TEXTURE, RESIDUAL STRESS AND STRUCTURAL ANALYSIS OF THIN FILMS USING A COMBINED X-RAY ANALYSIS

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Rietveld Texture Analysis (RiTA)

- Goals:
  - Obtain structure, microstructure, texture and residual stresses of thin films and multilayer by one step methodology
  - The analysis should not be limited by phase overlapping, strong texture or complex structures

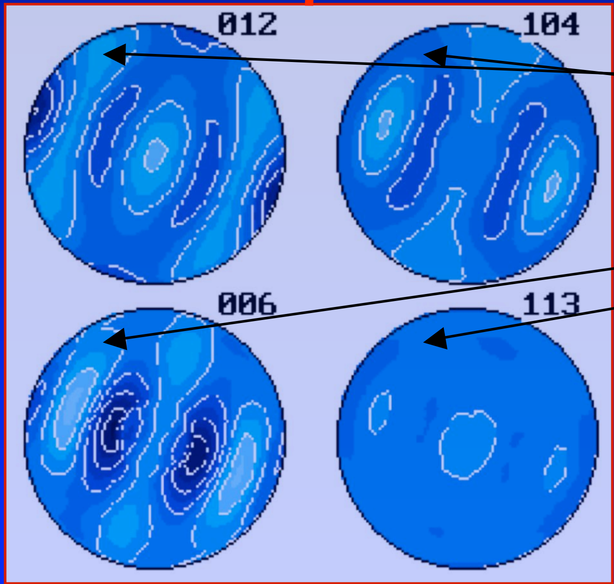
- How? -> Rietveld based analysis or full pattern fitting
  - The Rietveld method is a powerful fitting method of the diffraction pattern to refine the crystal structure.
  - We select and develop some particular methodologies for the analyses.
  - We incorporate in a Rietveld package all these methodologies from microstructure to texture, residual stress and reflectivity.
  - We build a machine to collect several full XRD spectra at different tilting position of the sample and reflectivity pattern.
  - The final program is Maud, developed inside the ESQUI European project

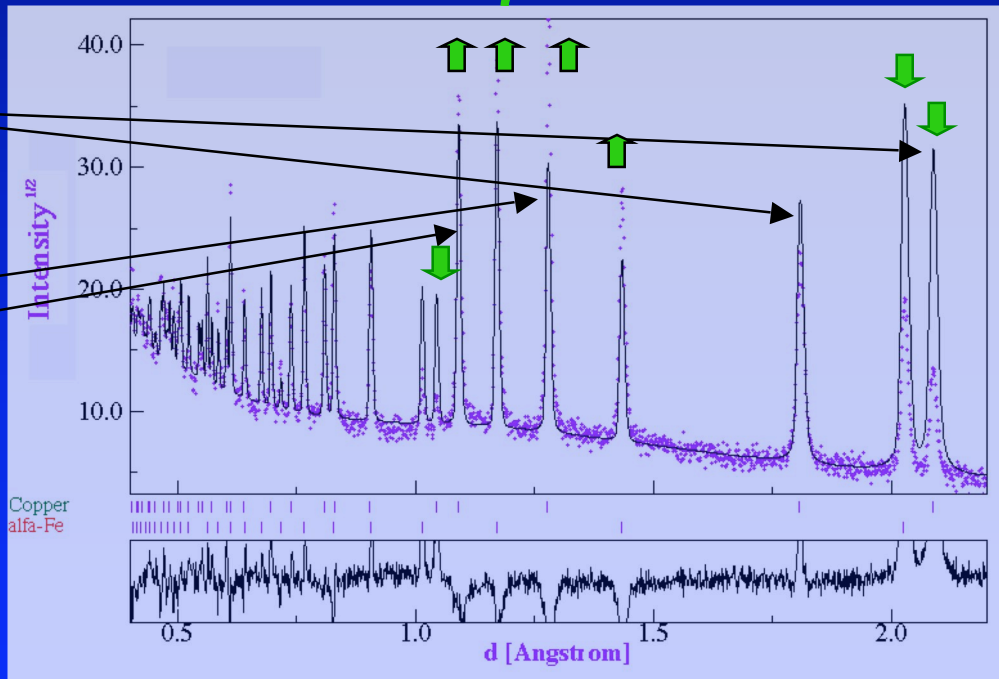
Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra





How it works (RiTA)

The equation:

$$I_i^{calc}(\chi,\phi) = \sum_{n=1}^{Nphases} S_n \sum_k L_k \left|F_{k;n}\right|^2 S\left(2\theta_i - 2\theta_{k;n}\right) P_{k;n}(\chi,\phi) A + bkg_i$$

Harmonic:

$$P_k(\chi,\phi) = \sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{n=-l}^{l} k_l^n(\chi,\phi) \sum_{m=-l}^{l} C_l^{mn} k_n^{*m}\left(\Theta_k \phi_k\right)$$

$$f(g) = \sum_{l=0}^{\infty} \sum_{m,n=-l}^{l} C_l^{mn} T_l^{mn}(g)$$

- C_l^{mn} are additional parameters to be refined
- Data (reflections, number of spectra) sufficient to cover the ODF

- Pro:
  - Easy implementation
  - Very elegant, completely integrated in the Rietveld
  - Fast, low memory consumption to store the ODF.
- Cons:
  - No automatic positive condition (ODF > 0)
  - Not for sharp textures
  - Low symmetries -> too many coefficients to refine (where are the advantages?)
  - Memory hog for refinement.
  - No ghost correction.

How it works (RiTA)

- WIMV
  - Discrete method. ODF space is divided in regular cells (ex. 5x5x5 degrees) and the function value is stored for each cell.
  - Numerical integration:

$$P_k(\chi,\phi) = \int_{\varphi} f(g,\varphi)\,d\varphi$$

  - For each refinement iteration:
    - P_k extracted (Le Bail method)
    - ODF computed (WIMV)
    - P_k recalculated
    - Fitting of the spectra
  - Advantages:
    - ODF > 0, always
    - Ok for sharp textures and low symmetries
  - Disadvantages:
    - Less elegant (require extraction and interpolation to a regular grid)
    - Tricky to implement
    - Slower in the Rietveld (high symmetries)

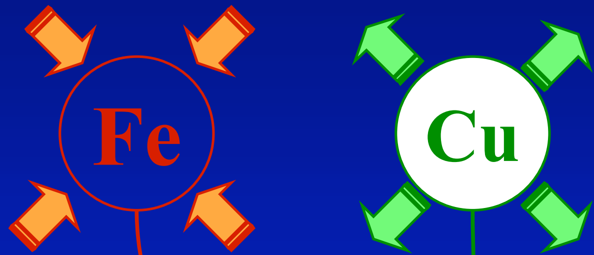
Residual Stresses and Rietveld

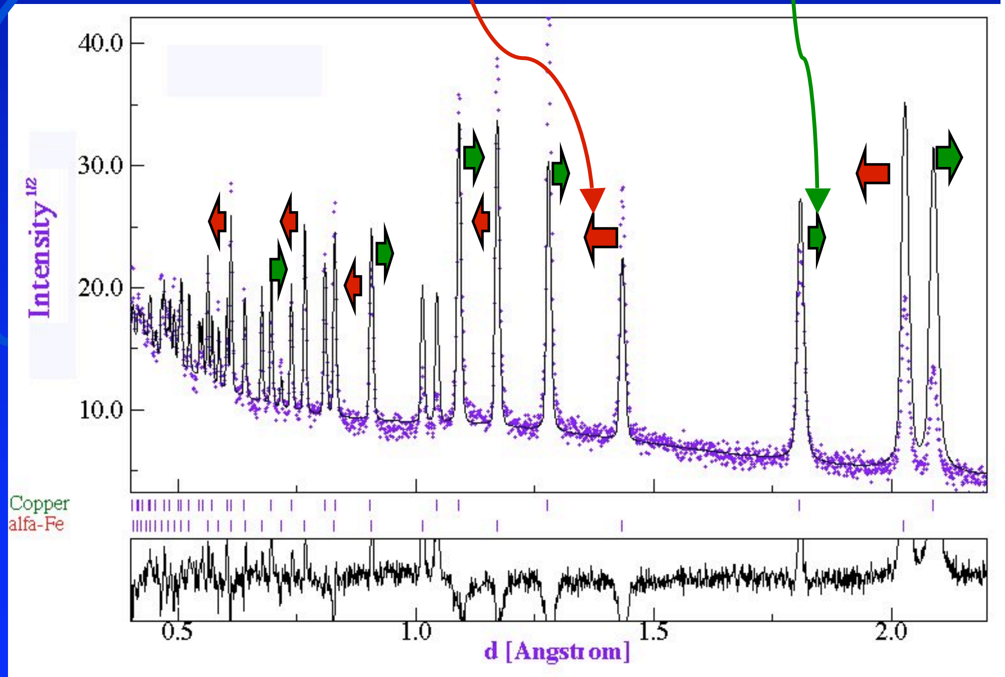
- Macro elastic strain tensor (I kind)
- Crystal anisotropic strains (II kind)

C

Macro and micro stresses

Applied macro stresses

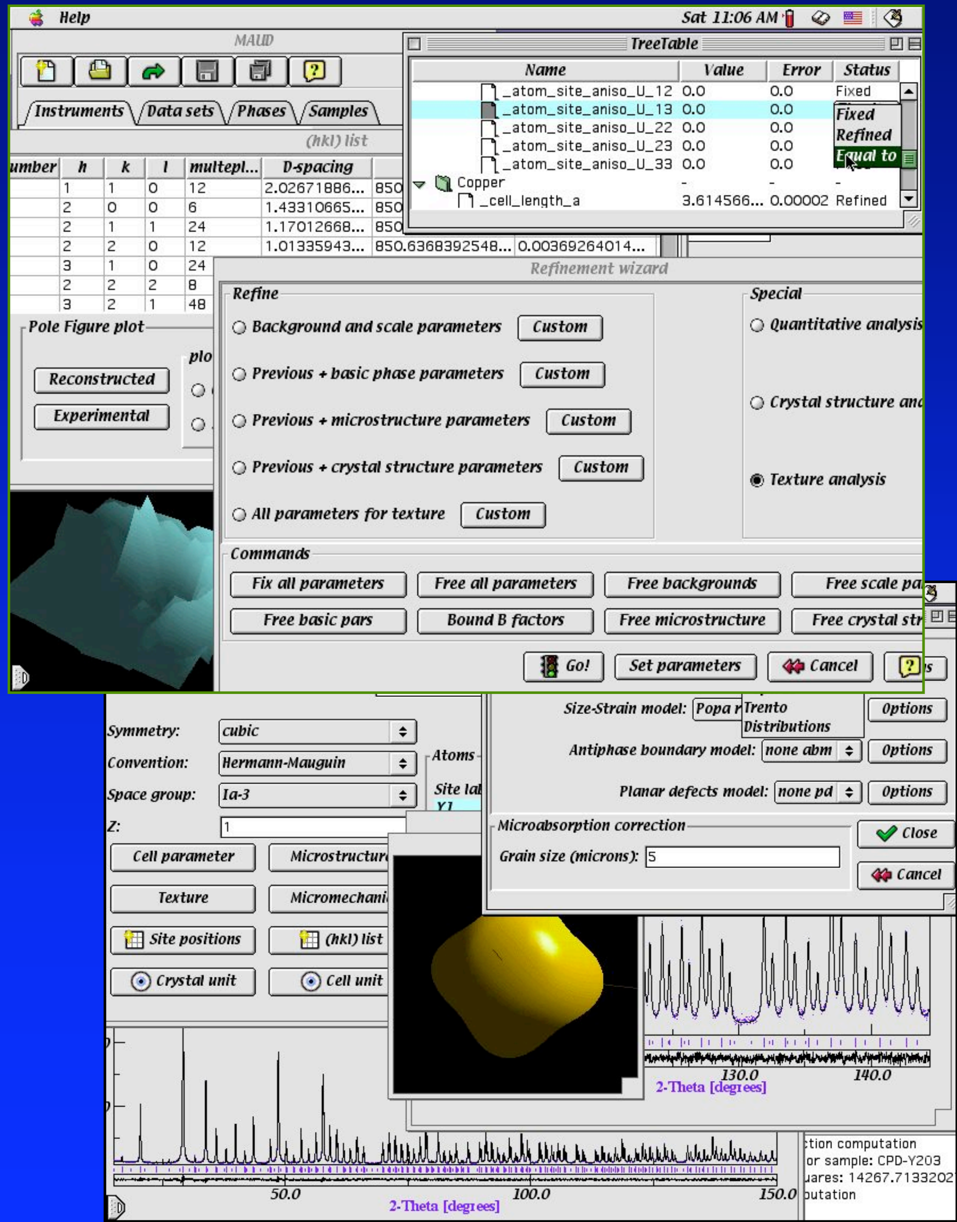




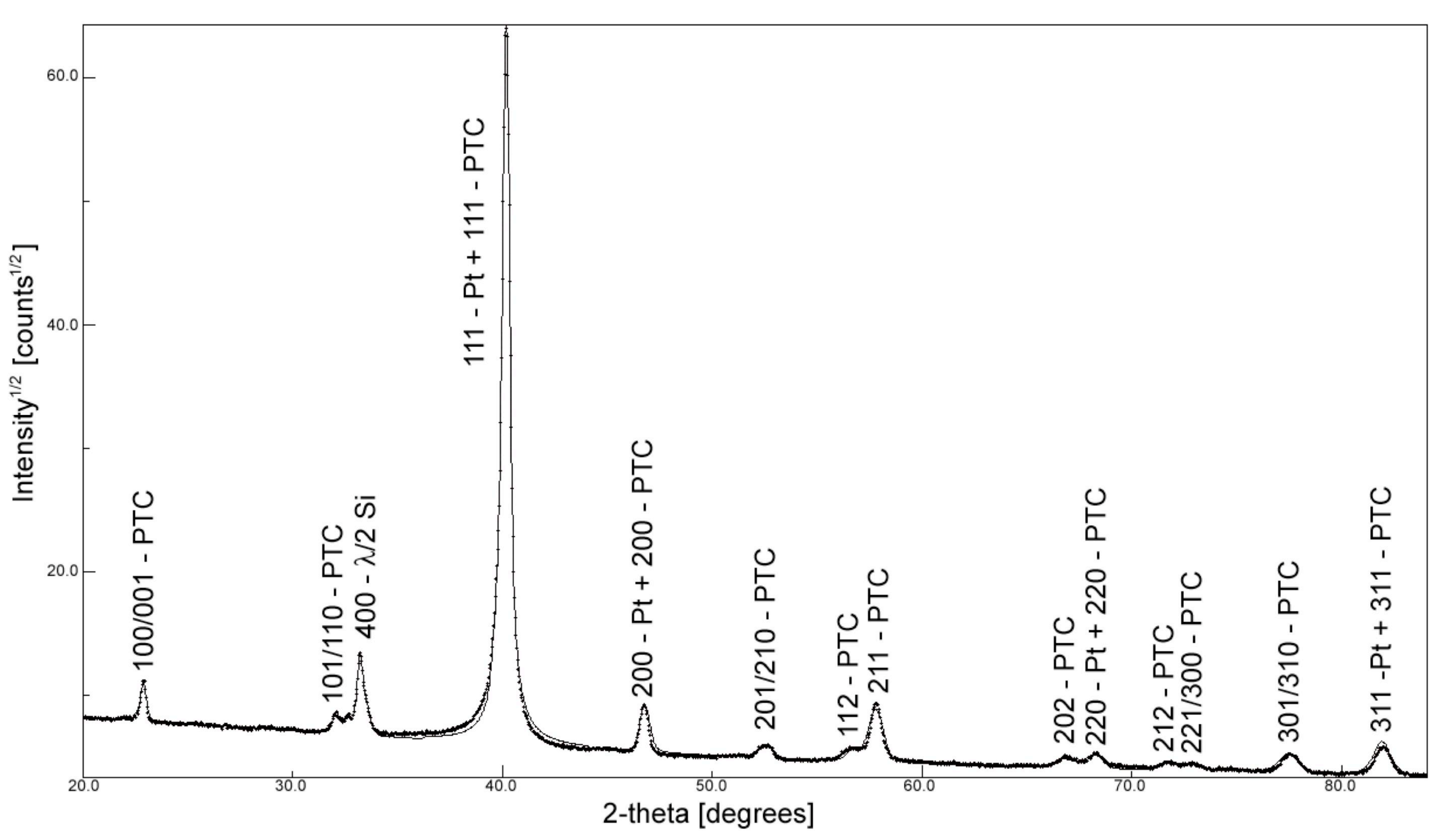
Methodology implementation

Maud program:

- *Rietveld based analysis software:*
  - *Crystal structure*
  - *Microstructure*
  - *Quantitative phase analysis*
  - *Layered sample model*
- *Texture:*
  - *WIMV*
  - *E-WIMV (modified)*
  - *Harmonic*
- *Residual Stresses*
  - *No texture: triaxial tensor*
  - *With texture: Reuss, Voigt, Geometrical mean*
- *Reflectivity*
  - *Matrix method*
  - *DWBA LS fit (electron density profile)*
  - *Genetic algorithm*
- *http://www.ing.unitn.it/~luttero/maud*
- *Supported by: ESQUI European project*

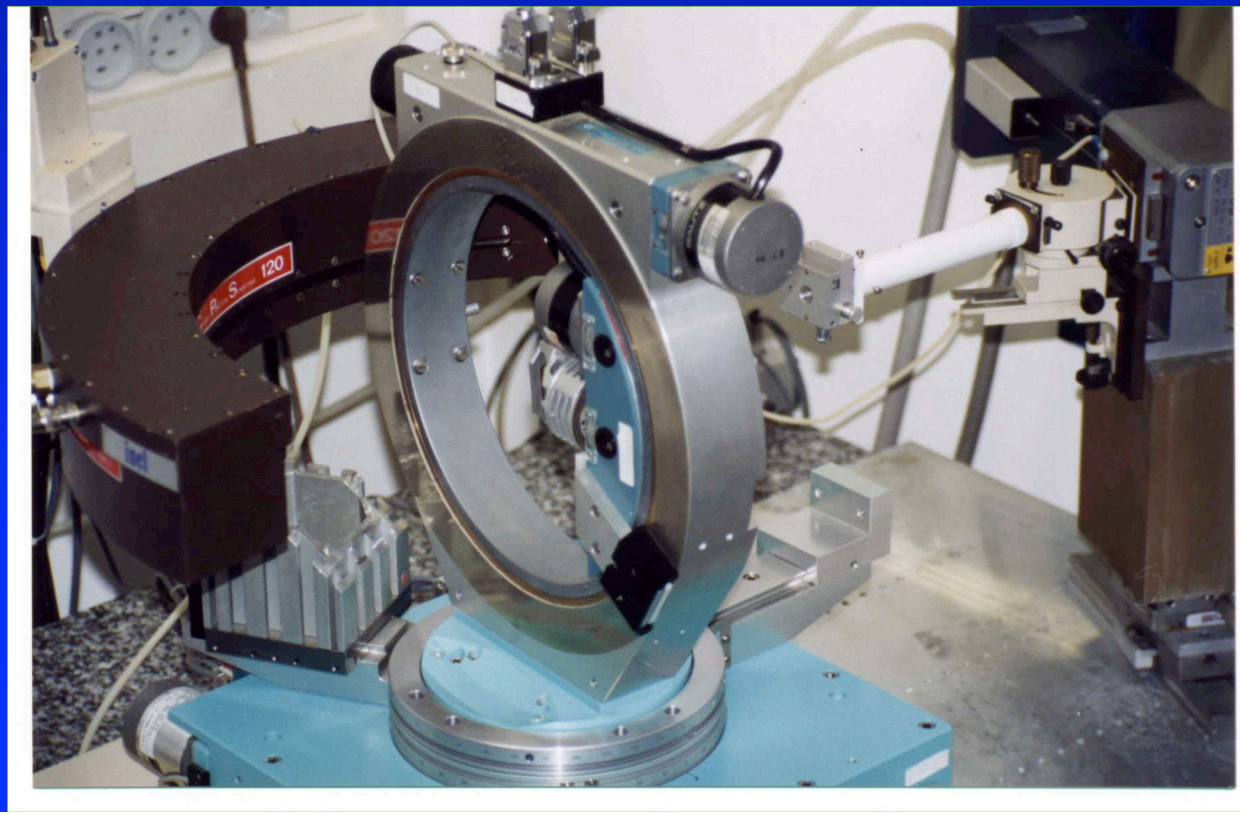


PTC film: the overlapping problem



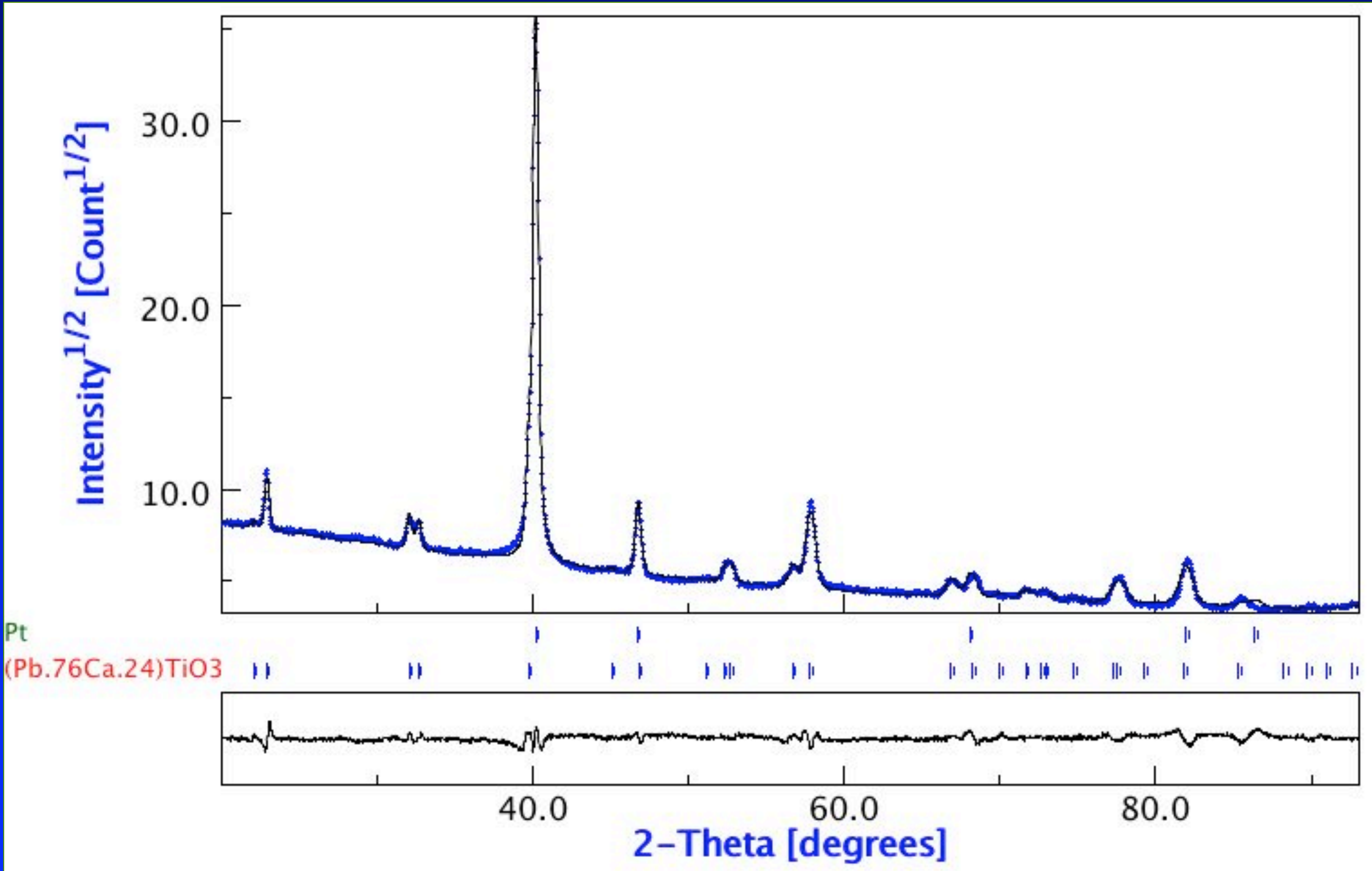
PTC film: the measurement

- Substrate: $TiO_2/SiO_2/Si(100)$
- 400 nm of $Pb_{0.76}Ca_{0.24}TiO_3$ (PTC) film deposited by spin coating of a sol-gel solution (CSIC Madrid).
- 50 nm of Pt buffer layer.
- Instrument: 120 degs curved position sensitive detector on a closed eulerian cradle, graphite primary monochromator (LPEC - Le Mans, France)
- Collected full spectra on a 5x5 degs grid in chi and phi. From 0 to 355 in phi and up to 50 deg in chi.



The LPEC, Le Mans instrument

PTC and Pt phase separation



PTC film: harmonic texture model

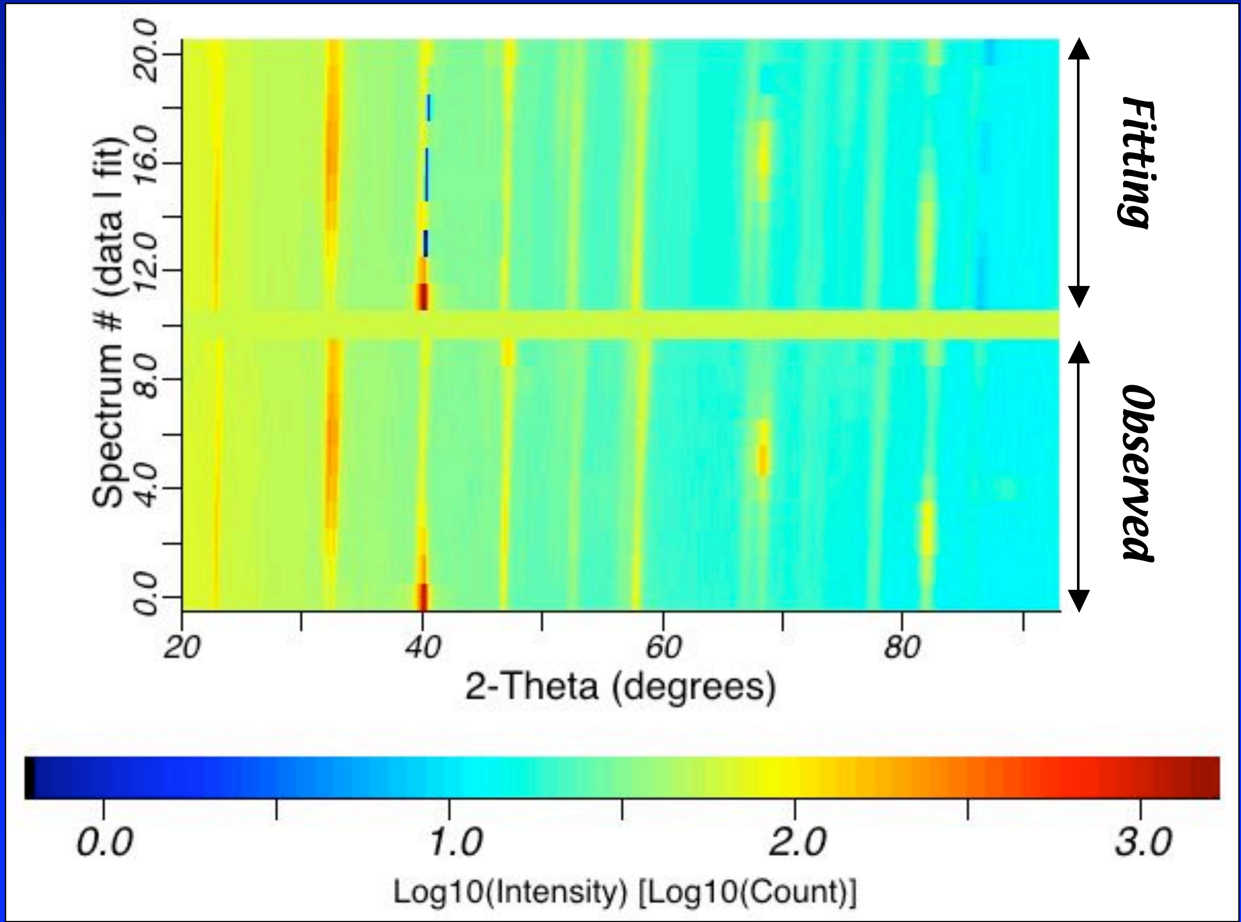
Triclinic sample symmetry: 1245 parameters only for PTC (L_{max} = 22)

Increasing sample symmetry to orthorhombic: 181 parameters

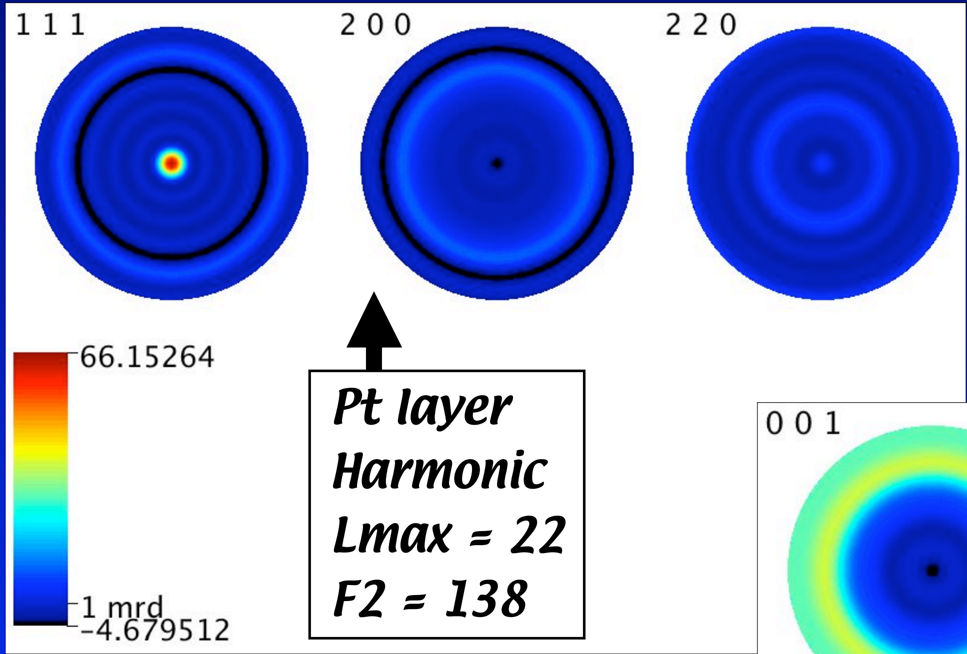
Reducing sample symmetry to fiber and L_{max} to 16: 24 parameters

For Pt layer: fiber texture, L_{max} = 22 -> 15 parameters

Rw (%) = 14.786048

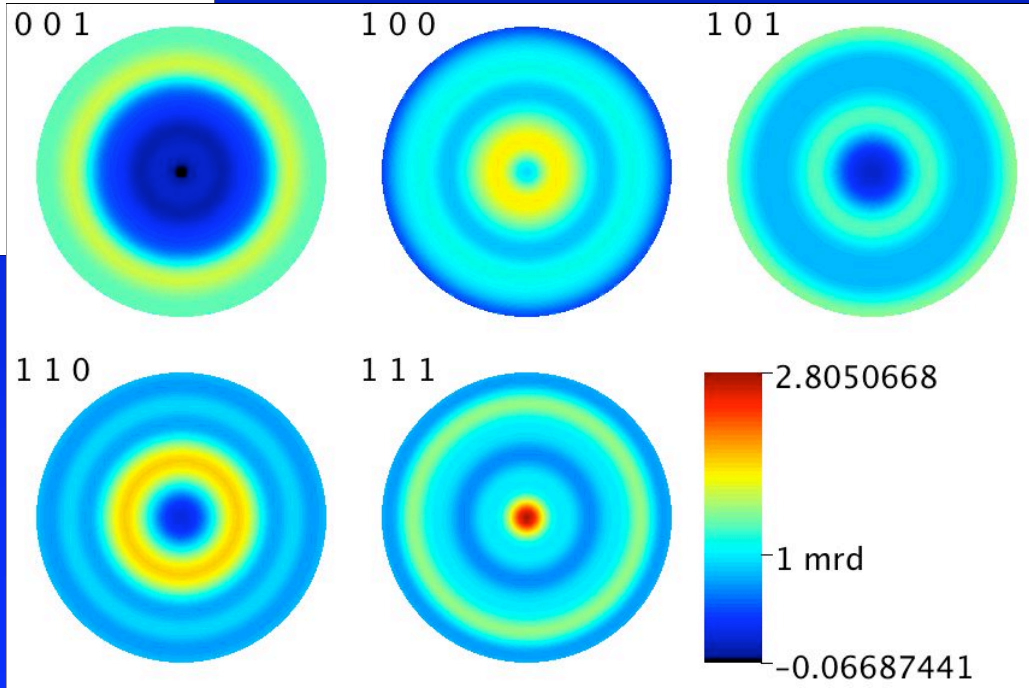


PTC film: harmonic reconstructed pole figures

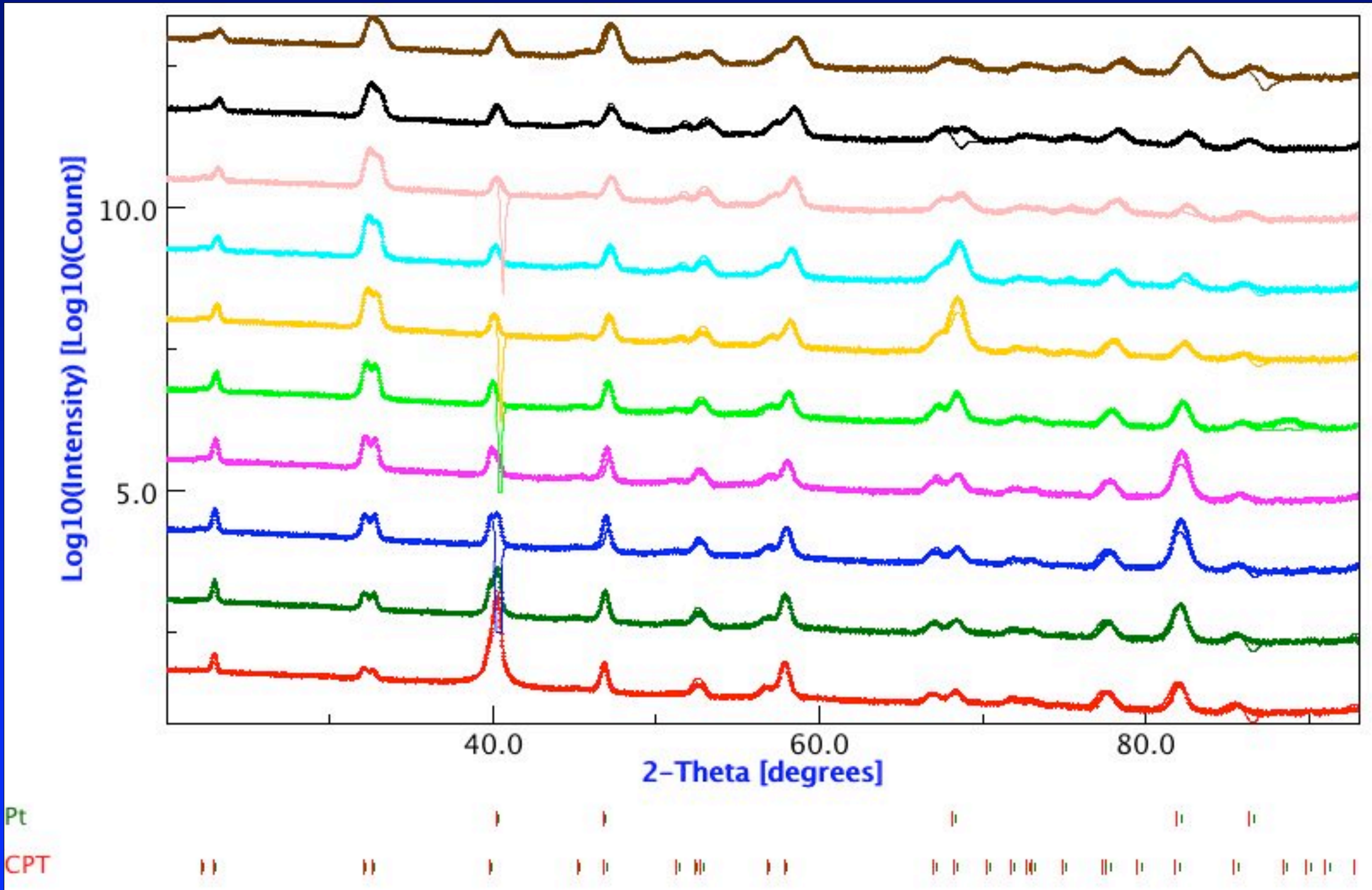


Pt layer
Harmonic
Lmax = 22
F2 = 138

CPT layer
Harmonic method
Lmax = 16
F2 = 1.55

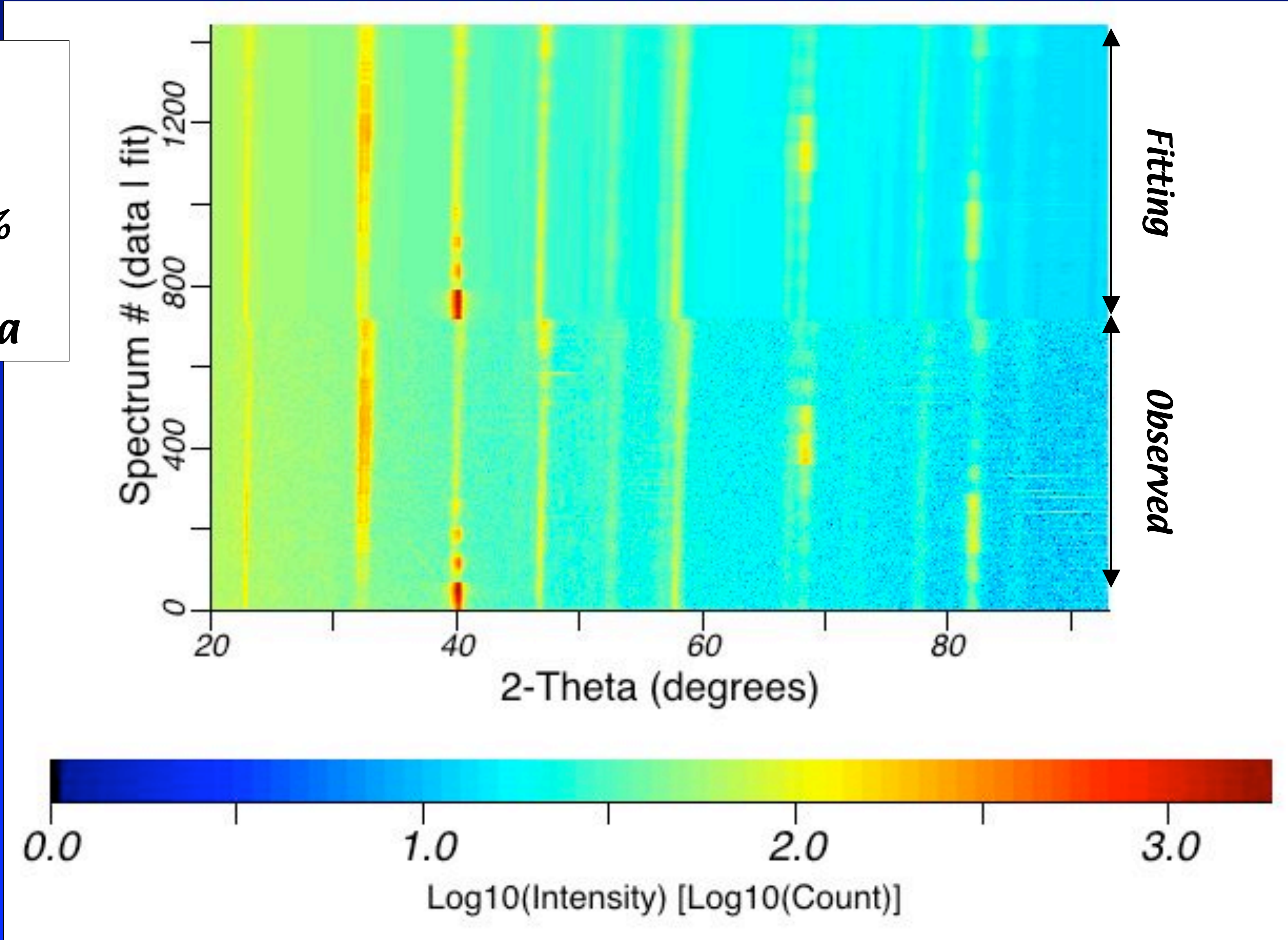


PTC film: harmonic fitting, the "Ghost" problem

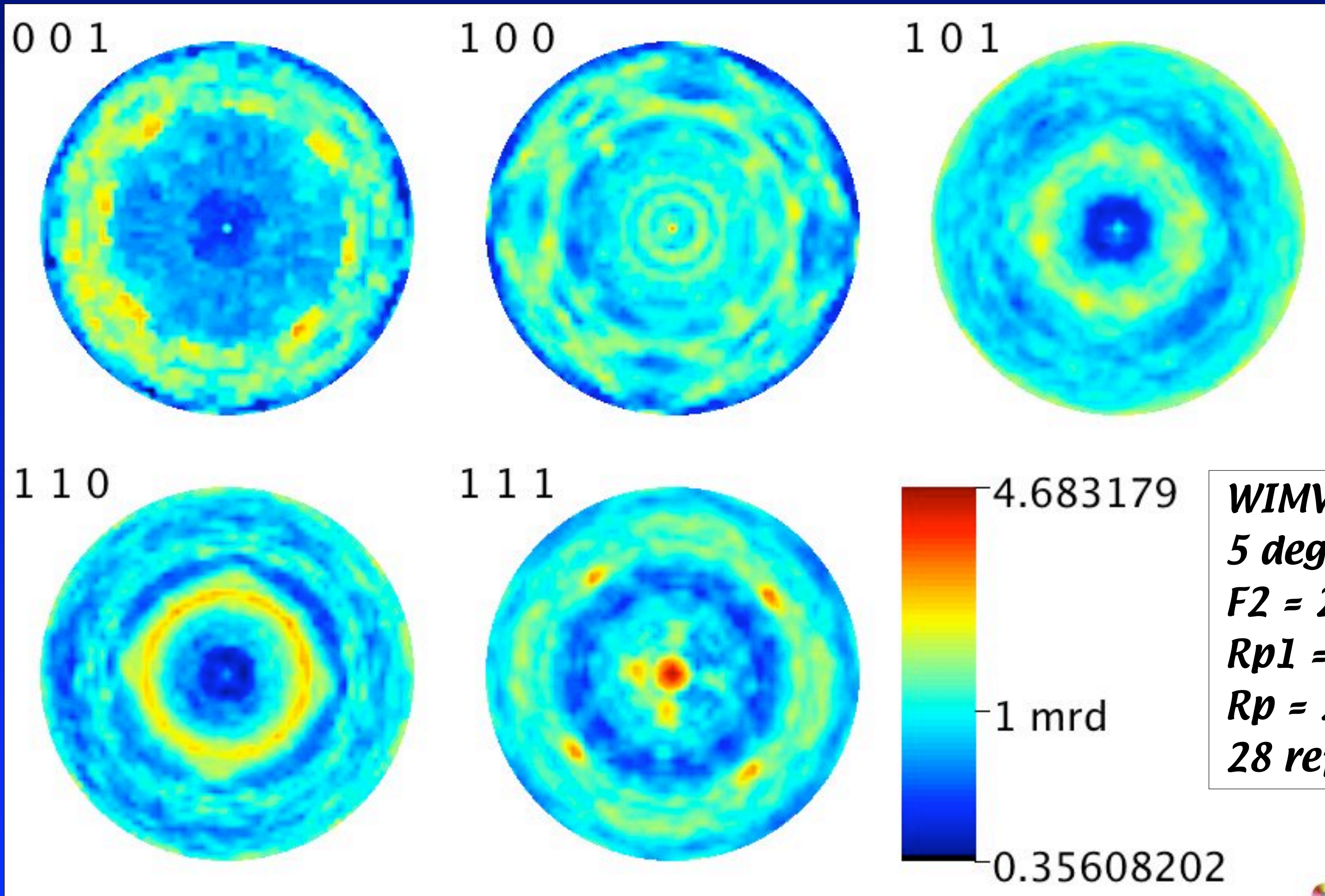


PTC film fitting: WIMV

WIMV
2 layers
2 phases
Rw = 25.5%
R = 42.6 %
792 spectra

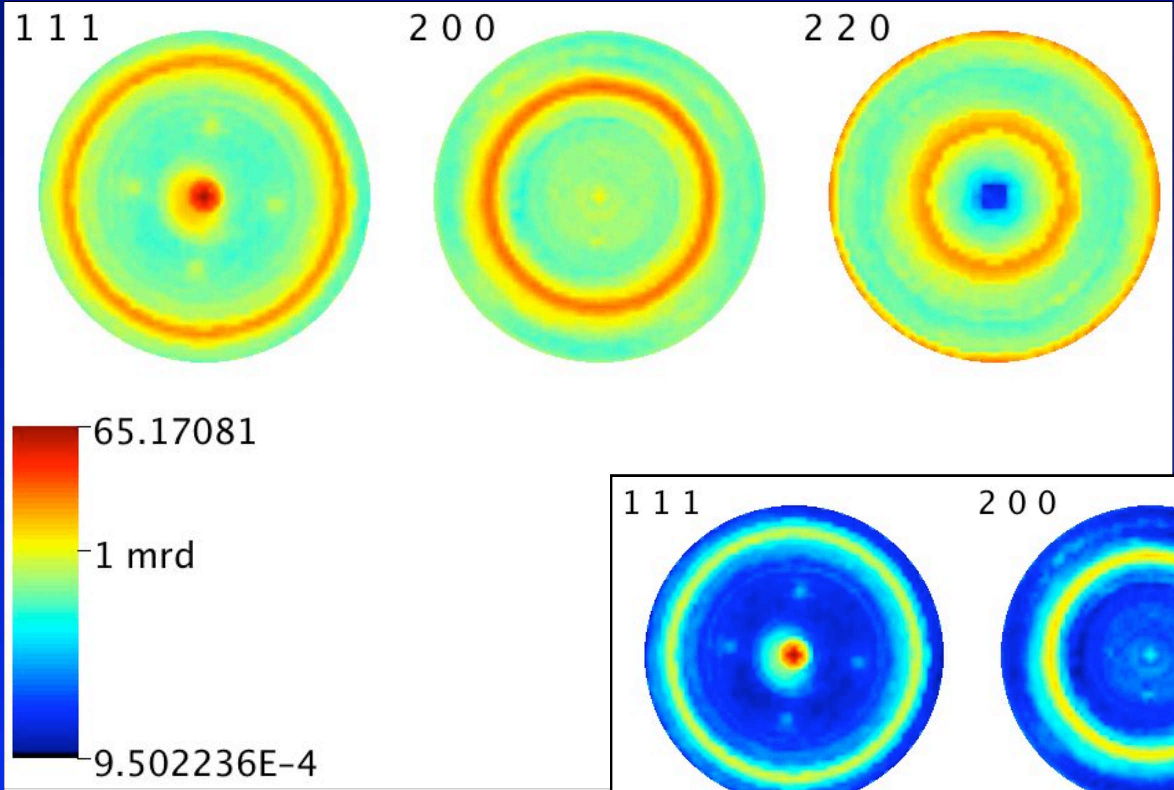


PTC film: CPT reconstructed pole figures, WIMV

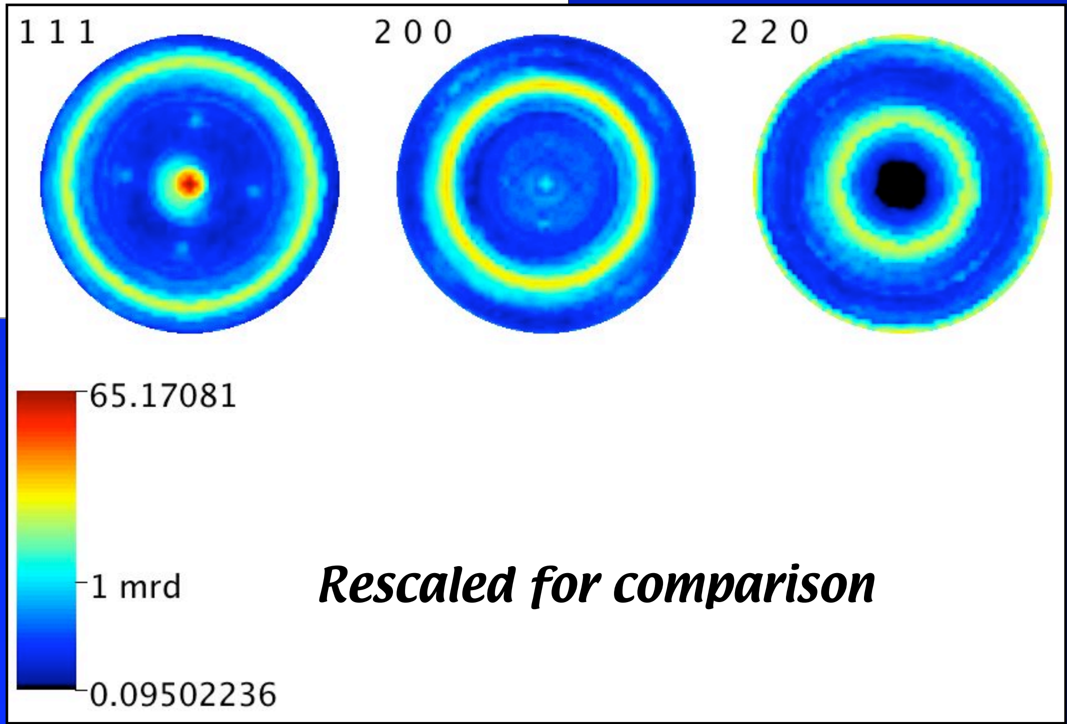


WIMV
5 deg cells
F2 = 25.88
Rp1 = 18.2 %
Rp = 25.0 %
28 reflections

PTC film: reconstructed Pt pole figures, WIMV



WIMV
5 deg cells
F2 = 2.13
Rp1 = 27.3 %
Rp = 28.6 %
5 reflections



E-WIMV

Modified WIMV algorithm for Rietveld Texture Analysis

Differences respect to WIMV:

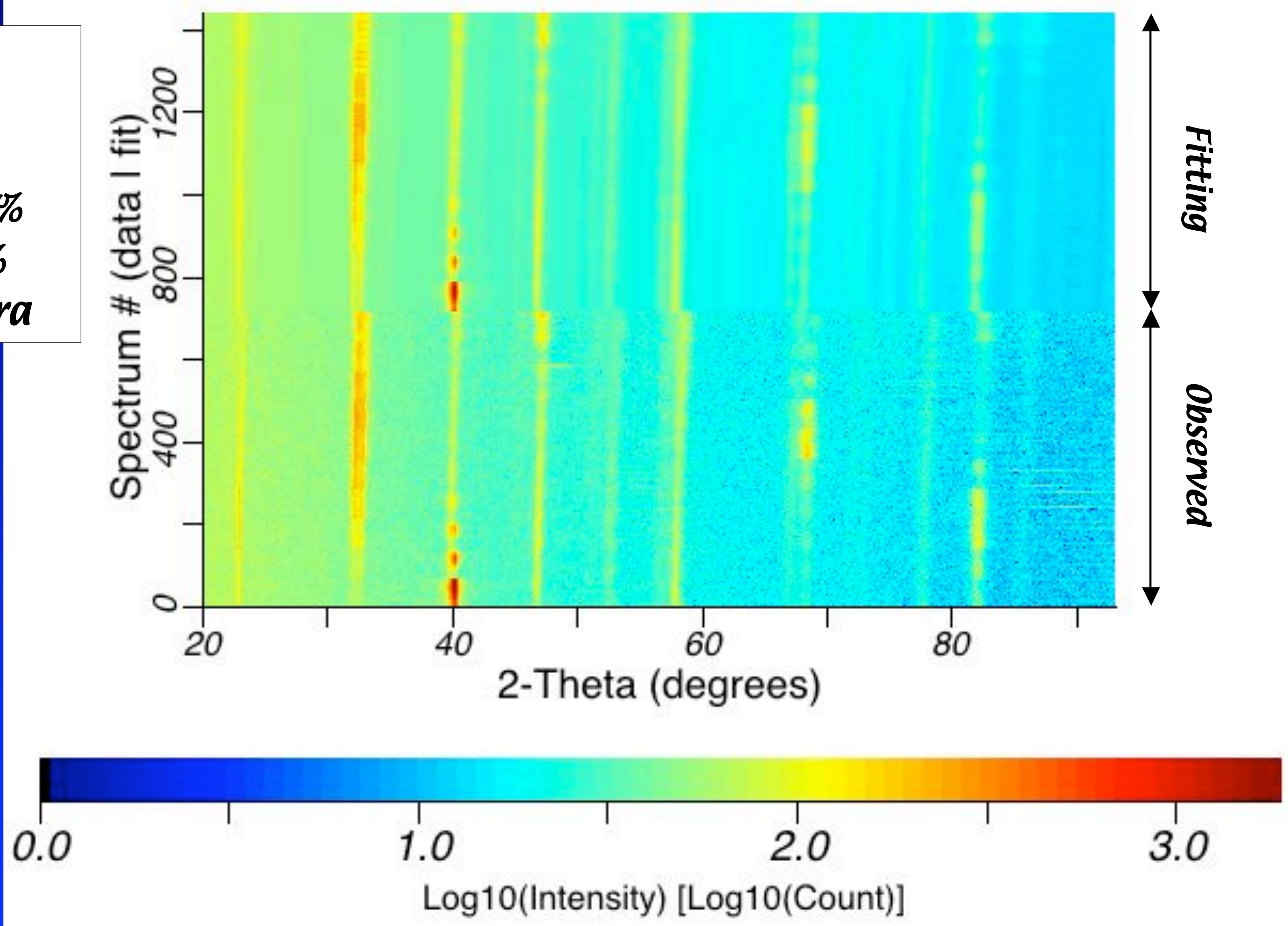
- *ODF cell path computed for each measured point (no interpolation of pole figures on a regular grid)*
- *Different cell sizes available (Ex: 15, 10, 7.5, 5, 2.5, 1.25, 1…..) in degs.*
- *Tube projection computation (similar to the ADC method)*
- *Minimization engine more entropy like*

Problems:

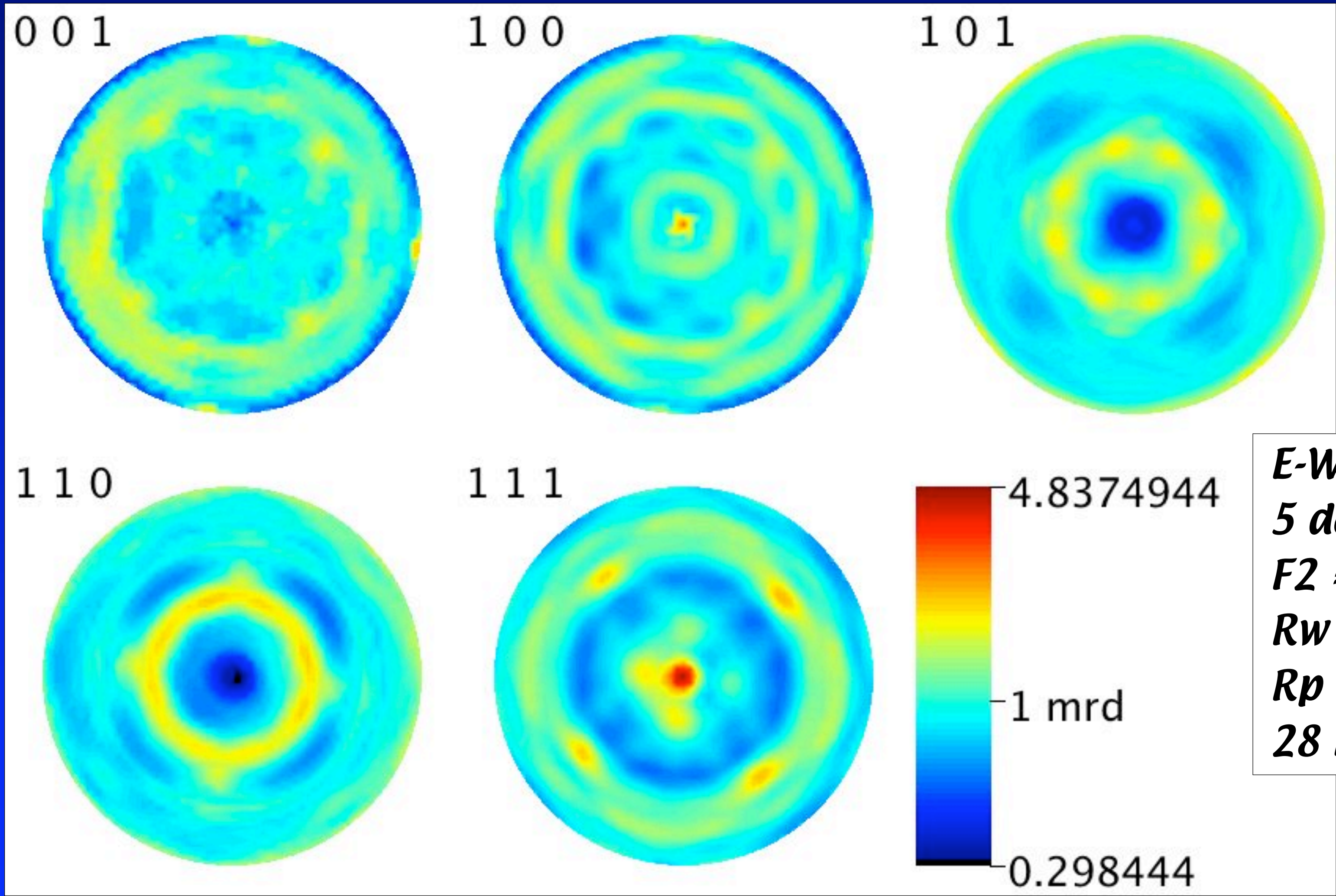
- *Path computation is slow for low symmetries (high number of data)*

PTC film fitting: E-WIMV

E-WIMV
2 layers
2 phases
Rw = 21.7%
R = 40.0 %
792 spectra

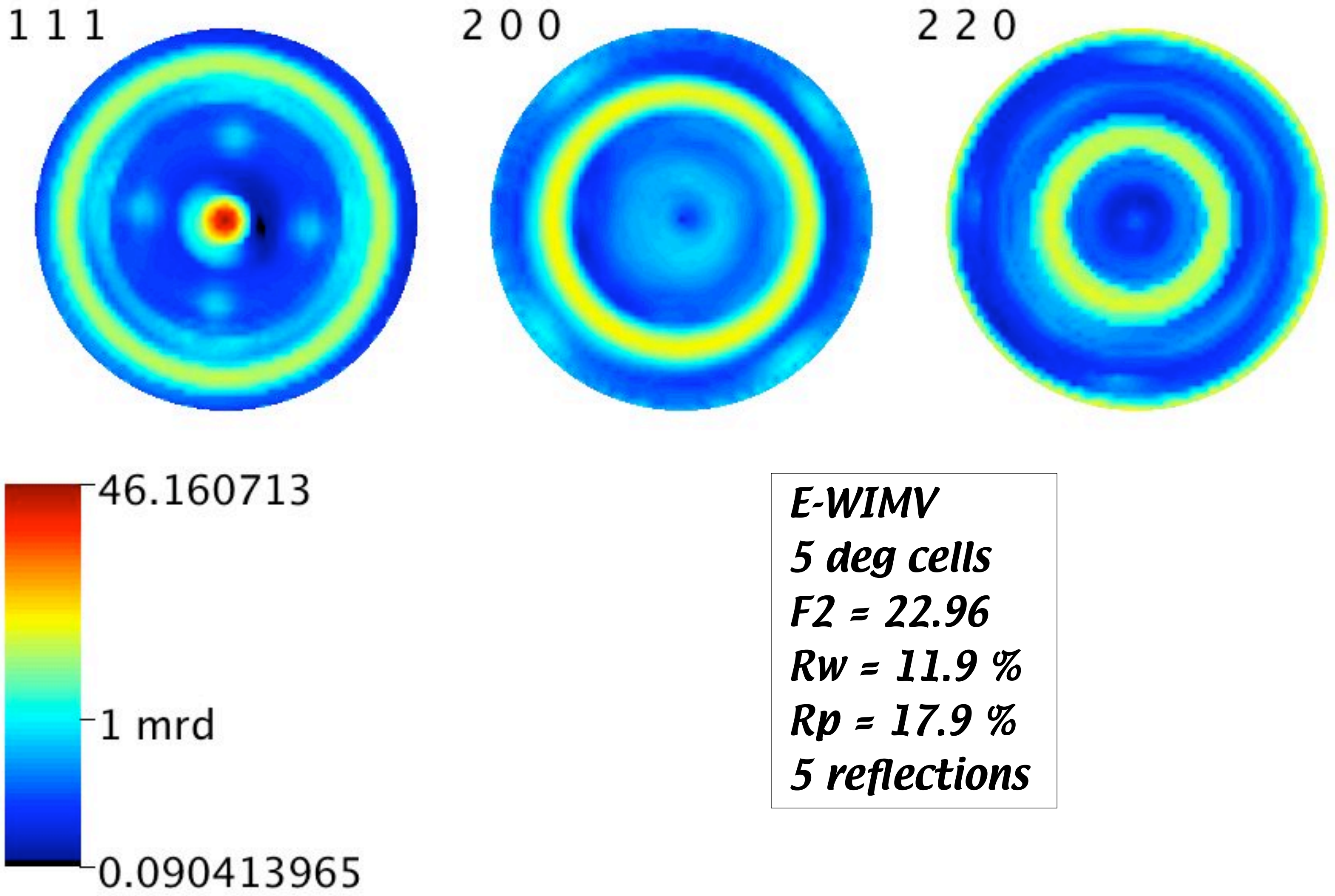


PTC film: PTC reconstructed pole figures



E-WIMV
5 deg cells
F2 = 1.962
Rw = 74.4 %
Rp = 24.9 %
28 reflections

Pt buffer layer: *reconstructed pole figures*



E-WIMV
5 deg cells
F2 = 22.96
Rw = 11.9 %
Rp = 17.9 %
5 reflections

Results on the PTC film

Layer/Phase	Cell parameters (Å)	Cryst. Size (Å)	r.m.s. microstrain	Layer thickness (Å)
Pt	3.955(1)	462(4)	0.0032(1)	458(3)
PTC	a=3.945(1) c=4.080(1)	390(7)	0.0067(1)	4080(1)

PTC crystal structure

Atom	Occupancy	x	y	z
Pb	0.76	0.0	0.0	0.0
Ca	0.24	0.0	0.0	0.0
Ti	1.0	0.5	0.5	0.477(2)
O1	1.0	0.5	0.5	0.060(2)
O2	1.0	0.0	0.5	0.631(1)

Substrate influence on Residual Stress and Texture

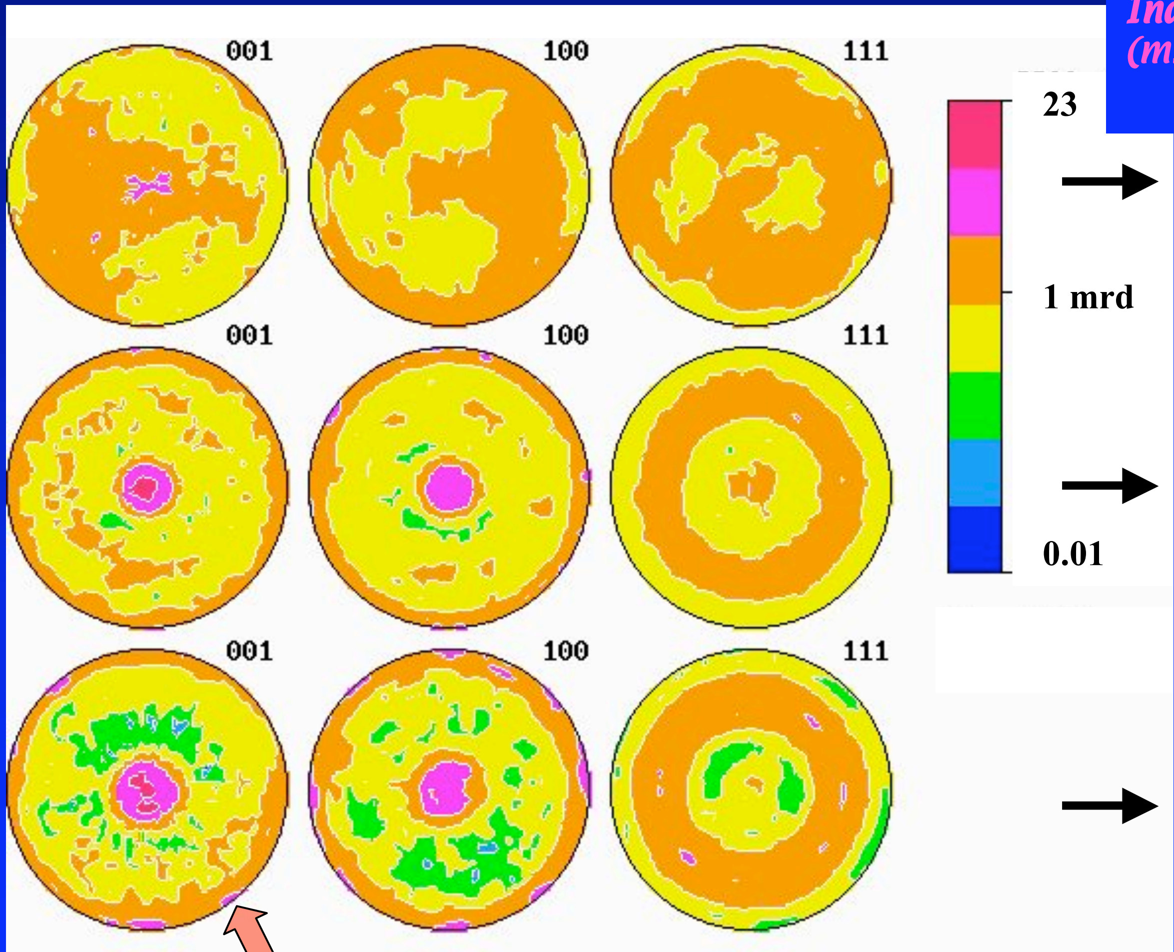
Tensile stress

PTCa on $Pt/TiO_2/(100)Si$

PTCa on $Pt/(100)MgO$

PTCa on $Pt/(100)SrTiO_3$

Compressive stress

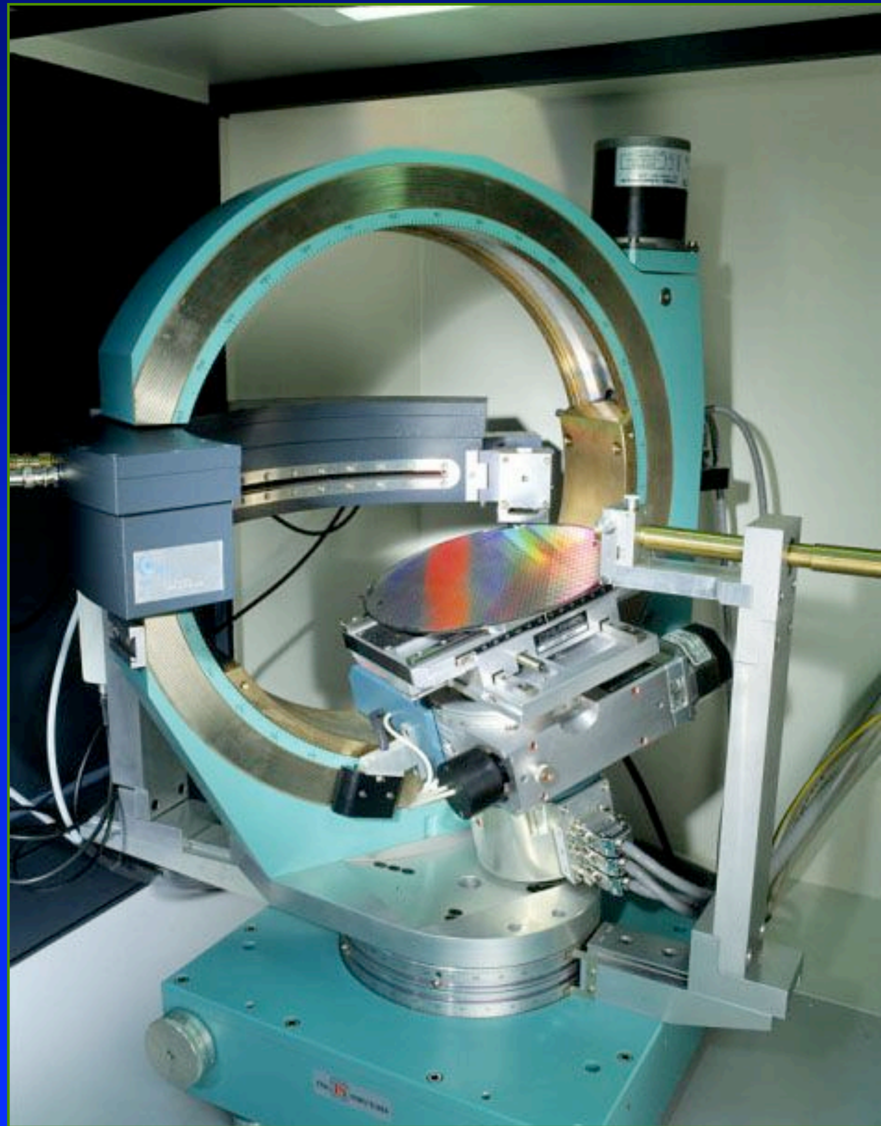


Texture Index (m.r.d.^{2})	Pyroelectric Coefficient (10^{-8}C cm^{-2} K^{-1})
2.1	0.3
5.1	1.5
7.9	1.1

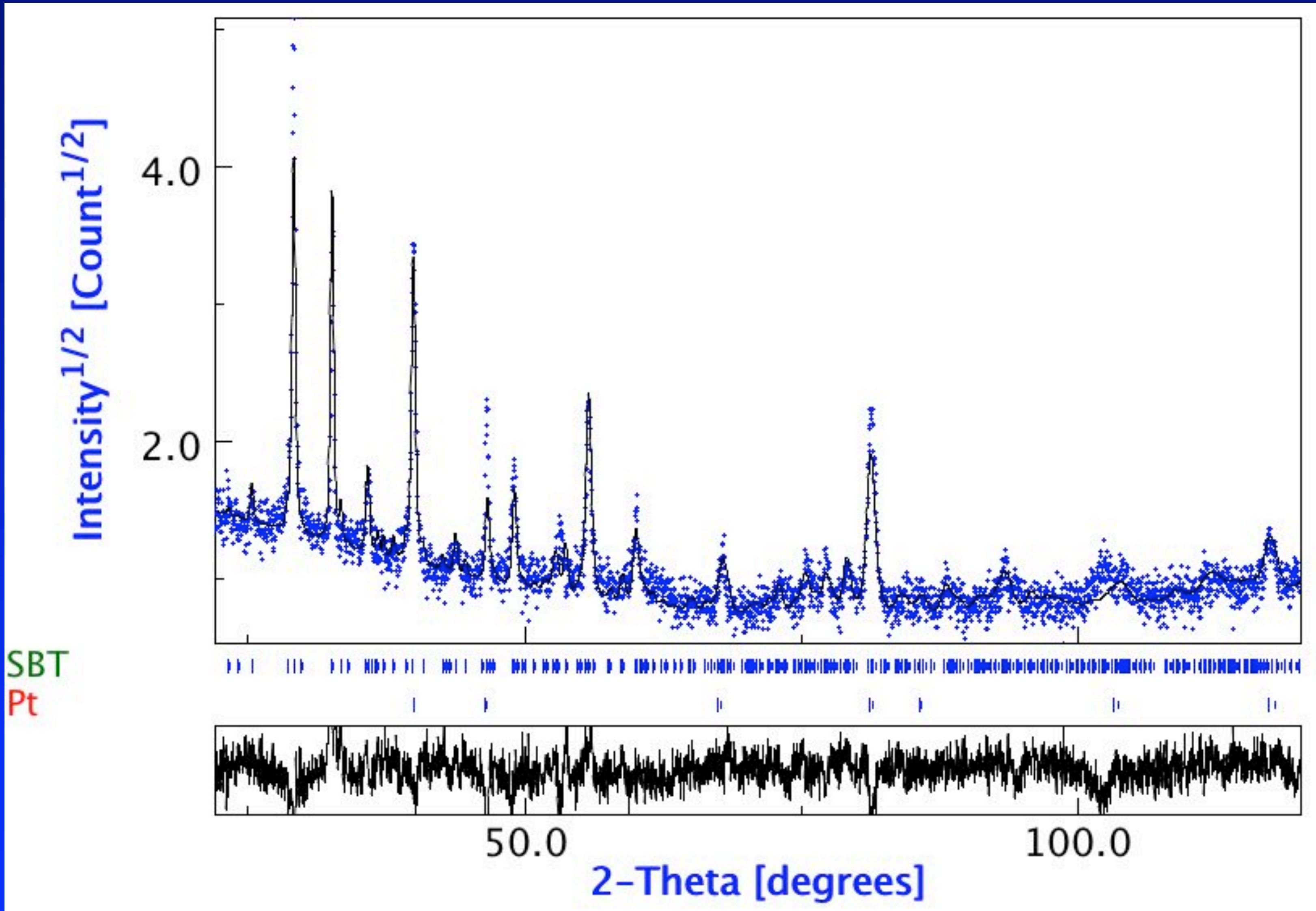
Enhancement of <001> texture?

SBT film

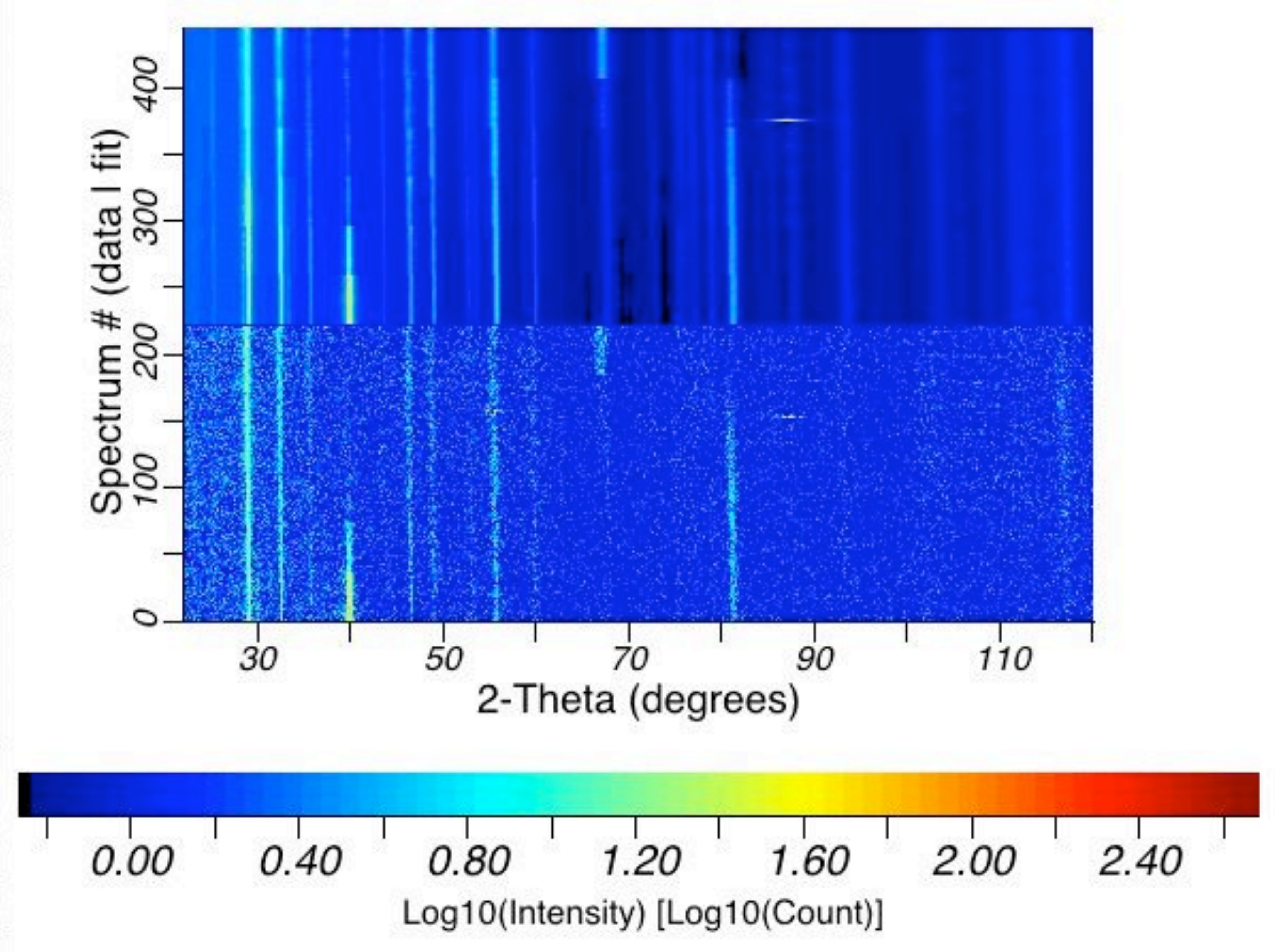
- Si Wafer + 50 nm Pt buffer layer
- ~ 300 nm of $(Sr_{0.82}Bi_{0.12})Bi_2Ta_2O_9$ - Orthorhombic A21am:-cba
- Spectra collection on the ESQUI diffractometer (right)
- 120 degs position sensitive detector on an eulerian cradle; multilayer as a primary beam monochromator
- Spectra collected in chi from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



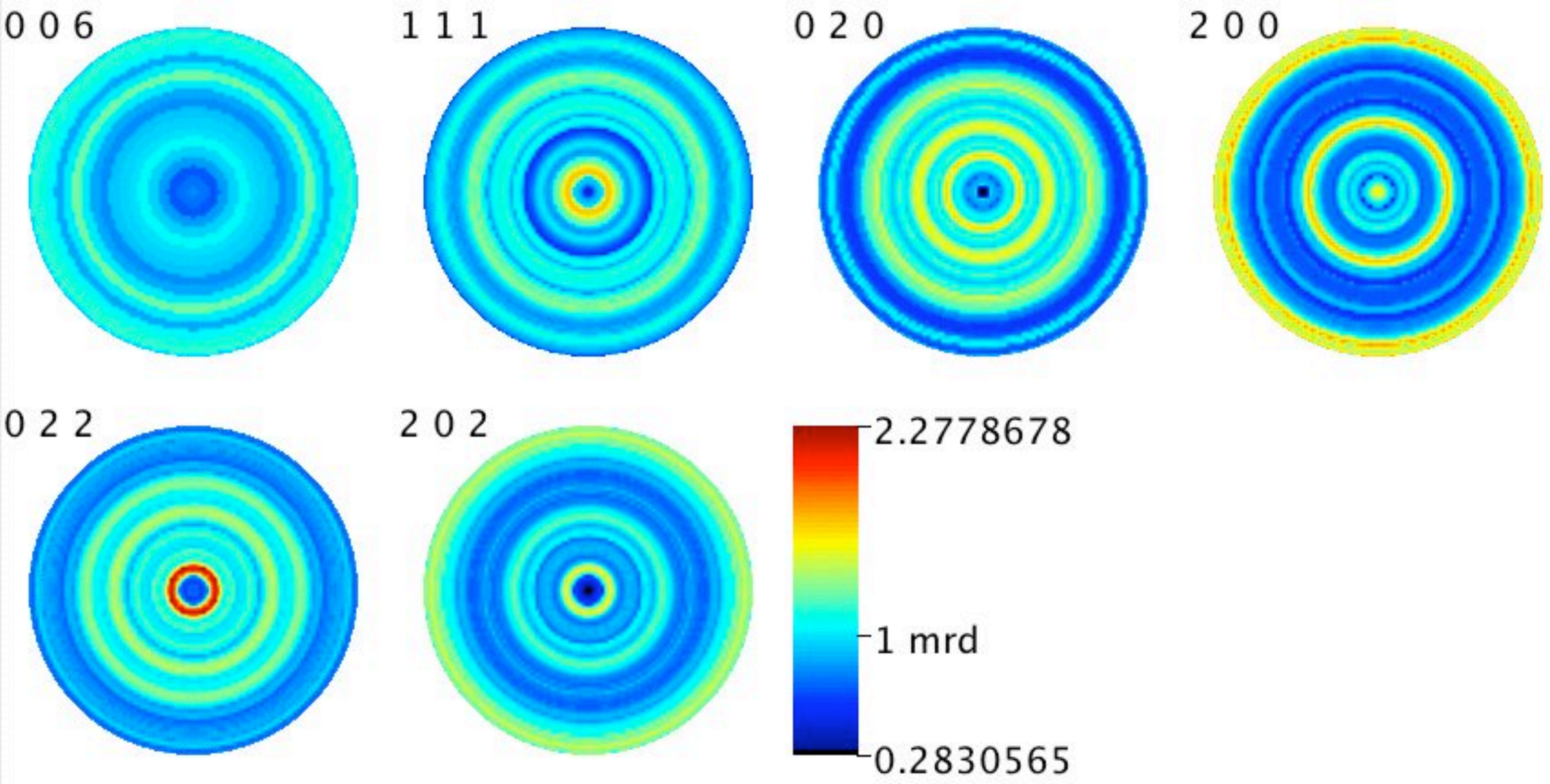
Rietveld Texture refinement



SBT thin film Rietveld fit



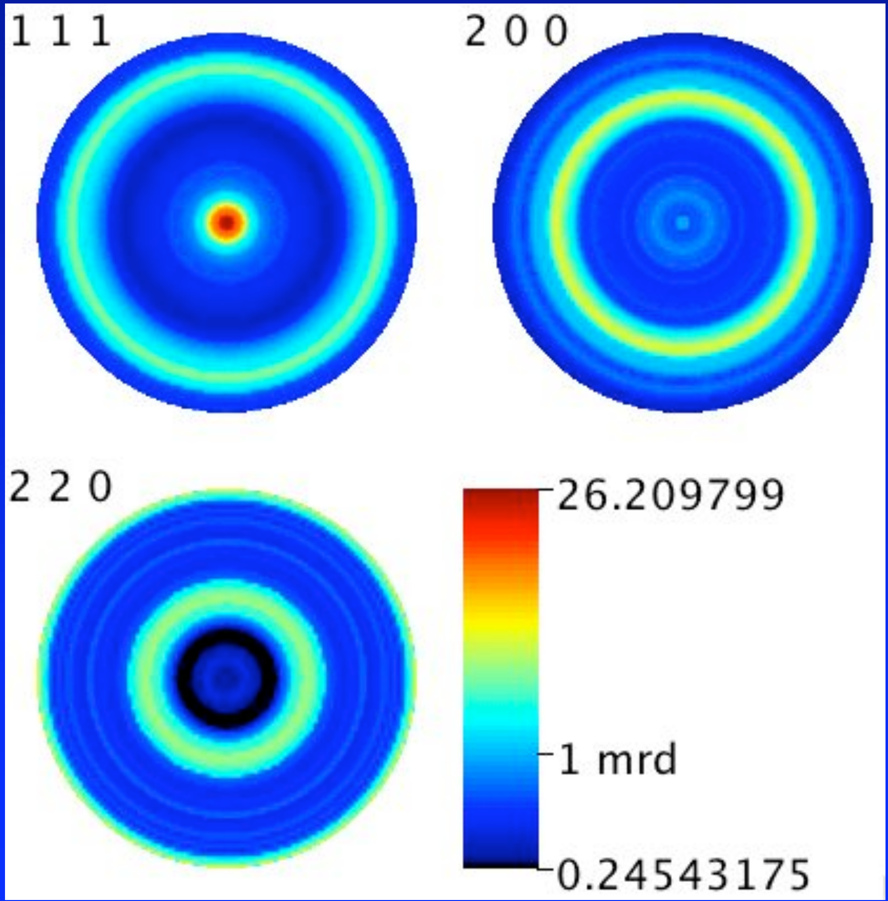
SBT pole figures reconstructed



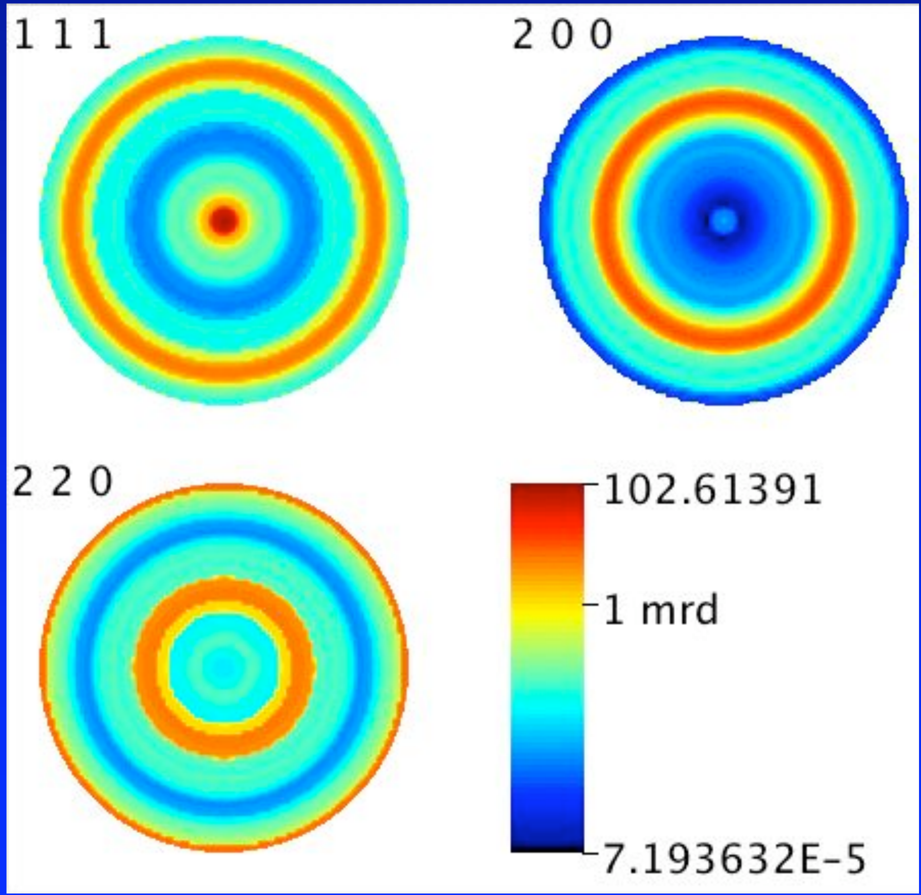
Pt texture too sharp for WIMV

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

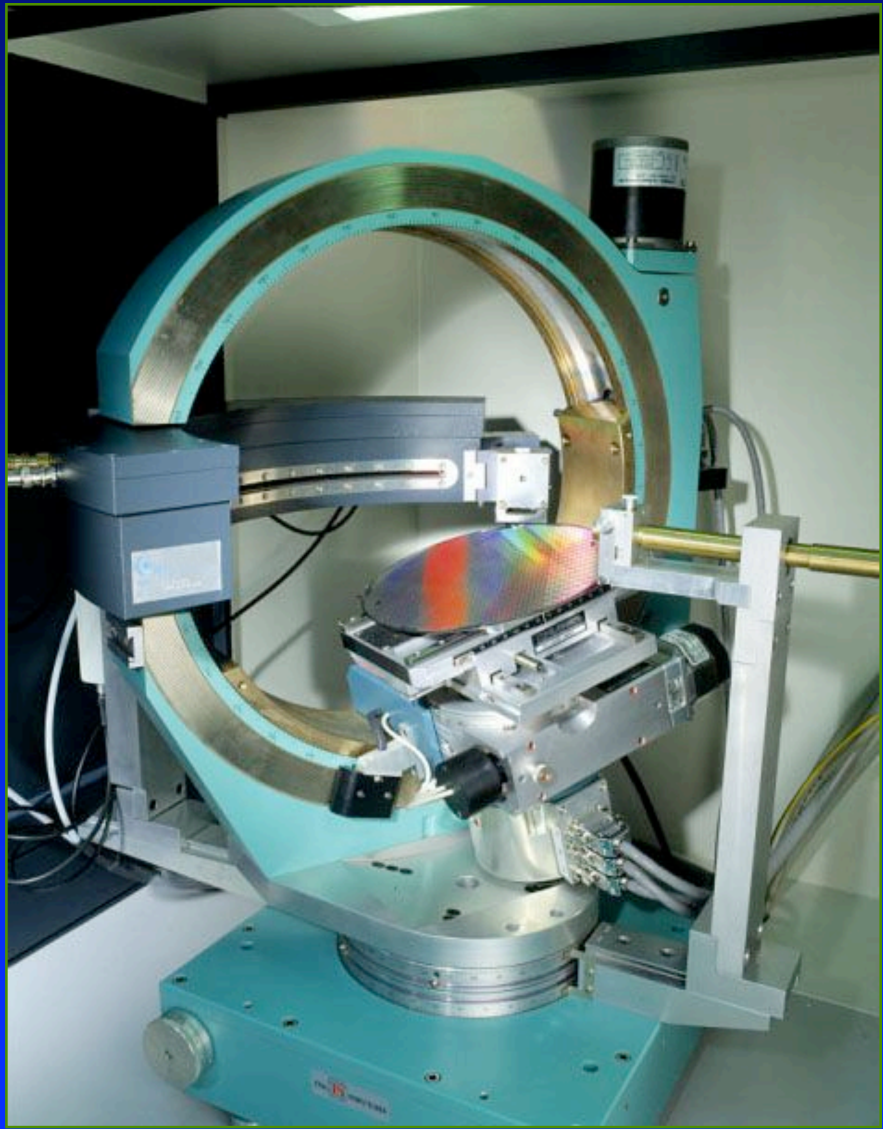
Si wafer substrate

Spectra collection on the ESQUI diffractometer (right)

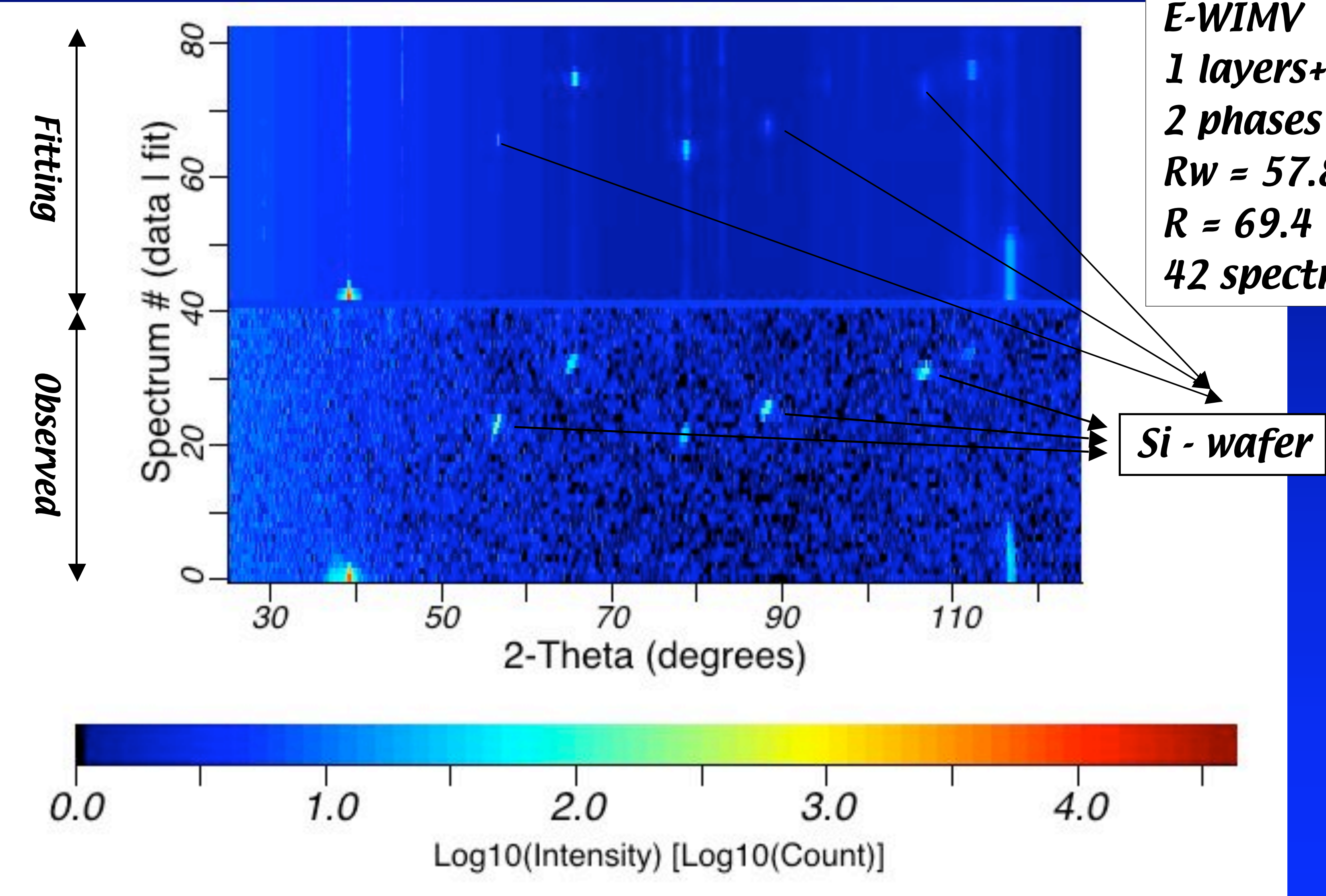
120 degs position sensitive detector on an eulerian cradle; multilayer as a primary beam monochromator

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

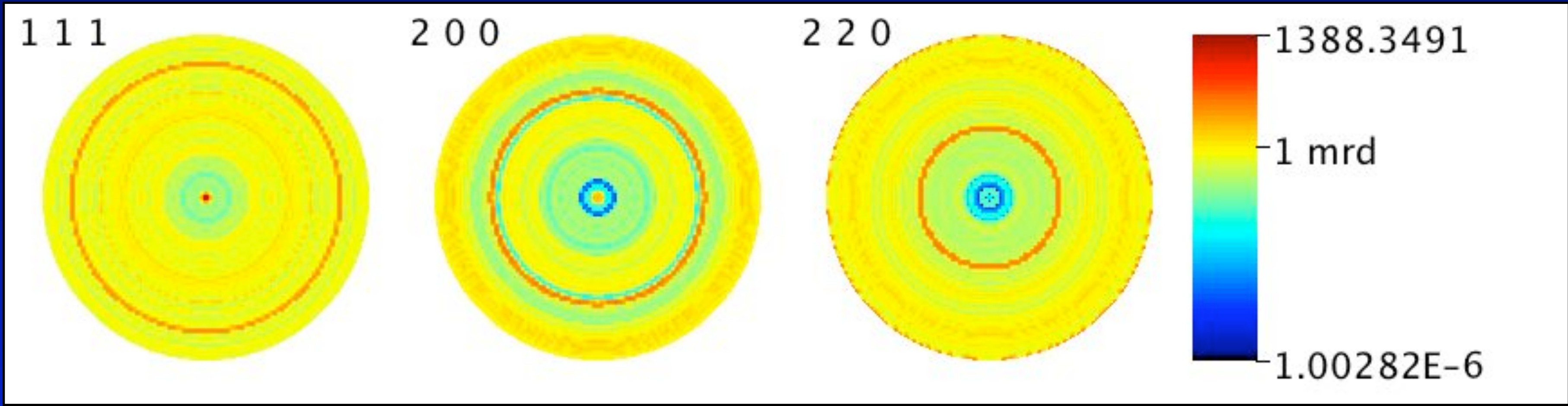


Al film: fitting the spectra



E-WIMV
1 layers+wafer
2 phases
Rw = 57.8%
R = 69.4 %
42 spectra

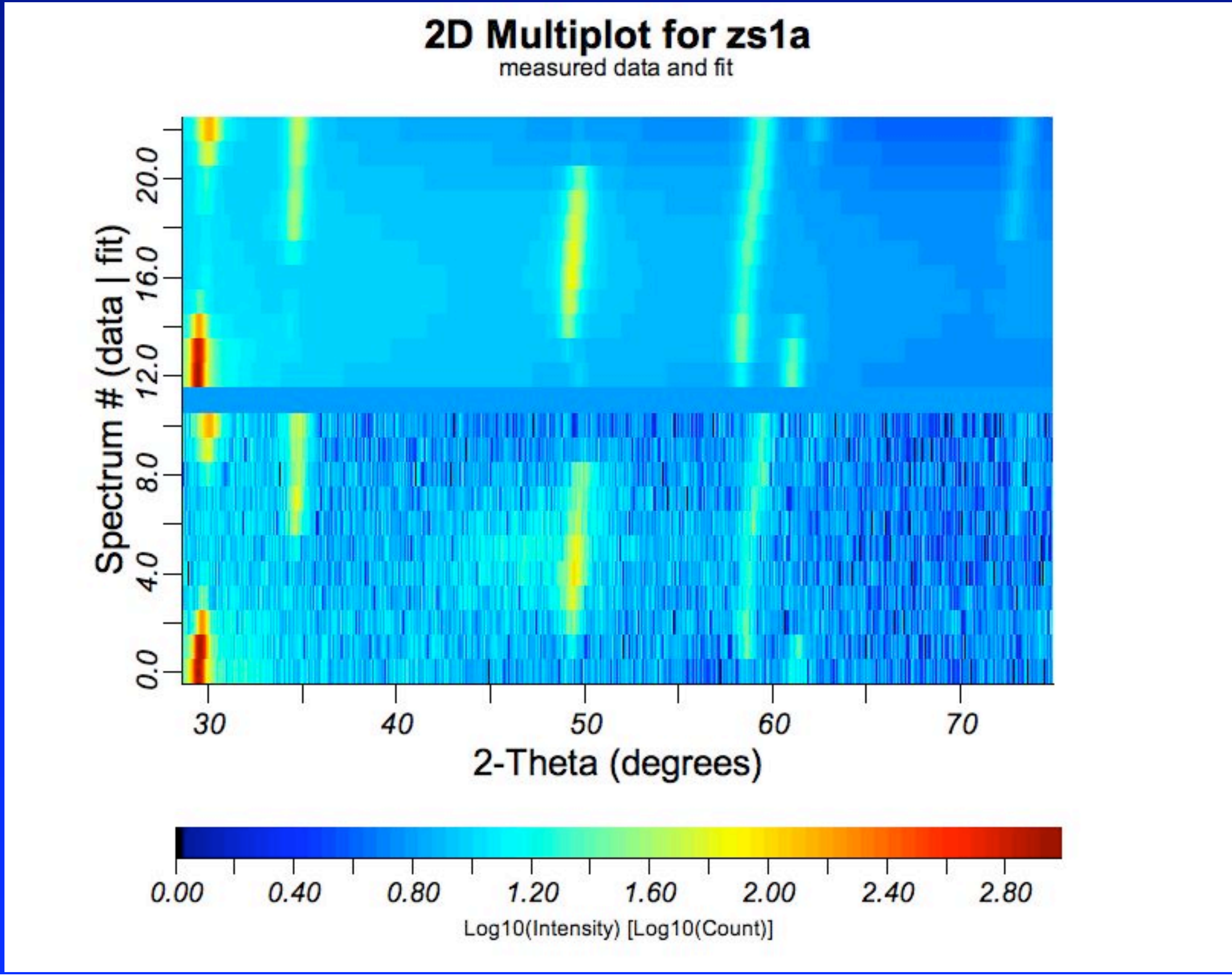
Al film: Al reconstructed pole figures



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

Cubic ZrO_2 thin film: stress-texture analysis

- Measurement by Huber stress-texture goniometer (point detector)
- EWIMV for texture and Geometrical mean for stress (BulkPathGEO method)



ZrO_2 film: results

Very high in plane residual stresses (compression):

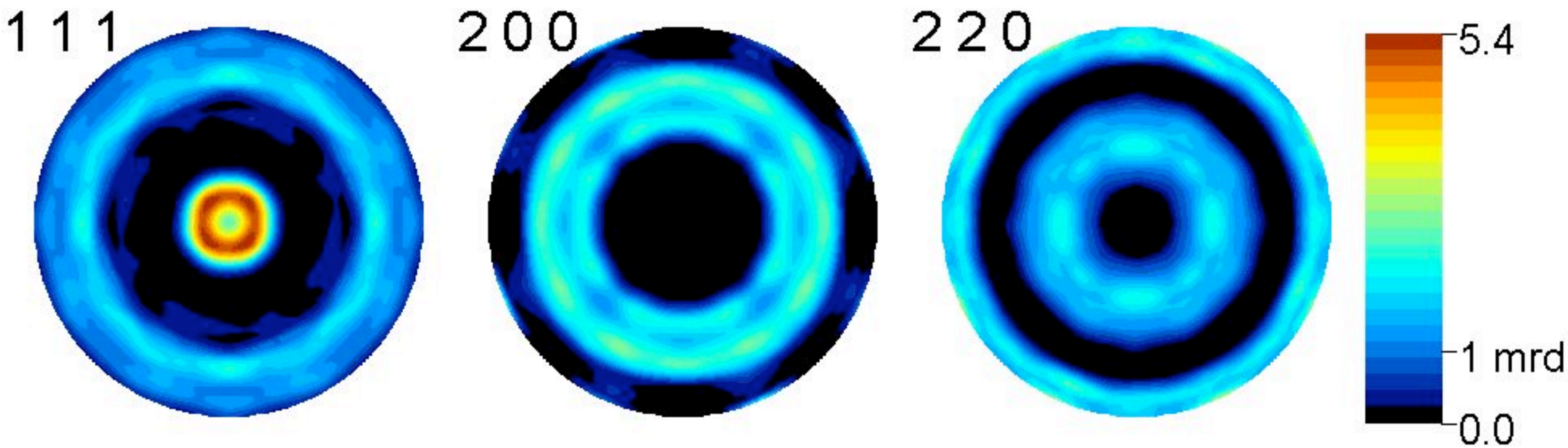
Reuss model: 3.6 GPa

Bulk Path GEO: 3.47(5) GPa

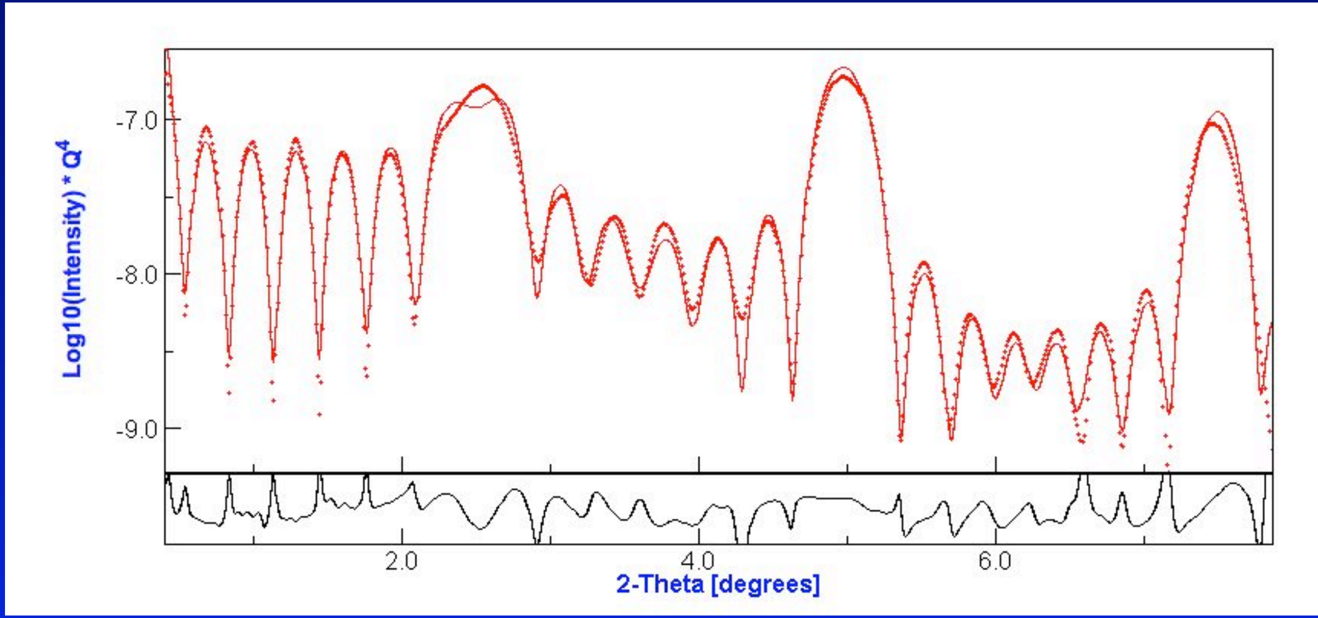
Curvature method: > 10 Gpa !?

Thickness: 320 Nanometer

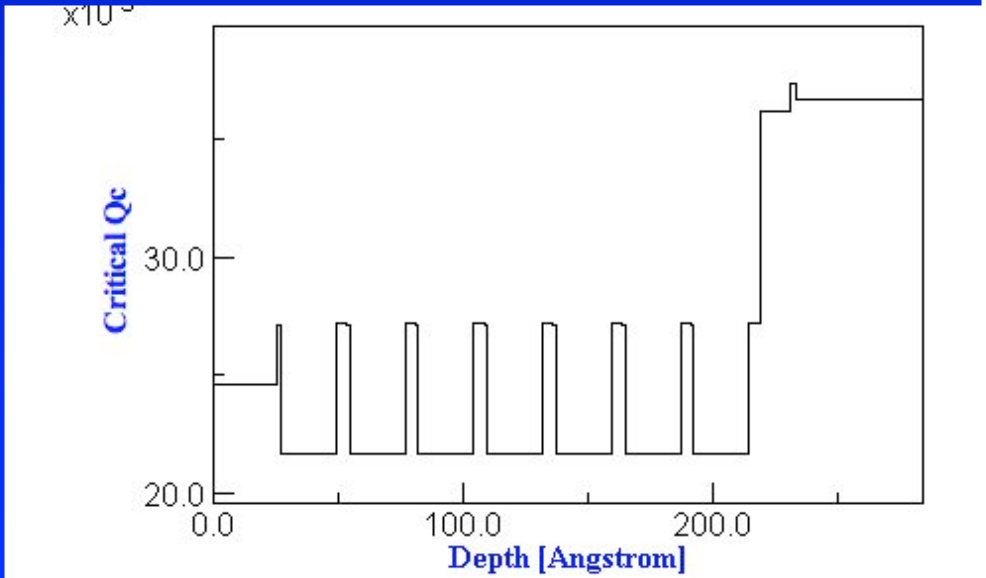
Reconstructed pole figures



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)



Conclusions

- Combined analysis (Rietveld, microstructure, texture, residual stresses and reflectivity) is very powerful for thin film
- Extremely sharp textures requires the new E-WIMV method
- Bulk Path GEO confirms to be powerful for macro residual stresses
- We need to decrease the measurement time
- Severe overlapping is no more a problem

The ESQUI European Project site:

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

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)