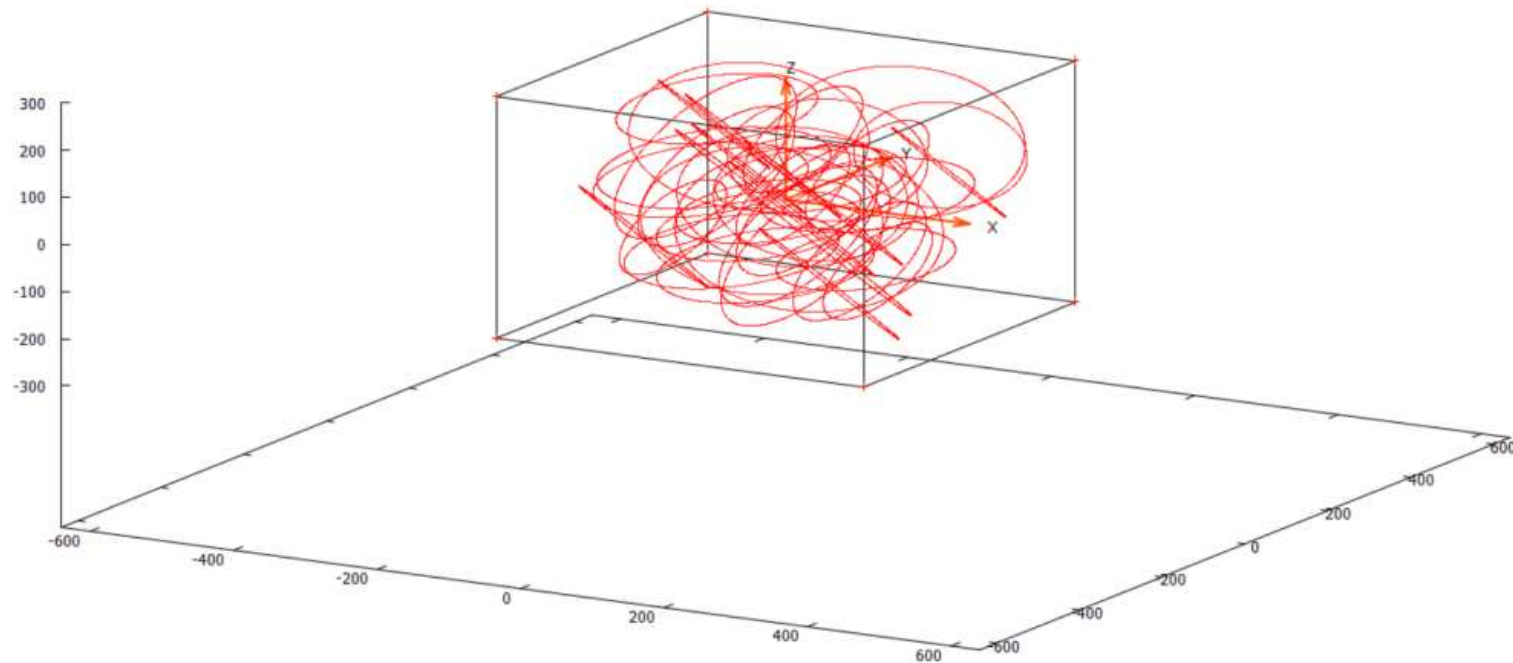
In this case the microstructure is known, it's the input of the method, however some preliminary information e.g. electron microscopy is needed.

The steps of the method:

- input: eigenstrains based on 3D microstructure
- relaxation: solving the stress-strain relation
- calculating the displacement field, then line profiles

It can be used for modeling 3D line profiles.

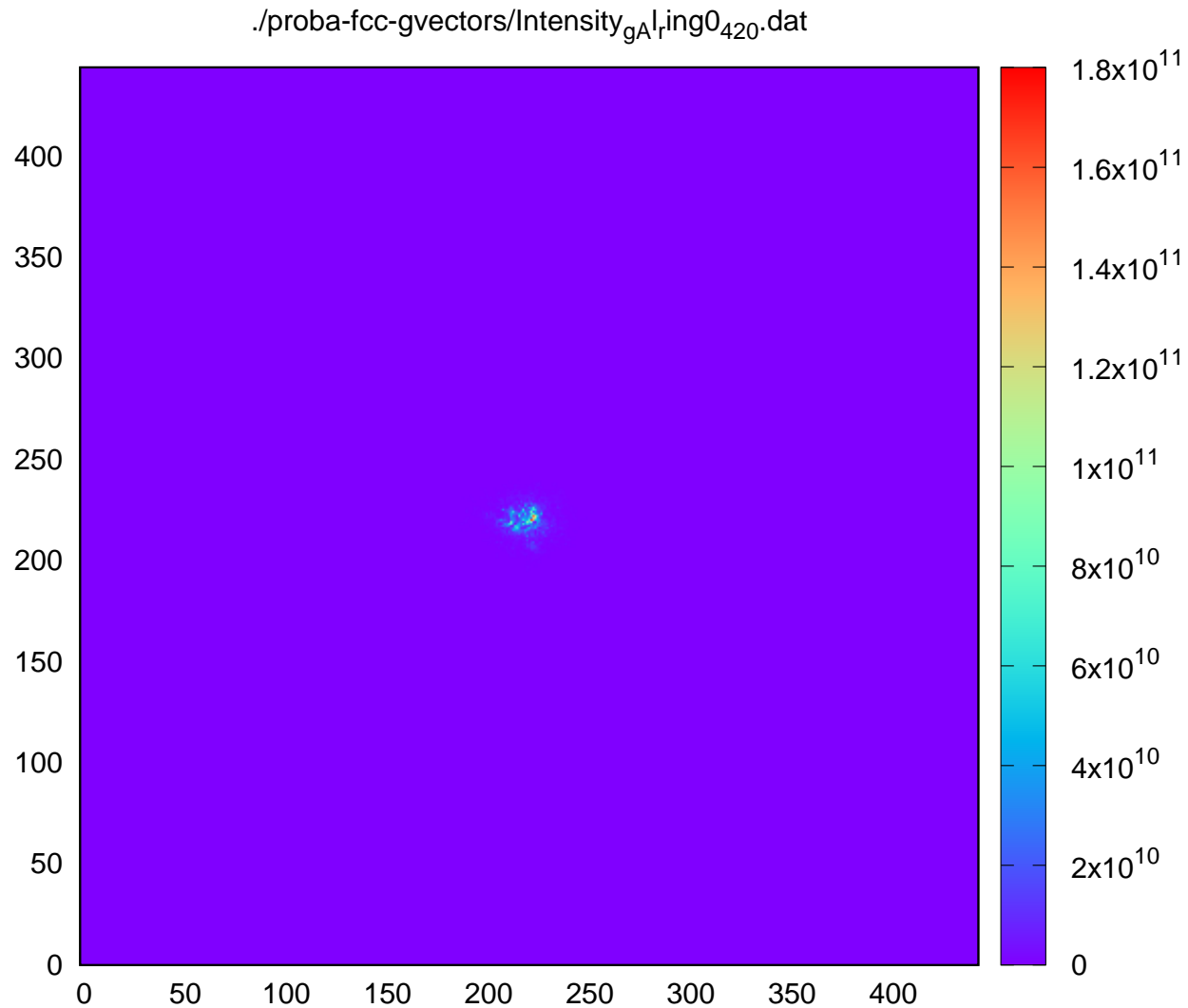
Example input: fcc Al, N=512, $0.5\mu\text{m}$



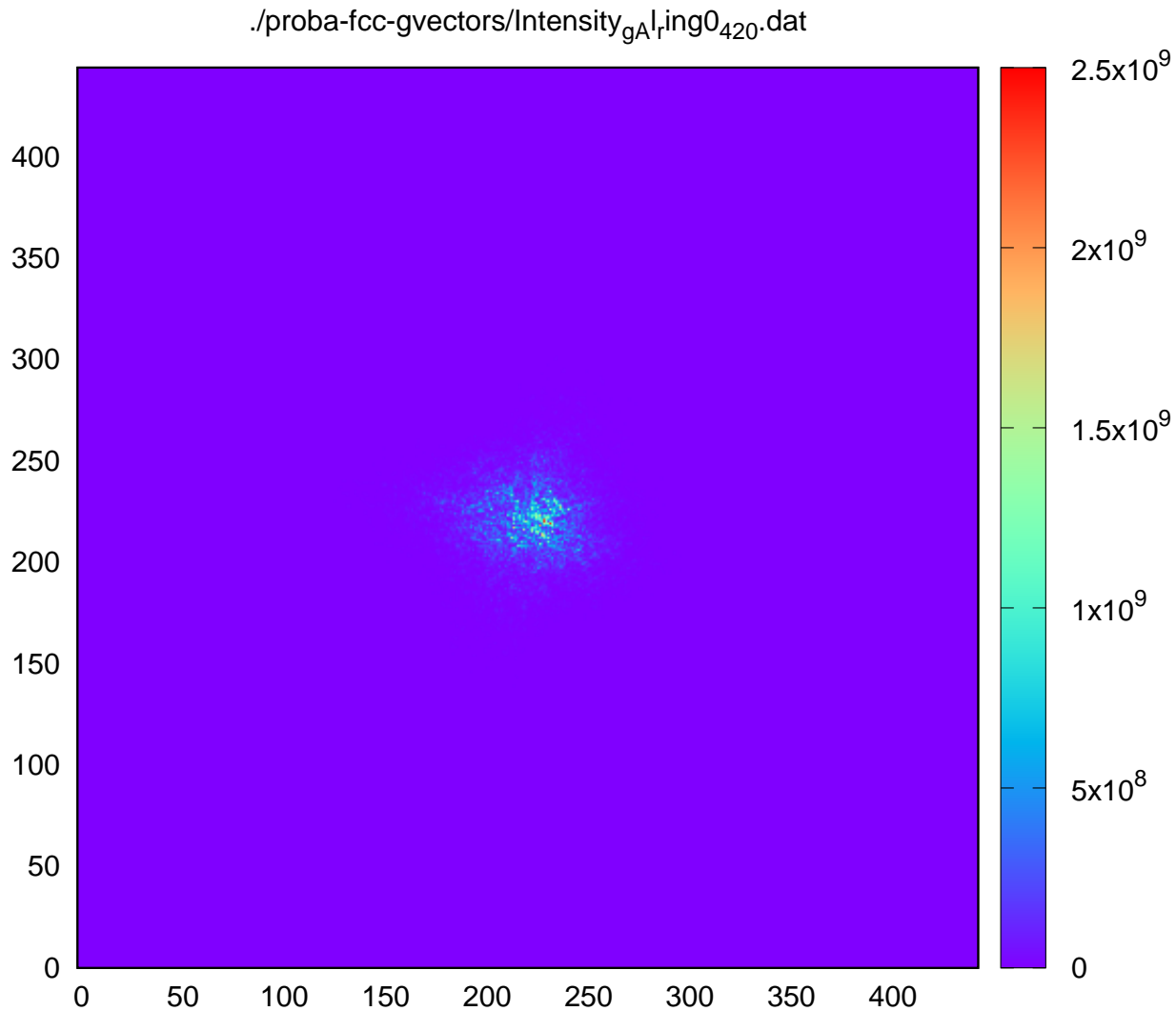
Output, solution files

- mechanical fields: 3D stress-strain-displacement field data
- X-ray output files: 3D-s line profiles, visualisation:
 - analysing 3D-s intensity distributions by slicing (in the case of modeling, the x-y-z resolutions are the same so the voxels are cubes, in the case of 3D synchrotron measurements, the ω resolution is usually weak, this means that the voxels are prolonged bricks)
 - 3D amplitude and phase distributions can also be calculated
 - 1D line profiles and 2D rocking curves

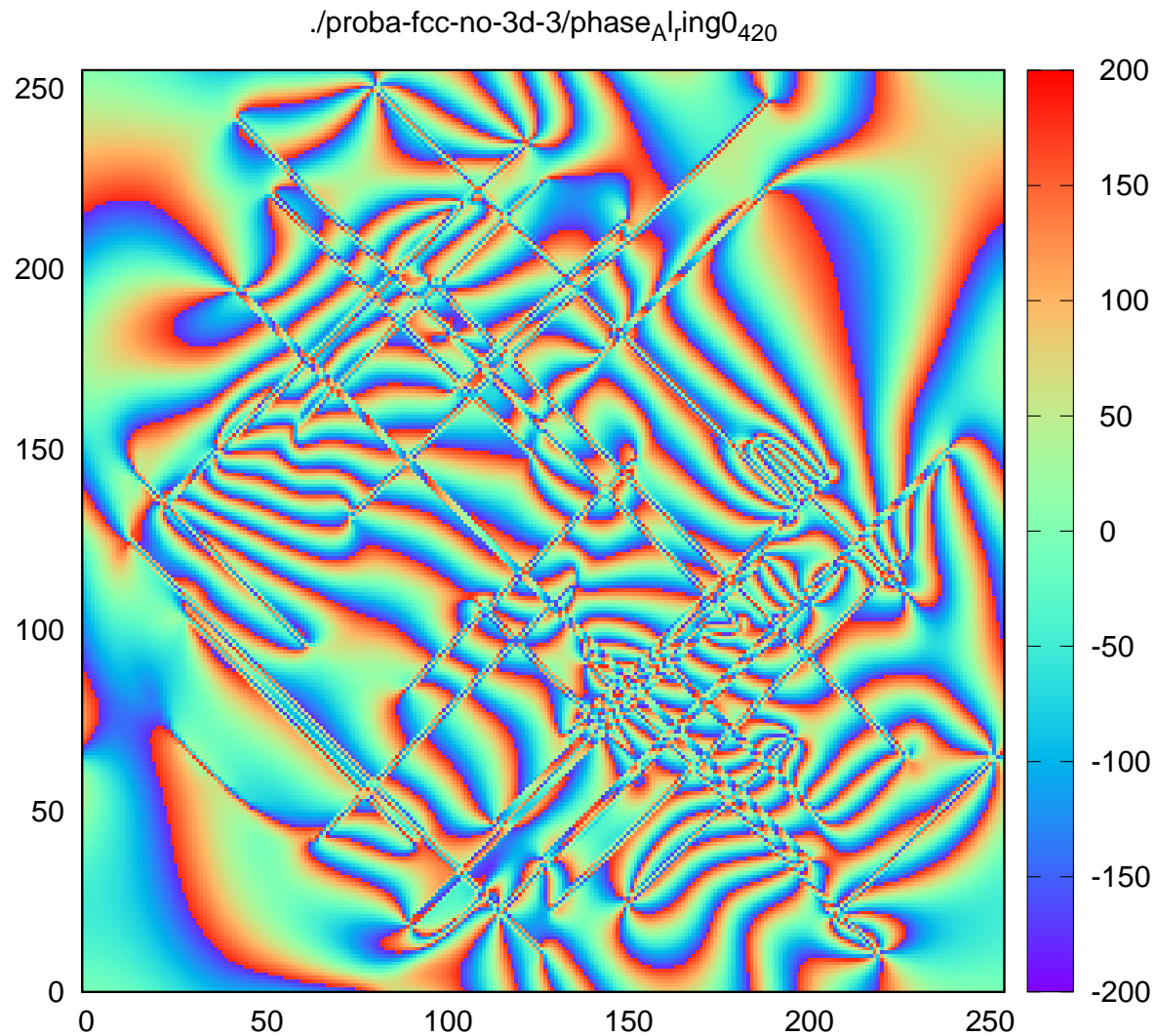
Example output: Al 420 $I_g(222, y, z)$



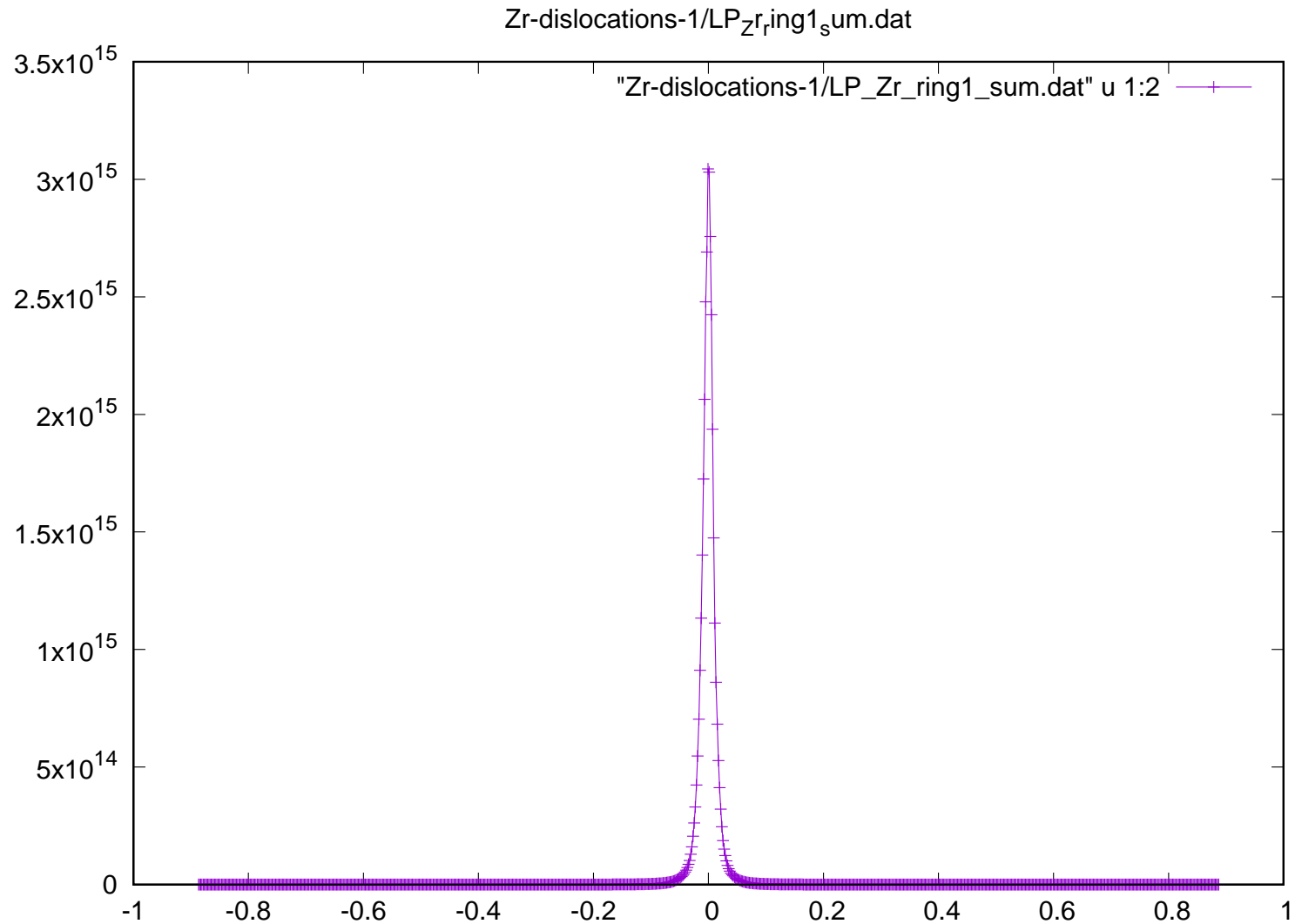
Example output: Al 420 $I_g(202, y, z)$



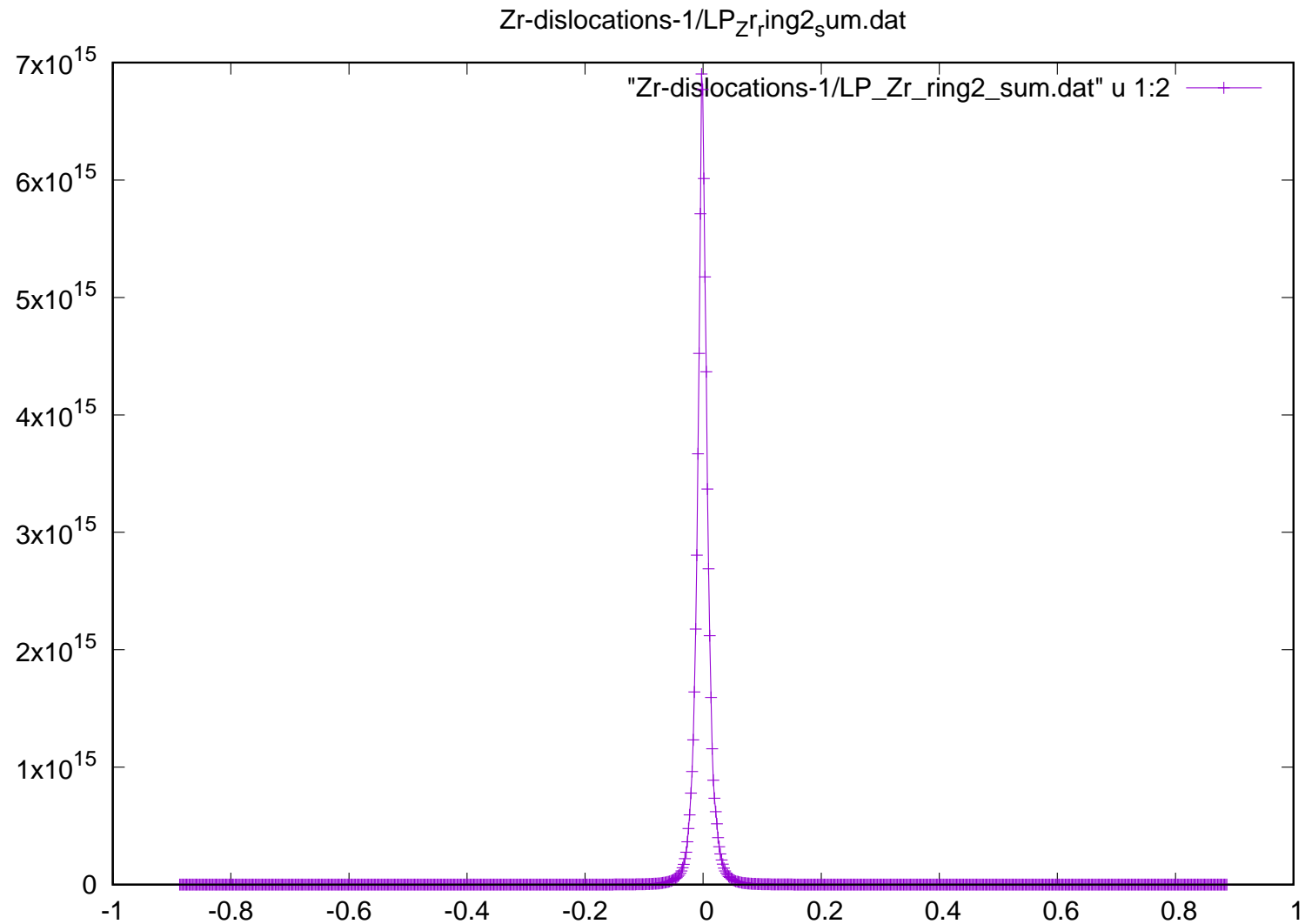
Example for phase: Al 420 $\varphi(128, y, z)$



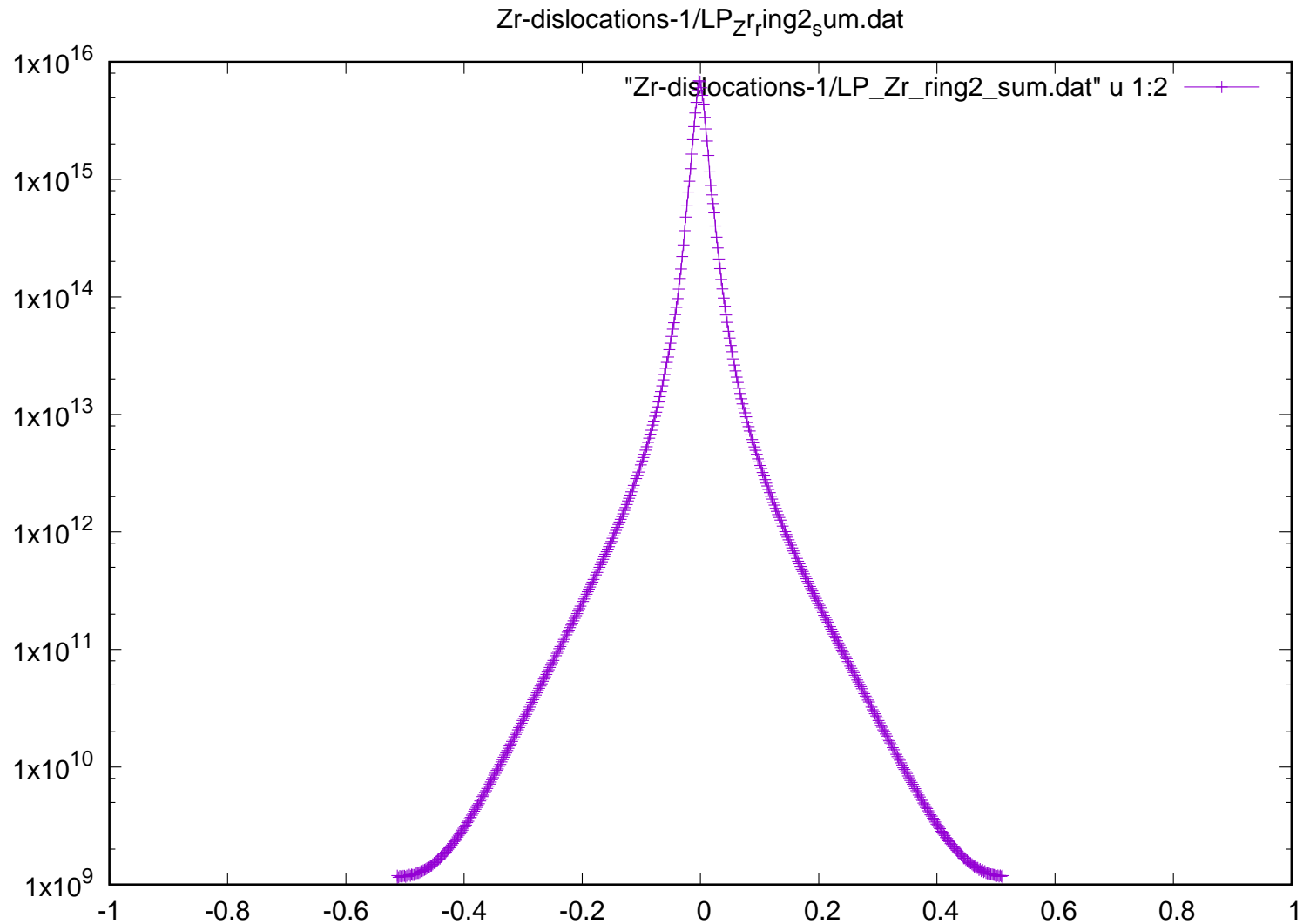
LP Zr (c-loops) 10.0



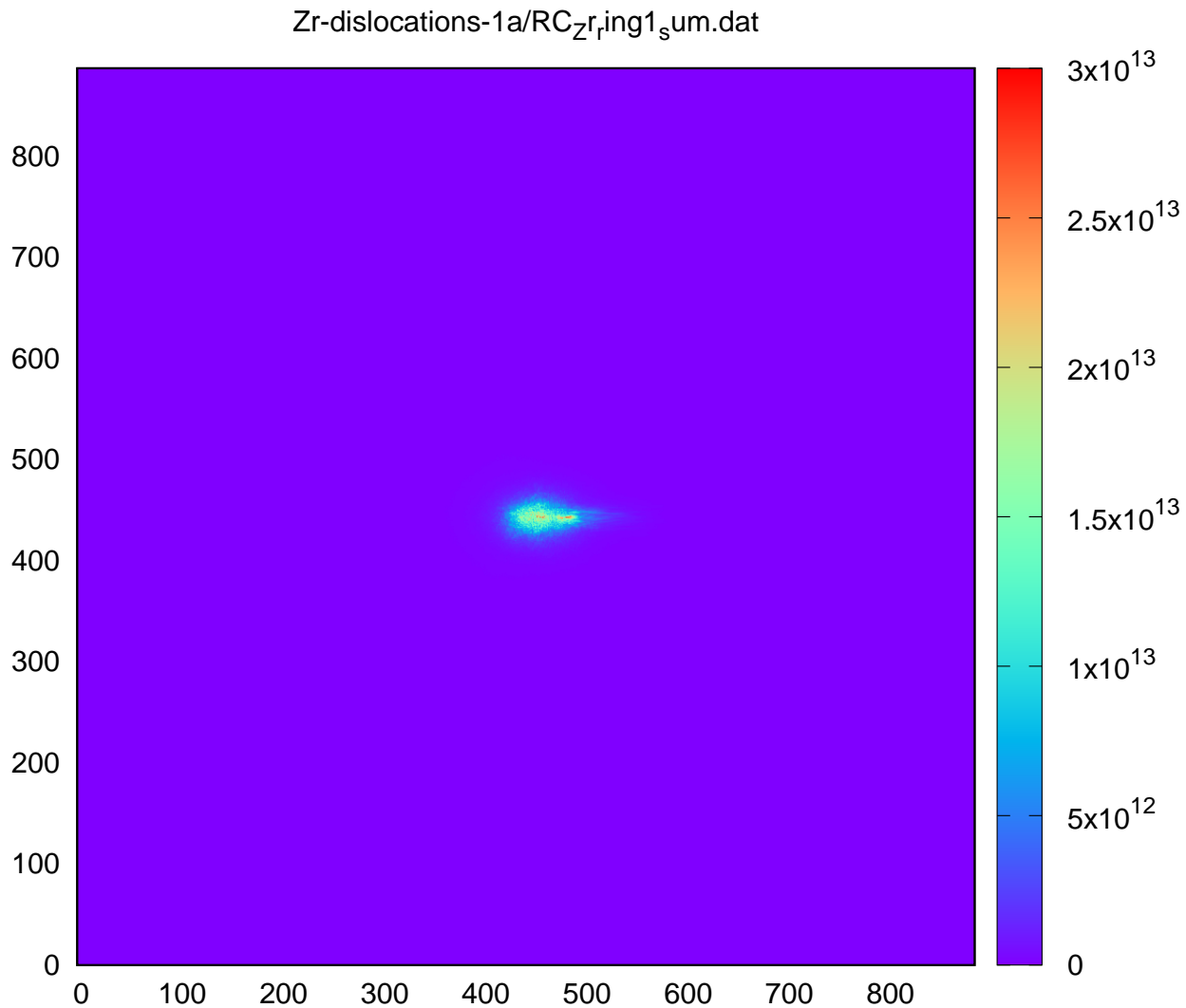
LP Zr (c-loops) 00.2



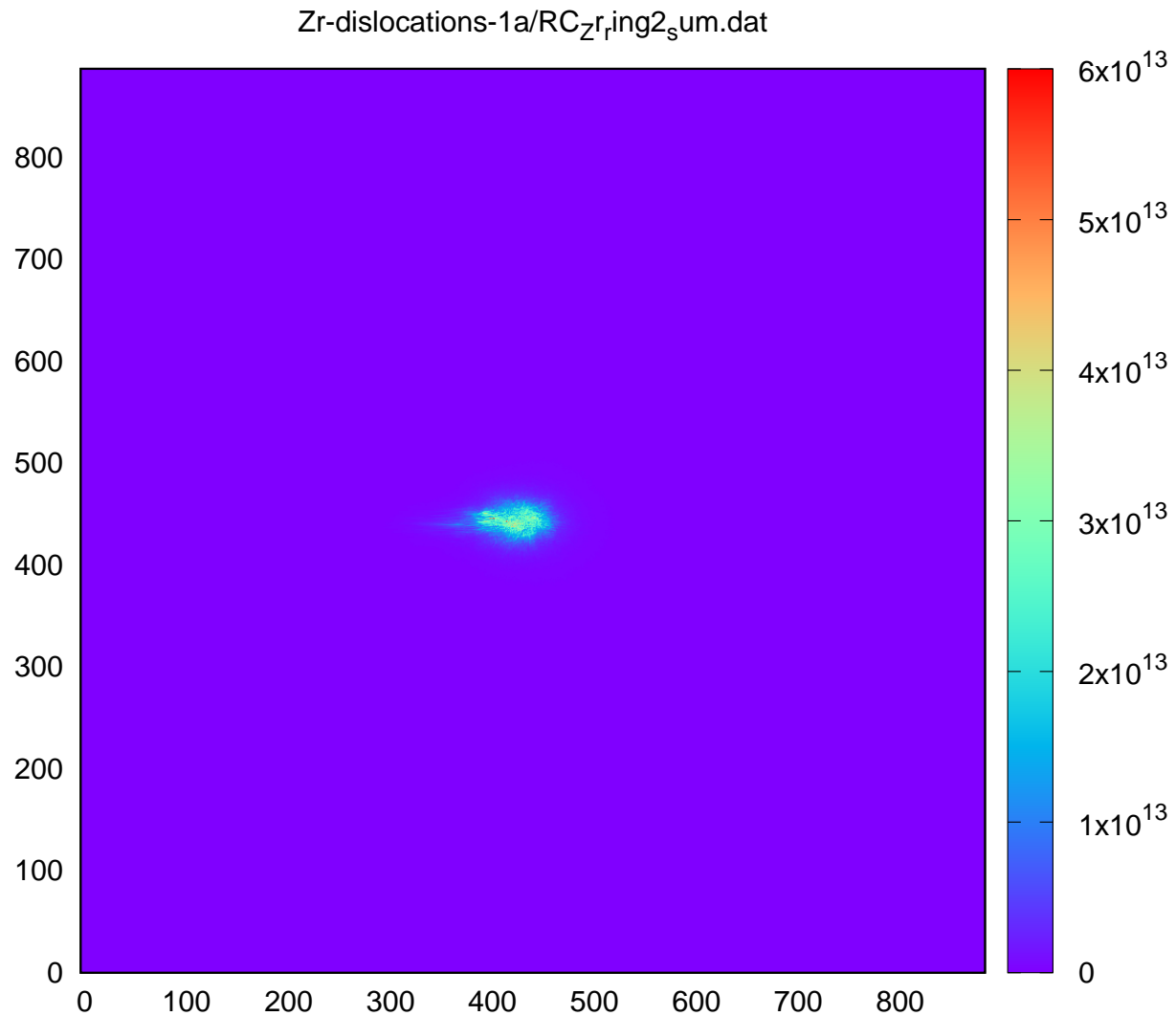
LP Zr (c-loops) 00.2



Zr (c-loops) rocking curve 10.0



Zr (c-loops) rocking curve 00.2



Thank you for your attention!