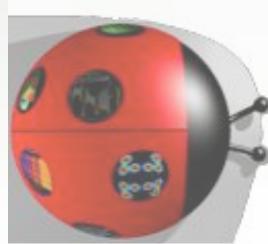


Combined Analysis: introduction

Luca Lutterotti

*Department of Materials
Engineering and Industrial
Technologies*

University of Trento - Italy



The Rietveld method

- 1964-1966 - Need to refine crystal structures from powder.
Peaks too much overlapped:
 - Groups of overlapping peaks introduced. Not sufficient.
 - Peak separation by least squares fitting (gaussian profiles). Not for severe overlapping.
- 1967 - First refinement program by H. M. Rietveld, single reflections + overlapped, no other parameters than the atomic parameters. Rietveld, Acta Cryst. 22, 151, 1967.
- 1969 - First complete program with structures and profile parameters. Distributed 27 copies (ALGOL).
- 1972 - Fortran version. Distributed worldwide.
- 1977 Wide acceptance. Extended to X-ray data.

"If the fit of the assumed model is not adequate, the precision and accuracy of the parameters cannot be validly assessed by statistical methods". Prince.



Principles of the Rietveld method

- **To minimize the residual function:**

$$WSS = \sum_i w_i (I_i^{\text{exp}} - I_i^{\text{calc}})^2, w_i = \frac{1}{I_i^{\text{exp}}}$$

- **where:**

$$I_i^{\text{calc}} = S_F \sum_k L_k |F_k|^2 S(2\theta_i - 2\theta_k) P_k A + bkg_i$$

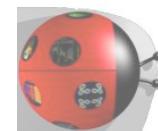
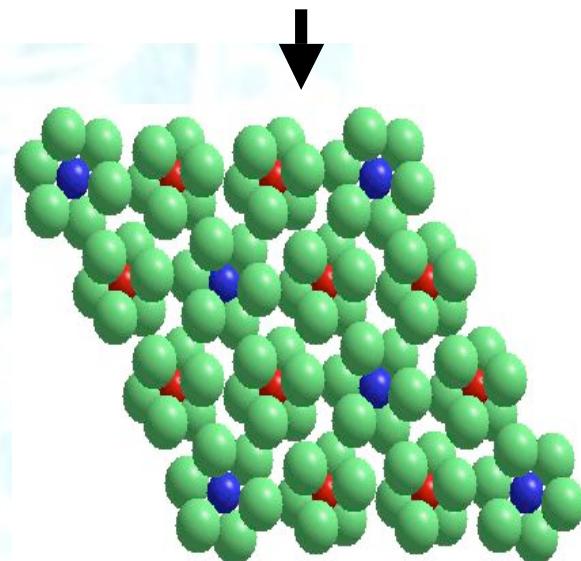
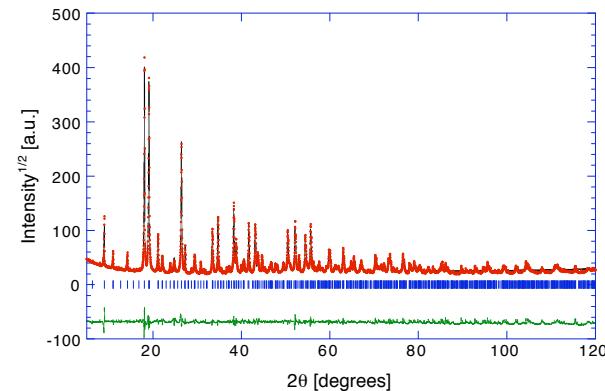
P_k = preferred orientation function

$S(2\theta_i - 2\theta_k)$ = profile shape function

(PV : η , HWHM)

$$\text{HWHM}^2 = U \tan^2 \theta + V \tan \theta + W$$

$$P_k = \left(r^2 \cos^2 \alpha + \frac{\sin^2 \alpha}{r} \right)^{-3/2}$$



Non classical Rietveld applications

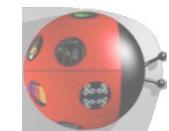
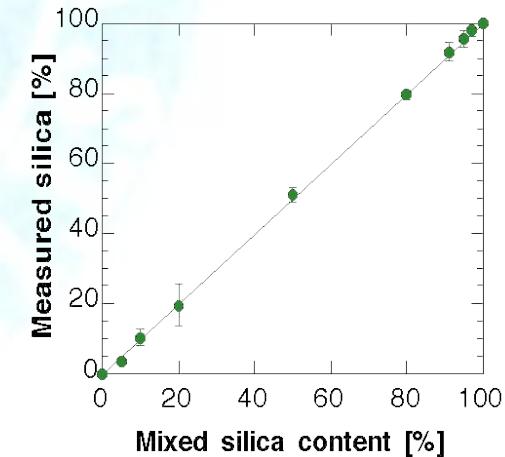
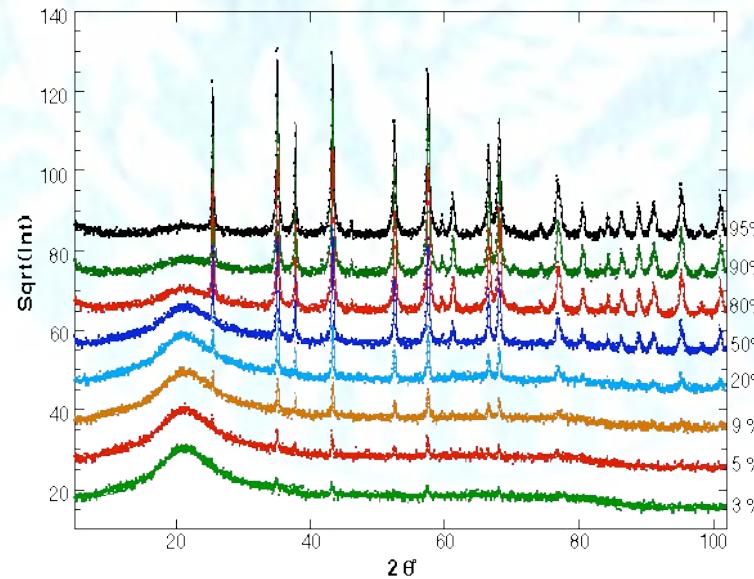
- *Quantitative analysis of crystalline phases (Hill & Howard, J. Appl. Cryst. 20, 467, 1987)*

$$I_i^{\text{calc}} = \sum_{n=1}^{N\text{phases}} S_n \sum_k L_k |F_{k;n}|^2 S(2\theta_i - 2\theta_{k;n}) P_{k;n} A + bkg_i$$
$$W_p = \frac{S_p (ZMV)_p}{\sum_{n=1}^{N\text{phases}} S_n (ZMV)_n}$$

Z = number of formula units
M = mass of the formula unit
V = cell volume

- *Non crystalline phases (Lutterotti et al, 1997)*

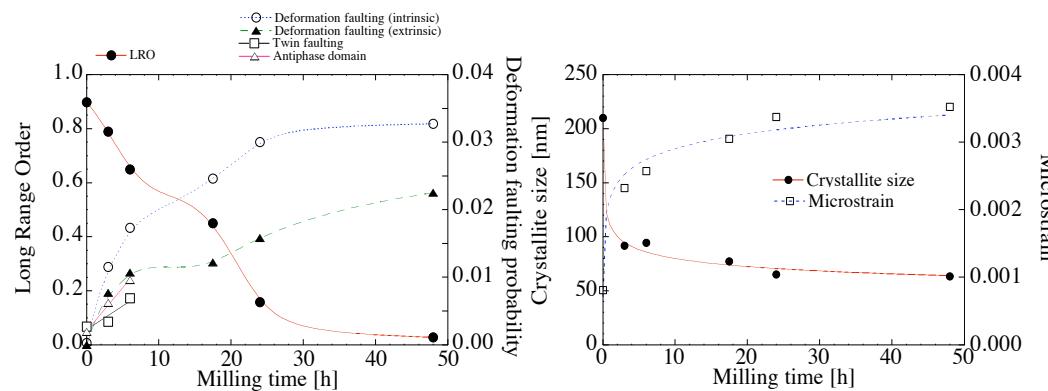
- *Using Le Bail model for amorphous (need a pseudo crystal structure)*



Non classical Rietveld applications

- Microstructure:

- Le Bail, 1985. Profile shape parameters computed from the crystallite size and microstrain values ($\langle M \rangle$ and $\langle \varepsilon^2 \rangle^{1/2}$)
 - More stable than Caglioti formula
 - Instrumental function needed
- Popa, 1998 (J. Appl. Cryst. 31, 176). General treatment for anisotropic crystallite and microstrain broadening using harmonic expansion.
- Lutterotti & Gialanella, 1998 (Acta Mater. 46(1), 101). Stacking, deformation



Rietveld Texture Analysis (RiTA)

- *Characteristics of Texture Analysis:*
 - *Powder Diffraction*
 - *Quantitative Texture Analysis needs single peaks for pole figure meas.*
 - *Less symmetries -> too much overlapped peaks*
- *Solutions: Groups of peaks (WIMV, done), peak separation (done)*
- *What else we can do? -> Rietveld like analysis?*
 - *1991. Berar & Garnier present a poster with a program including the harmonic treatment for texture.*
 - *1992. Popa -> harmonic method to correct preferred orientation in one spectrum.*
 - *1994. Ferrari & Lutterotti -> harmonic method to analyze texture and residual stresses. Multispectra measurement.*
 - *1994. Wenk, Matthies & Lutterotti -> Rietveld+WIMV for Rietveld Texture analysis.*
 - *1997. GSAS got the harmonic method (wide acceptance?).*

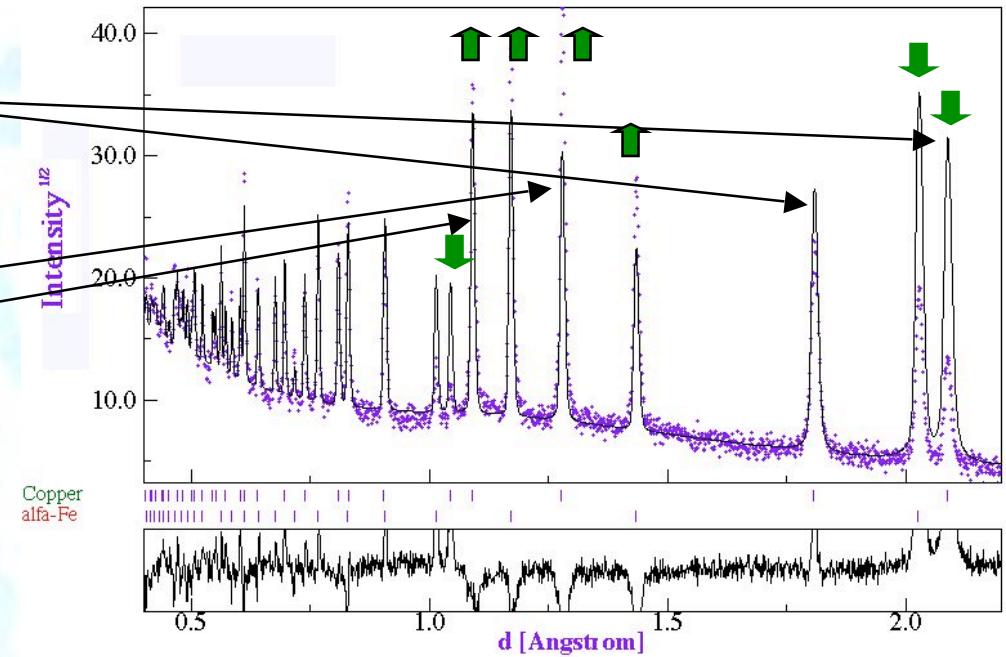
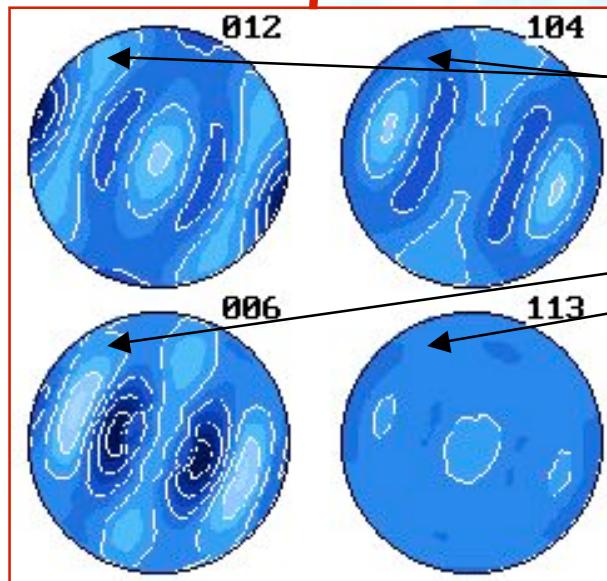


Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra



How it works (RiTA)

- **The equation:** $I_i^{calc}(\chi, \phi) = \sum_{n=1}^{N_{phases}} S_n \sum_k L_k |F_{k;n}|^2 S(2\theta_i - 2\theta_{k;n}) P_{k;n}(\chi, \phi) A + bkg_i$
- **Harmonic:**

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

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

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

- **Advantages:**

- Easy implementation
- Very elegant, completely integrated in the Rietveld
- Fast, low memory consumption to store the odf.

- **Disadvantages:**

- 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.



How it works (RiTA)

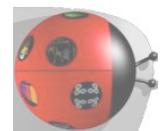
- **WIMV**

- *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 cycle:*
 - *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 for implementation*
 - *slower*

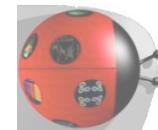
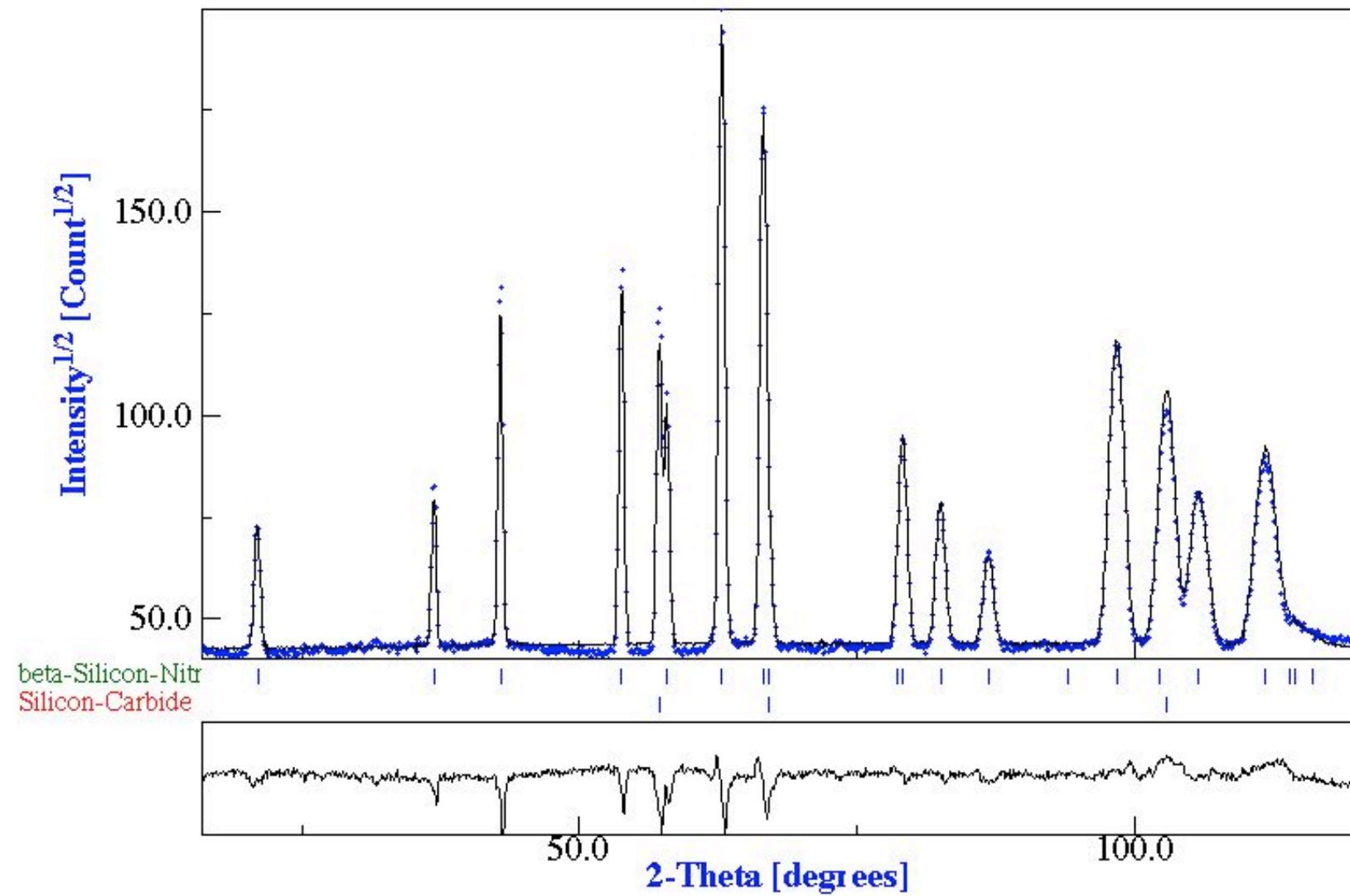


Analysis of Composites: Si_3N_4+SiC

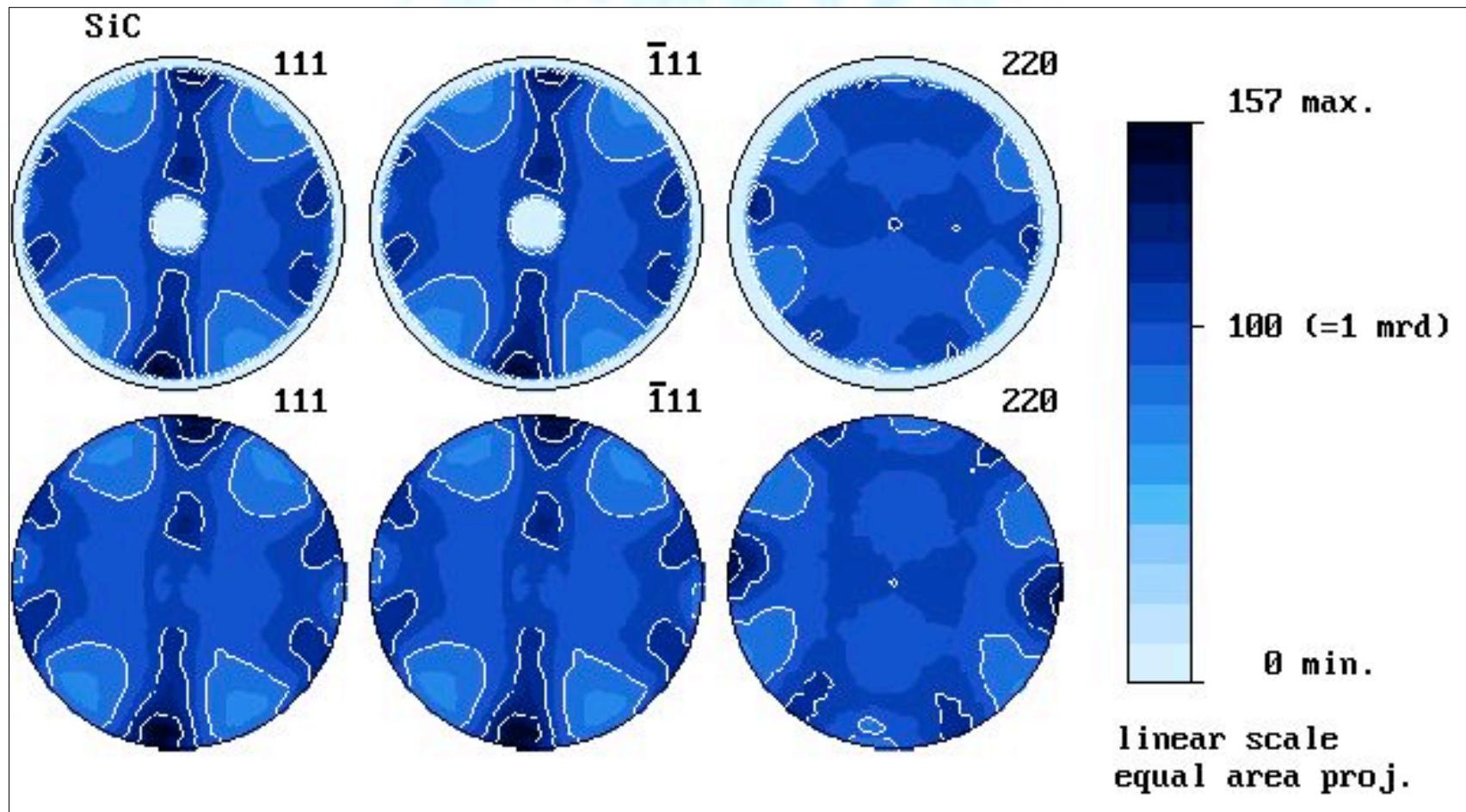
- *SiC whiskers: (111) along fiber direction*
- *Matrix: $\beta-Si_3N_4$*
- *Minor glass quantity (for sintering aid)*
- *Composite obtained by HIP*
- *Diffraction measurements:*
 - *D20-ILL: neutron, PSD, Eulerian cradle*
 - *720 spectra, $10^\circ \times 10^\circ$ grid on χ and ϕ , 2 ω positions*
- *Analyzed by Maud using RiTA (Rietveld Texture Analysis)*



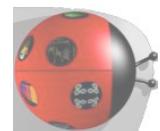
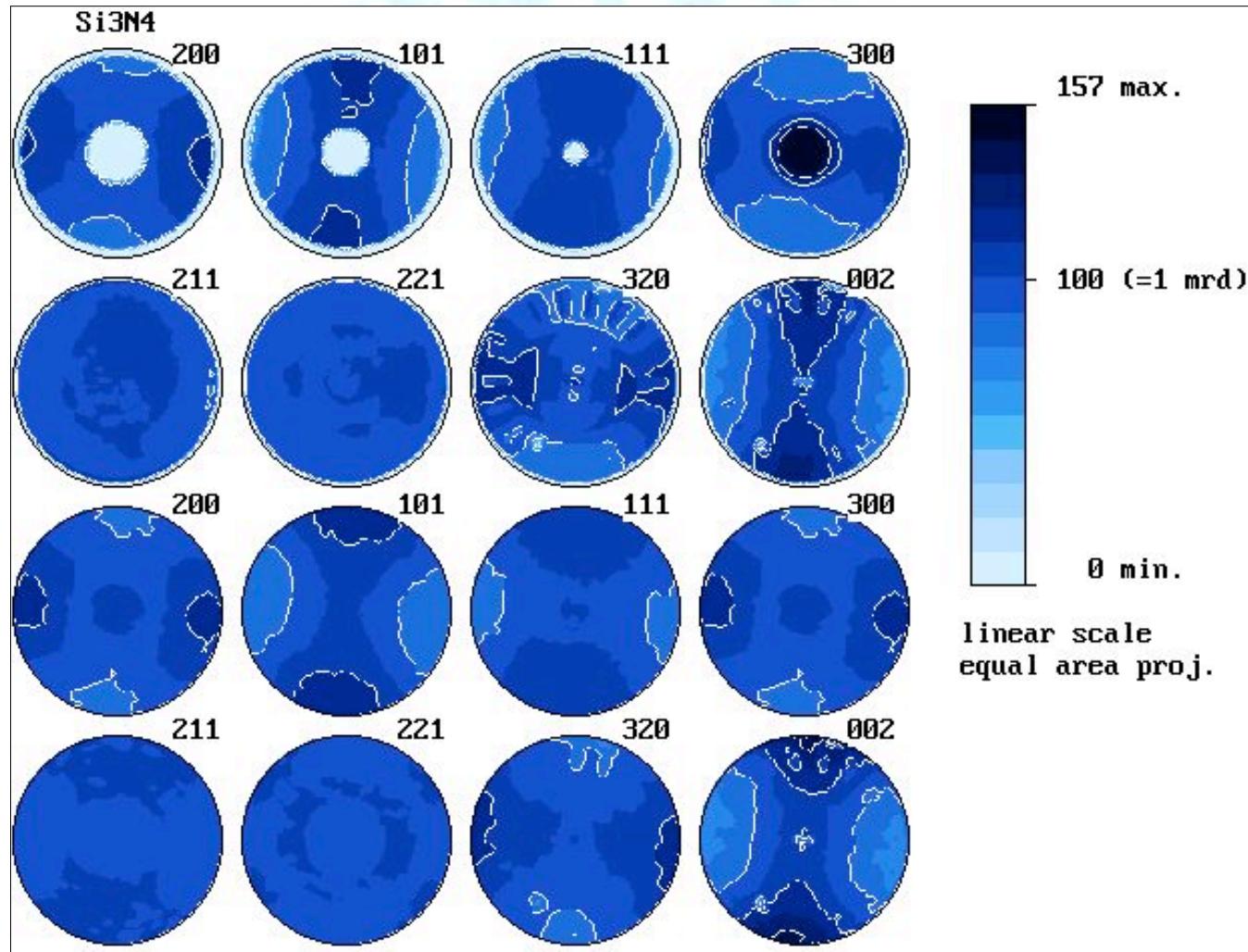
Fitting the spectra



SiC whiskers pole figures



Si₃N₄: experimental and reconstructed pole figures



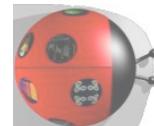
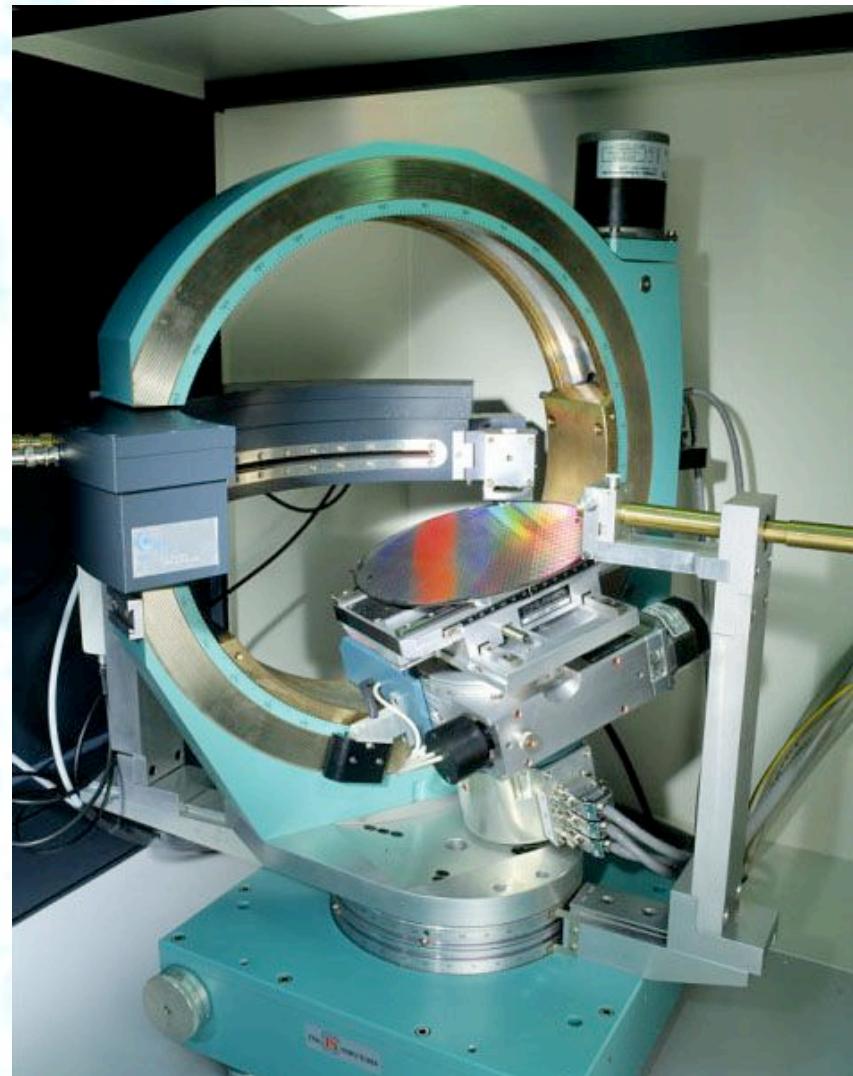
Kryptonite results

- *SiC distributed mainly in the basal plane of the composite*
 - *Optimum in plane mechanical properties of the composites*
- $\beta\text{-}Si_3N_4$ has a random ODF
- *SiC volume fraction: 24.2 %*



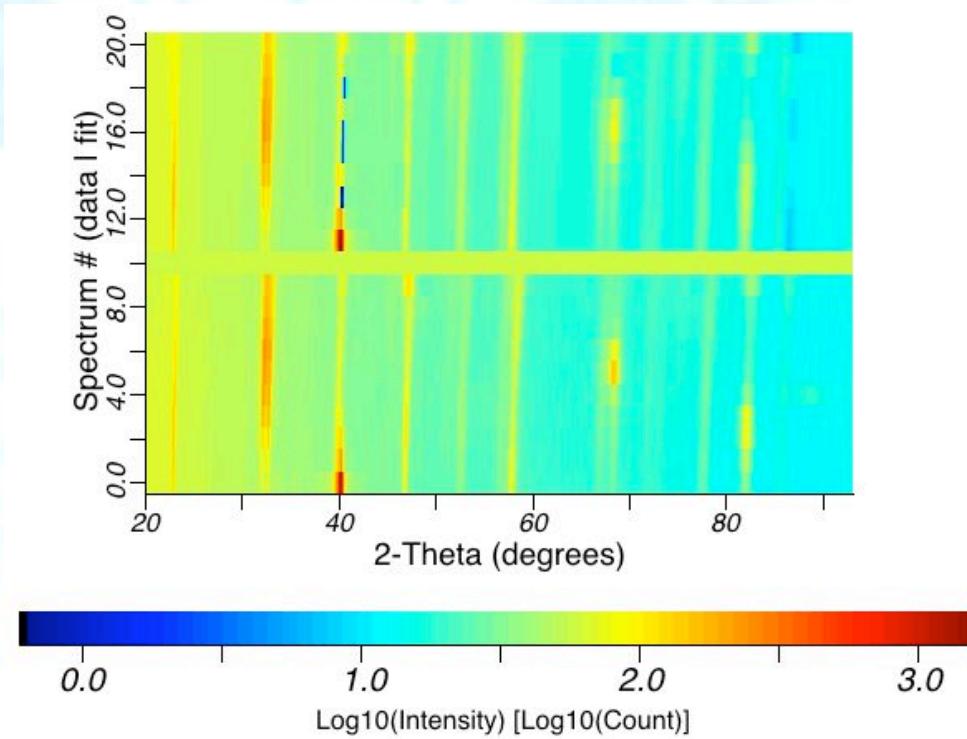
CPT film: experimental

- *Substrate: Pt/TiO₂/SiO₂/Si(100)*
- *400 nm of Pb_{0.76}Ca_{0.24}TiO₃ (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 (Le Mans, France)*
- *Collected full spectra on a 5x5 degs grid in chi and phi up to 50 deg in chi.*

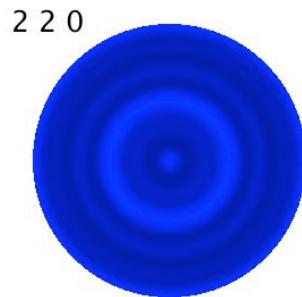
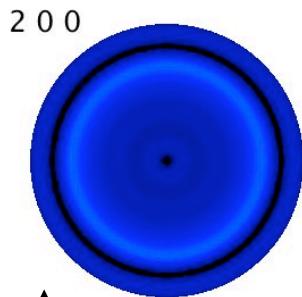
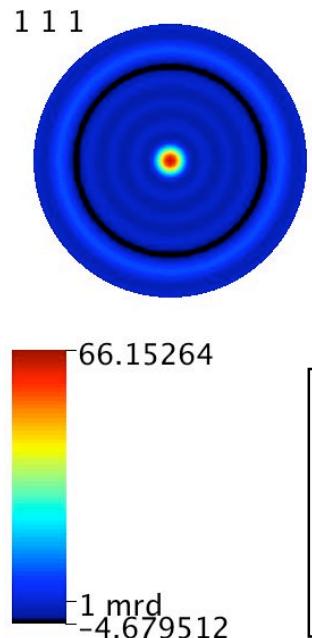


CPT film: harmonic texture model

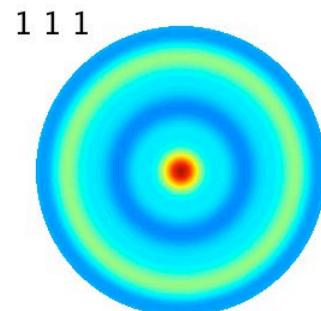
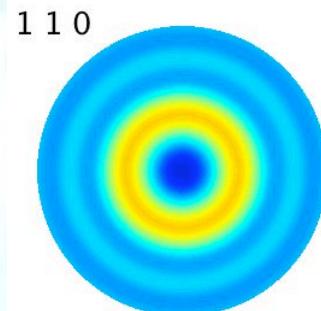
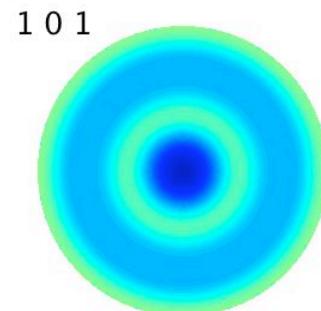
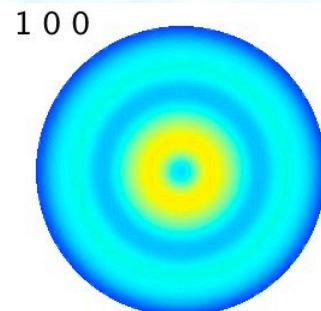
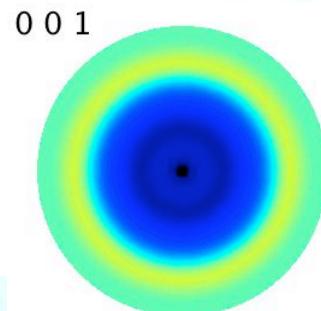
- Triclinic sample symmetry: 1245 parameters only for CPT ($L_{max} = 22$)
- Increasing sample symmetry to orthorhombic: 181 parameters
- Reducing sample symmetry to fiber and L_{max} to 16: 24 parameters
- For Pt layer: fiber texture, $L_{max} = 22 \rightarrow 15$ parameters
- $Rw (\%) = 14.786048$



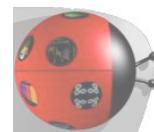
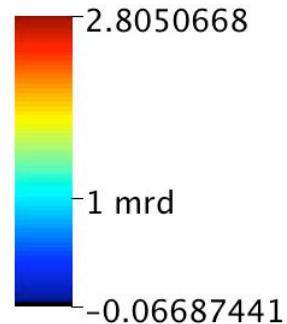
CPT film: harmonic reconstructed pole figures



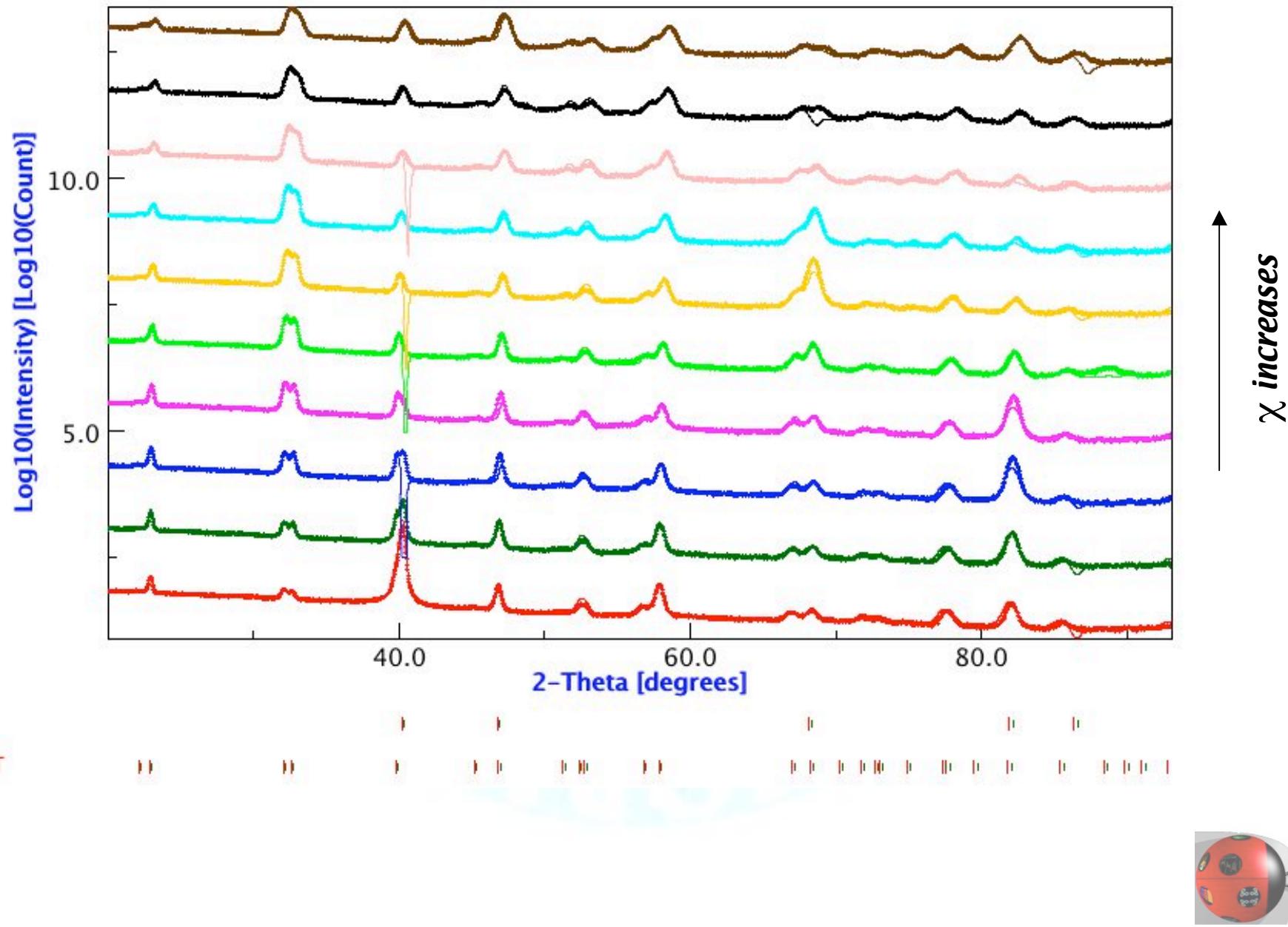
- Pt layer
- Harmonic
- $L_{max} = 22$
- $F2 = 138.0$



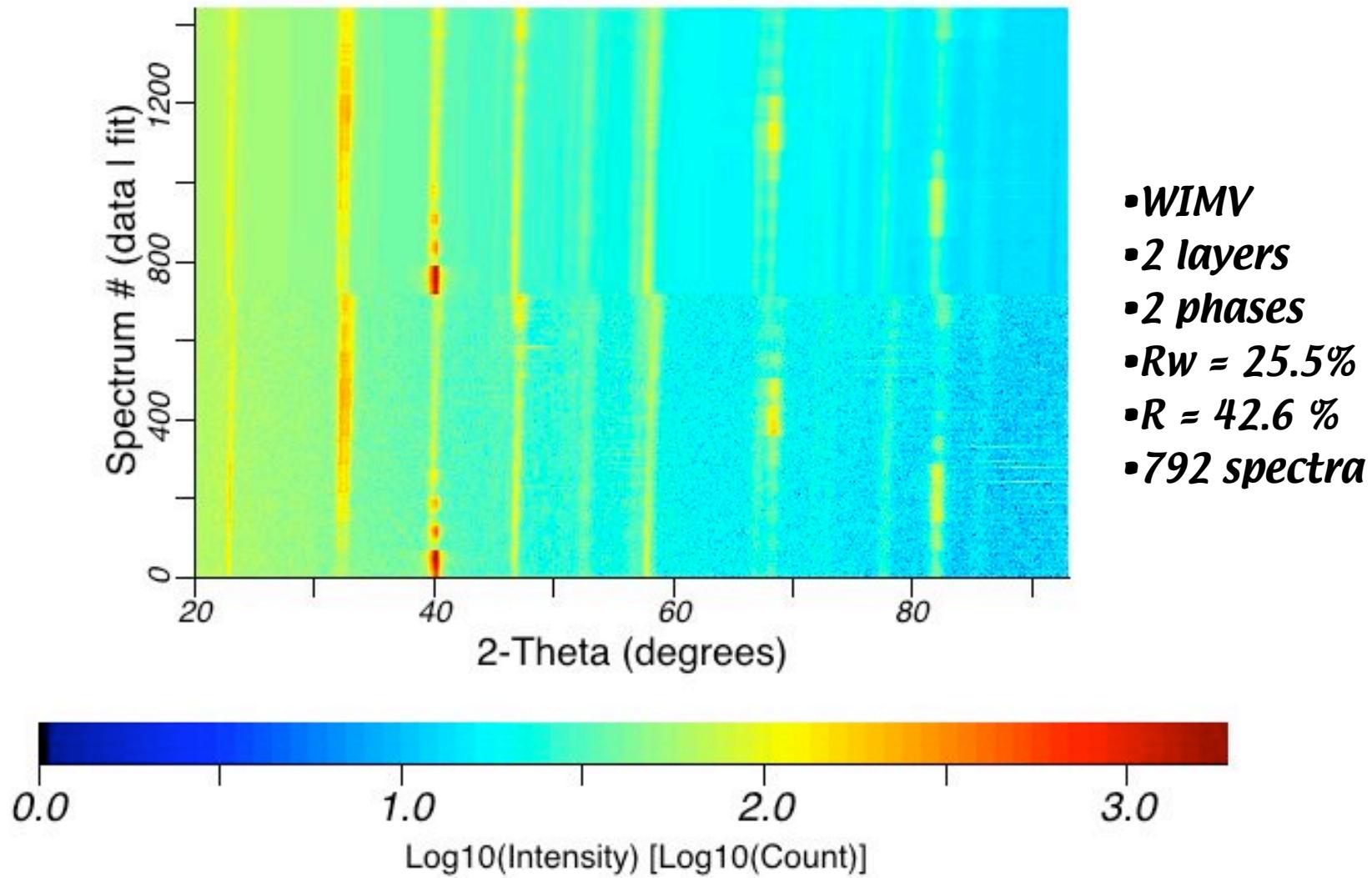
- CPT layer
- Harmonic method
- $L_{max} = 16$
- $F2 = 1.55$



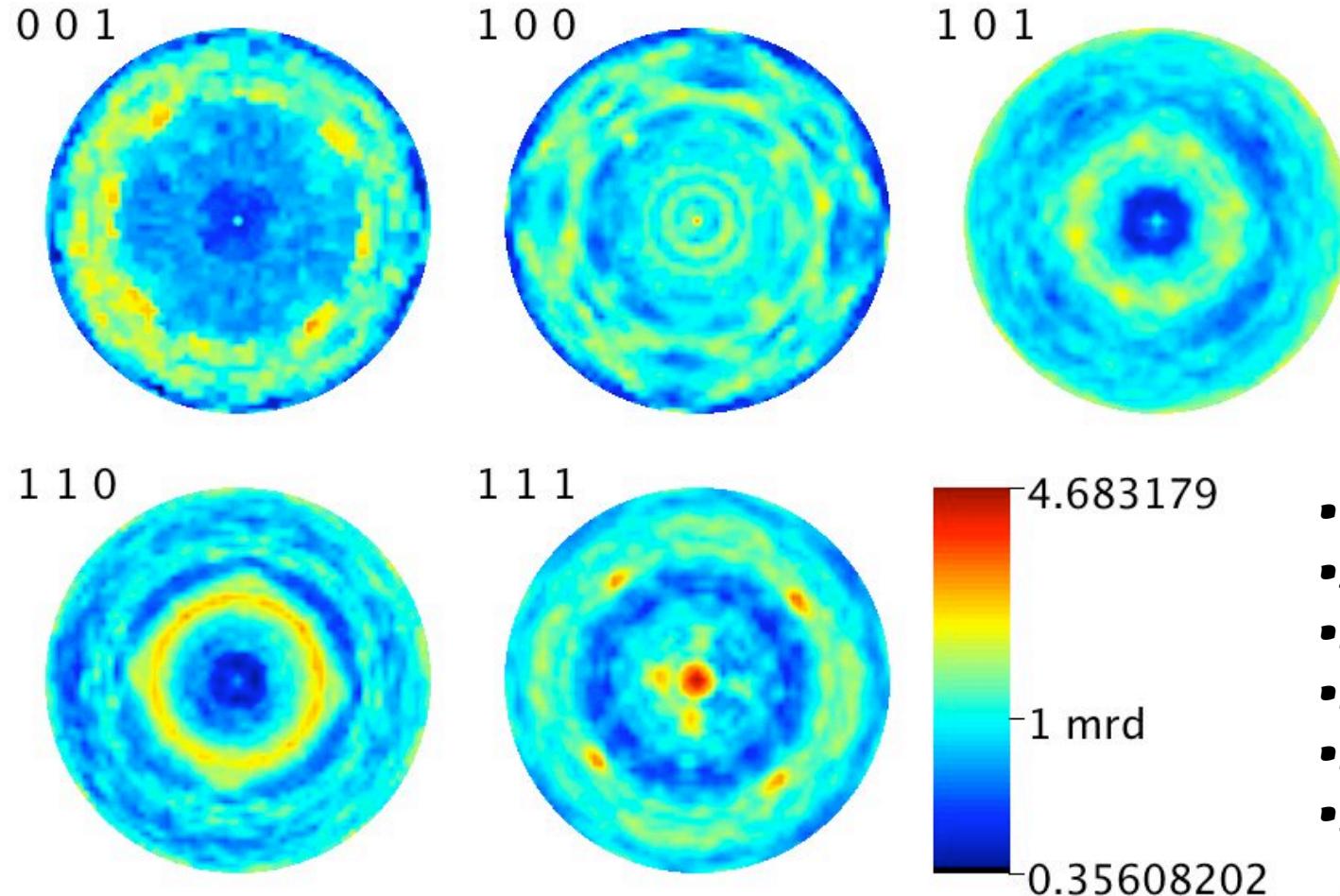
CPT film: harmonic fitting, the problem



CPT film fitting: WIMV



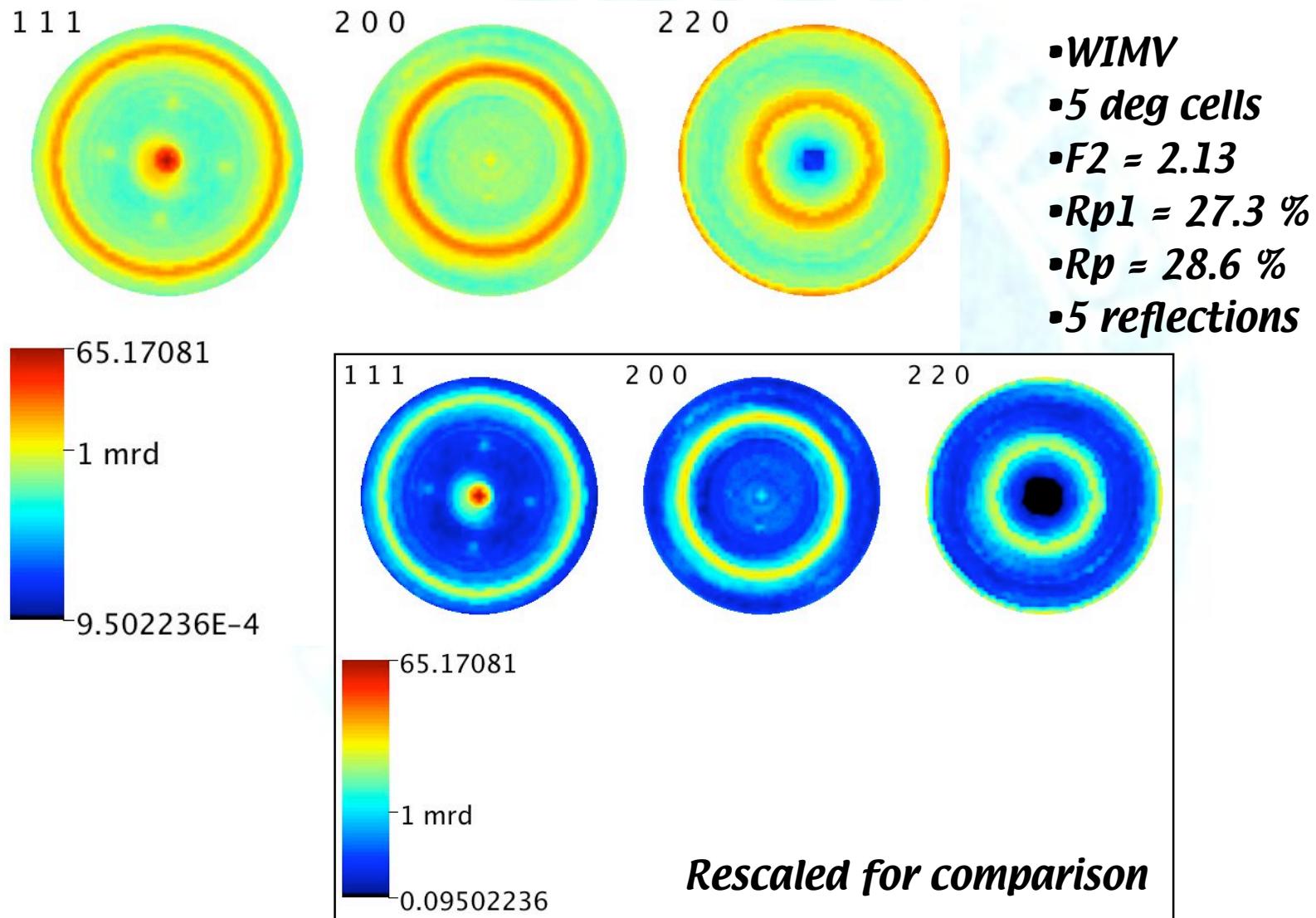
CPT film: CPT reconstructed pole figures, WIMV



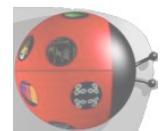
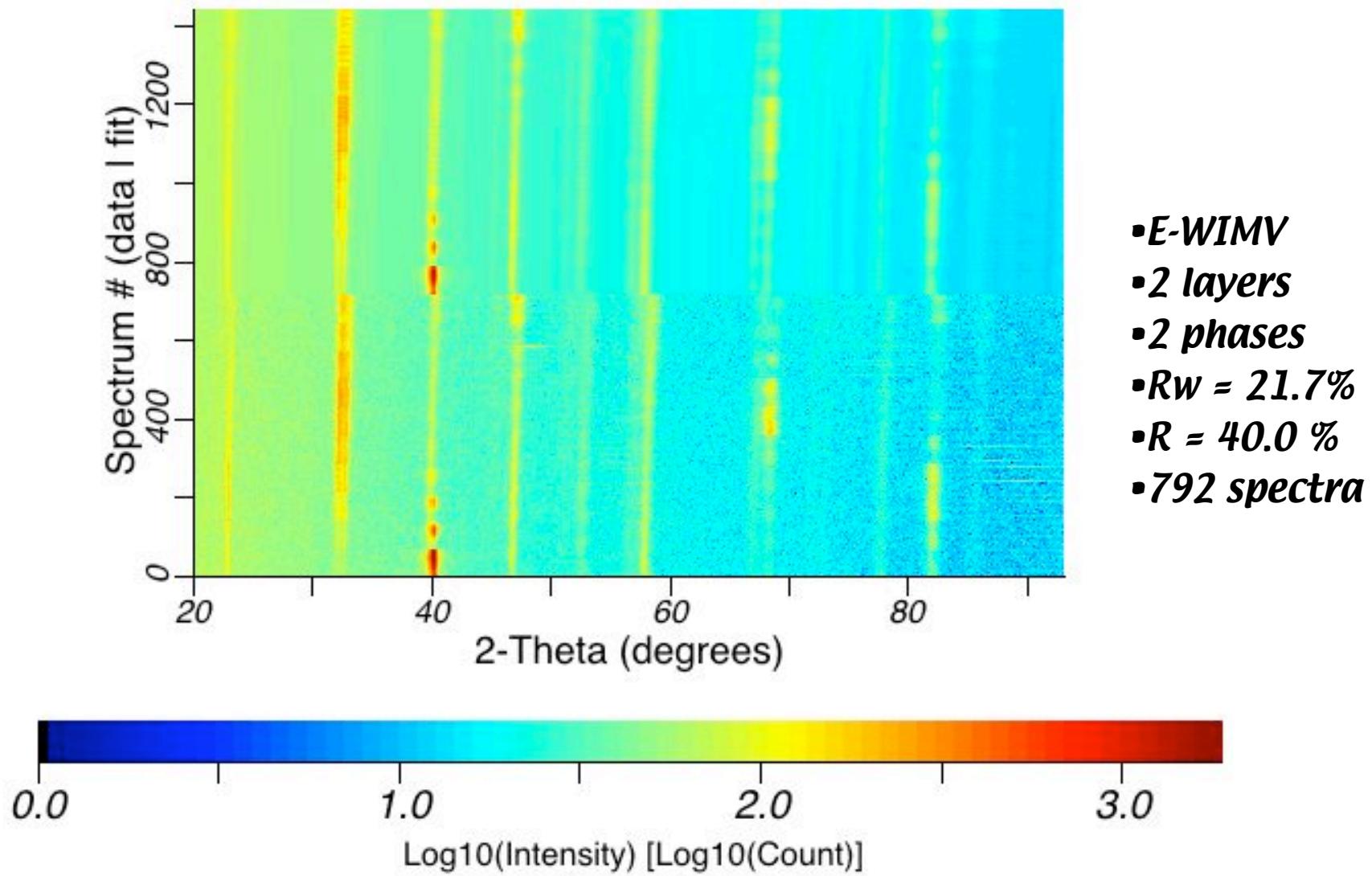
- *WIMV*
- *5 deg cells*
- $F2 = 25.88$
- $Rpl = 18.2 \%$
- $Rp = 25.0 \%$
- *28 reflections*



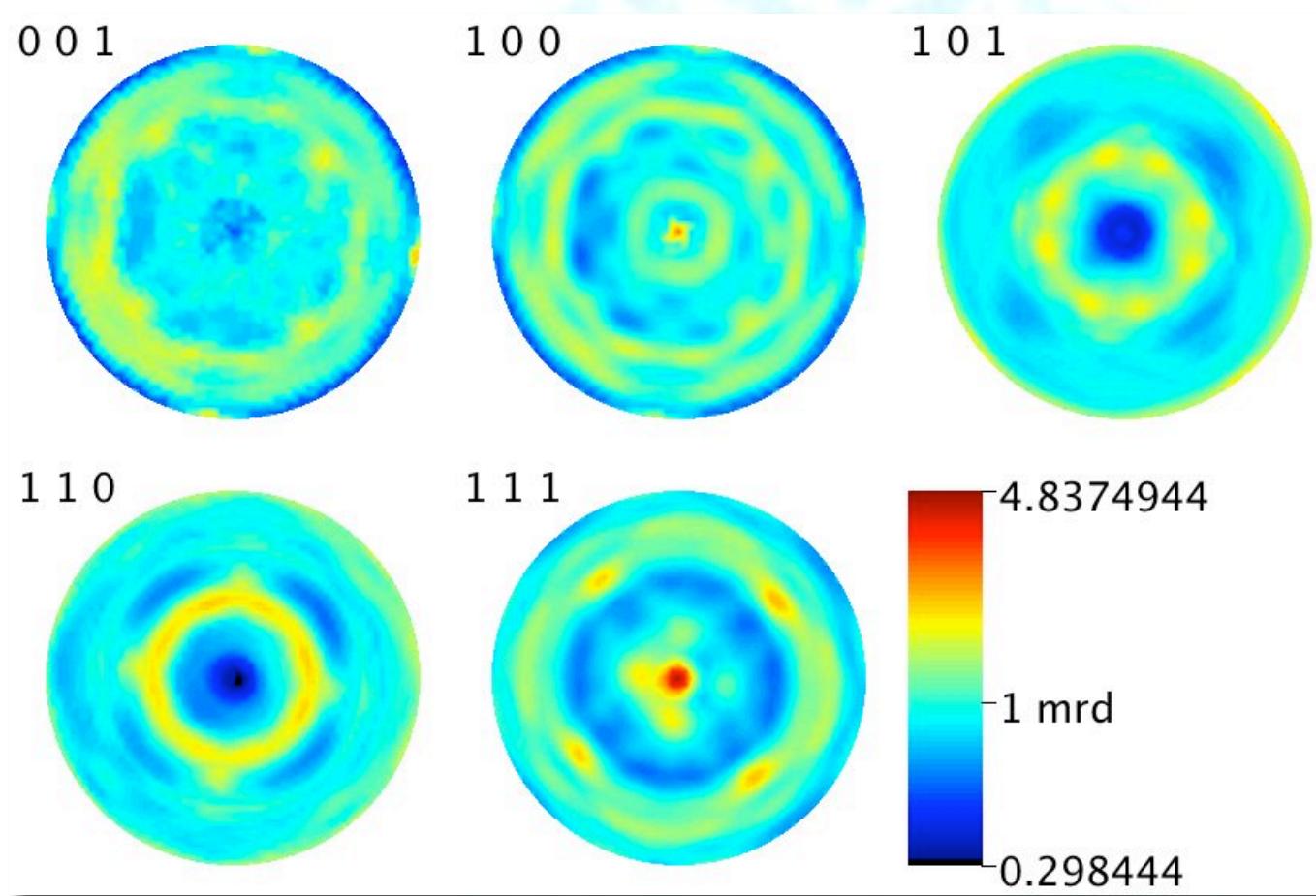
CPT film: reconstructed Pt pole figures, WIMV



PCT film fitting: E-WIMV



PCT film: PCT reconstructed pole figures

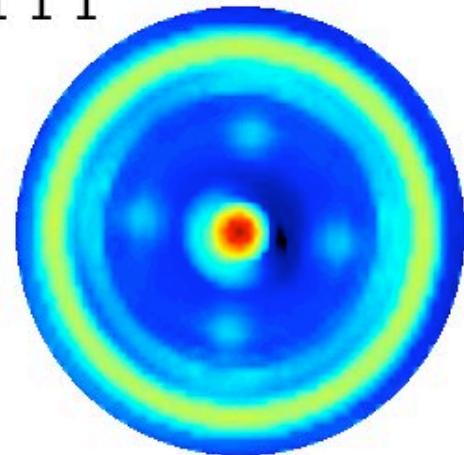


- E-WIMV
- 5 deg cells
- $F2 = 1.962$
- $Rw = 74.4 \%$
- $Rp = 24.9 \%$
- 28 reflections

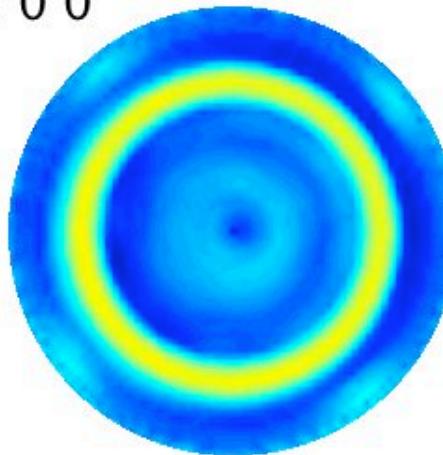


Pt buffer layer: reconstructed pole figures

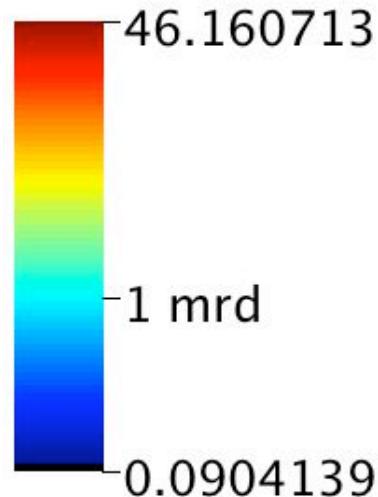
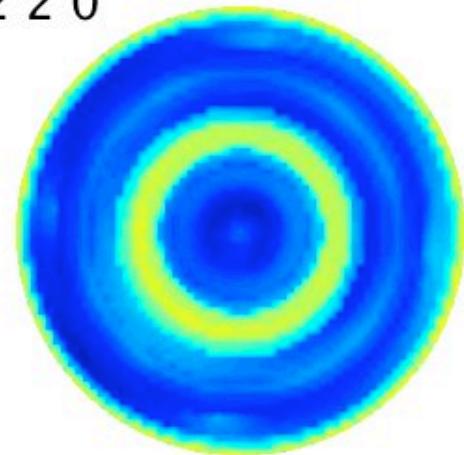
1 1 1



2 0 0



2 2 0

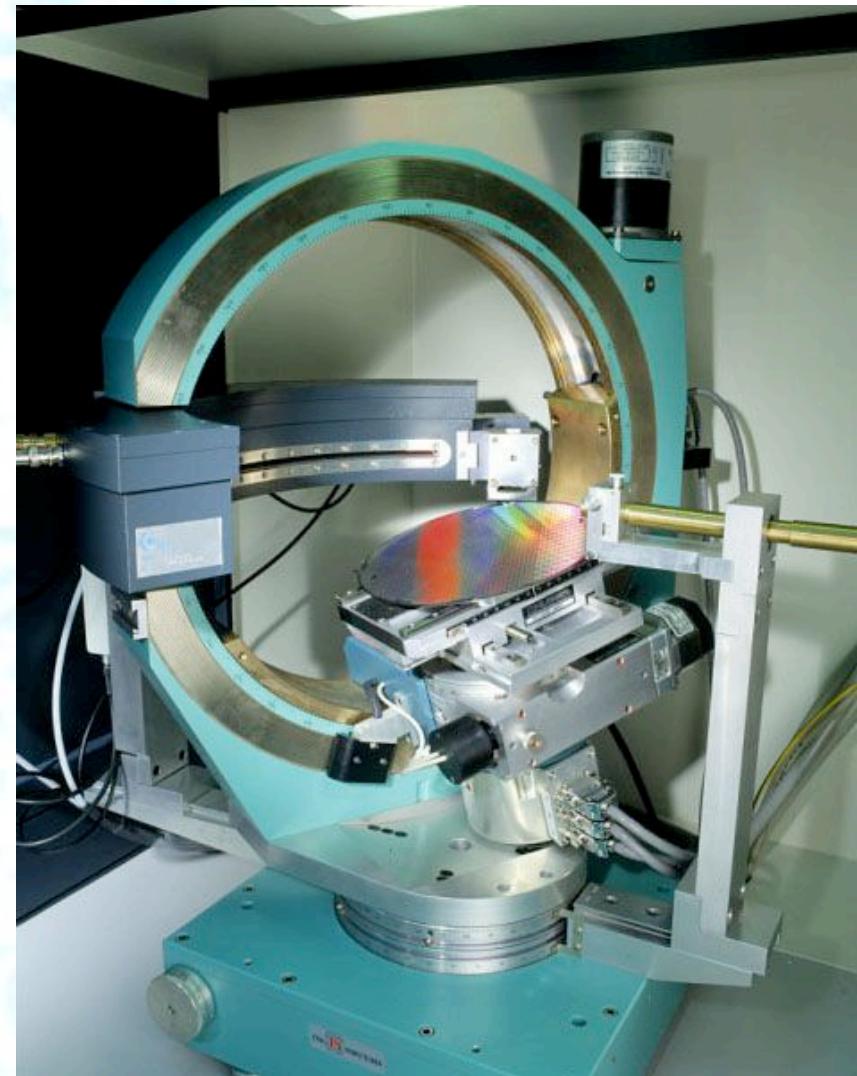


- *E-WIMV*
- *5 deg cells*
- $F2 = 22.96$
- $Rw = 11.9 \%$
- $Rp = 17.9 \%$
- *5 reflections*

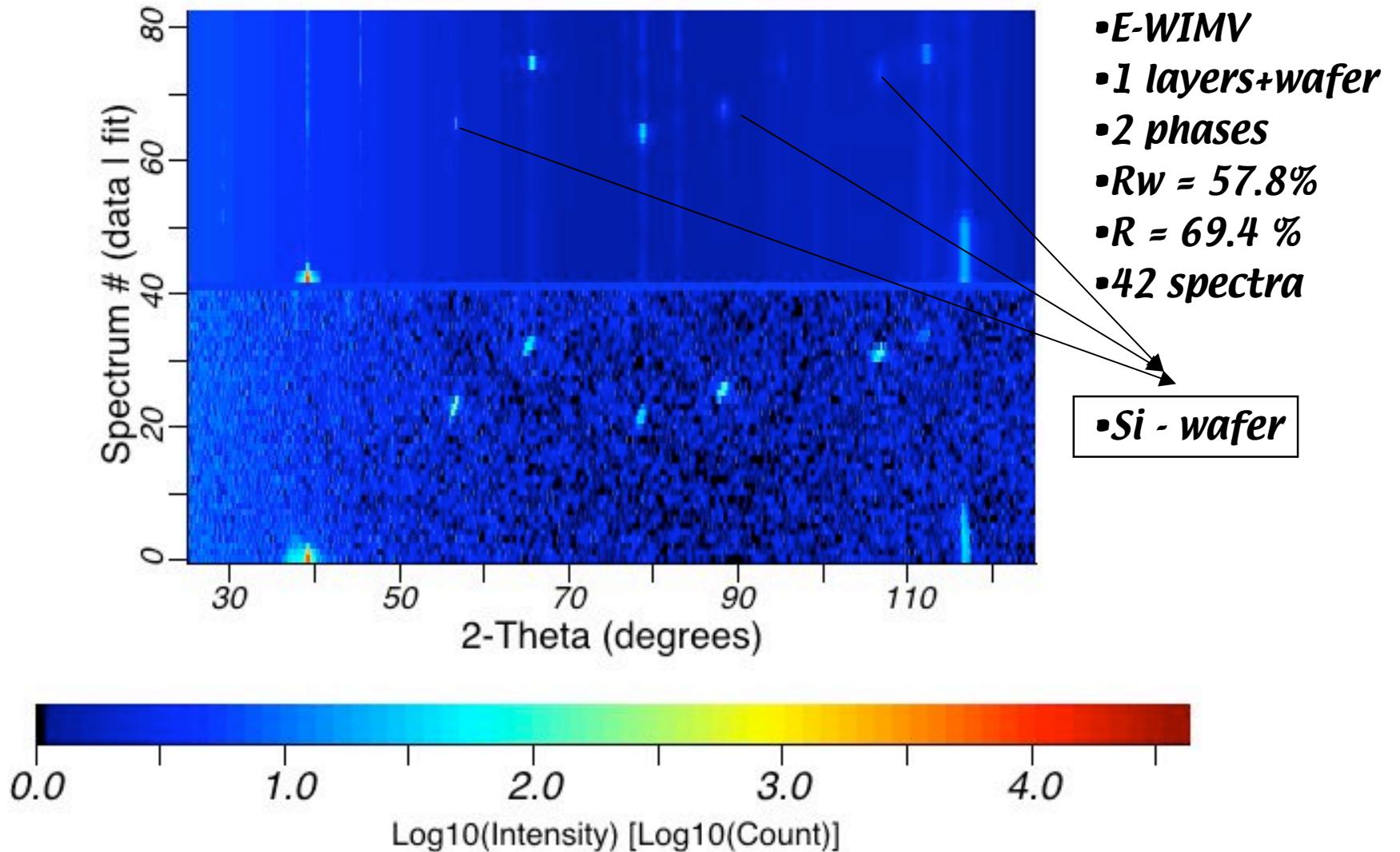


Extremely sharp Al film (ST microelectronics)

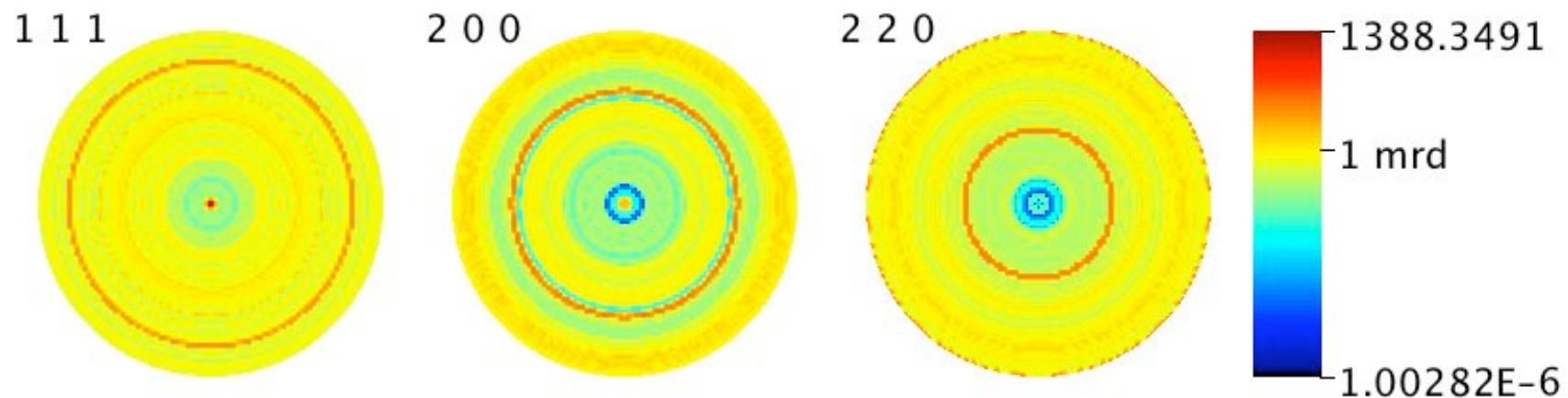
- *Aluminum film*
- *Si wafer substrate*
- *Spectra collection on the ESQUI diffractometer (right)*
- *120 degs position sensitive detector on an eulerian cradle; multilayer as a primary beam monochromator*
- *Spectra collected in chi from 0 to 45 degrees in step of 1 deg turning continuously the phi motor (fiber texture)*
- *E-WIMV used only; too sharp texture for even WIMV*



Al film: fitting the spectra



Al film: Al reconstructed pole figures

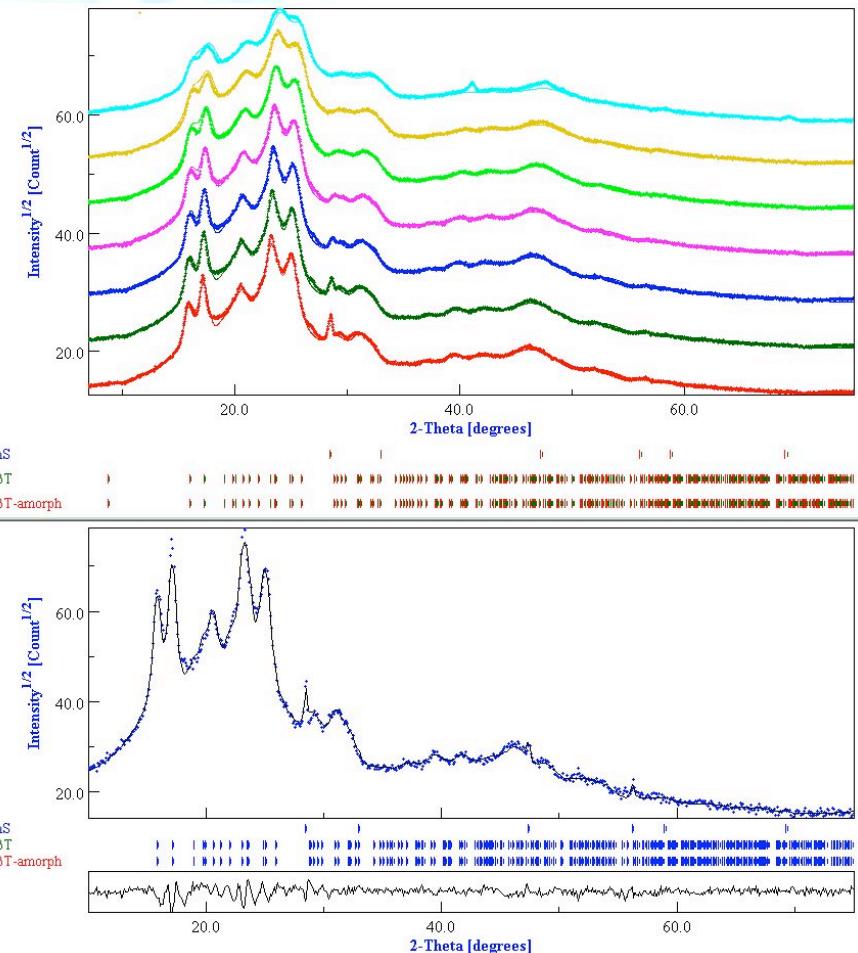


- *E-WIMV*
- *1 deg cells*
- $F2 = 1100.9$
- $Rw = 15.4 \%$
- $Rp = 19.5 \%$
- *8 reflections*

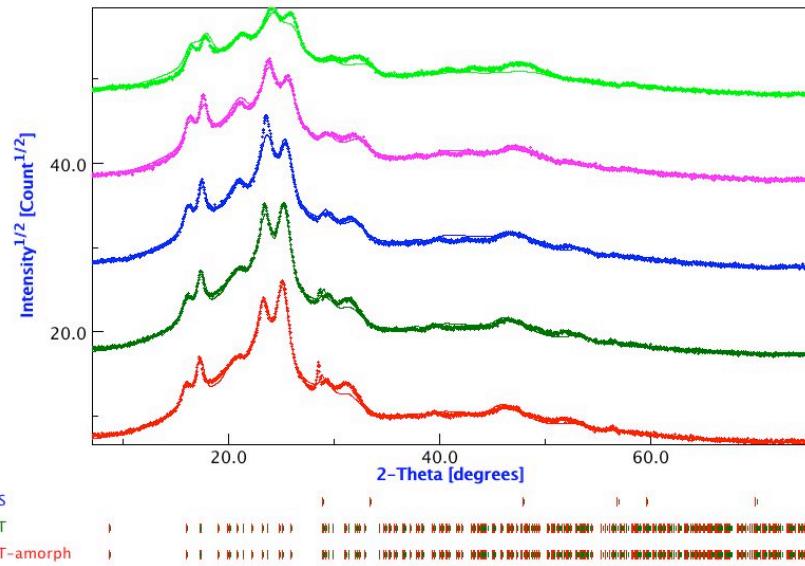


PBT polymer: texture analysis

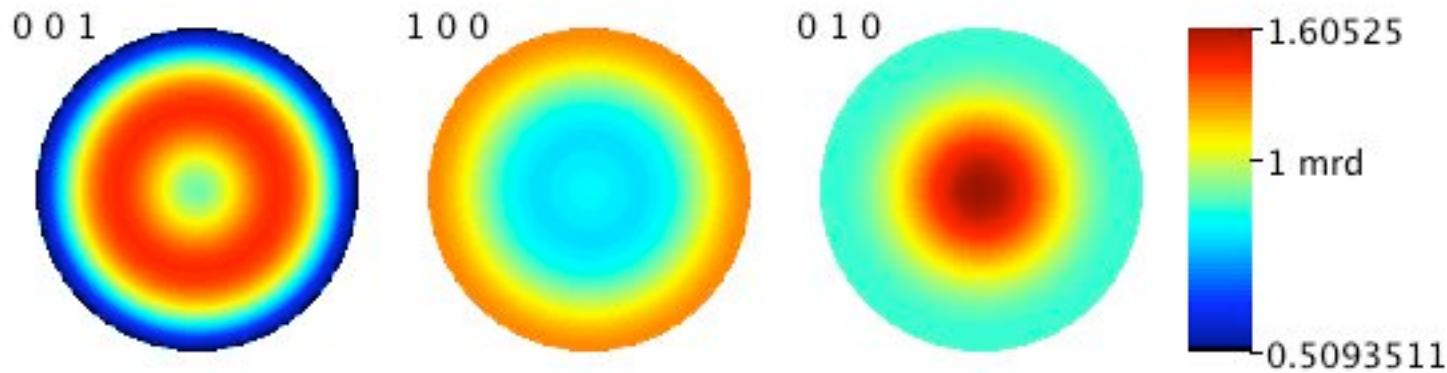
- *Polybutylentereftalate: triclinic*
 - *Only partially crystallized*
 - *Deformed at different rate
(uniassial compression)*
 - *Annealed*
 - *Spectra for both deformed and
deformed+annealed samples
collected in Le Mans (CPS 120
and eulerian cradle)*
 - *Analyzed by Maud assuming
amorphous and crystallized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



PBT results

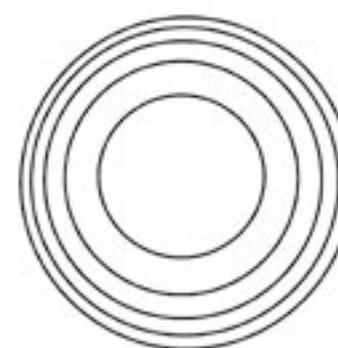
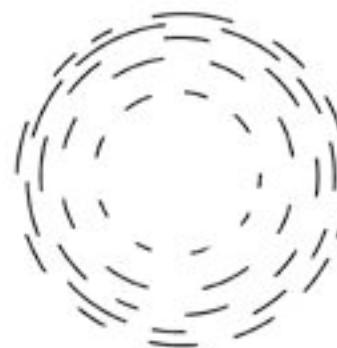
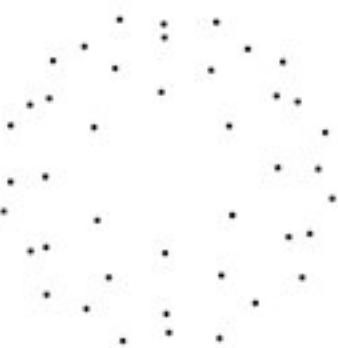
- *Deformed samples become textured at higher deformation values*
- *Crystallite sizes decrease with deformation and microstrains (paracrystallinity) increase.*
- *With the annealing crystallite sizes recuperate their original dimension and microstrains decrease. Texture remains and becomes more evident. Residual deformation is not recuperated.*
- *No texture on the amorphous PBT -> no good fitting*
- *Evidence of texture on amorphous polymers?*



What more? Ab initio structure solution

- IUCr 1999: McKusker and Baerlocher group present a crystal structure determination by powder diffraction using texture.

Single crystal Textured sample Powder sample



- *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)*
 - $F_{hkl} \rightarrow$ *structure solution*
- *Only one measurement step required*
- *Only one step for texture and F_{hkl} extraction*



Future

- *Driving the experiment (ODF coverage etc.). Using Genetic Algorithms?*
- *Sharp textures -> continuous coverage -> 2D detectors*
- *Structure solution problems:*
 - *Textured sample preparation*
 - *Data collection (fast, reliable, high resolution)*
- *Programming?*



Coupling Texture and Residual Strain models in the Maud/Rietveld package

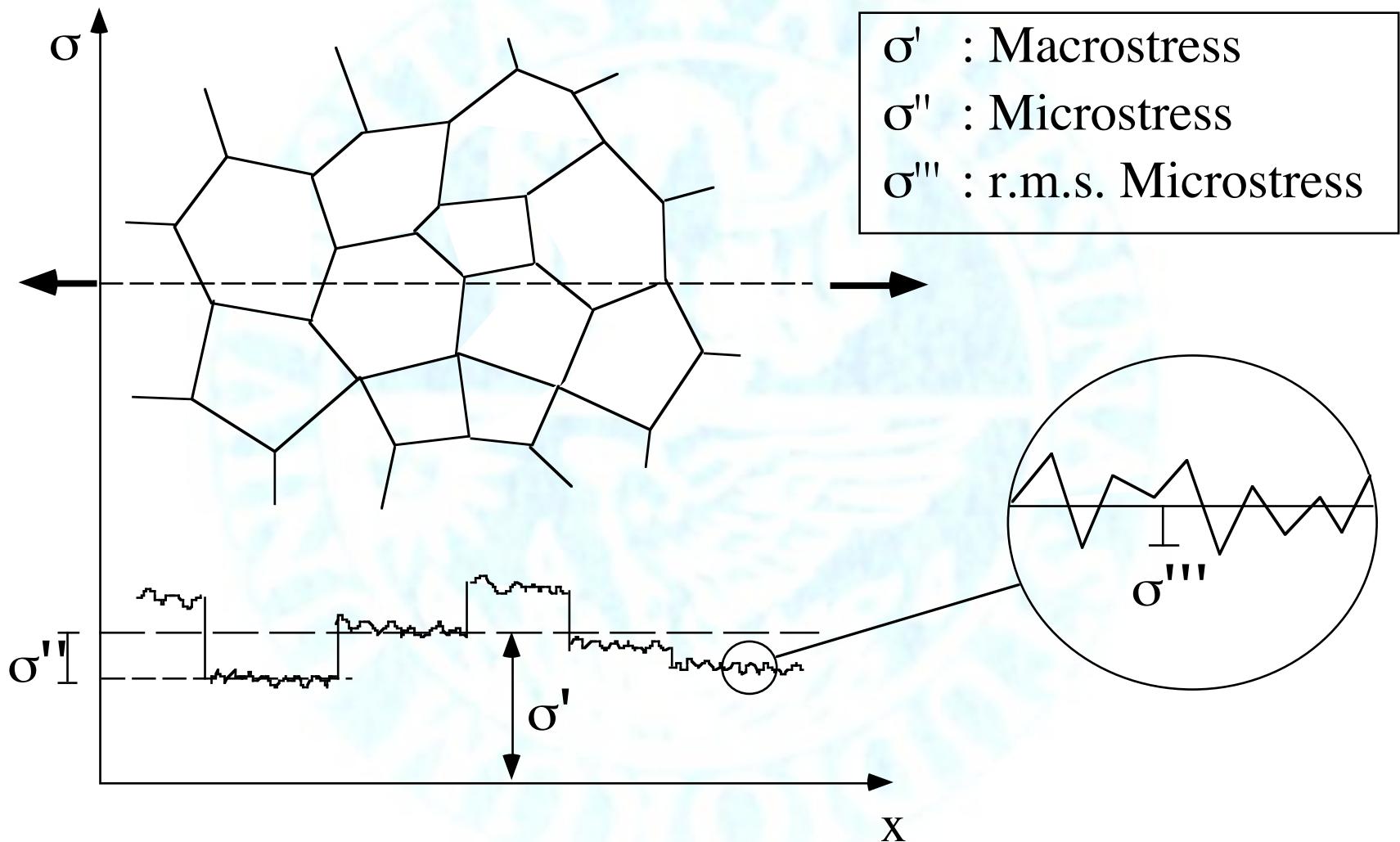
Luca Lutterotti

Department of Materials Engineering

University of Trento - Italy

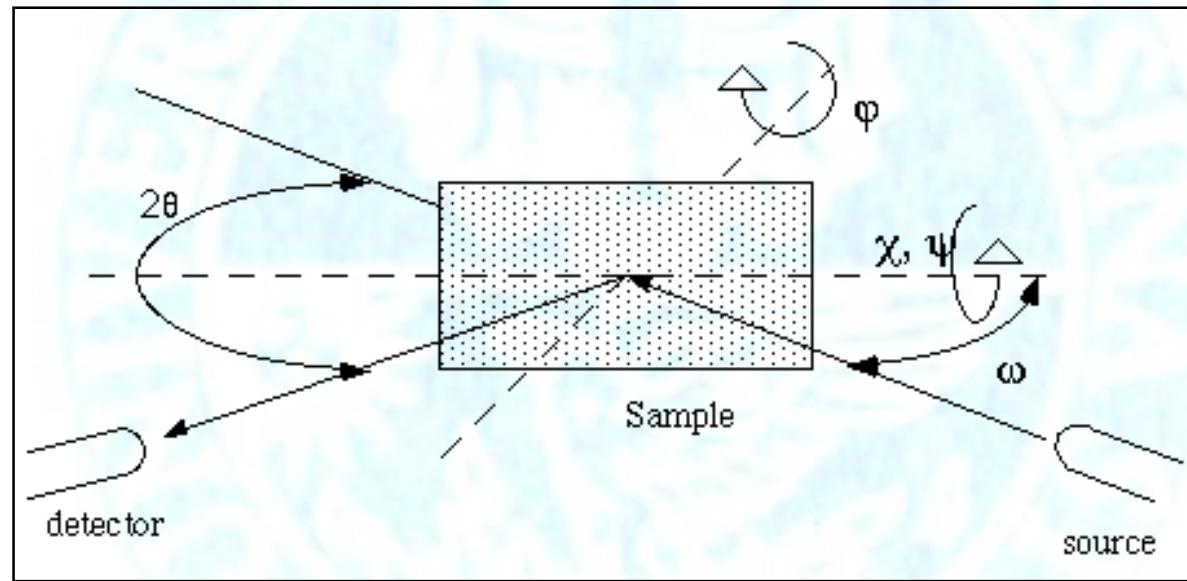


Residual Stress/Strain definition



Residual macrostress analysis

- *The classical analysis in diffraction employ the so-called $\sin^2\psi$*
- *Measurement setup:*



- *The simple behaviour is a linear relation between the d -spacing measured and the $\sin^2\psi$.*

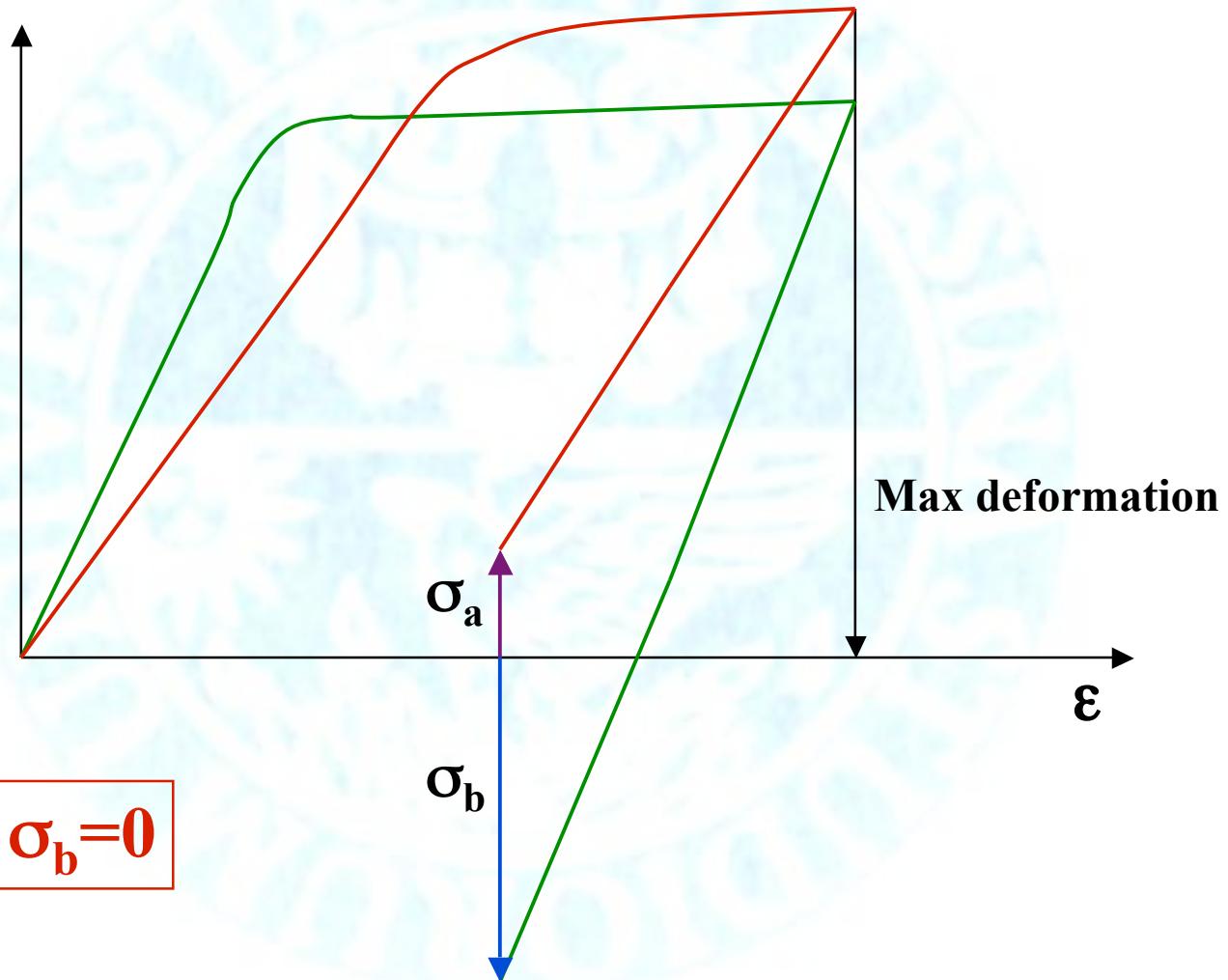


Non linear behaviour

- In many cases oscillation of d vs. $\sin^2\psi$ are observed; some possible causes:
 - Textured sample -> the elastic tensor is anisotropic.
 - Plastic deformation: anisotropy of the plasticity behaviour and elastic tensor results in anisotropy of the residual stresses/strains
 - Thermal expansion anisotropy
 - Shear stresses normal to the surface
 - Coherent and semicoherent interfaces (in thin film....)
 -
- Dollé in 1979 (J. Appl. Cryst., 12, 489) analyzed the problem in general and was followed by other authors: Noyan and Nguyen for the plastic deformation, Barral et al. for the texture connection.

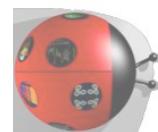


Anisotropy of plastic deformation



Plastic deformation

- *The distribution of local stresses and local strain are controlled by:*
 - *The stress equilibrium equations*
 - *The local yield criterion and the normality rule or the Maximum Work Principle*
 - *The fact that no plastic volume change takes place*
 - *The stress and strain boundary conditions.*
- *Different models can be used:*
 - *Sachs model: uniform stress, geometrical incompatibility of the strain results*
 - *Taylor model: the plastic strain rate is homogeneous, the stress depends on the crystallite orientation g*
 - *Elastic-plastic self-consistent models: intermediate solution between Sachs and Taylor models. Assumes that strain rate and stress are uniform inside the crystallite.*



Residual stresses in textured samples

- Just loading a stress-free polycrystalline material the local stresses and local elastic strains assume spatial distributions governed by:
 - The stress equilibrium equations
 - Hooke's law
 - The strain compatibility equations
 - The stress and strain boundary conditions at grain boundaries and outer surfaces.
- Different models can be used:
 - Reuss model: σ is homogeneous throughout the sample. As a consequence the strain change from grain to grain and with different orientation g .
 - Voigt model: ε is homogeneous throughout the sample. The stress will be heterogeneous.
 - Hill model and Self consistent models: both stress and strain are heterogeneous.



Goals of the residual stress/strain analysis

- *Separation of the microstrain/microstress of I and II kind.*
 - *It is sufficient to determine the sum of them:*

$$\sigma_{ij} = \sigma_{ij}^I + \sigma_{ij}^{II}, \text{ but } <\sigma_{ij}> = \sigma_{ij}^I$$

$$\text{and as a result: } \sigma_{ij}^{II} = \sigma_{ij}^I - <\sigma_{ij}>$$

Or for strains:

$$\varepsilon_{ij} = \varepsilon_{ij}^I + \varepsilon_{ij}^{II}, \text{ and } \varepsilon_{ij}^{II} = \varepsilon_{ij}^I - <\varepsilon_{ij}>$$

- *Dilemma:*
 1. *Extracting pure strain -> no models needed*
 2. *Extracting stresses -> unique solution*



Needs

- To extract the local anisotropic stress/strain we need to measure not only different ψ and ϕ , but also as many hkl peaks as possible -> Rietveld method
 - Ferrari & Lutterotti, 1994, introduced a combined treatment for texture and residual stresses based on the Rietveld method to obtain the local stress/strain tensor (method 2, employing models).
 - Balzar, Von Dreele, Bennett & Ledbetter, 1998, used the Rietveld method (GSAS) to extract pure strain data (method 1), to be processed later.
 - Wang, Lin Peng & McGreevy, 1999, introduced the SODF (Stress Orientation Distribution Function) has a general treatment to analysis residual stresses. They were using as many peaks as possible (non Rietveld) (method 2).
 - Popa & Balzar, 2001, proposed a Strain Orientation Distribution Function to be used in a Rietveld program, to extract more strain information than previous methods (method 1).



Ferrari & Lutterotti model

The local stress tensor is written as:

$$\bar{\underline{\tau}}(g) = \underline{B}\underline{\tau}^0 + \underline{\tau}^*$$

So the local strain tensor :

$$\bar{\underline{e}}(g) = \underline{S}^C (\underline{B}\underline{\tau}^0 + \underline{\tau}^*) \quad \text{Then :}$$

$$\bar{e}^j(hkl) = \frac{\int_0^{2\pi} \bar{e}_{33}(g') f(g') d\omega}{\int_0^{2\pi} f(g') d\omega}$$

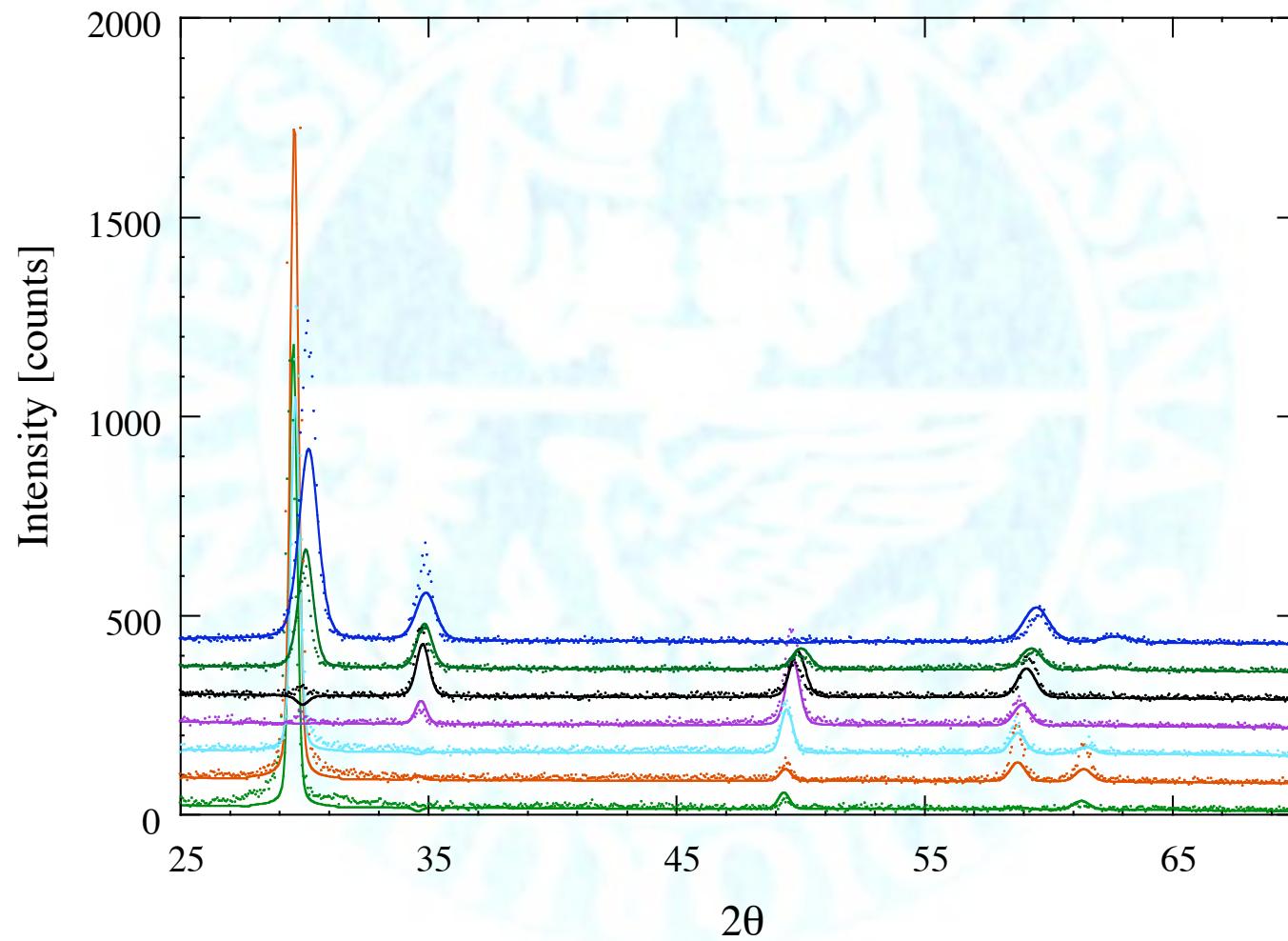
$$\text{and} \quad d_{hkl}^j = d_{hkl}^0 \left(1 + \bar{e}^j(hkl) \right)$$

The stress concentrator tensor B can be used to compute the effective elastic constant: $\underline{S} = \langle \underline{S}^C \underline{B} \rangle$

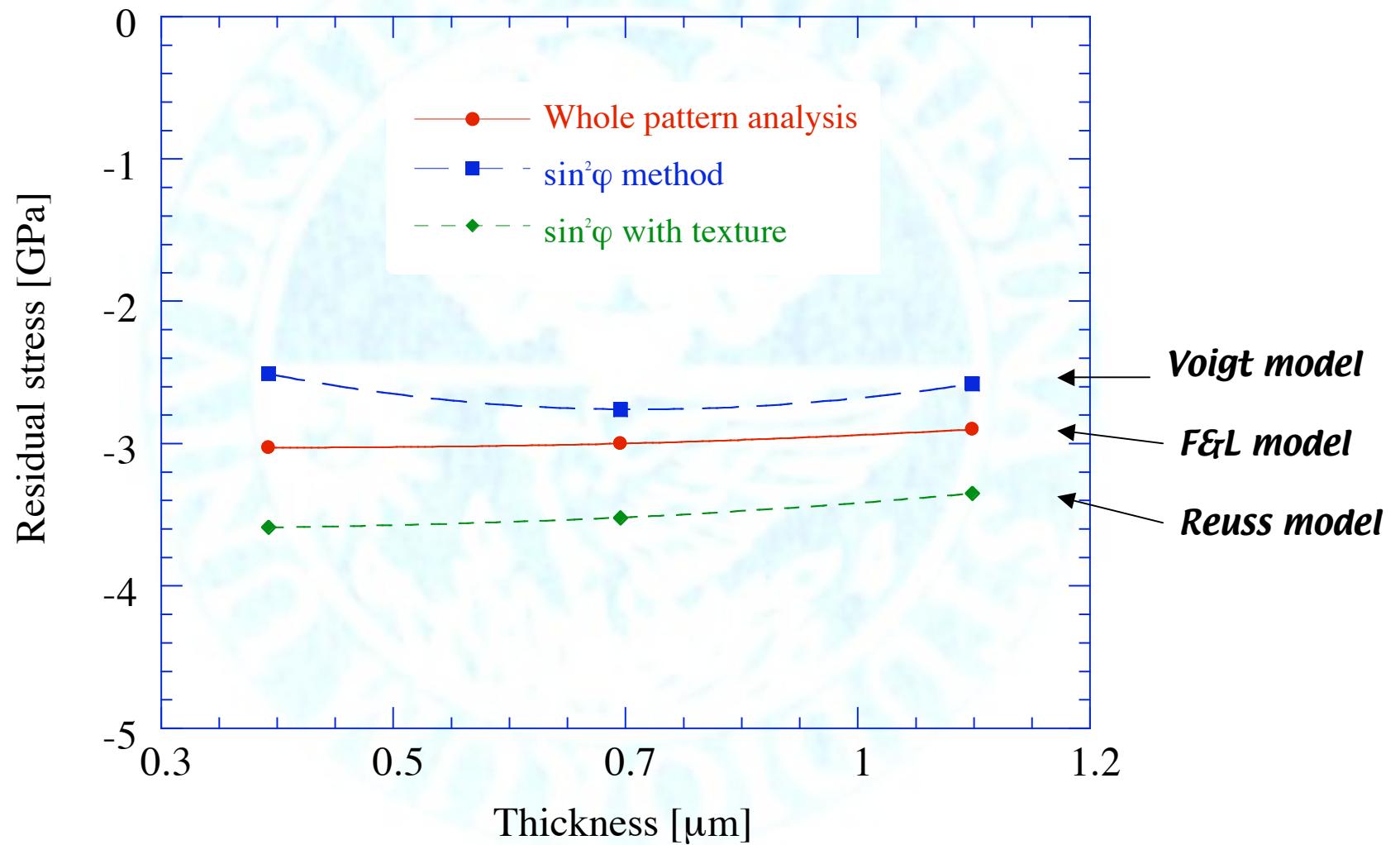
It's a mixed model in between Reuss and Voigt ones.



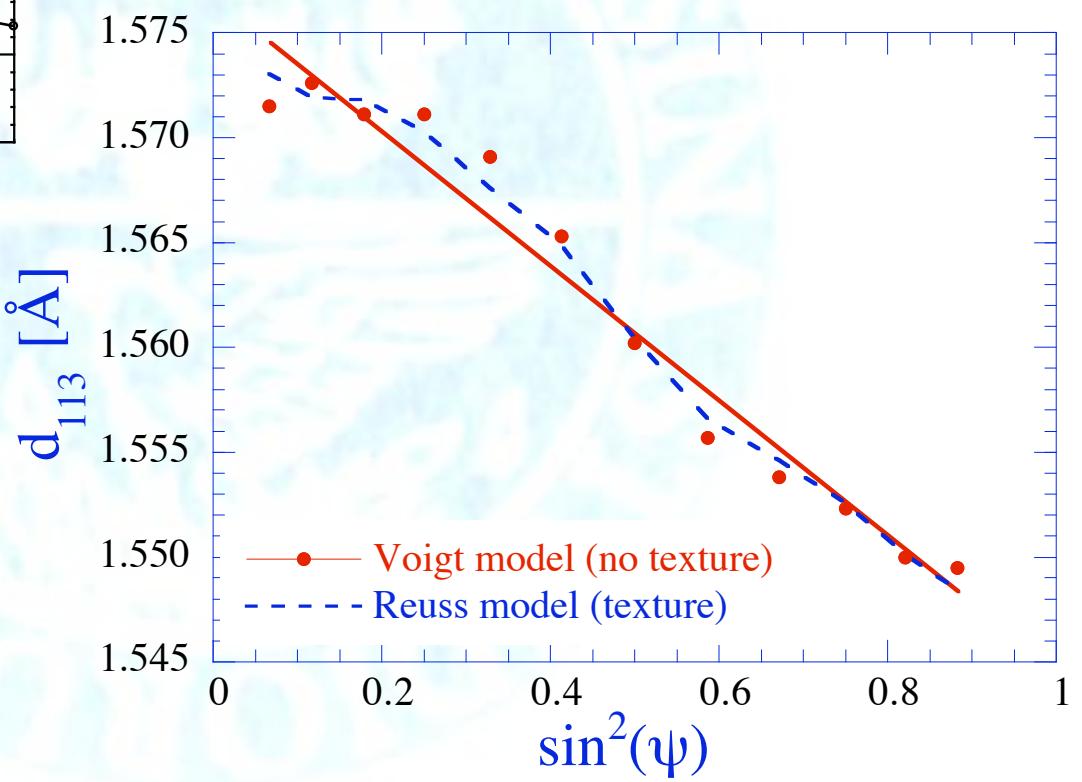
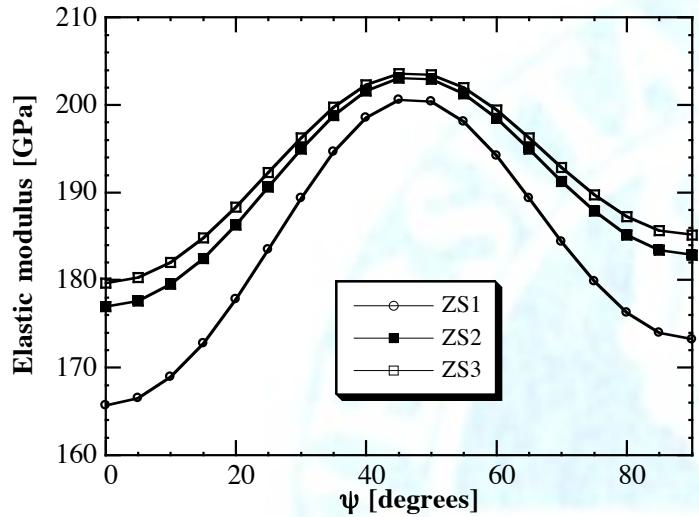
Testing the model: ZrO₂ thin films



Macro residual stress on the ZrO₂ serie

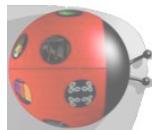
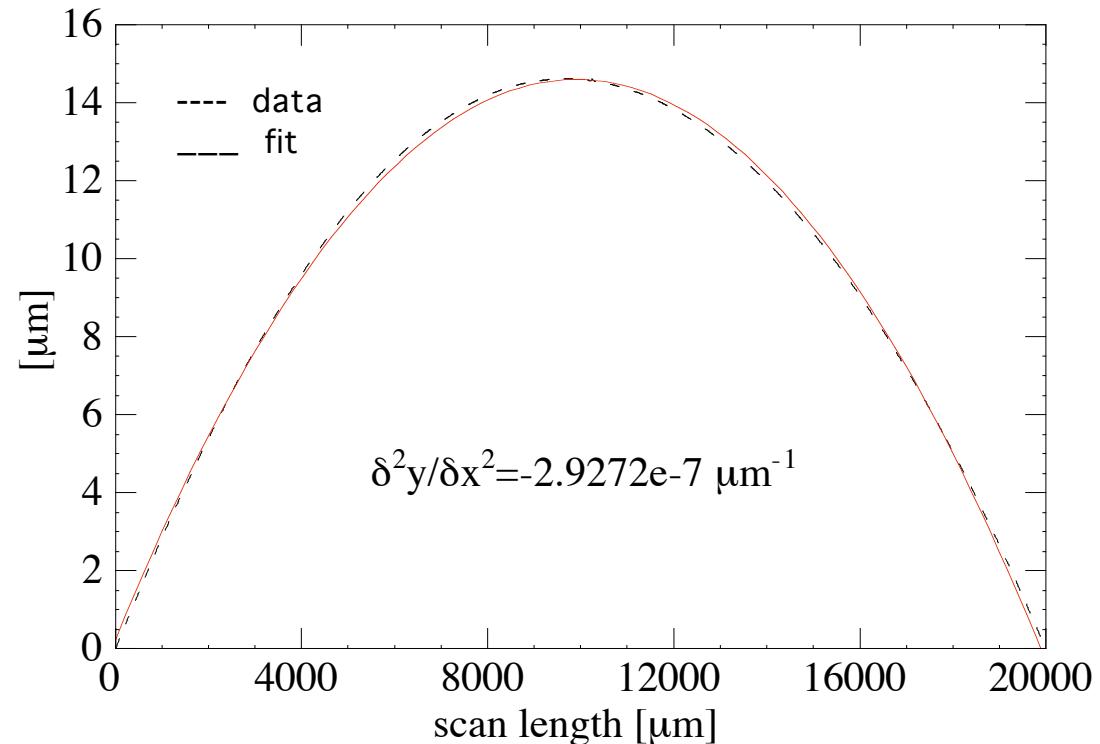


Traditional methods for the ZrO₂ films



Measuring the stress also by the curvature

$$\sigma^* = K \cdot \frac{d_s^2}{d_f} \cdot \frac{a_{11}}{2}$$



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:*

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



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*
- **Disadvantages:**
 - *6 ODF functions to be determined -> huge amount of unknowns.*
 - *Enormous amount of data required.*
 - *Uniquity of 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, too much unknown respect to the data.*
- *General remark:*

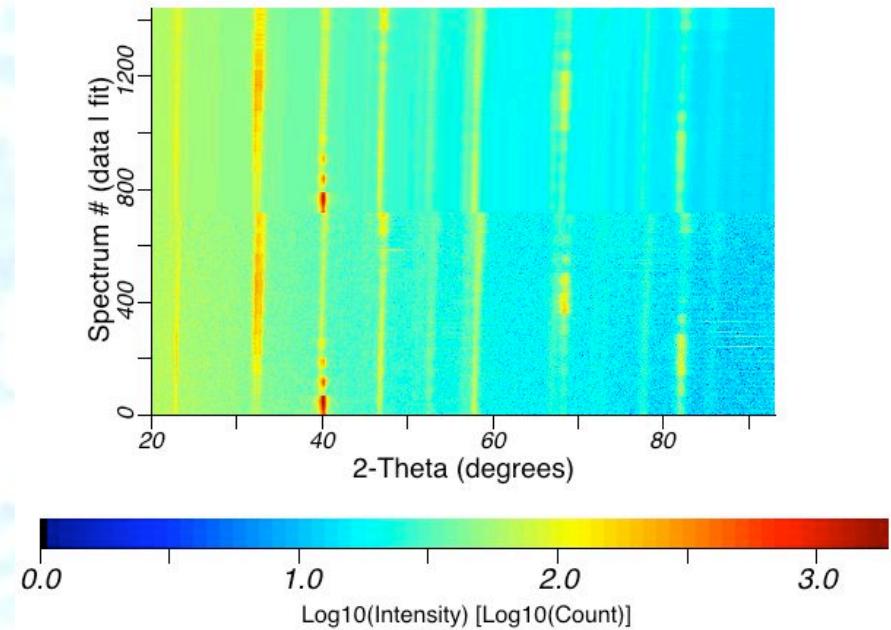
The SODF is used in an integral computation with the ODF ->

- *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.*



Experimental errors

- Example: the CPT film shows big shift of the peaks increasing χ .
- The shift is not smaller at low 2theta angle.
- In the fitting was perfectly reproduced by a beam 0.59 mm higher than the goniometer center.
- Using the Rietveld method peak shifts from low angle positions are also used normally -> good sample positioning required, perfect alignment of the instrument also.



Future

- *Using the Geometrical mean for Rietveld Residual Stress/Texture analysis.*
 - *The GEO method (Matthies) gives the same solution as the self-consistent method in the polycrystal case and can be used to overcome the dualism Voigt-Reuss.*
- *Comparison of SODF methods with stress model function (GEO)*



Acknowledgments

- *H.-R. Wenk and S. Matthies*
- *The ESQUI group (MDM Agrate (Mi), LPEC Le Mans, CSIC Madrid)*
- *S. Gialanella, L. Cont (Trento)*

