Rietveld combined analysis: examples

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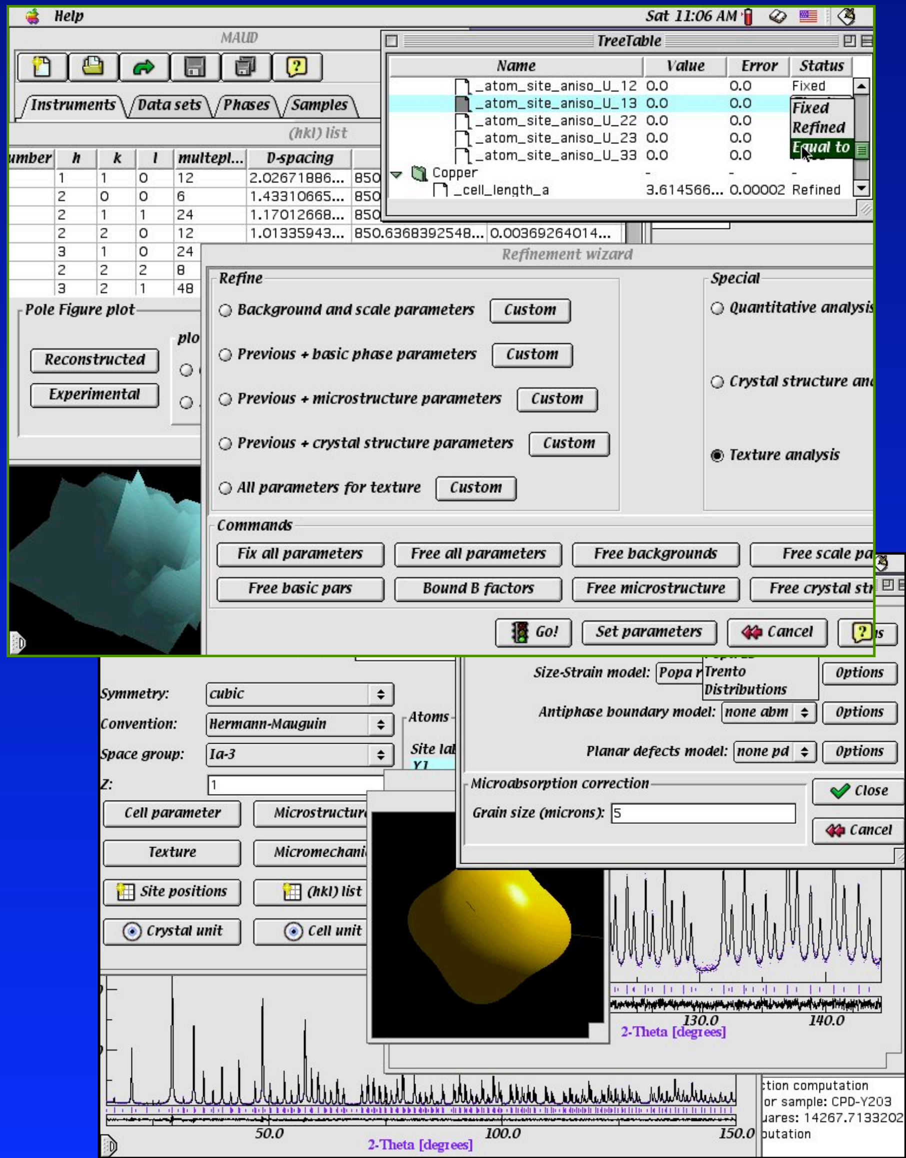
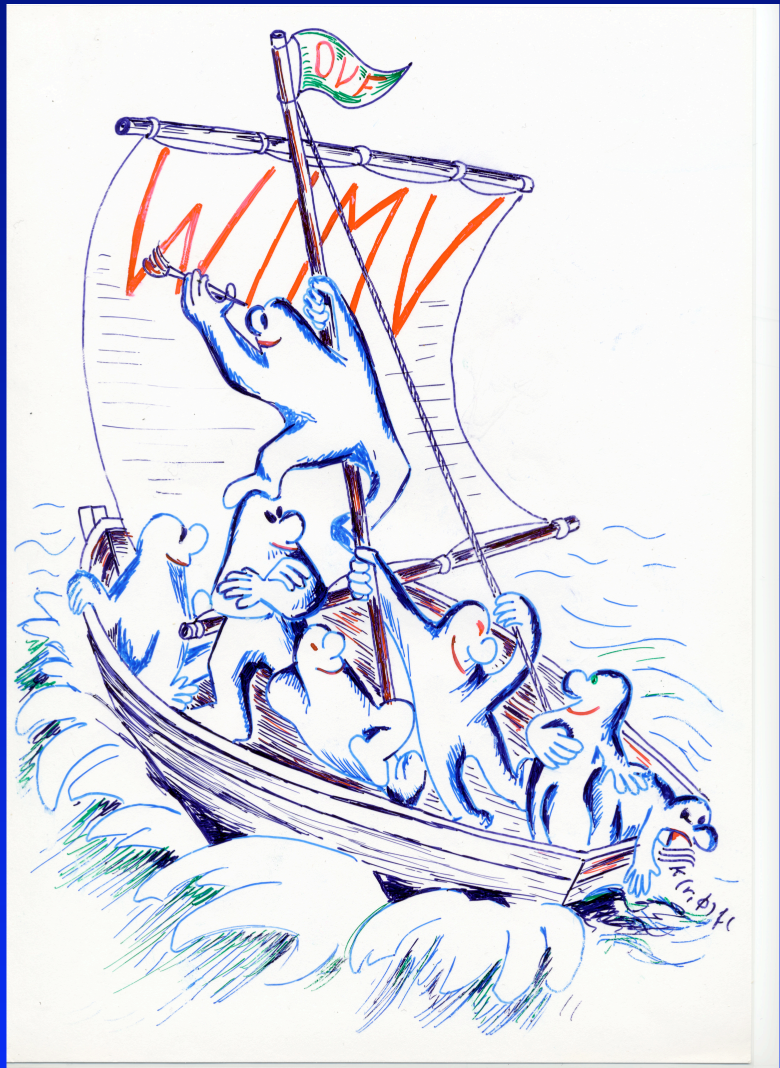
Methodology implementation

Maud program:

- Rietveld based analysis software:
  - Crystal structure
  - Ab initio structure solution (2.0)
  - Quantitative phase analysis
  - Layered sample model
- Microstructure
  - Isotropic or anisotropic size-strains
  - Crystallites-microstrains distributions (2.0)
- Texture:
  - WIMV
  - E-WIMV (modified)
  - Harmonic
  - Standard functions (2.0)
- Residual Stresses
  - No texture: tri-axial tensor
  - With texture: Reuss, Voigt, Geometrical mean
  - SODF (2.0)
- Reflectivity
  - Matrix method
  - DWBA LS fit (electron density profile)
  - Genetic algorithm
  - Cells method (DCD)



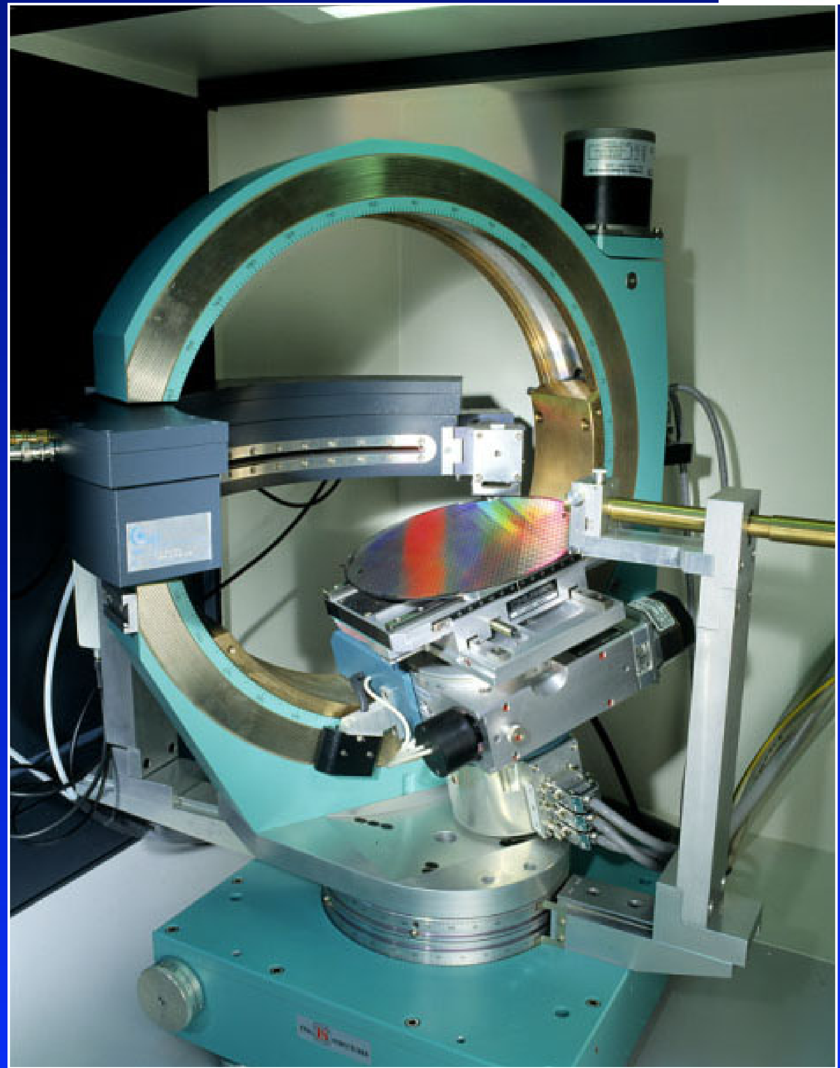
Analysis examples



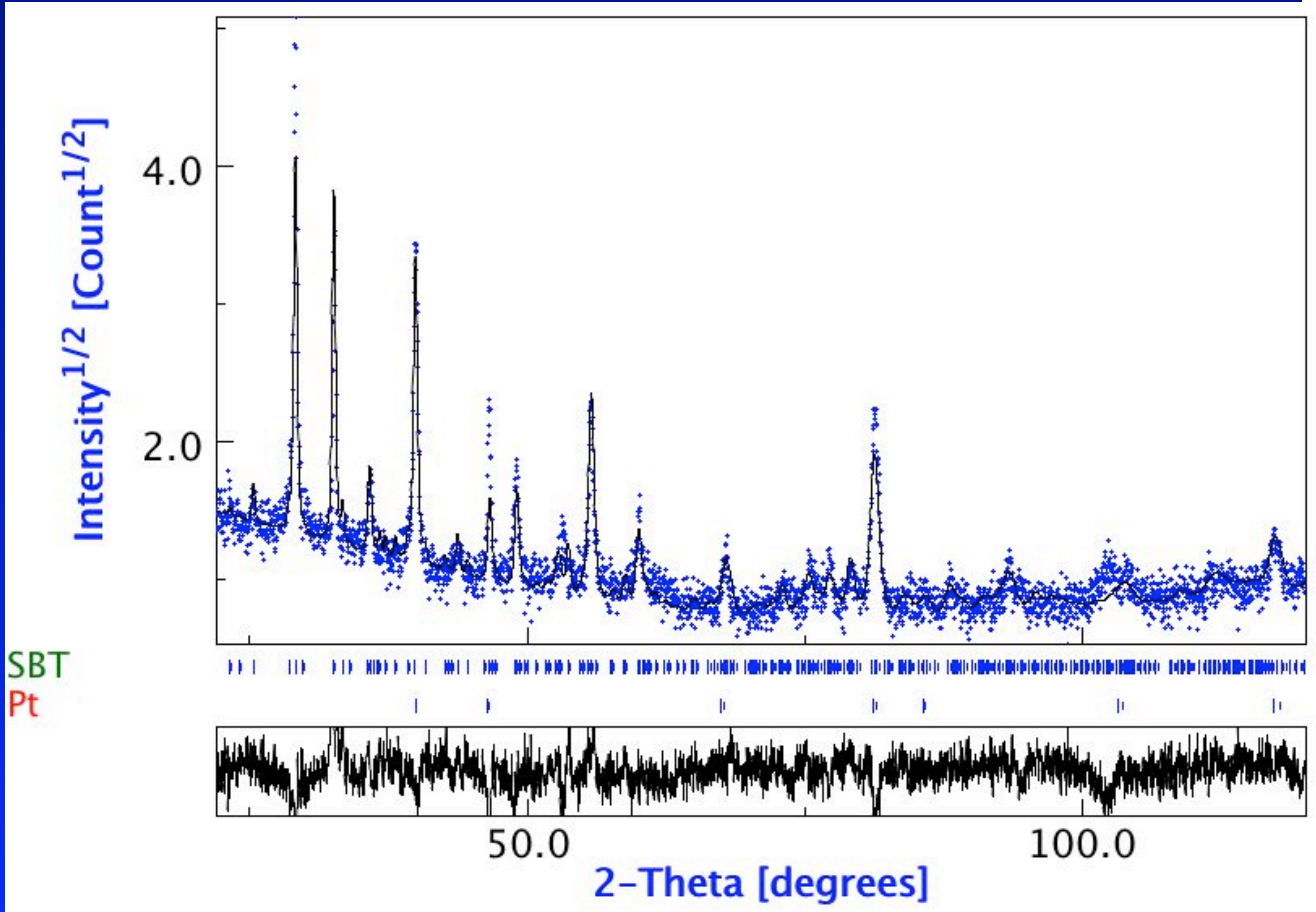
by S. Matthies

SBT film

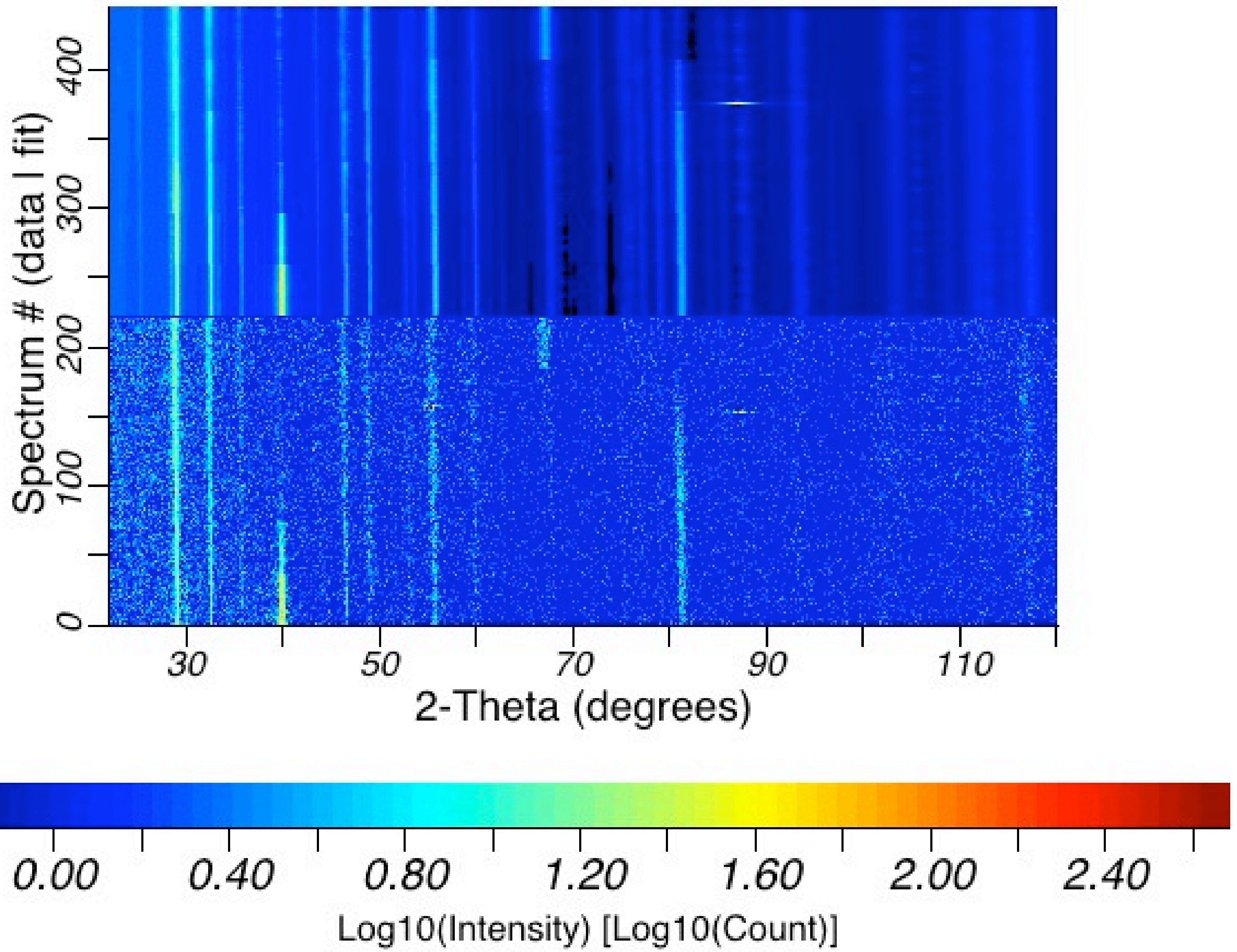
- Si Wafer + 50 nm Pt buffer layer
- ~ 300 nm of $(Sr_{0.82}Bi_{0.12})Bi_2Ta_2O_9$ - Orthorhombic A21am:-cba
- Spectra collection on the ESQUI diffractometer (right)
- 120 degs position sensitive detector on an eulerian cradle; multilayer as a primary beam monochromator
- Spectra collected in chi from 0 to 45 degrees in step of 5 deg for chi and 0 to 180 in steps of 5 deg for phi
- Structure refined



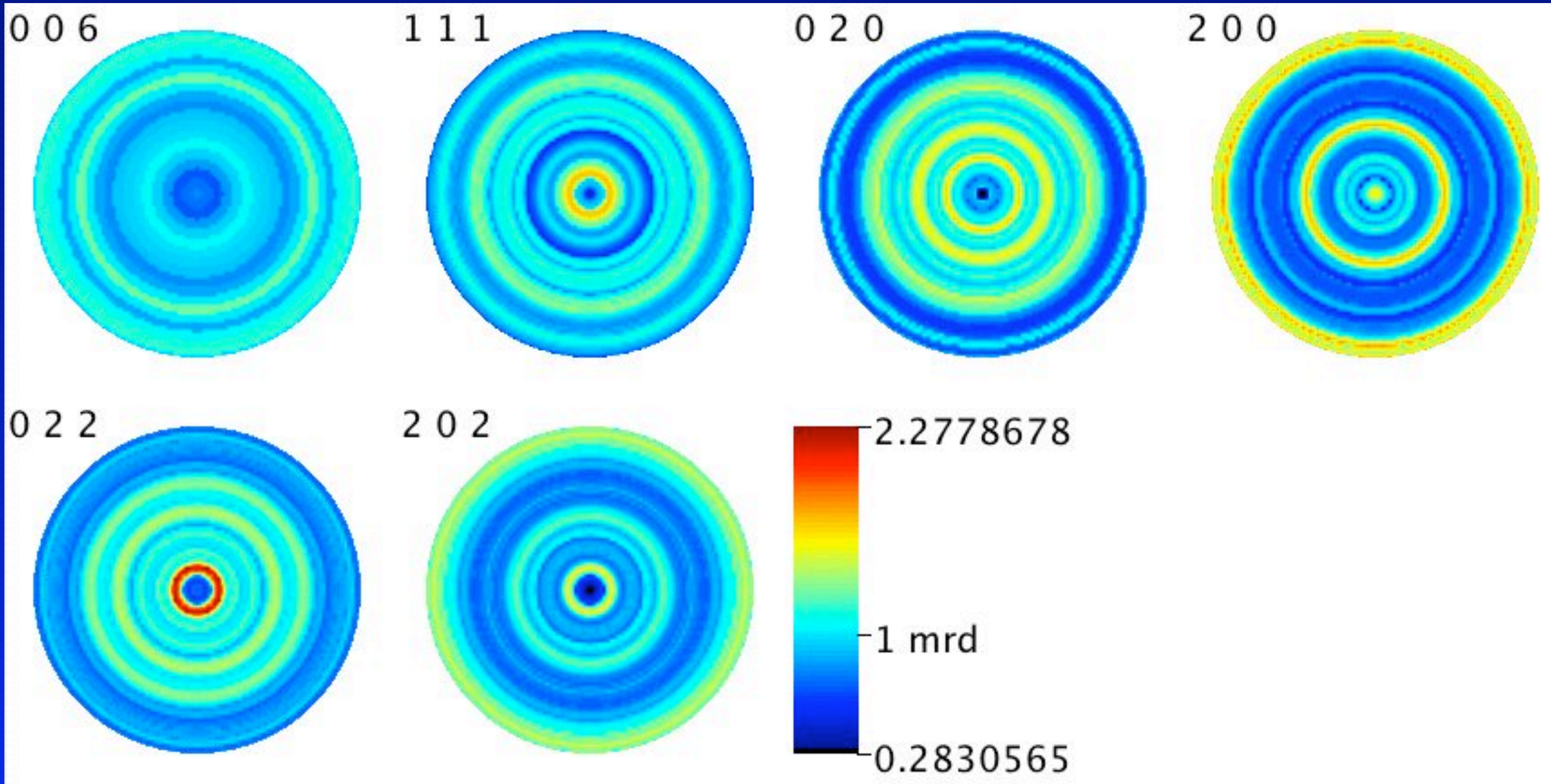
Rietveld Texture refinement



SBT thin film Rietveld fit



SBT pole figures reconstructed



E-WIMV

Modified WIMV algorithm for Rietveld Texture Analysis

Differences respect to WIMV:

- ODF cell path computed for each measured point (no interpolation of pole figures on a regular grid)
- Different cell sizes available (Ex: 15, 10, 7.5, 5, 2.5, 1.25, 1…..) in degs.
- Tube projection computation (similar to the ADC method)
- Minimization engine is an entropy like

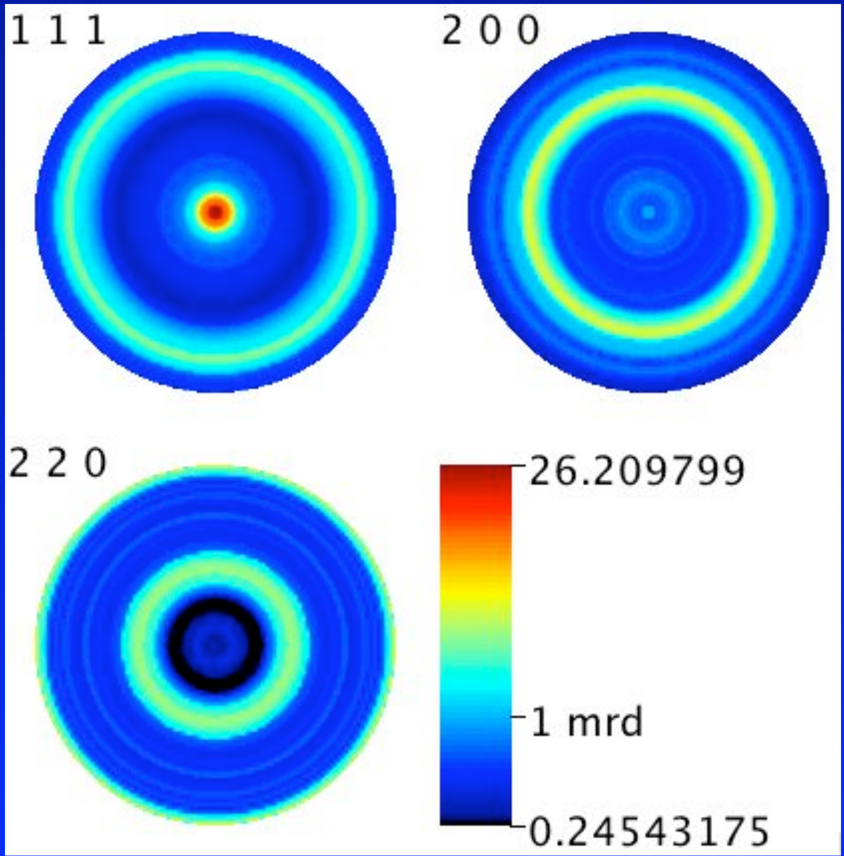
Problems:

- Path computation is slow for low symmetries (high number of data)

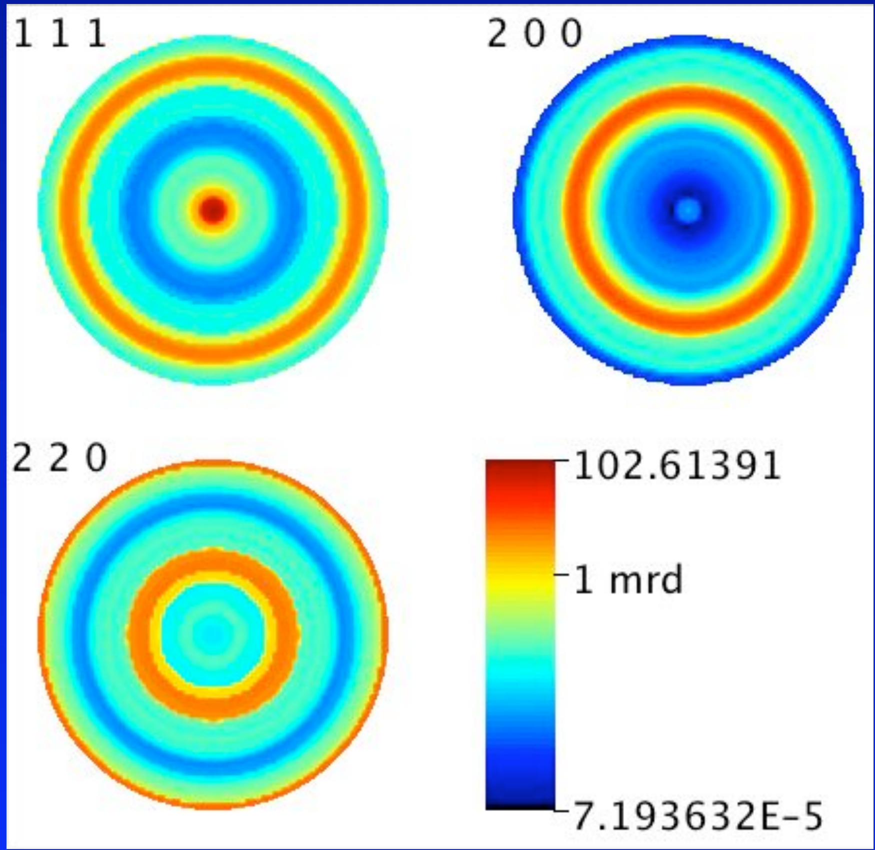
Pt texture too sharp for WIMV

Special texture methodology for Rietveld developed: Entropy based WIMV using tube projections. Interpolation of pole figures avoided.

WIMV

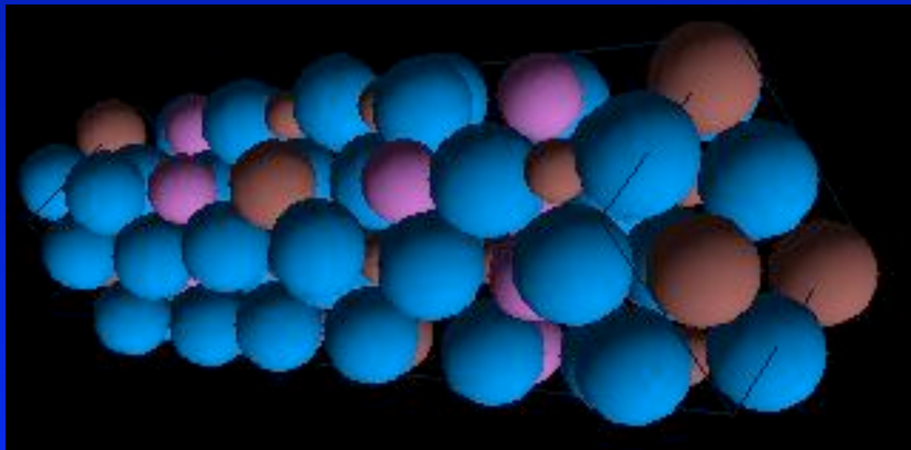


E-WIMV



SBT film microstructure and crystal structure

	Cell parameters (Å)	Cryst. Size (Å)	Microstrain	Layer thickness (Å)
SBT	a ≈ b = 5.5473(2) c = 25.316(2)	565(5)	0.0037(3)	3579(72)
Pt	3.9411(1)	317(4)	0.0029(2)	557(15)



Space group: A21am:-cba

14 atomic position parameters refined

Extremely sharp Al film (ST microelectronics)

Aluminum film

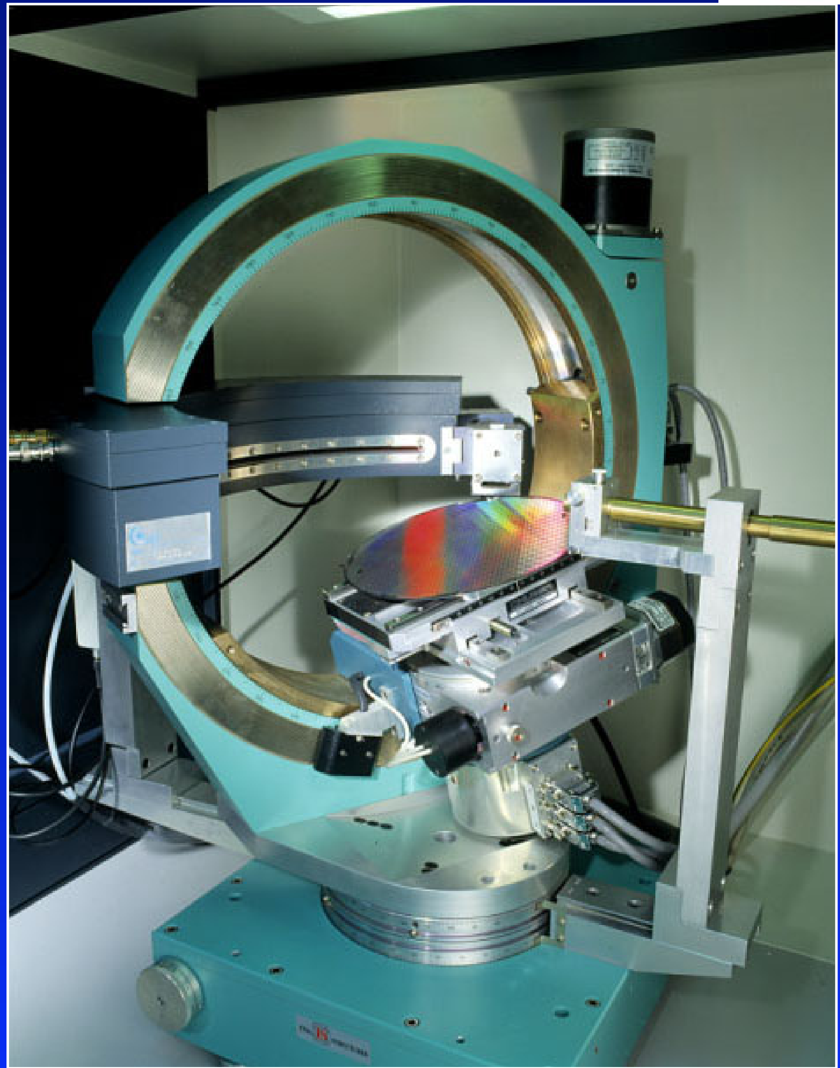
Si wafer substrate

Spectra collection on the ESQUI diffractometer (right)

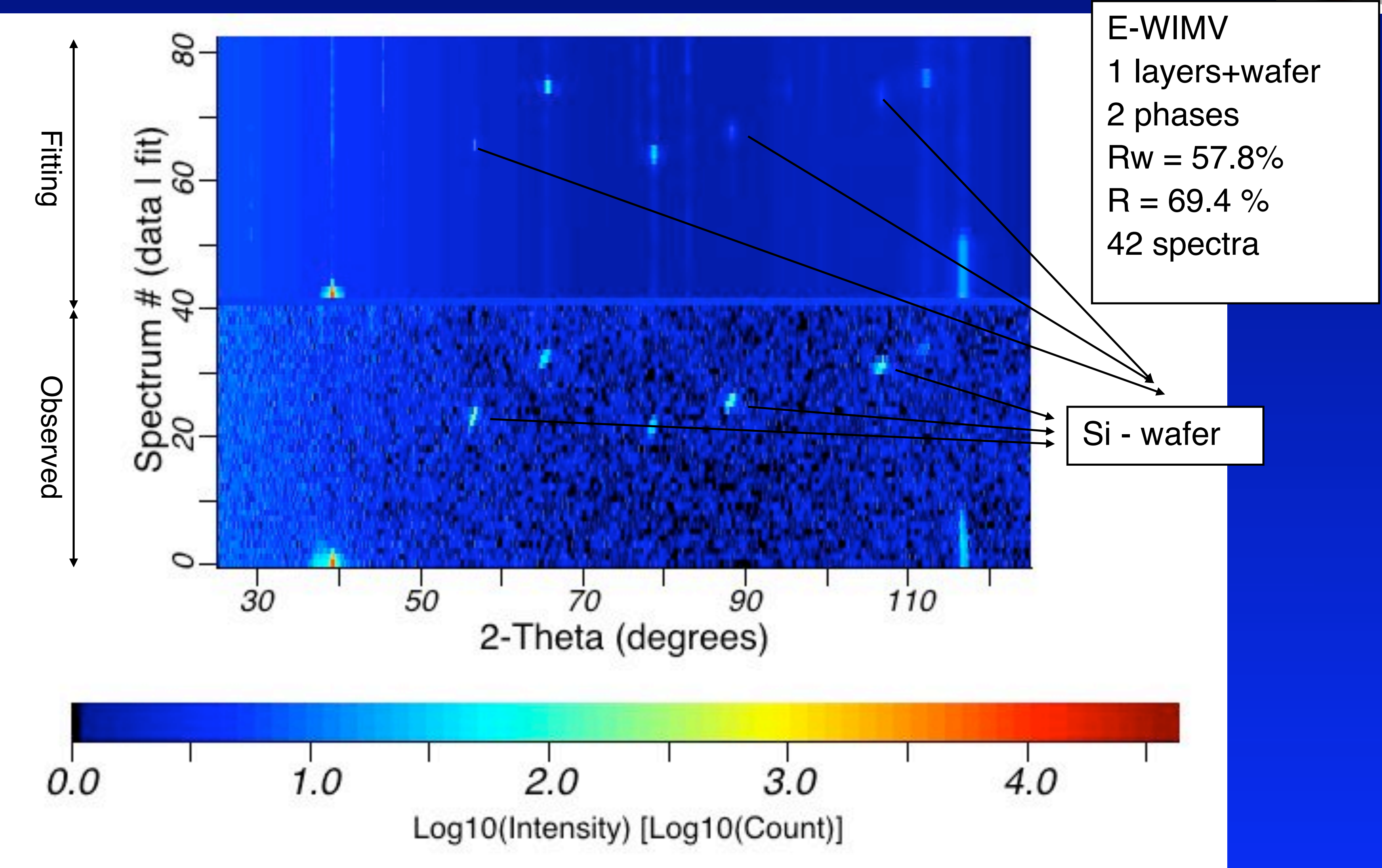
120 degs position sensitive detector on an eulerian cradle; multilayer as a primary beam monochromator

Spectra collected in chi from 0 to 45 degrees in step of 1 deg turning continuously the phi motor (fiber texture)

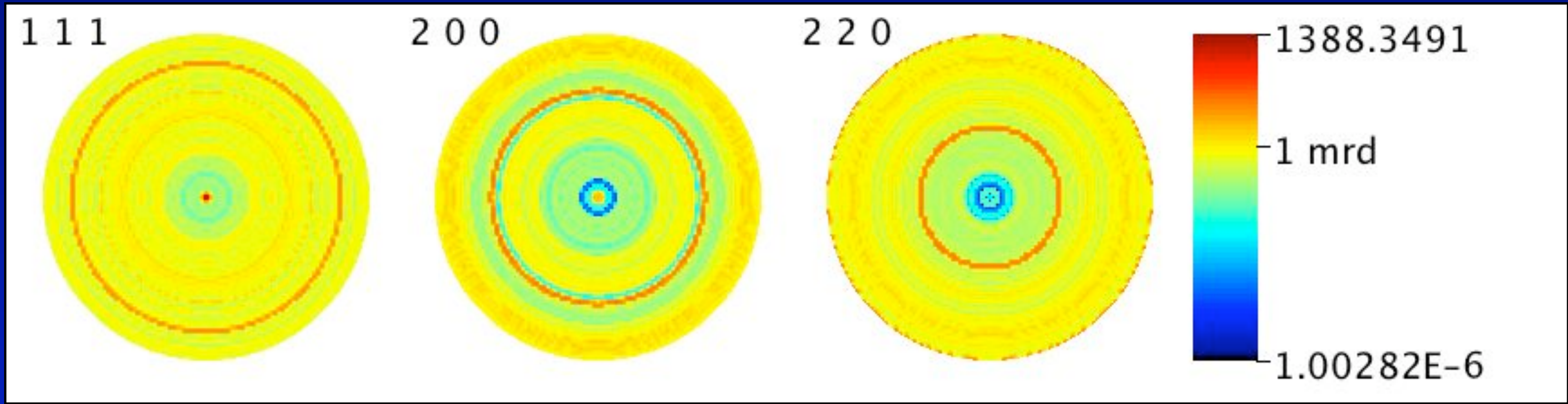
E-WIMV used only; too sharp texture even for WIMV



Al film: fitting the spectra



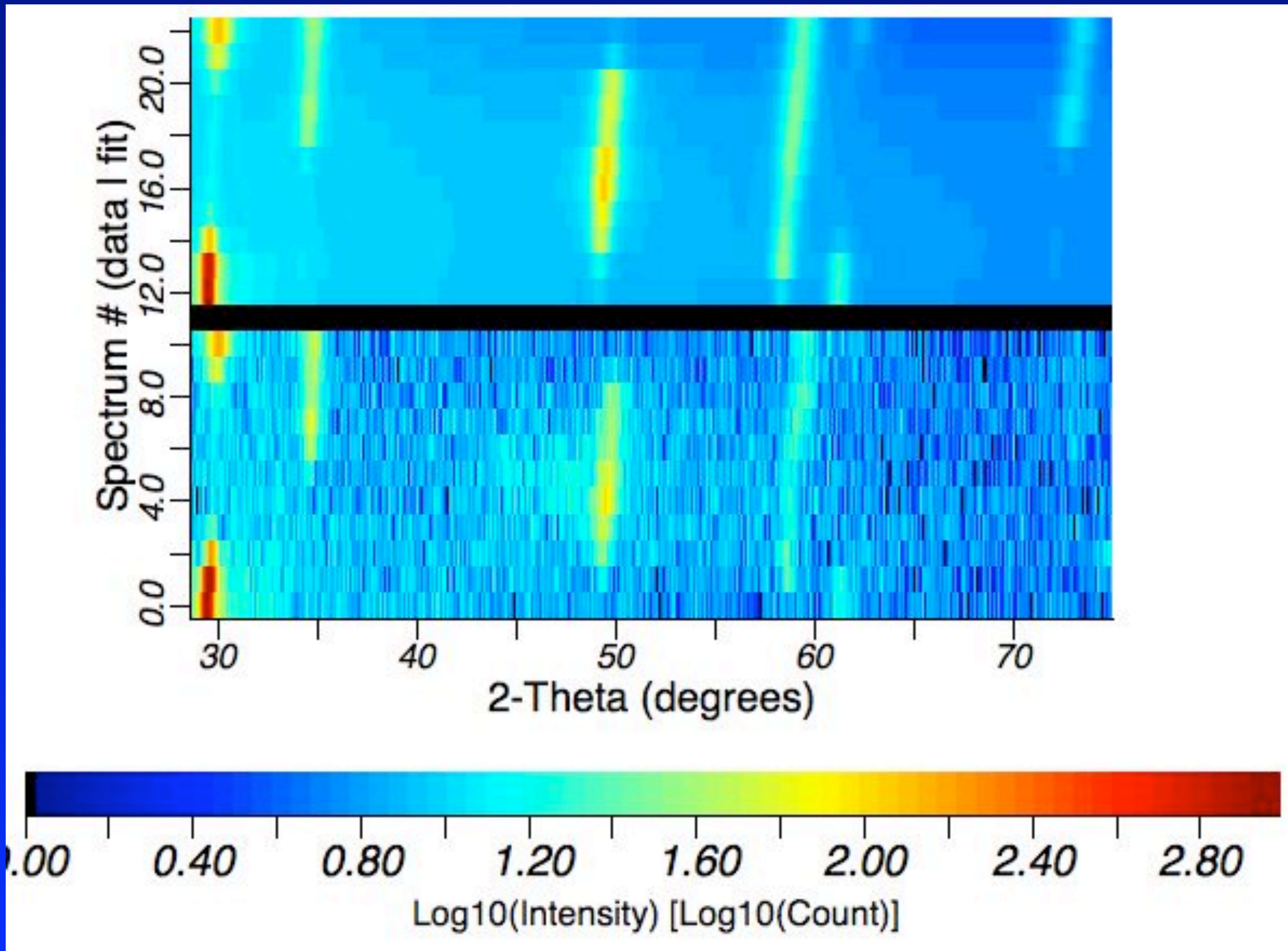
Al film: Al reconstructed pole figures



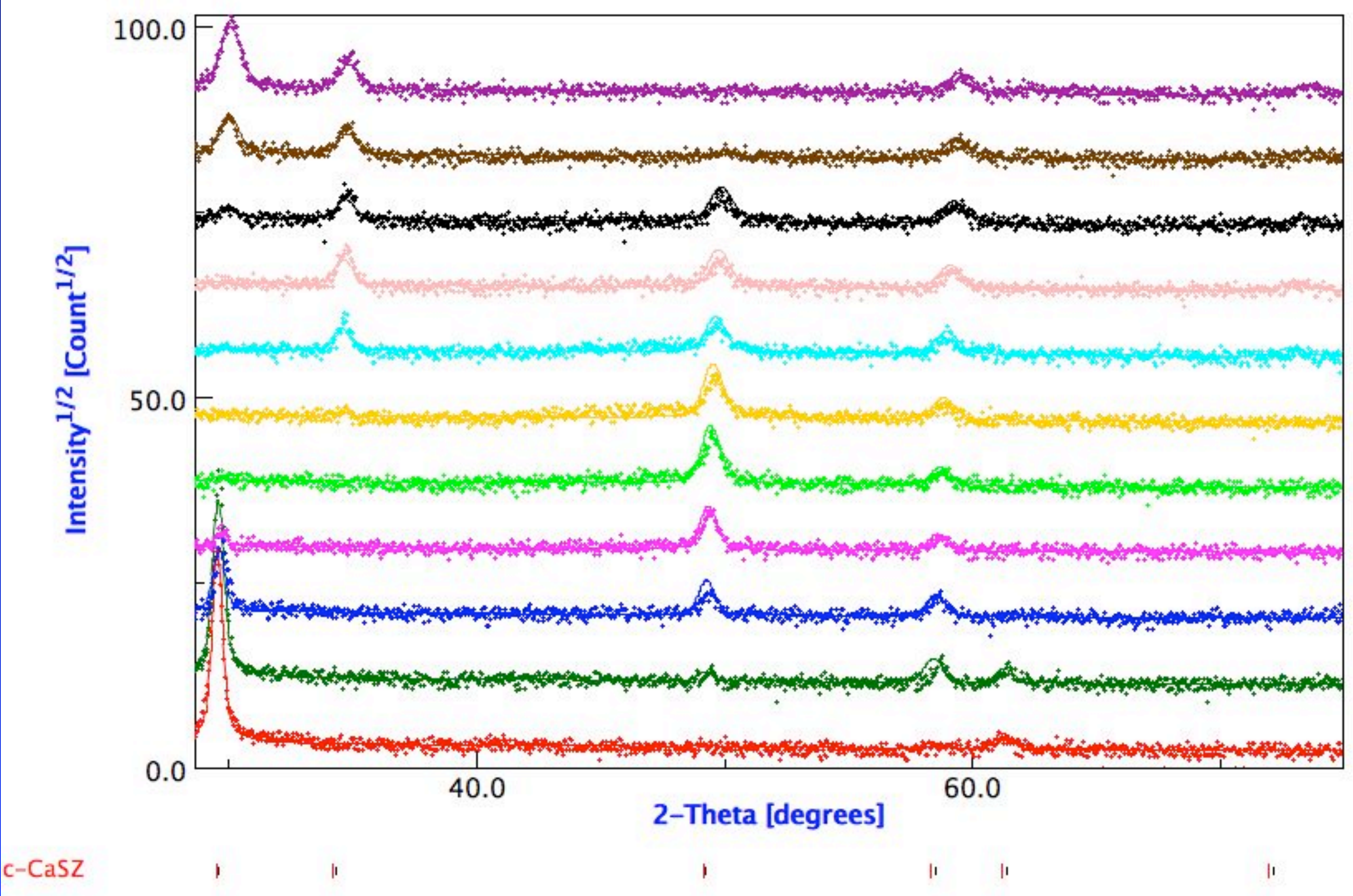
E-WIMV
1 deg cells
F2 = 1100.9
Rw = 15.4 %
Rp = 19.5 %
8 reflections

Residual Stresses/Texture analysis

- Voigt model + WIMV



Multi-plot for the zirconia film (WIMV)

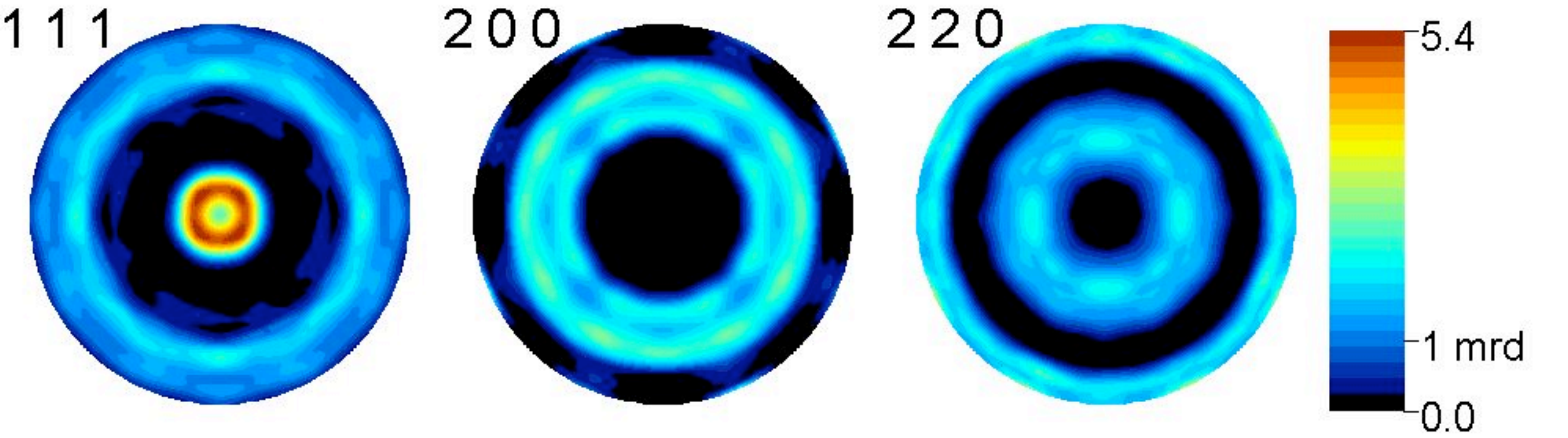


ZrO_2 film: results

Very high in plane residual stresses (compression):
Reuss model: 3.6 GPa
Bulk Path GEO: 3.47(5) GPa
Curvature method: > 10 Gpa !?

Thickness: 320 Nanometer

Reconstructed pole figures



The -GEO methods

- Averaging elastic constants (composite case: c=composite, m=matrix, f=fiber or inclusion, ϕ=inclusion fraction):
  - Voigt: $E_{cv} = E_m (1-\phi) + \phi E_f$
  - Reuss: $E_{cr}^{-1} = E_m^{-1} (1-\phi) + \phi E_f^{-1}$

Arithmetic mean

  - $E_{cr} < E_{cv}$ and also S_c is not the inverse of E_c for the arithmetic mean (?!)
  - Hill: $E_{ch} = (E_{cv} + E_{cr}) / 2$
  - ……(Self-consistent etc.)
  - Geometrical mean (GEO): $\log E_c = (1-\phi) \log E_m + \phi \log E_f$
    - Inversion property is guaranteed: $S_{GEO} = E^{-1}_{GEO}$

- We can use the Geometrical mean framework to relate strain-stresses in residual stress analysis (PathGEO, BulkPathGEO)
- Advantages:
  - Correct description for strain-stress compatibility
- Cons:
  - Not exact when grain shape and texture are correlated

The SODF method

- SODF = Stress Orientation Distribution Function (or II kind microstresses):

$$\sigma_{ij}(g) = \sum_{l=0}^{L\max} \sum_{m=-l}^{l} \sum_{n=-l}^{l} \Gamma_{lmn}^{ij} T_l^{mn}(g)$$

- The I kind stress (average) becomes:

$$\tilde{\sigma}_{ij} = \sum_{l=0}^{L\max} \sum_{m=-l}^{l} \sum_{n=-l}^{l} (-1)^{m+n} \Gamma_{lmn}^{ij} C_l^{\overline{mn}}$$

- Diffraction strain computed as in Ferrari & Lutterotti using the ODF from the texture analysis.
- To ensure unique solution should be minimized (actually this has been replaced by enforcing a self-consistent compatibility bound):

$$\Pi_{index} = \sum_{l=0}^{L\max} \sum_{m=-l}^{l} \sum_{n=-l}^{l} (\Gamma_{lmn}^{ij})^2$$

The SODF method: pro & cons

- Advantages:
  - Very flexible function to store the orientation dependent local stress
  - Easy to implement in Rietveld programs
  - High L_{max} expansion not needed
  - Can be used also as a strain distribution function (more appropriate for epitaxial films or in general residual strains due to growth and misfit)

- Disadvantages:
  - 6 ODF functions to be determined -> huge amount of unknowns.
  - Enormous amount of data required.
  - Unique solution not guaranteed.
  - Slow computation with texture.
  - Missing data for sharp textures.

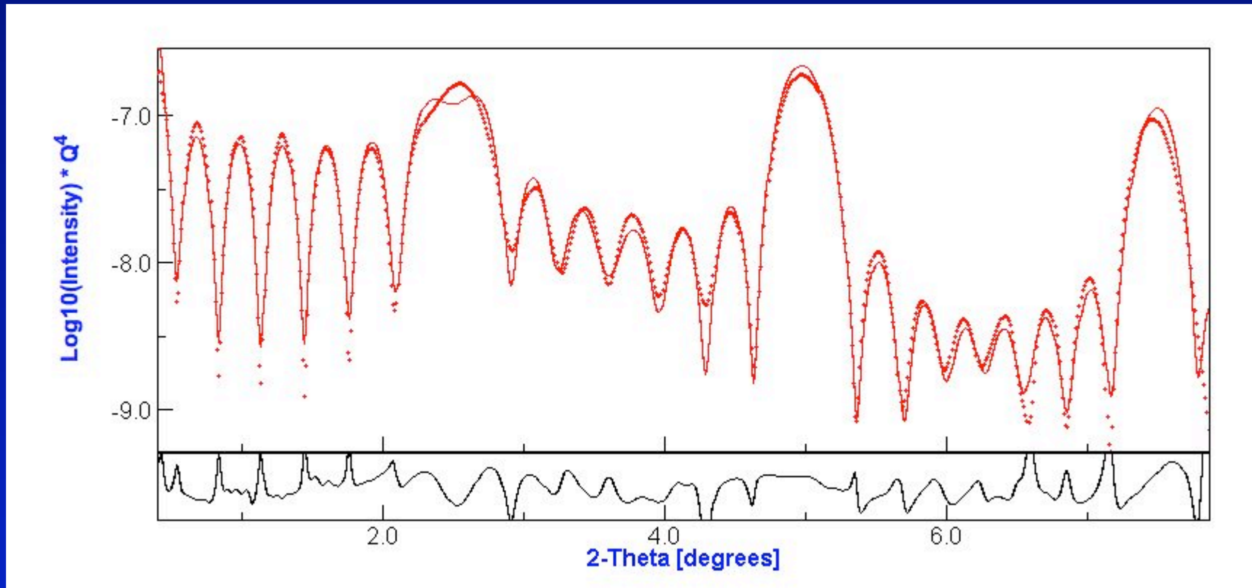
The modified SODF method

- Popa and Balzar introduced a Strain Orientation Distribution Function for Rietveld implementation.
- Main differences respect to the original SODF:
  - Extracting strain data instead of residual stresses
  - The modified SODF contains already the texture weights -> faster computation
  - Additional symmetries introduced to reduce the number of unknown.
- Possible problems:
  - Same as for the original SODF, to much unknown respect to the data.
- General remark:
- The SODF is used in an integral computation with the ODF :
  - we may have more solutions for the same result
  - If a texture weight is zero or very low, the correspondent strain value may assume every values.

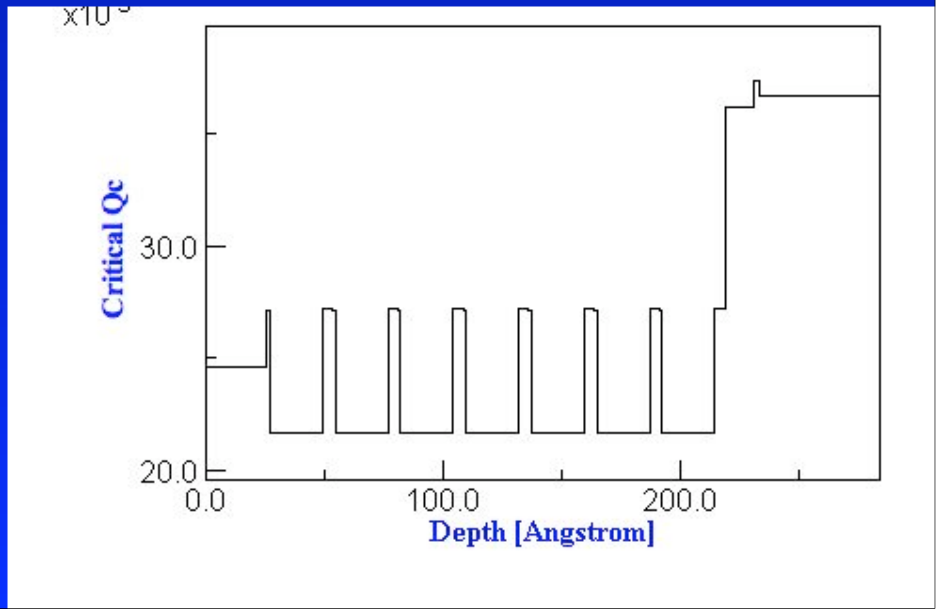
Reflectivity

- Advantages of combining diffraction and reflectivity:
  - Thickness is much more accurate from reflectivity -> can be used to correct absorption path in diffraction
  - Phase content in layers is accurate in diffraction (and cell parameters) -> can be used to compute electron densities for reflectivity
- Cons:
  - few samples are sufficiently thick to get diffraction and sufficiently thin to get reflectivity
- In Maud:
  - Matrix method (layered model)
  - DWBA (electron density profile)
  - Genetic algorithm to obtain a first approximate model to be used in the matrix method
  - Discrete Cell Density approach

Reflectivity for multilayer analysis



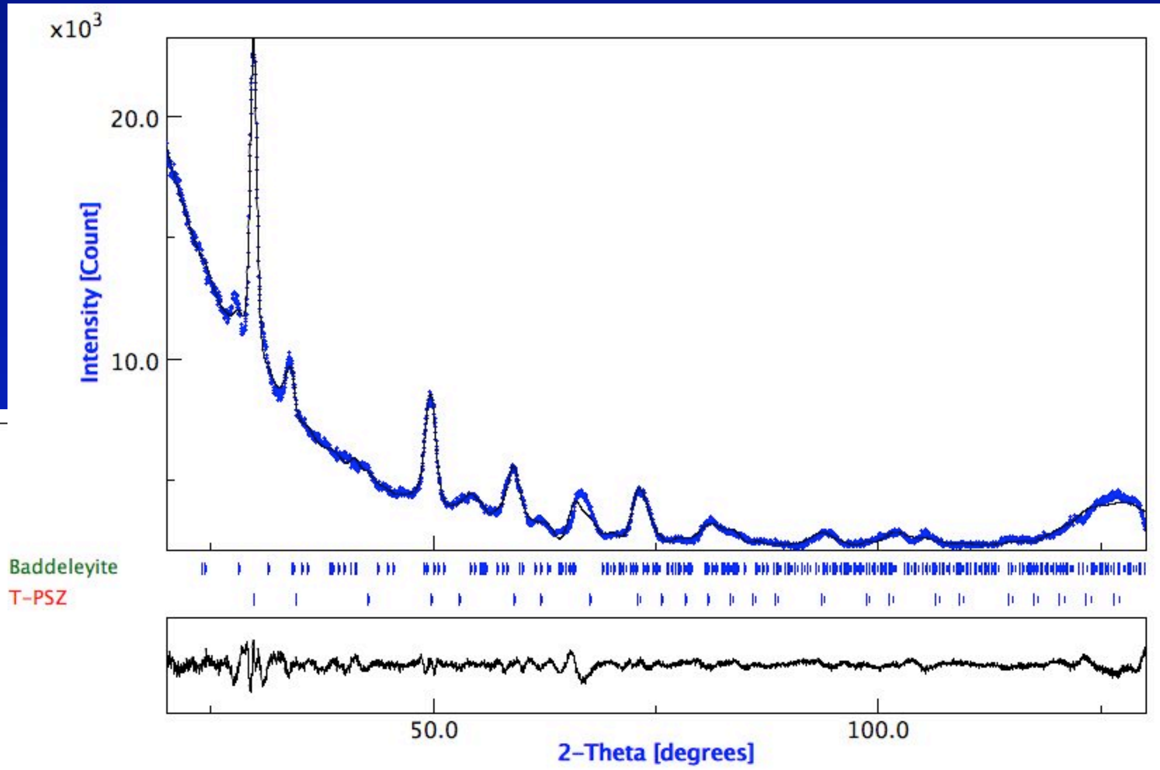
- Langmuir-Blodgett film
- 24 layers sequence
- Matrix method used for the analysis in Maud
- Film and data collected by A. Gibaud (LPEC, Le Mans)

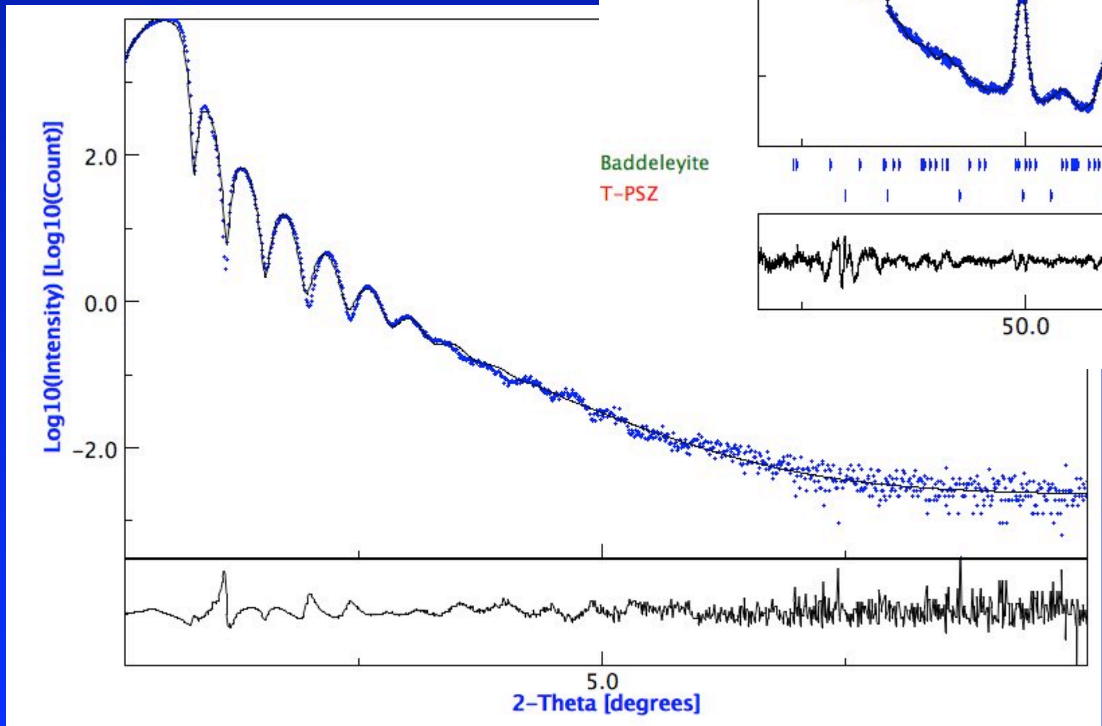


ZrO_2 film (reflectivity and diffraction)

- Zirconia film (about 20 nm thick)
- Contains tetragonal and monoclinic phases
- One reflectivity and one diffraction spectra collected (time constraint?)
- Analysis by Maud:
  - Layered model (matrix):
    - Si wafer
    - Buffer layer
    - ZrO_2 layer
    - Air
  - ZrO2 layer composed by monoclinic + tetragonal zirconia textured:
    - Fiber texture assumed
    - Harmonic model used (only one spectrum)
- We want:
  - ZrO_2 layer thickness
  - Phase fraction, microstructure (and texture?)

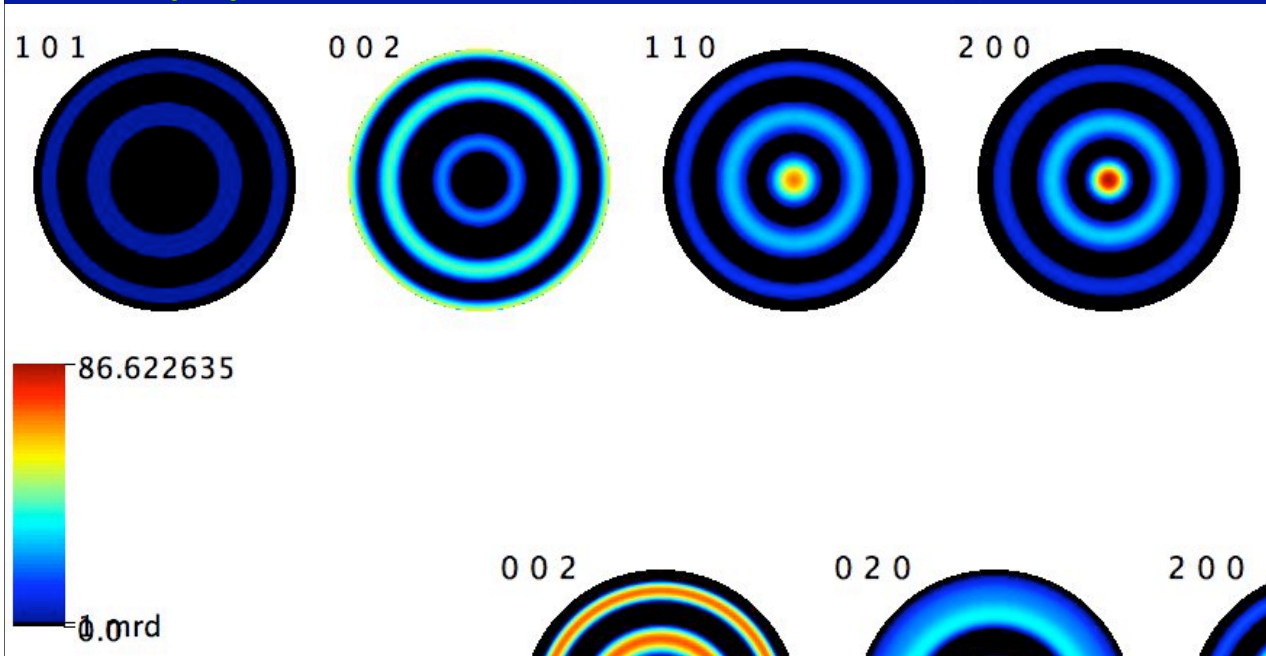
ZrO_2 results - 1



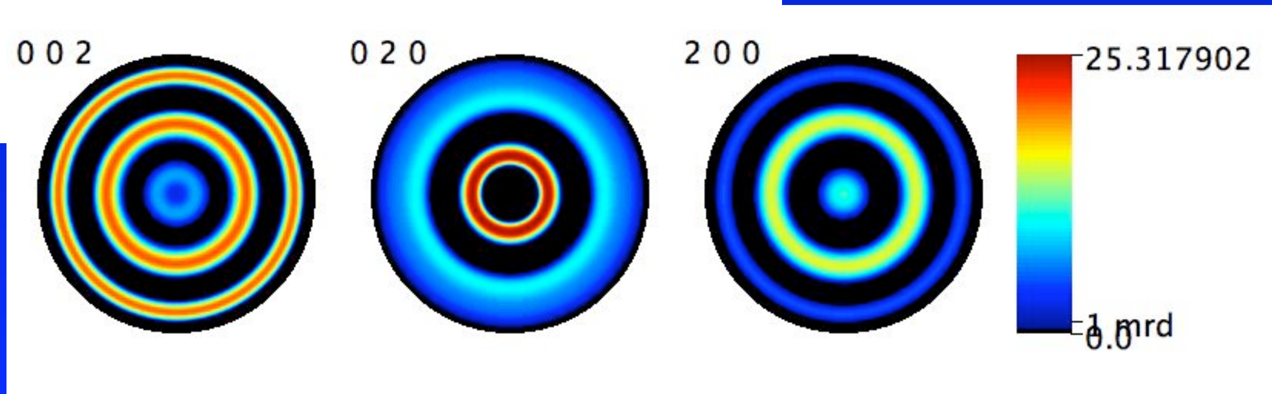


ZrO_2 results - 2

- ZrO_2 thickness: 196(1) Angstrom
- Baddeleyte: $\langle D \rangle$ = 28(1)Å, $\langle \varepsilon^2 \rangle^{1/2}$= 0.0027(1), volume fraction = 0.53()
- Tegragonal: $\langle D \rangle$ = 130(7) Å, $\langle \varepsilon^2 \rangle^{1/2}$= 0.017(1)



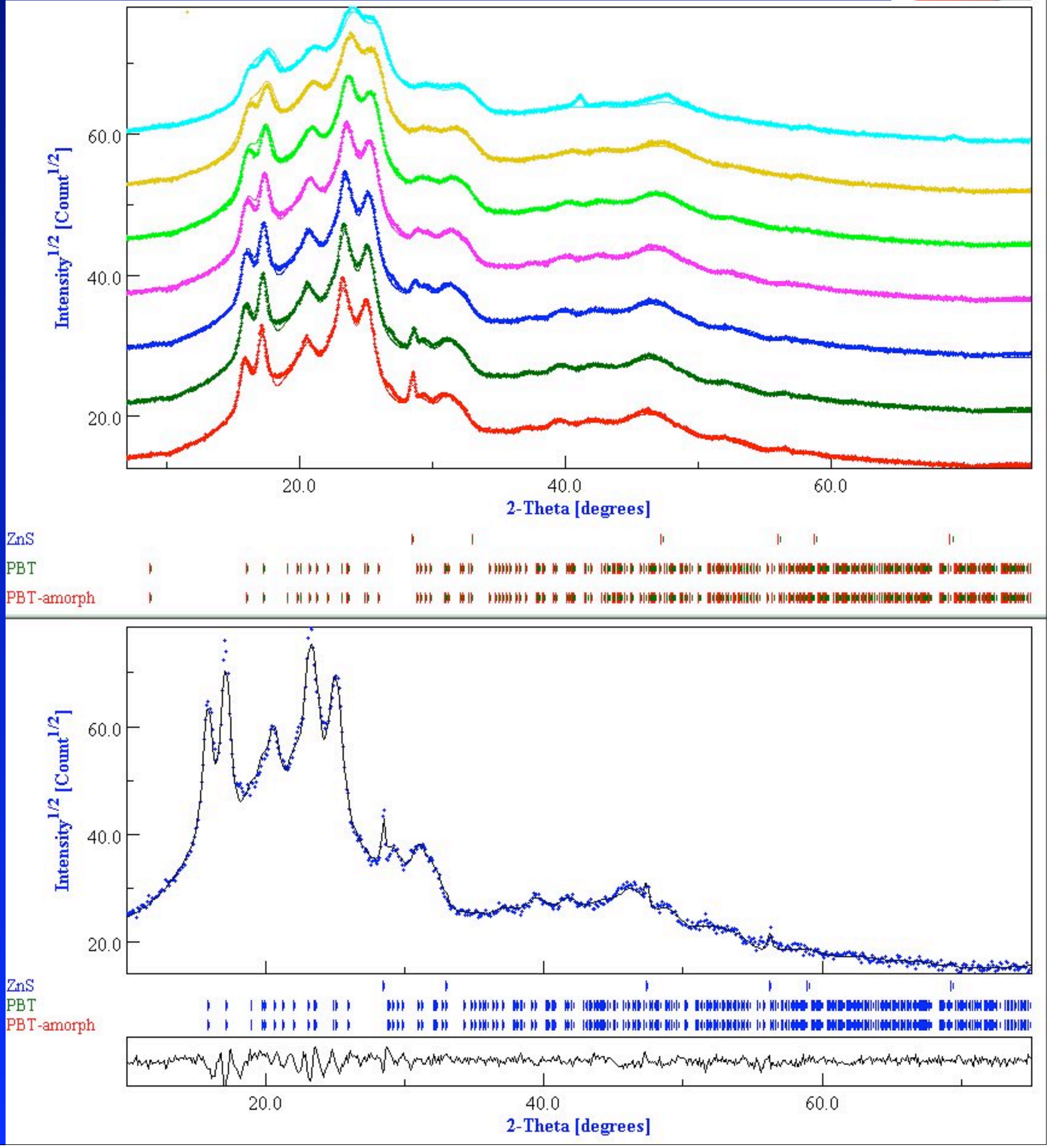
Tetragonal



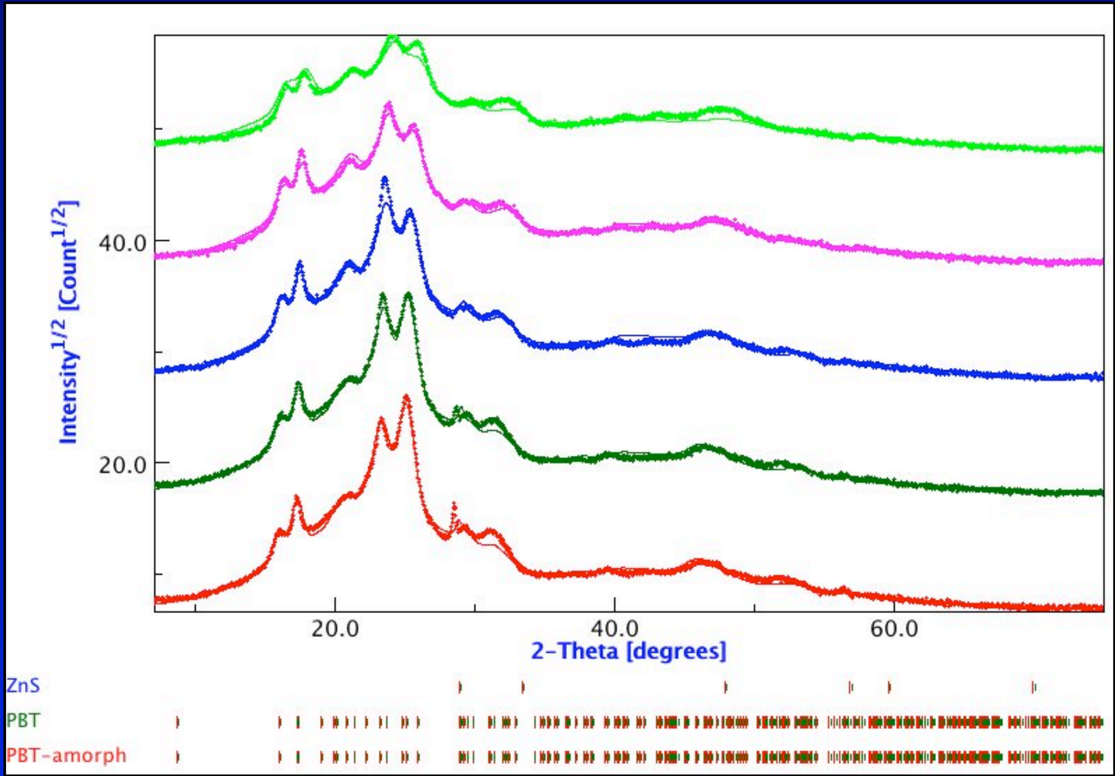
Monoclinic

PBT polymer (thick film): texture analysis

- Polybutilentereftalate: triclinic
- Only partially crystallized
- Deformed at different rate (uniassial compression)
- Annealed
- Spectra for both deformed and deformed+annealed samples collected in Le Mans (CPS 120 and eulerian cradle)
- Analyzed by Maud assuming amorphous and crystallized phases having:
  - Same structure
  - Same texture



PBT deformed and annealed



Harmonic

L_{max} = 4

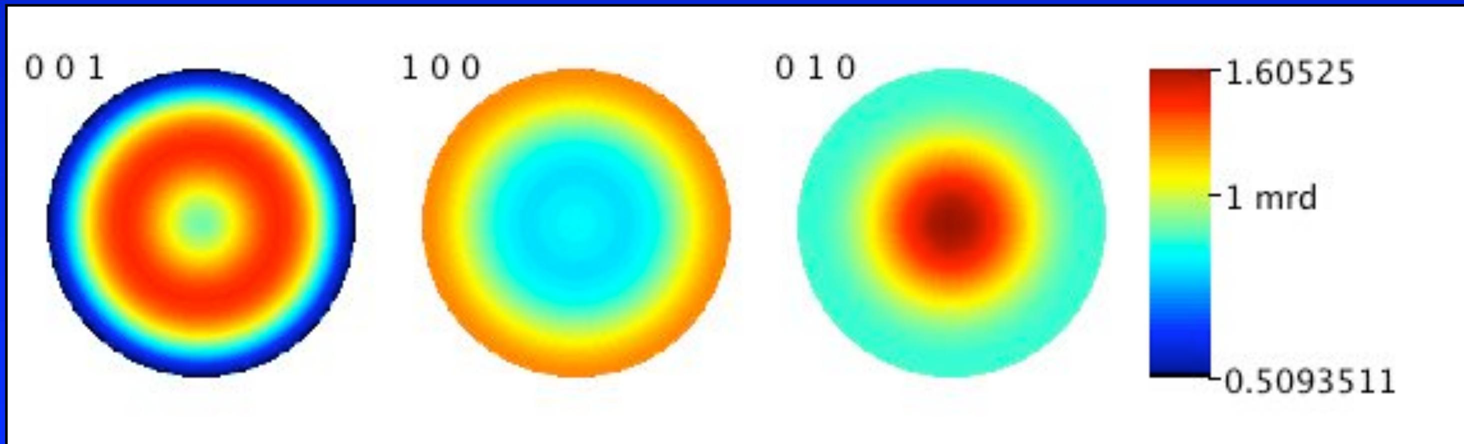
F^2 = 1.37

R_w = 6.27 %

R_p = 22.1 %

>300 reflections

Reconstructed pole figures

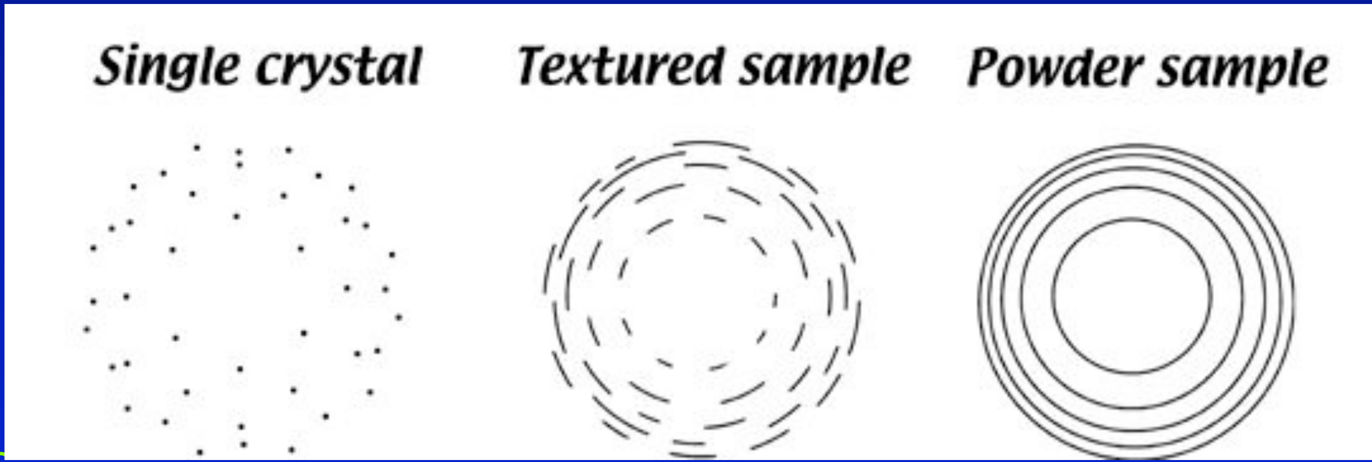


PBT results

- Deformed samples become textured at higher deformation values
- Crystallite sizes decrease with deformation and microstrains (paracrystallinity) increase.
- With the annealing crystallite sizes recuperate their original dimension and microstrains decrease. Texture remains and becomes more evident. Residual deformation is not recuperated.
- Good fitting requires the use of the texture on the amorphous PBT

What more? Ab initio structure solution

- IUCr 2000: McKusker and Berlocher group present a crystal structure determination by powder diffraction using texture.

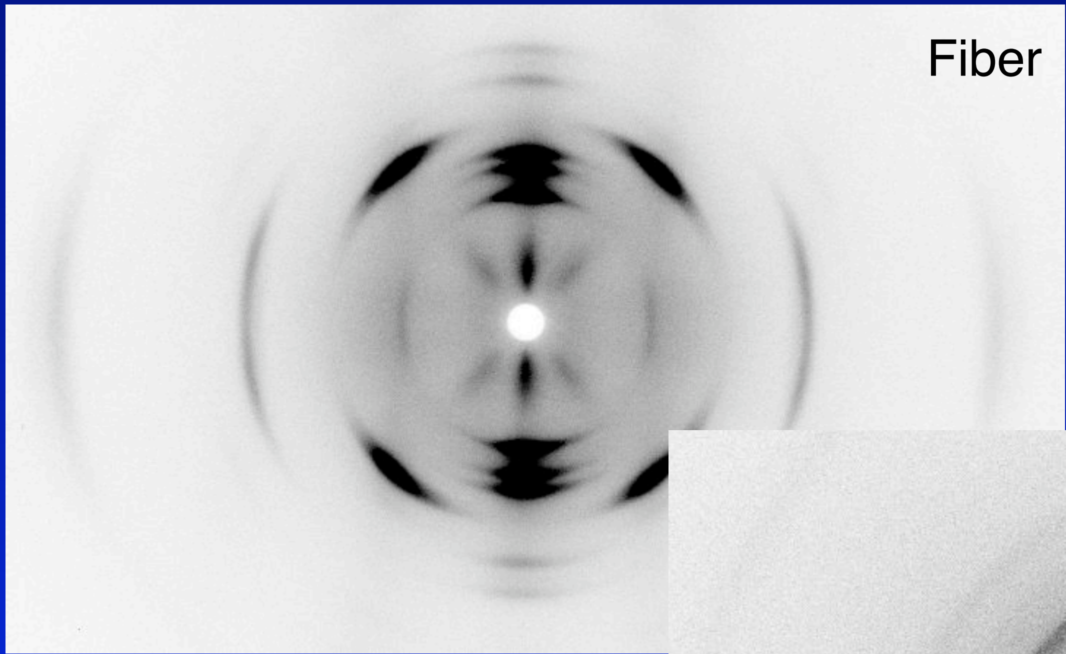


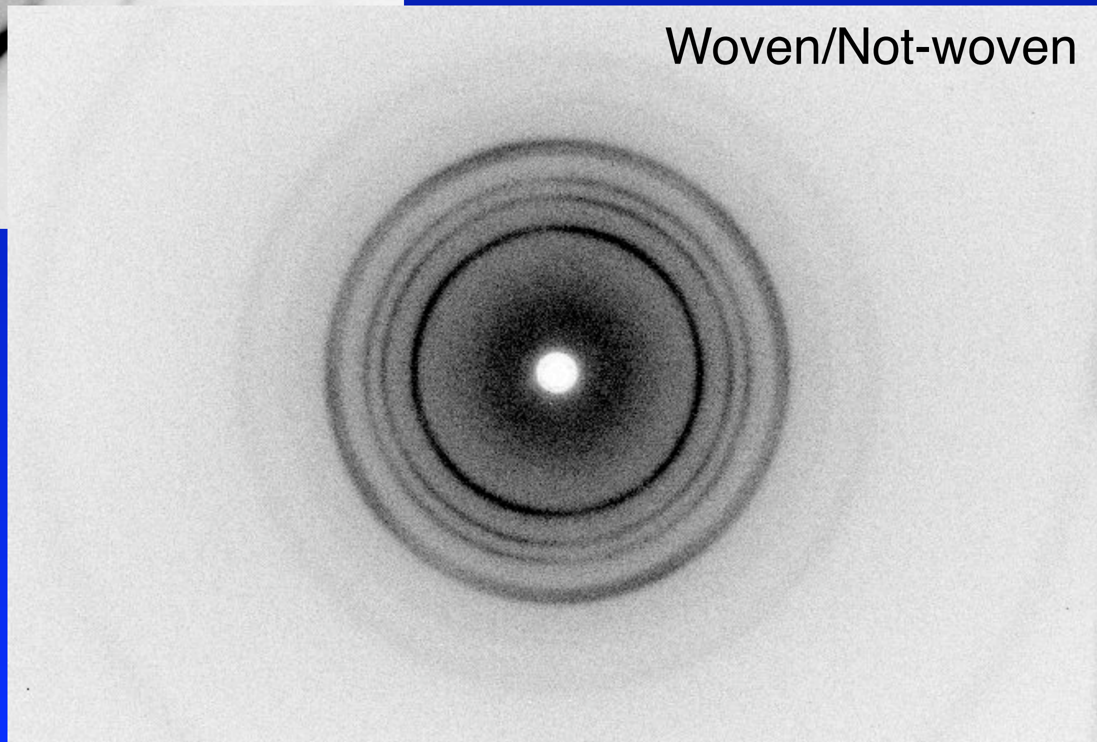
- Steps:
  - Indexing
  - Pole Figure collection and texture analysis
  - Spectra collection and F_{hkl} extraction using texture correction
  - F_{hkl} -> crystal structure determination using single crystal methods

Ab initio structure determination

- Improvement through RiTA:
  - Steps:
    - Spectra collection
    - Indexing
    - Rietveld Texture Analysis extracting F_{hkl} and computing texture (automatic correction)
    - F_{hkl} -> structure solution
- Only one measurement step required
- Only one step for texture and F_{hkl} extraction

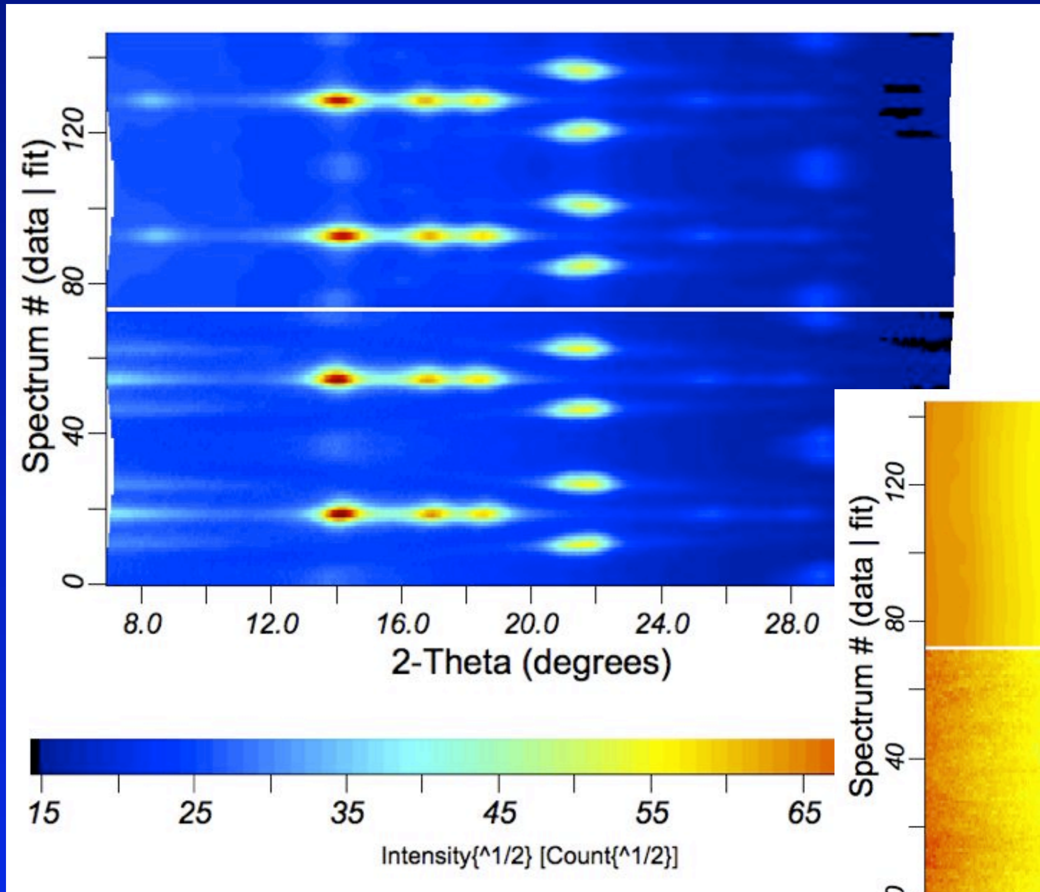
Polypropilene and the Laue camera (IP)

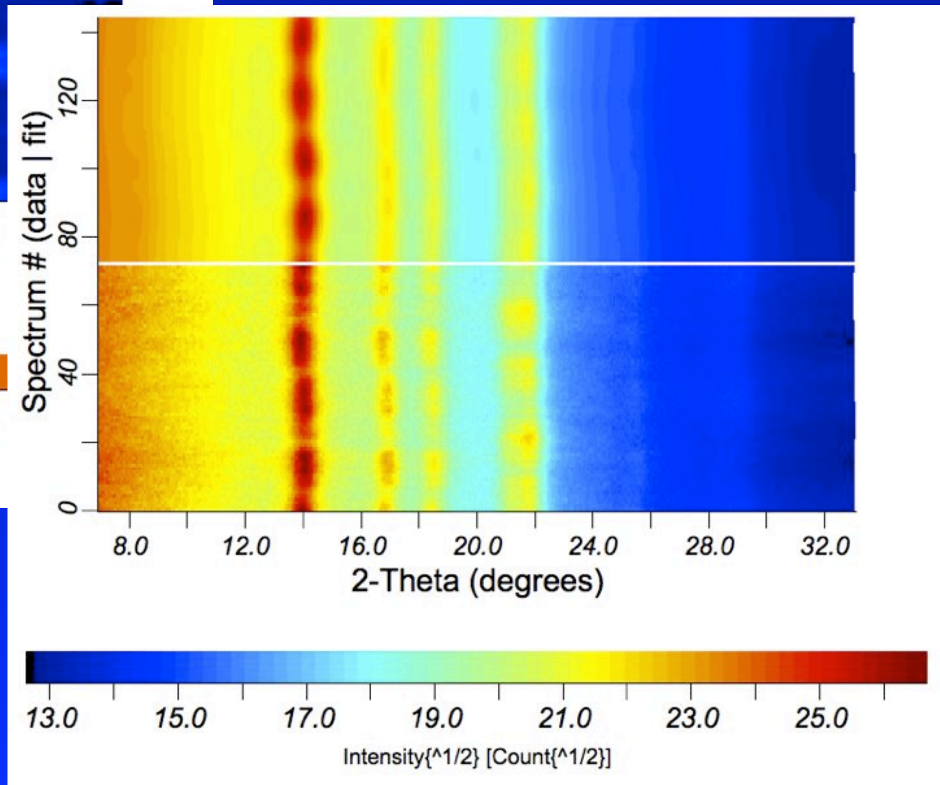




Maud fitting

Fiber PP

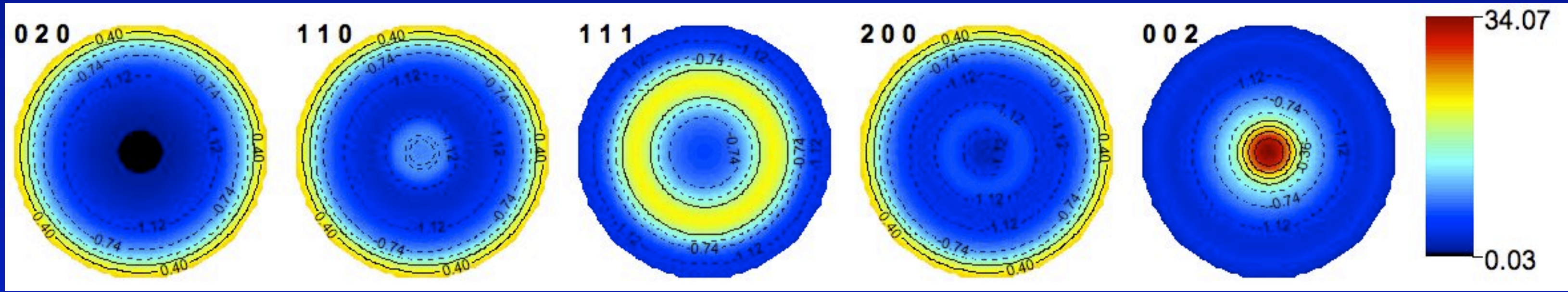




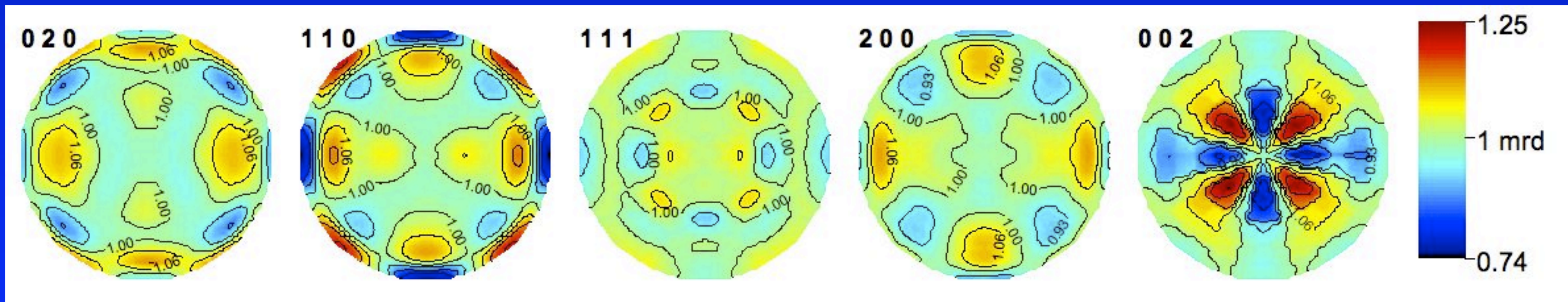
Woven/not-woven

Texture (reconstructed pole figures from ODF)

PP fiber (log scale), using standard functions



Woven/not-woven PP, using EWIMV



On the edge: the C182 sample

Amorphous carbon film ?

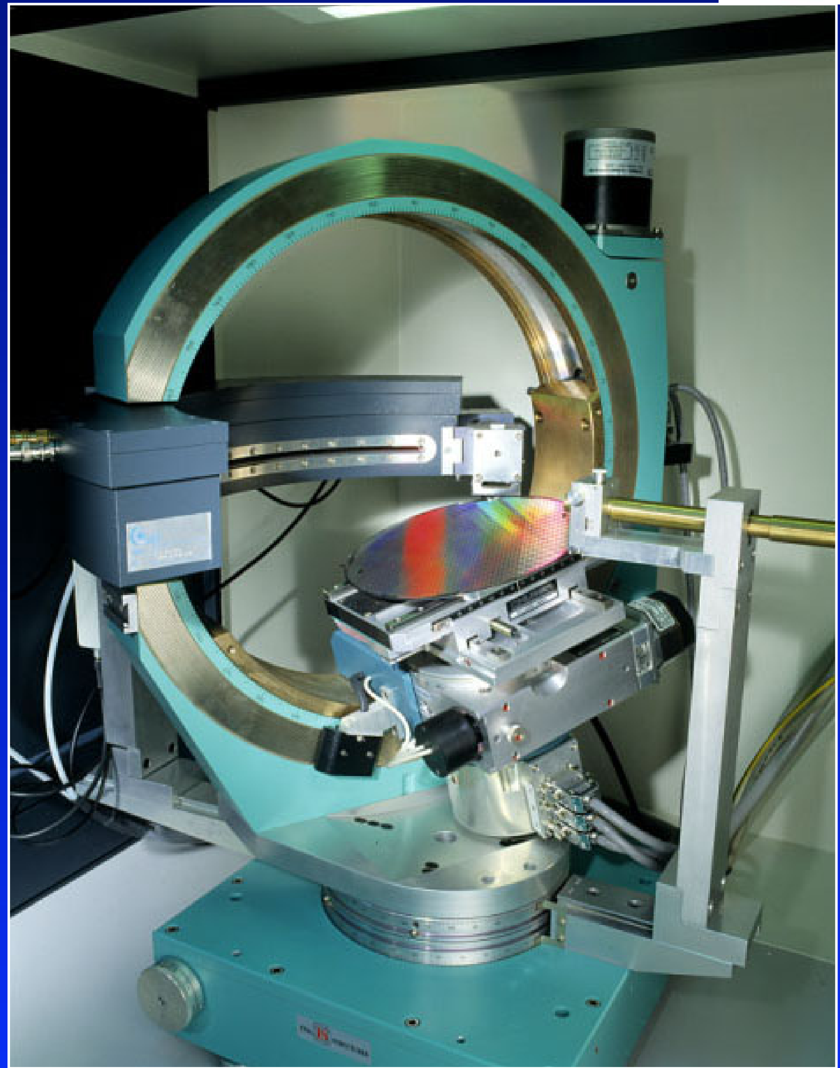
Si wafer substrate

Spectra and reflectivity collected on the ITS HR-XRD diffractometer (right)

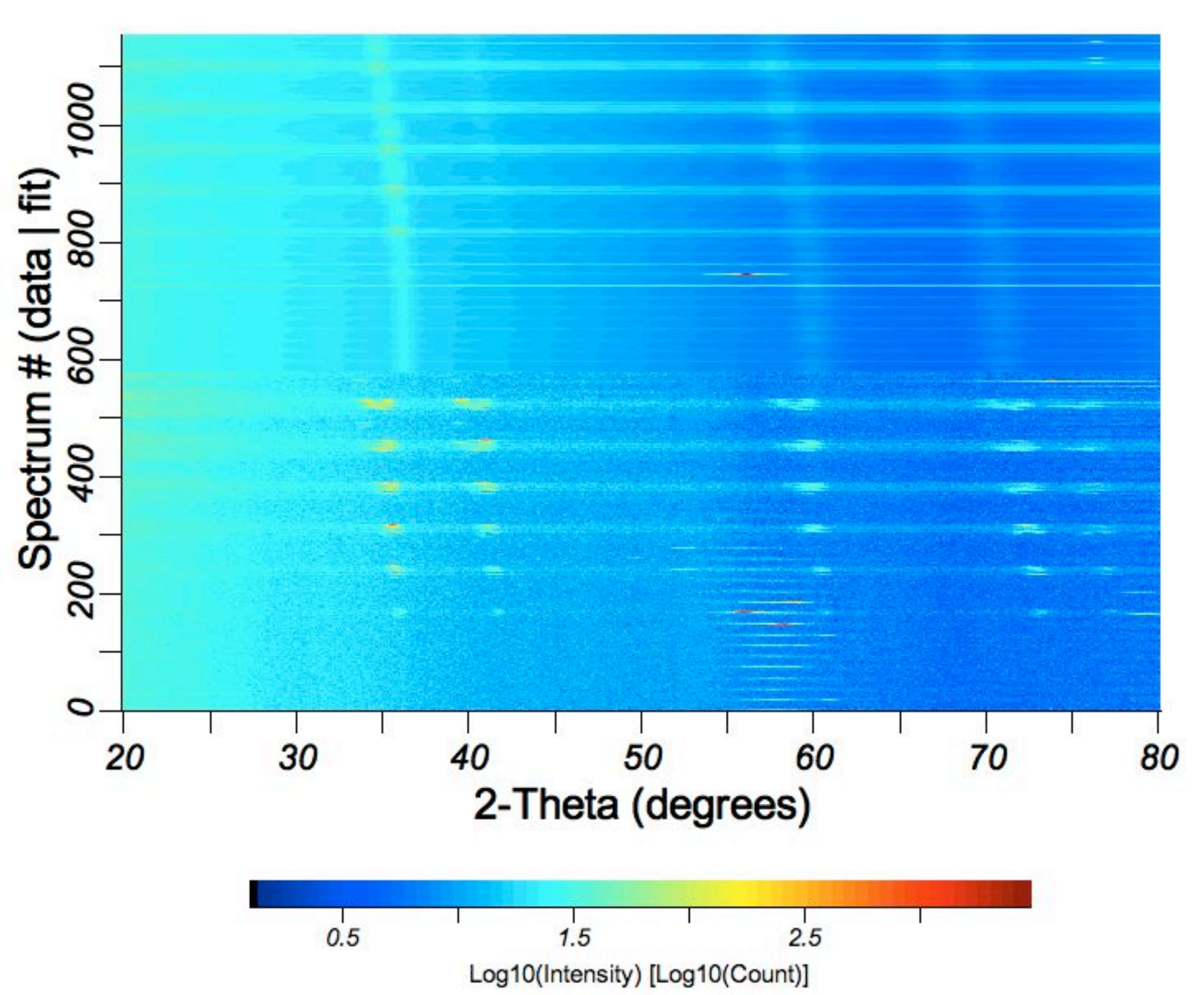
120 degs position sensitive detector on an eulerian cradle; multilayer as a primary beam monochromator

Spectra collected in chi from 0 to 50 degrees in step of 5 deg and phi from 0 to 360 in step of 5 also

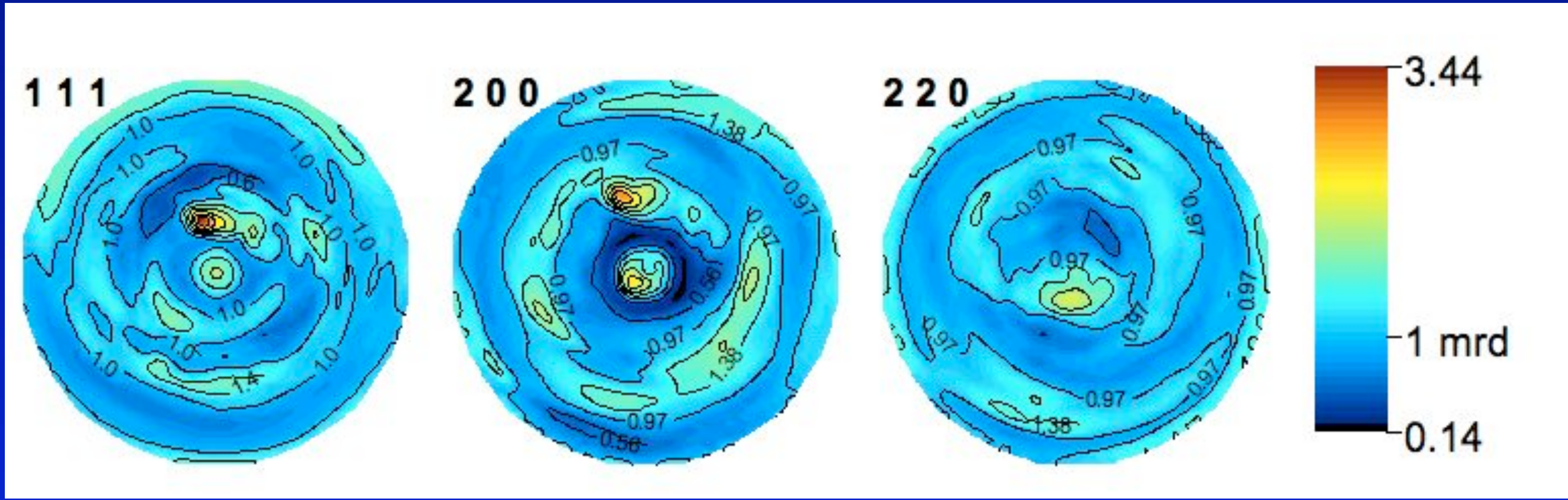
E-WIMV and standard function for Si substrate



C182 Texture



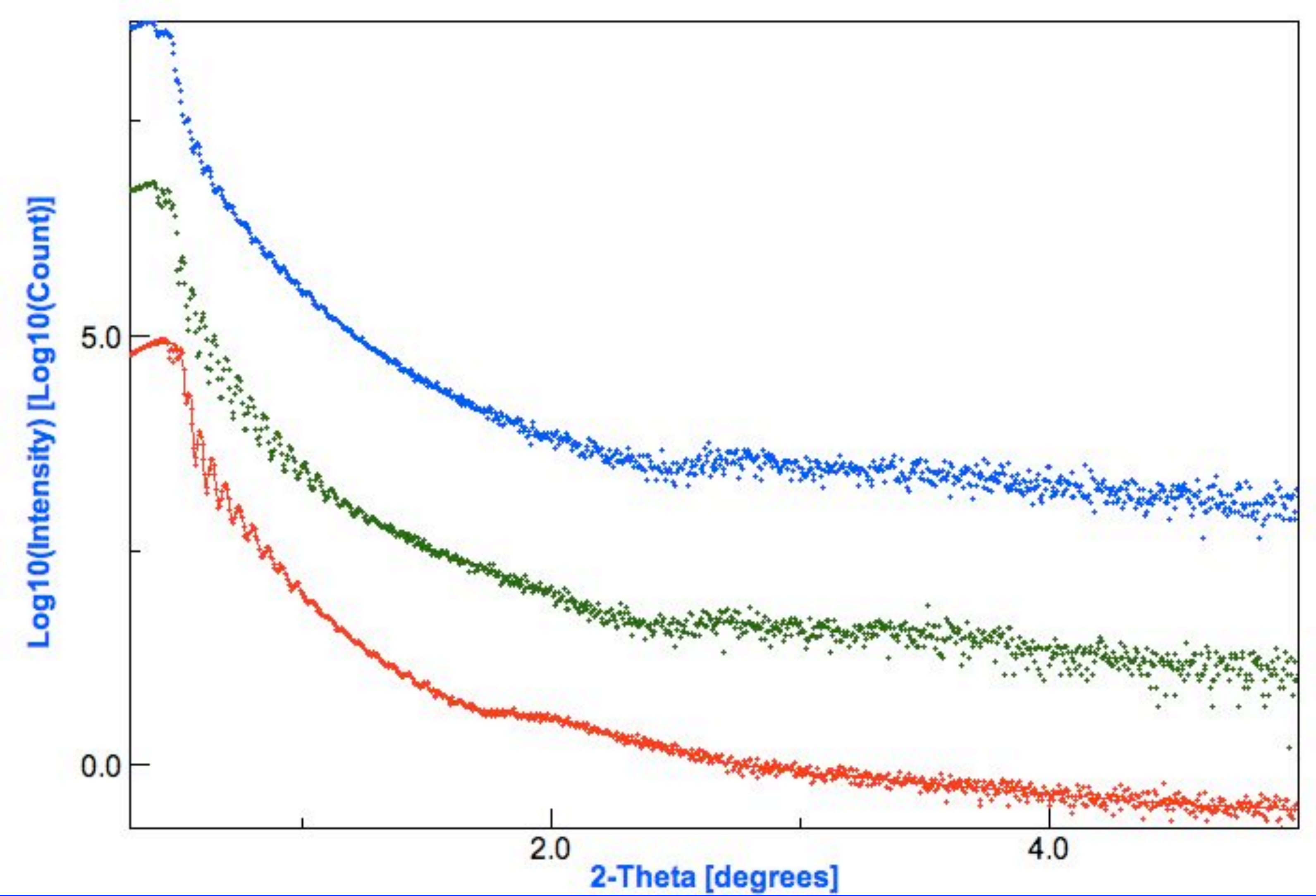
C182 Reconstructed pole figures



C182 diffraction result

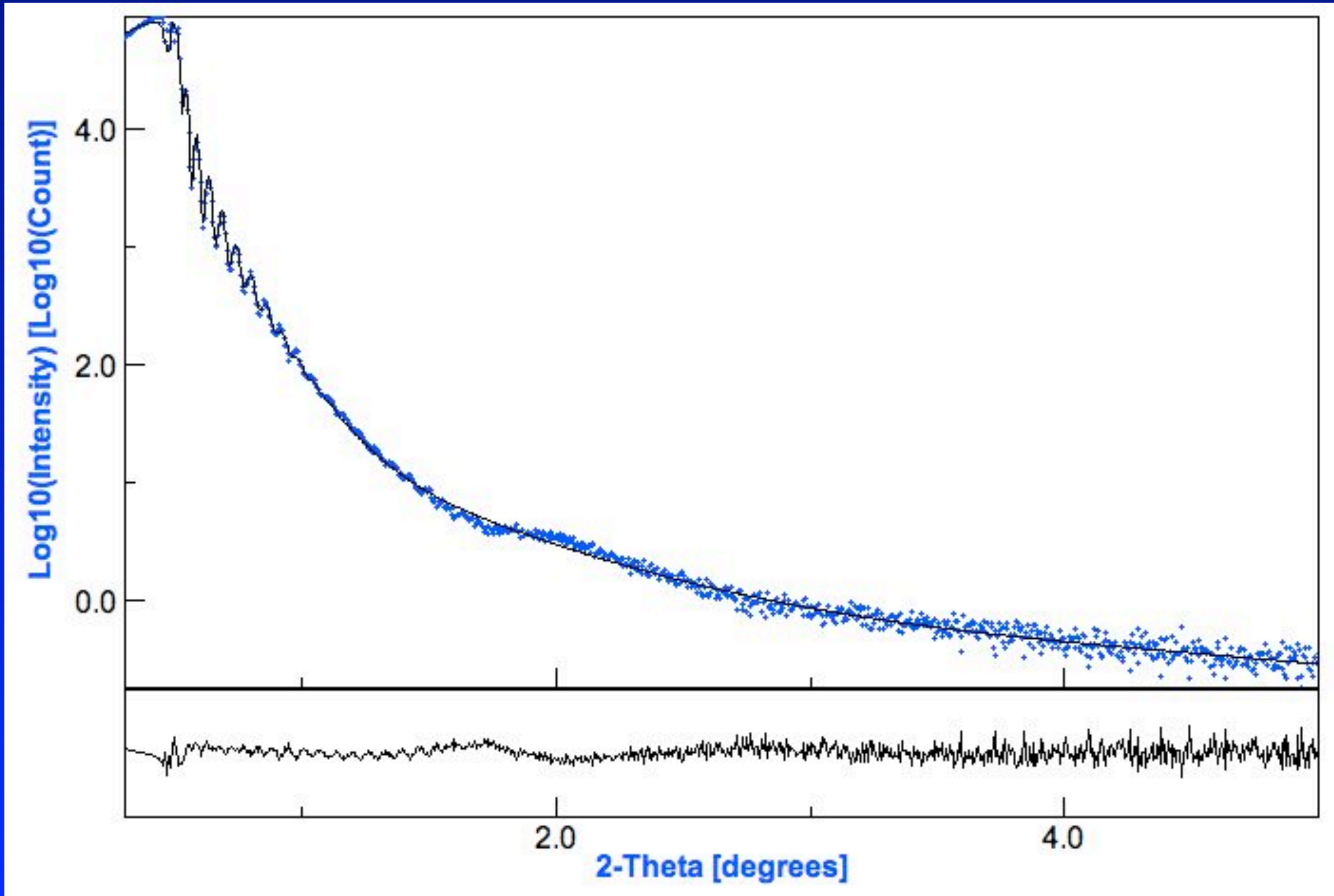
- Phase: SiC structure ??
- Texture as shown before
- Strain: very high in plane strain ~0.1 ??
- Relevant second kind microstress (not modeled)
- Crystallite size ~400 Angstrom, microstrain ~0.1

C18x reflectivity

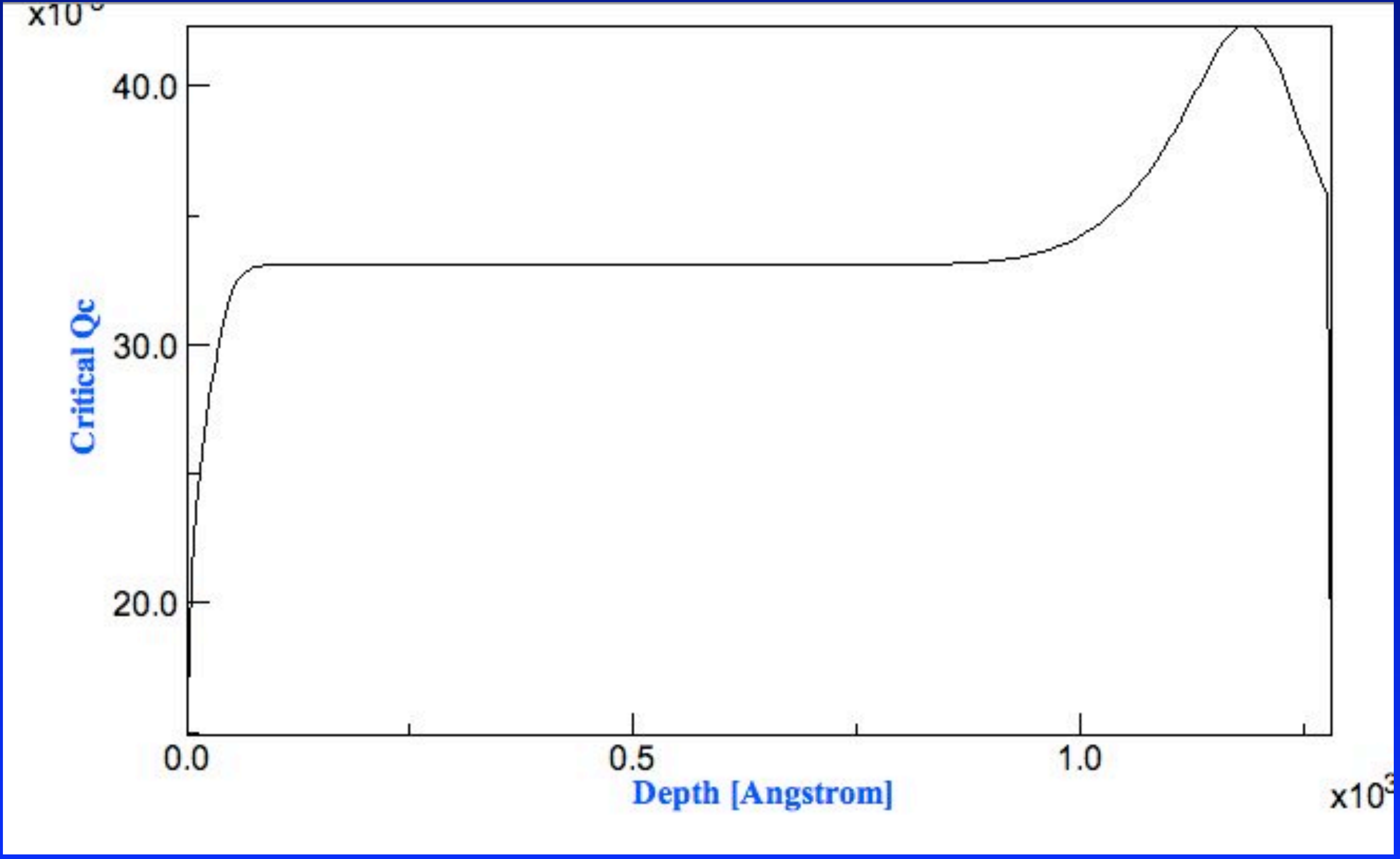


- C184
- C182
- C181

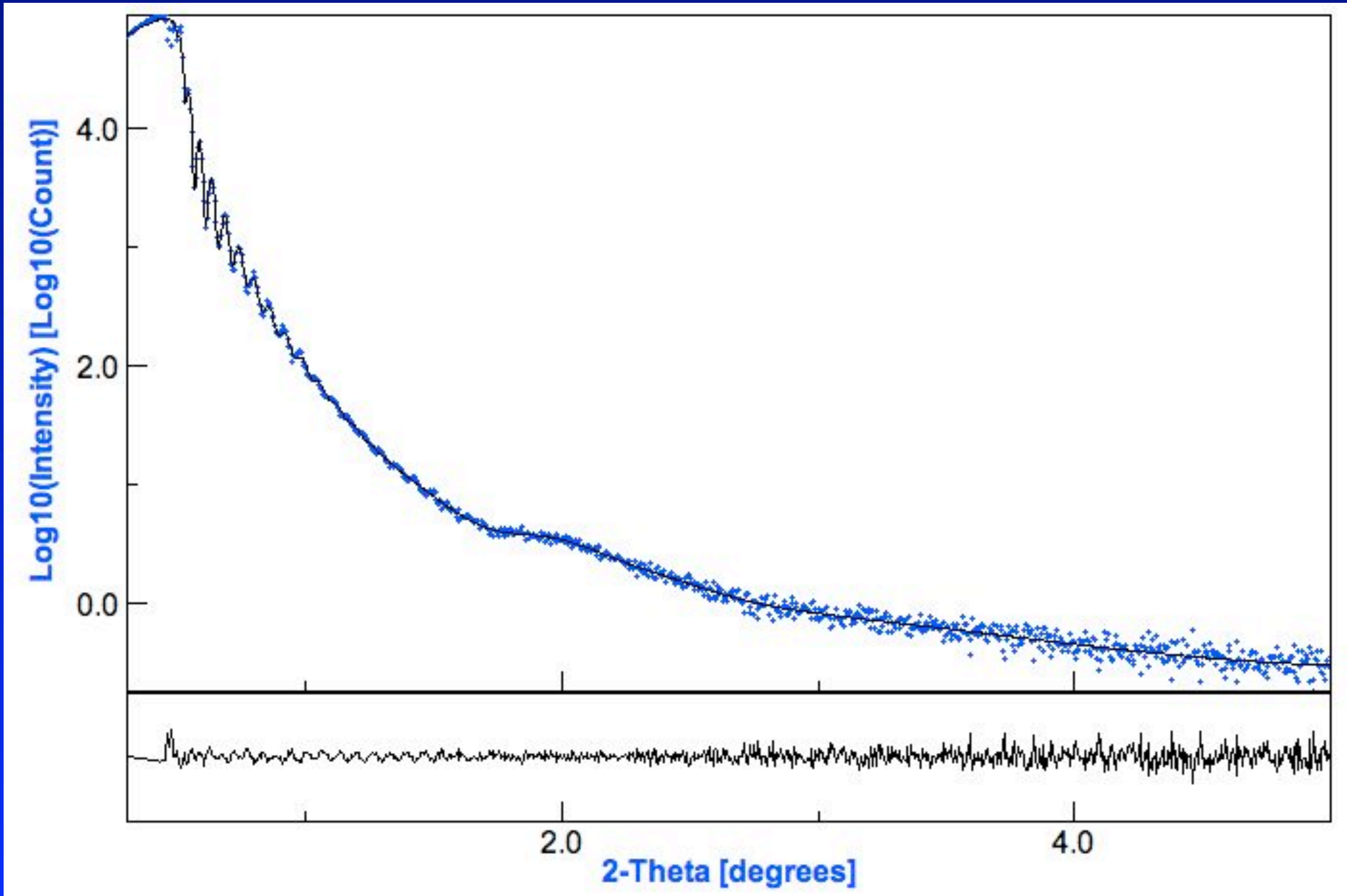
C181 sample - 3 layers model



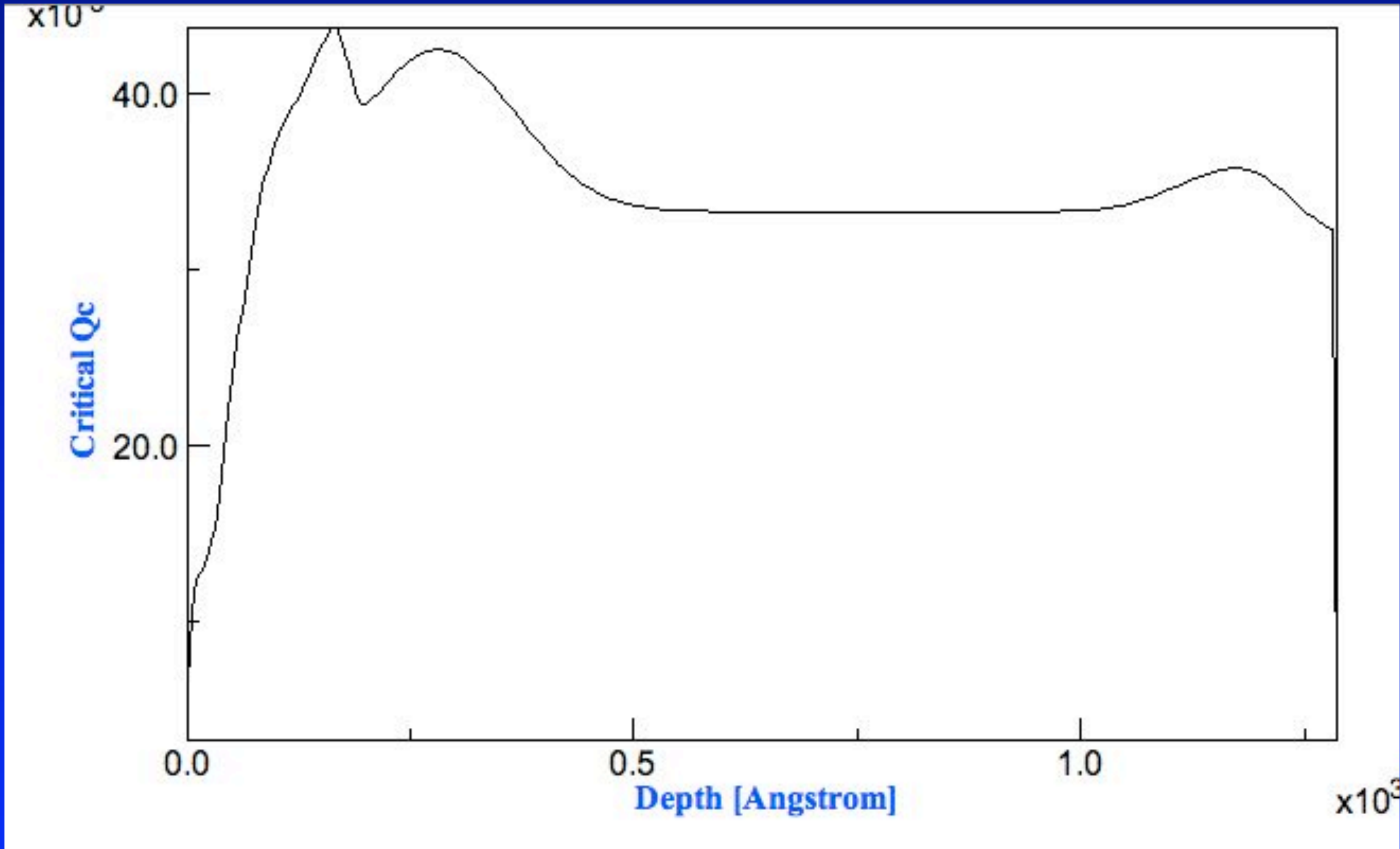
C181 sample - 3 layers model



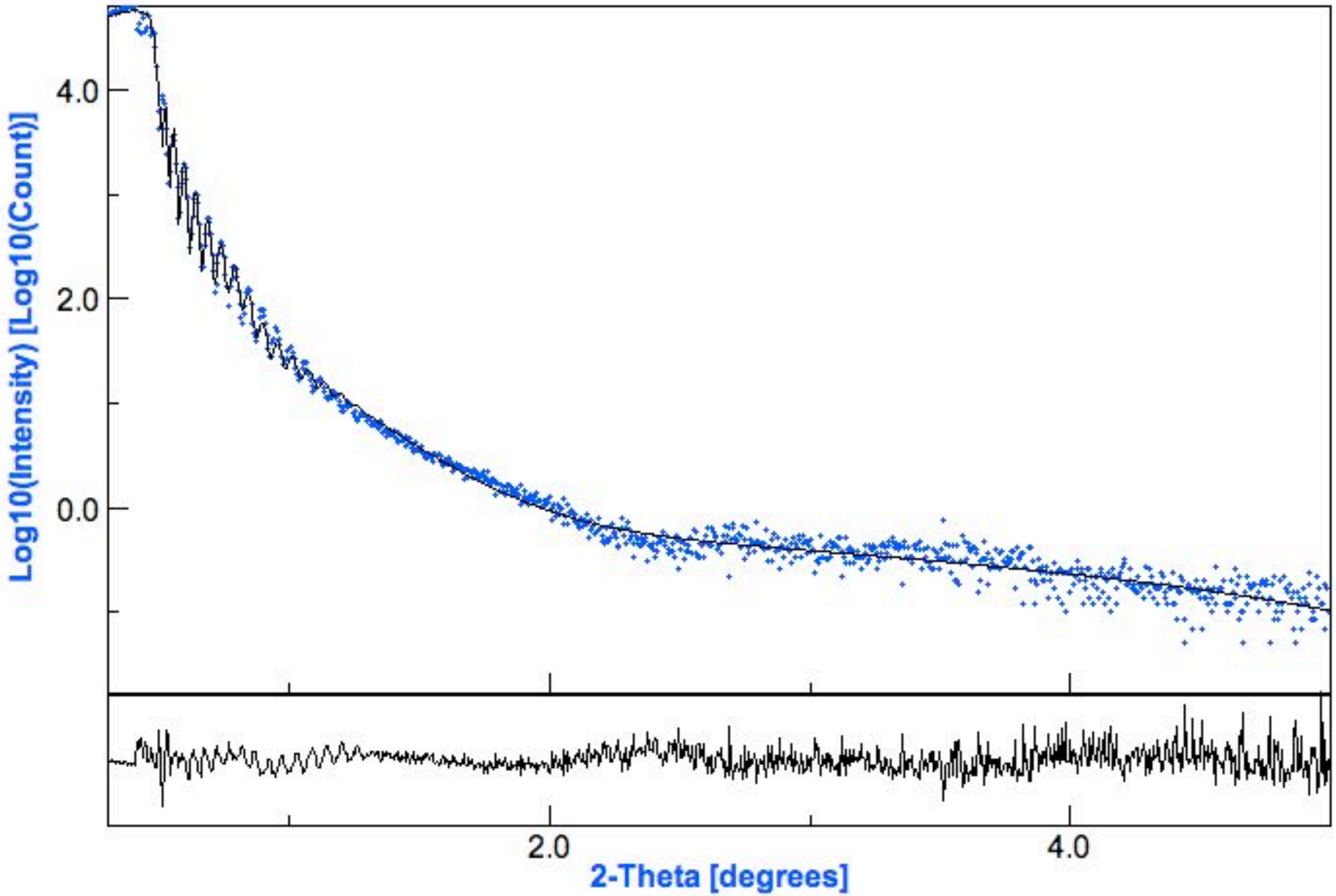
C181 - DCD model



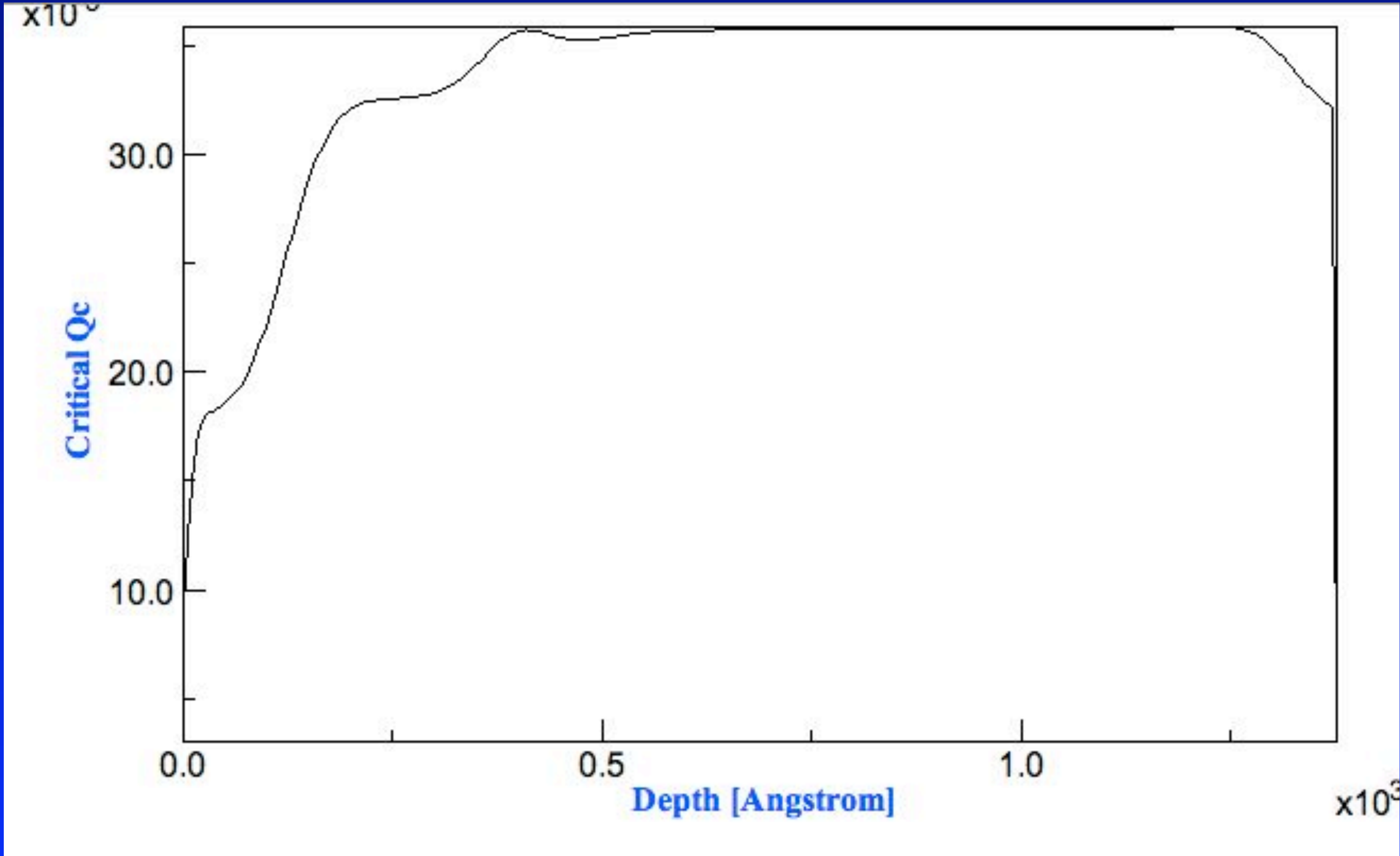
C181 - DCD model



C182 - DCD model



C182 - DCD model



Conclusions

- Combined analysis (Rietveld, microstructure, texture, residual stresses and reflectivity) is very powerful for thin films
- Extremely sharp textures requires special methodologies for texture
- Residual stresses cannot be treated by the simple $\sin^2\psi$ method in thin films
- Reflectivity and diffraction can be combined but the useful overlapping range is very small
- We need to improve the measurement time
- Still the knowledge of the sample is important
- Severe overlapping is no more a problem

The Maud program site:

http://www.ing.unitn.it/~luttero/maud

Future work (in progress)

- Driving the experiment (ODF coverage etc.). Using Genetic Algorithms?
- Sharp textures -> continuous coverage -> 2D detectors -> 2D fitting?
- Ab initio structure solution. Problems:
  - Textured sample preparation
  - Data collection (fast, reliable, high resolution)
- Reflectivity: off specular computation (reciprocal map fitting)

Off specular reflectivity