Étude structurale de matériaux sous forme de couches minces par diffraction des rayons X en incidence rasante

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Collaborations et examples d'applications:

S. Bouffard (Cimap, Caen), P. Lecoeur (IEF, Orsay)

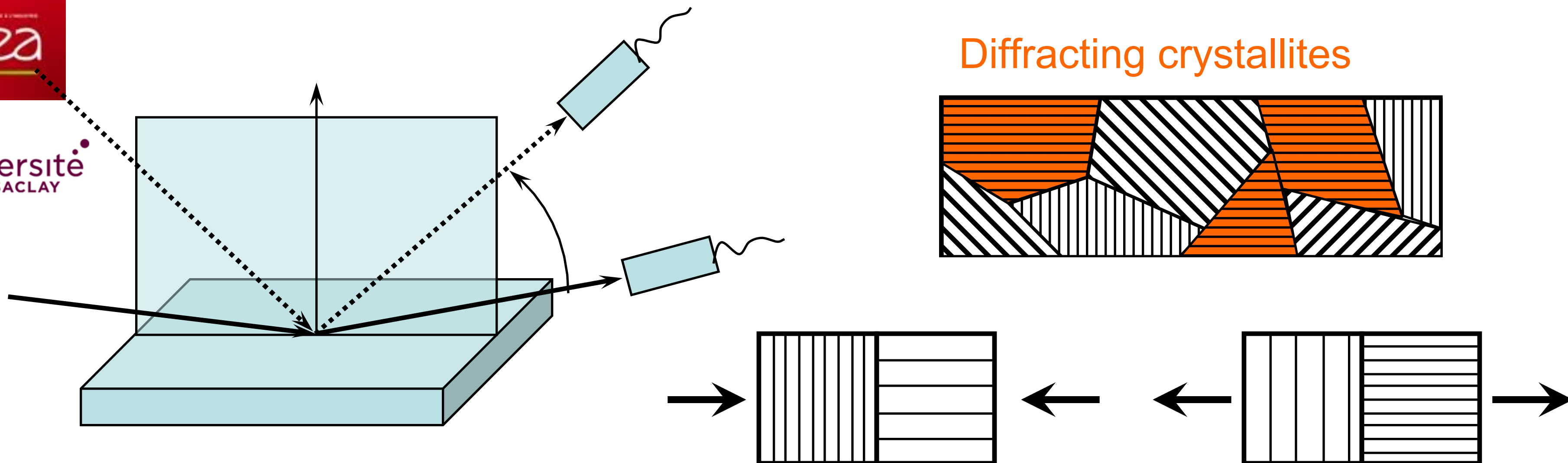
C. Laberty-Robert, C. Sanchez (LCMC, Jussieu)

ANR-06-BLAN-0292, C'nano IDF Solnac 2009,
Triangle de la Physique Instrumat 2011-074T, ANR-10-LABX-0039

Outline

- Diffraction basics – Glancing angle (incidence) XRD
- Rietveld method and GA-XRD
- Structures & microstructures
- Examples
- Conclusion

Conventional X-ray diffraction



+ Reliable information on
    - the preferred orientation of crystallites
    - the crystallite size and lattice strain (in one direction)

– No information on the residual stress (constant direction of the diffraction vector)

– Low scattering from the layer (large penetration depth)

Penetration depth of X-rays

L.G. Parratt, Surface Studies of Solids by Total Reflection of X-rays, Physical Review 95 (1954) 359-369.

$$n = \sqrt{1+\chi} \approx 1 + \frac{\chi}{2} = 1 - \frac{r_e \lambda^2}{2\pi}\rho$$

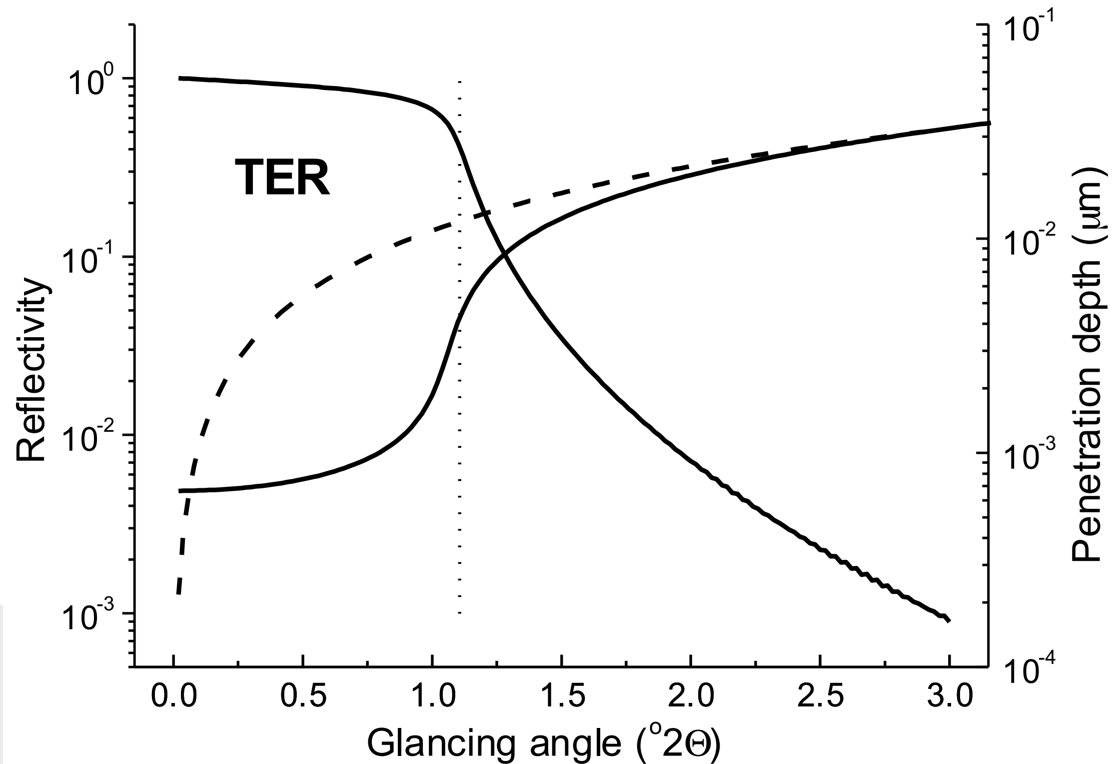
$$n \approx 1 - \frac{r_e \lambda^2}{2\pi}\rho_e\left(f_0 + f' - if''\right)$$

$$n \approx 1 - \delta + i\beta \leq 1$$

Example: Gold (CuKα)
$\delta = 4.2558 \times 10^{-5}$
$\beta = 4.5875 \times 10^{-6}$

$$n_V \cos\theta = n_j \cos\theta_j \quad ; \quad n_j = \cos\theta_c$$

$$1 - \frac{r_e \lambda^2}{2\pi}\rho \cong 1 - \frac{\theta_c^2}{2} \quad ; \quad \theta_c \cong \sqrt{\frac{r_e \lambda^2}{\pi}\rho}$$

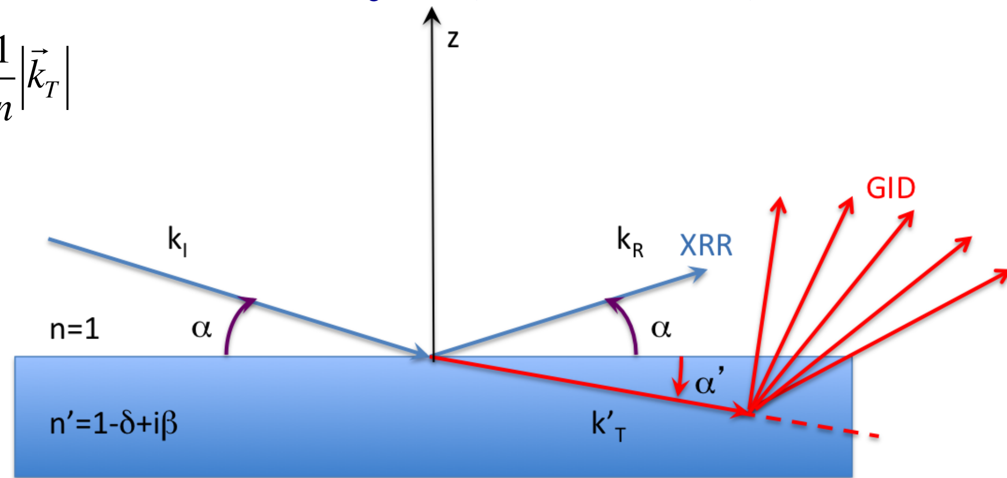


Snell, Fresnel laws for X-rays (GAXRD)

$\psi_j = a_j e^{i\vec{k}_j\cdot\vec{r}}$; j=I, T or R $\quad k = |\vec{k}_I| = |\vec{k}_R| = \frac{1}{n}|\vec{k}_T|$

$$C^1 \begin{cases} a_T = a_I + a_R \\ a_T k_T = a_I k_I + a_R k_R \end{cases}$$

$$\begin{cases} n\cos\alpha' = \cos\alpha \\ (a_I + a_R)\, n\sin\alpha' = (a_I - a_R)\sin\alpha \end{cases}$$



$$n = 1-\delta+i\beta \equiv 1-\frac{\alpha_c^2}{2}+i\beta \;;\; \alpha_c^2 \equiv \left(\frac{4\pi}{k^2}\right)\rho \;,\; \beta=\frac{\mu}{2k}$$

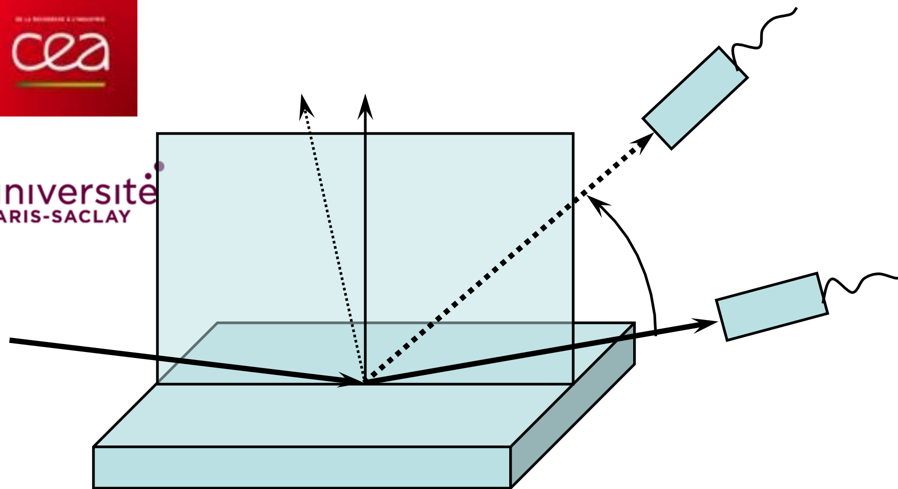
$$\left(1-\frac{\alpha_c^2}{2}+i\beta\right)\left(1-\frac{\alpha'^2}{2}\right)=\left(1-\frac{a^2}{2}\right) \rightarrow \alpha'^2 = \alpha^2-\alpha_c^2+2i\beta$$

Snell's Law

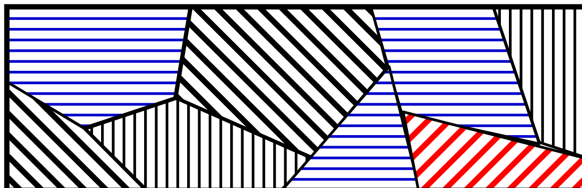
$$\left(1+\frac{a_R}{a_I}\right)\alpha' = \left(1-\frac{a_R}{a_I}\right)\alpha \rightarrow R \equiv \frac{a_R}{a_I} = \frac{\alpha-\alpha'}{\alpha+\alpha'}$$

Fresnel's Law

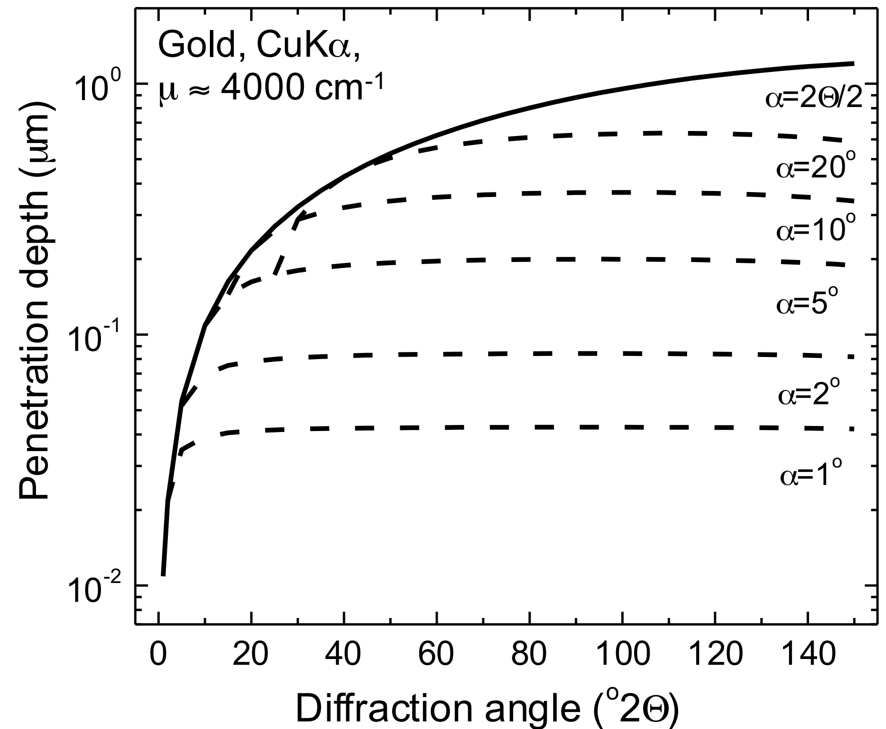
Glancing angle X-ray diffraction GAXRD



GAXRD



$$t: \frac{dI}{dz} = I_0 \frac{1}{e}\, ; x_e = \frac{\sin\theta_i \cdot \sin\theta_o}{\mu(\sin\theta_i + \sin\theta_o)}$$



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GAXRD Basics

- **Parallel, monochromatic X-ray beam impinges on a sample surface at a fixed angle of incidence (α_I) and diffraction profile is recorded by detector-only scan.**
- **When the angle of incidence (α_I) of X-ray beam decreases, since the refractive index in the sample is less than unity, total external reflection of X-rays occurs below the critical angle of incidence α_C. The diffracted and scattered signals at the angle 2θ arise mainly from a limited depth below the surface of the specimen.**

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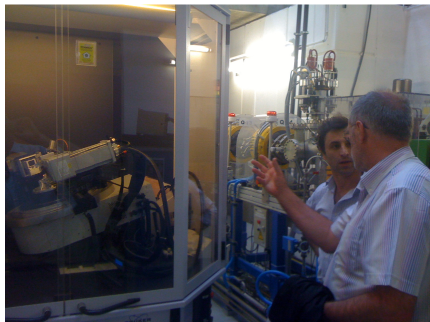

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Polycrystalline Thin Film

Angle of incidence α

Goebel mirror

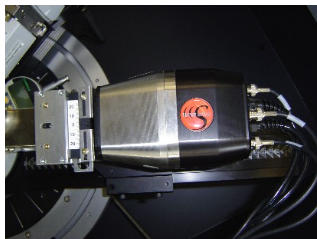
X-ray source

Diffraction angle, 2θ

Sample inclination, ψ

Sample rotation, ϕ

Diffraction vector

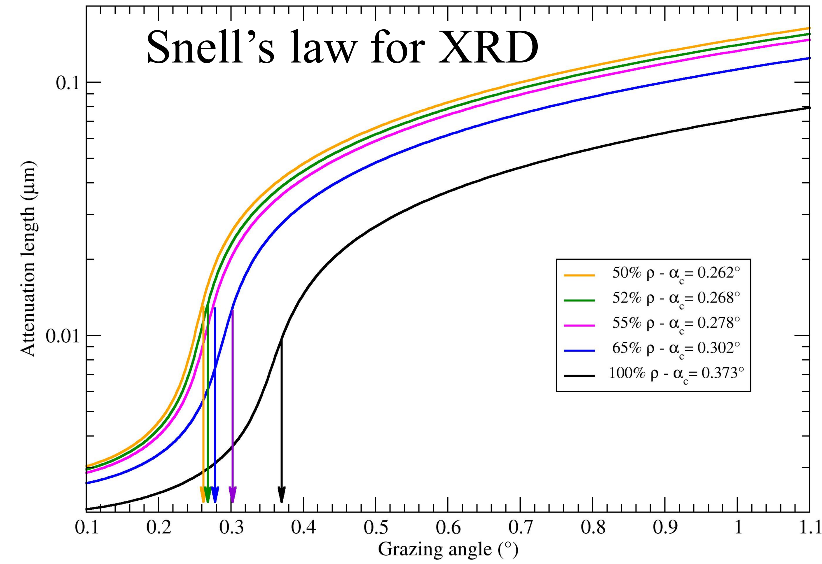


Sample Normal

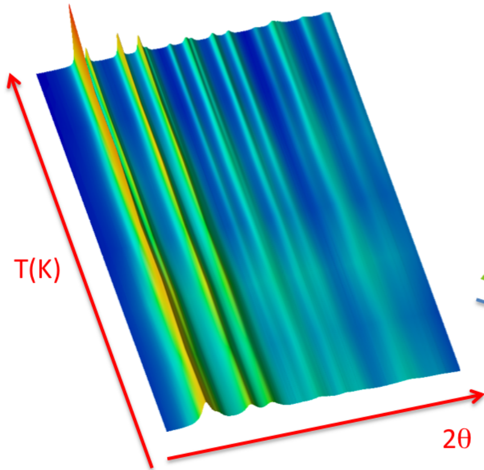
Analyzer Crystal

AFC 2016
Congrès de l'Association Française de Cristallographie
Marseille, France, 4 – 7 juillet 2016

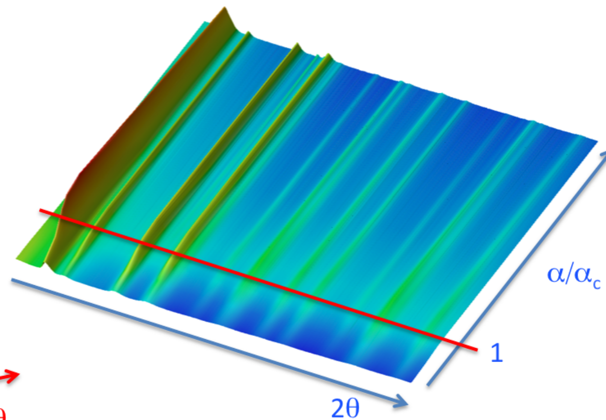
- **Quantitative phase analysis**
- **Symmetry**
- **Crystal structure (Rietveld)**
- **Crystallite size and strain determination**



Isothermal annealing



Microstructure vs. depth



$$1+R(\alpha)=T(\alpha)\rightarrow T(\alpha)=\frac{2\alpha}{\alpha+\alpha'}$$

$$\mathrm{T}(\alpha)=\frac{2\alpha/\alpha_c}{\alpha/\alpha_c+\sqrt{\left(\alpha^2/\alpha_c^2-1\right)}} \text{ for } \alpha>\alpha_c$$

$$T(\alpha)=2\frac{\alpha}{\alpha_c} \text{ for } \alpha\leq\alpha_c$$

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Reflections shape and breadth …

- **Instrumental broadening**
- **Specimen-related broadening**
  - **Crystallite finite size**
  - **Microstrain**
    - Non-uniform Lattice Distortions
    - Faults
    - Dislocations
    - Antiphase domain boundaries
    - Surface Relaxation
    - …
- **The peak profile is a convolution of the effects from all of these contributions**

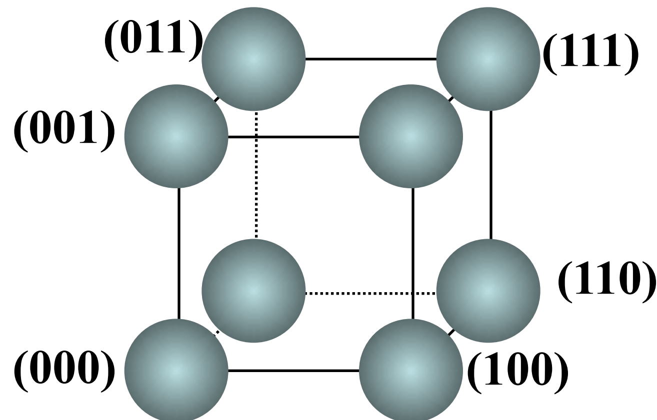
Typical sources of instrumental broadening

- X-ray Source Profile
  - Natural emission linewidths of $K\alpha_1$ and $K\alpha_2$ lines
  - Size of the X-ray source
- Goniometer Optics
  - Divergence and Receiving Slit widths
  - Imperfect focusing
  - Beam size
  - Penetration into the sample
  - …

Specimen broadening

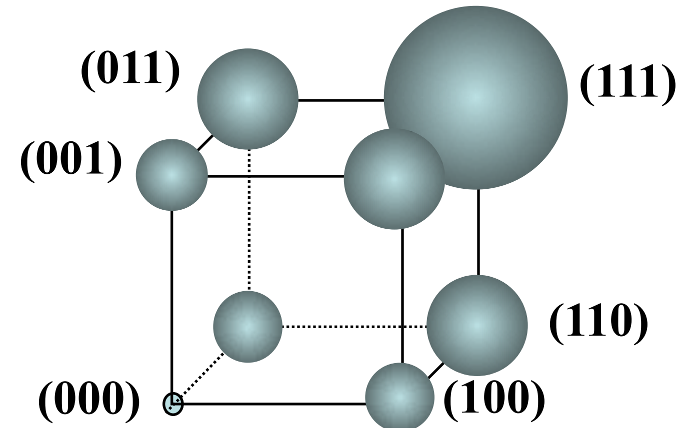
Crystallite size

- Fourier transformation of finite objects (with limited size)
- Constant line broadening (with increasing diffraction vector)



Lattice strain

- Local changes in the d-spacing
- Line broadening increases with increasing ***q*** (a result of the Bragg equation in the differential form)



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Rietveld and GAXRD: XND software

- Empirical profile matching is sometimes difficult:
  - overlapping peaks
  - a mixture of nanocrystalline phases
  - a mixture of nanocrystalline and microcrystalline phases
- Rietveld profile analysis (more information about the sample)
  - how much of each phase is present in a mixture
  - lattice parameter refinement
    - nanophase materials often have different lattice parameters from their bulk counterparts
  - atomic structure, site occupancy, thermal displacement parameters, …
  - better compensation of profile-related errors

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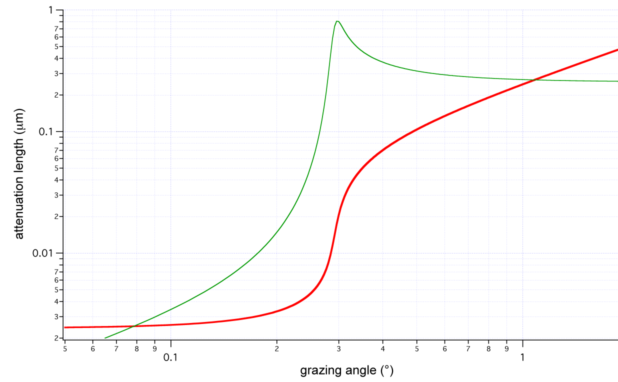
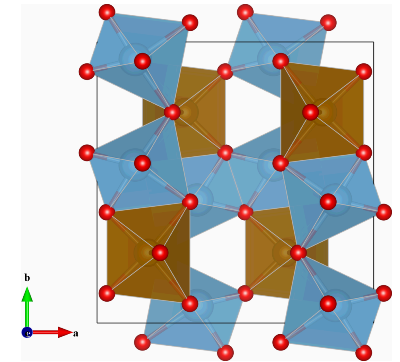
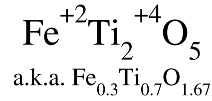
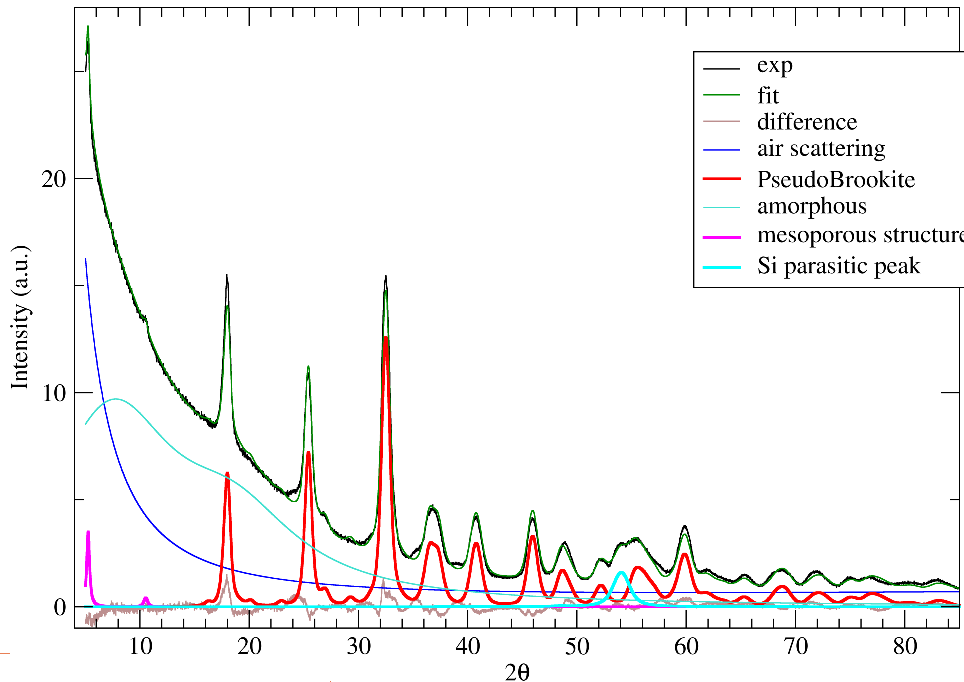
Rietveld analysis of multi-phase thin films









- Accurate retrieval of “domain” size and microstrain once instrumental broadening is corrected for
- Increased sensitivity to layers immediately below the surface
- In-situ measurements (irradiation and/or annealing phases)

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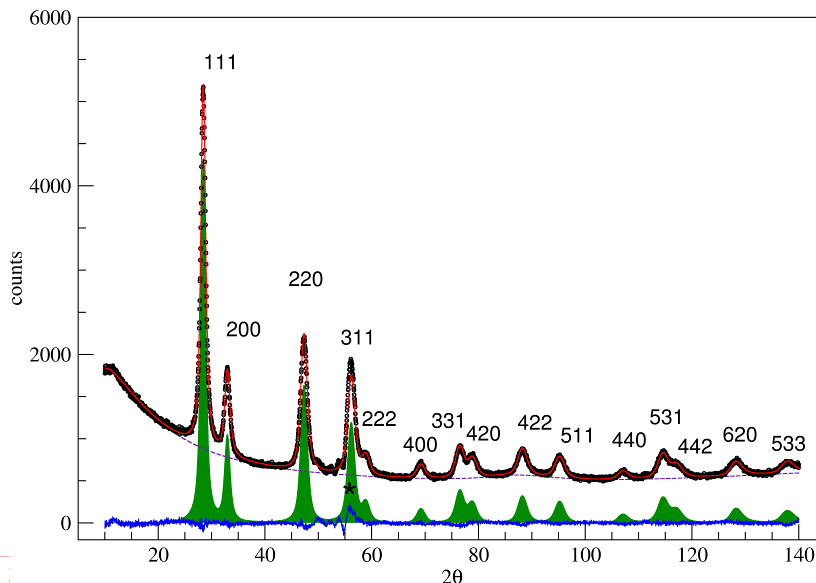
Measuring structure and strain in a thin layer: thin films & the problem of ion irradiation

The GAXRD setup

- **Accurate retrieval of “domain” size and microstrain once instrumental broadening is corrected for**
- **Increased sensitivity to layers immediately below the surface**
- **In-situ measurements (irradiation and/or annealing phases)**



Typical GAXRD pattern obtained on a fluorite phase

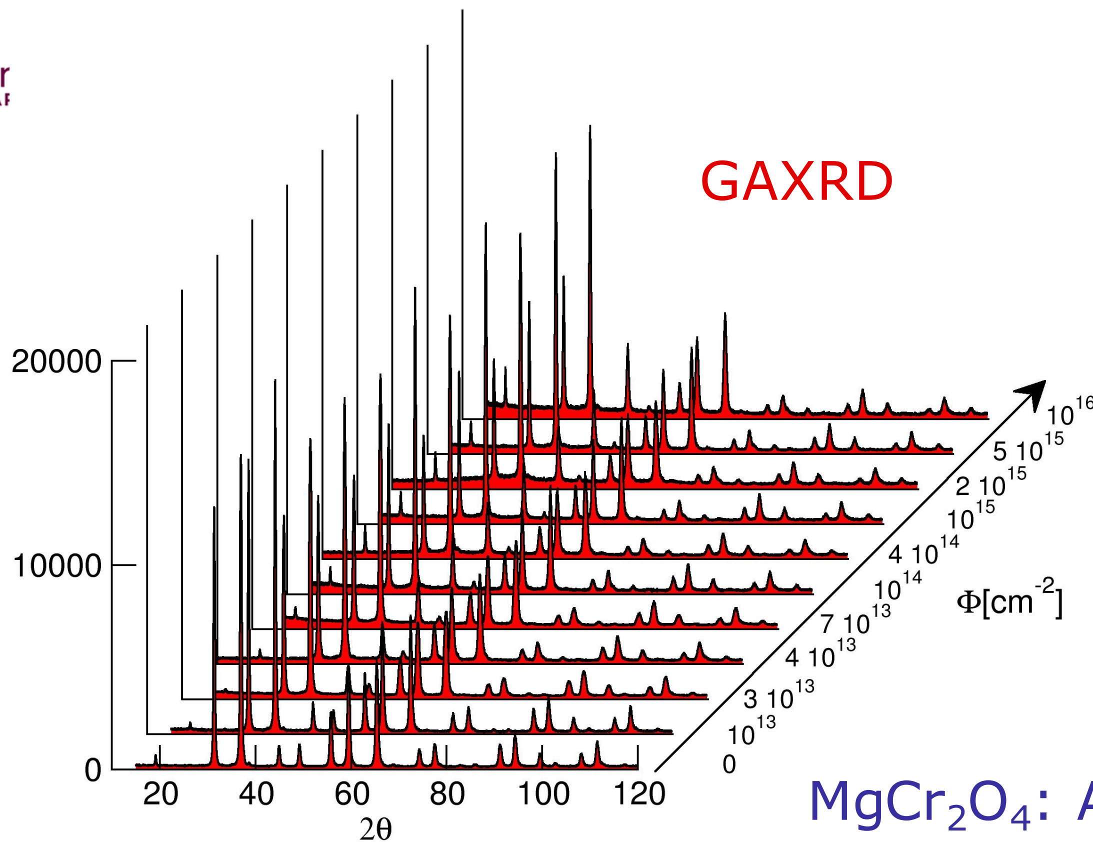
Structural evolution of spinels under irradiation

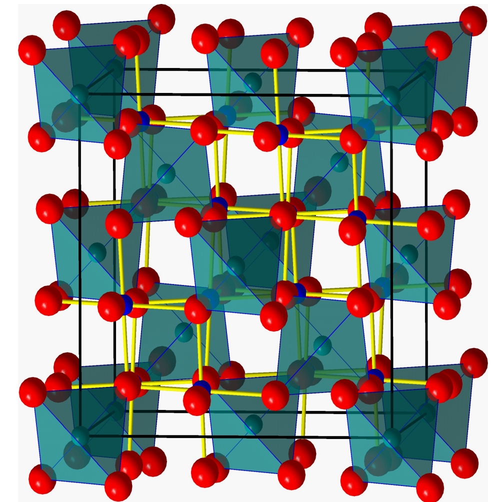
Behavior of spinel under irradiation: Modification of Diffraction patterns

	$MgAl_2O_4$	$MgCr_2O_4$	$ZnAl_2O_4$
High E. ions @RT	**Vanishing of odd Bragg reflexions** D. Simeone, J. Nucl. Mat. 2002 K Yasuda, MINB 2006, JNM 2007…	**Vanishing of odd Bragg reflexions** G. Baldinozzi, Nucl. Inst Meth B. 2007	**Non vanishing of odd Bragg reflexions** D. Simeone, J. Nucl. Mat. 2002
Low E. ions @ 140 K	**Vanishing of odd Bragg reflexions** L.M. Wang, MRS 1995, R. Devanathan, Phil Mag Let 1995		
Low E. ions @ RT	**Non vanishing of odd Bragg reflexions** D. Gosset, J. Eur. Ceram. 2005	**Vanishing of odd Bragg reflexions** D. Gosset, J. Eur Ceram Soc, 2005	**Non vanishing of odd Bragg reflexions** G. Baldinozzi, Nucl. Inst Meth B. 2005

Spinel irradiation at room temperature

Simulation of neutron irradiation by low energy ions (cascades) and of fission products by swift heavy ions



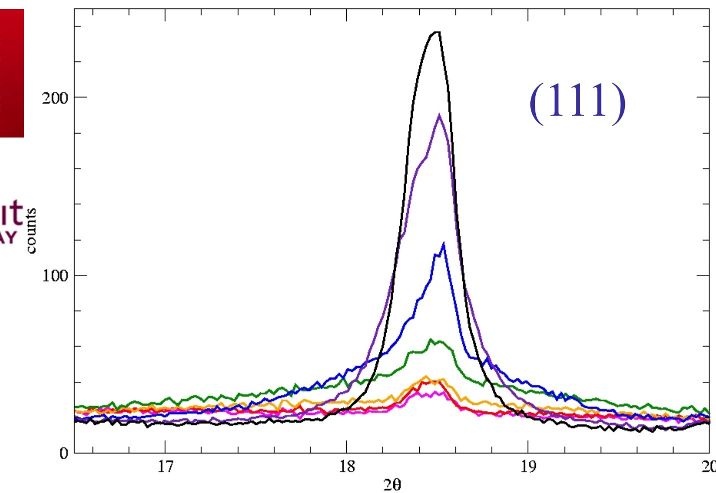


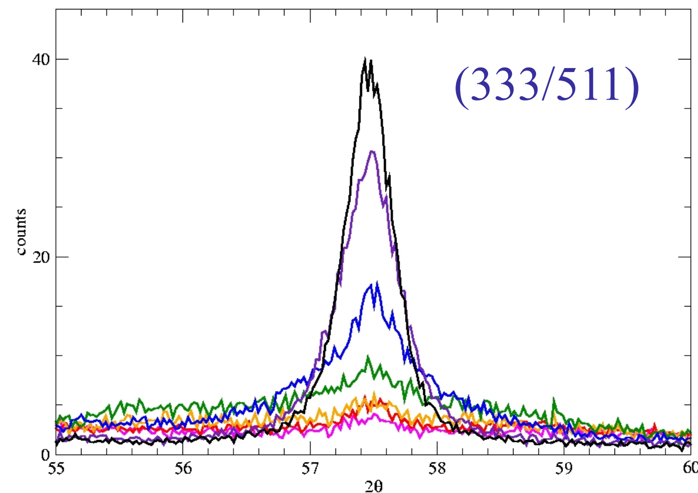
GAX-Ray diffraction:

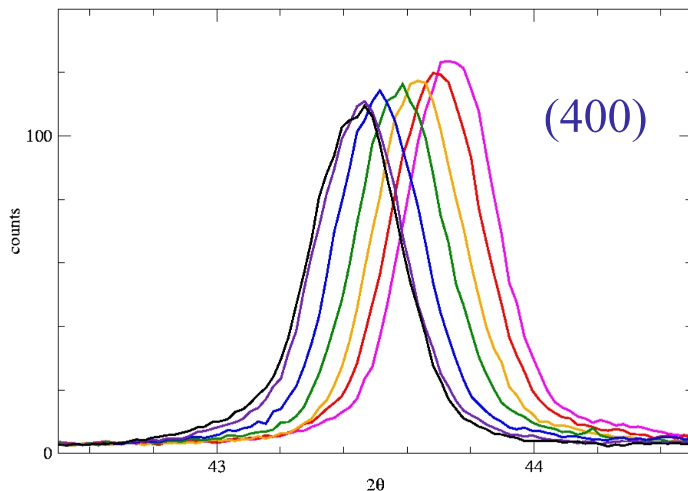
Asymmetric reflection setup (fixed, grazing impinging beam)

$MgCr_2O_4$: Au @ 4 MeV

$MgCr_2O_4$: thermal annealing after irradiation







- **Temperature restores the normal structure.**
- **The annealing of the extended defects increases the size of the coherent diffracting domains.**

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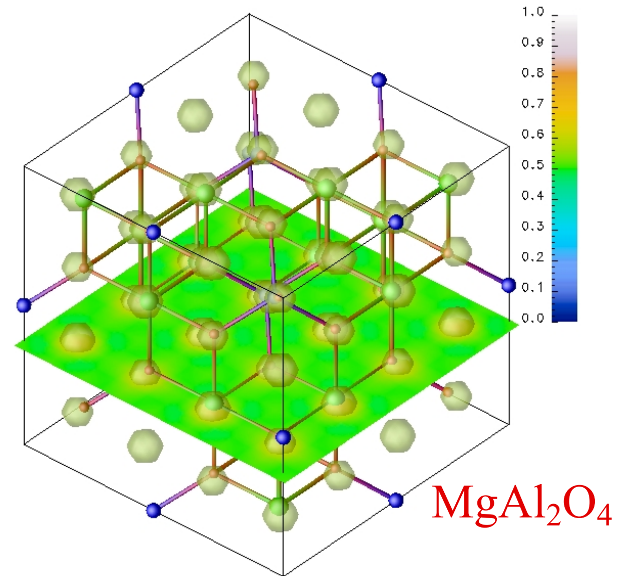
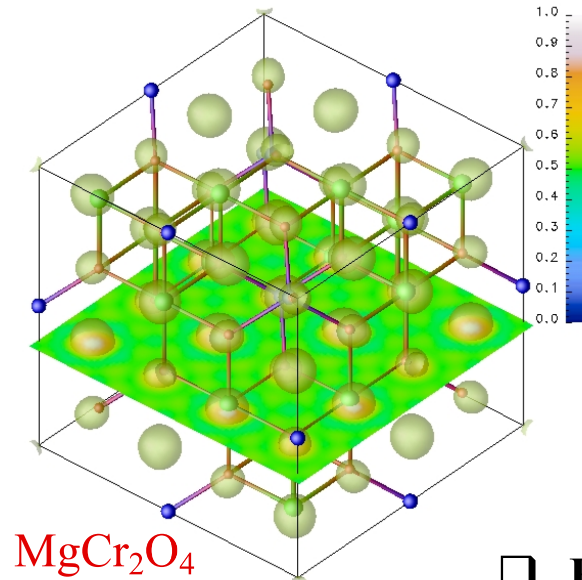
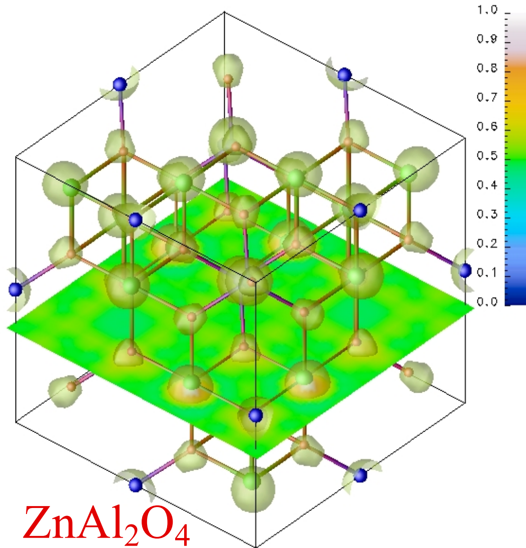
Electron density from X-ray diffraction



$MgAl_2O_4$



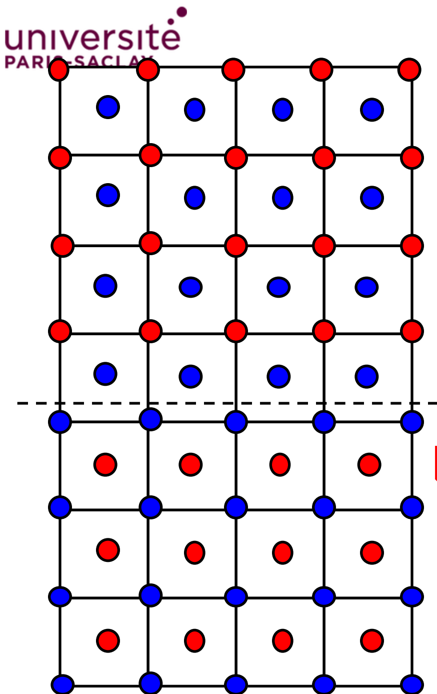
$MgCr_2O_4$



$ZnAl_2O_4$

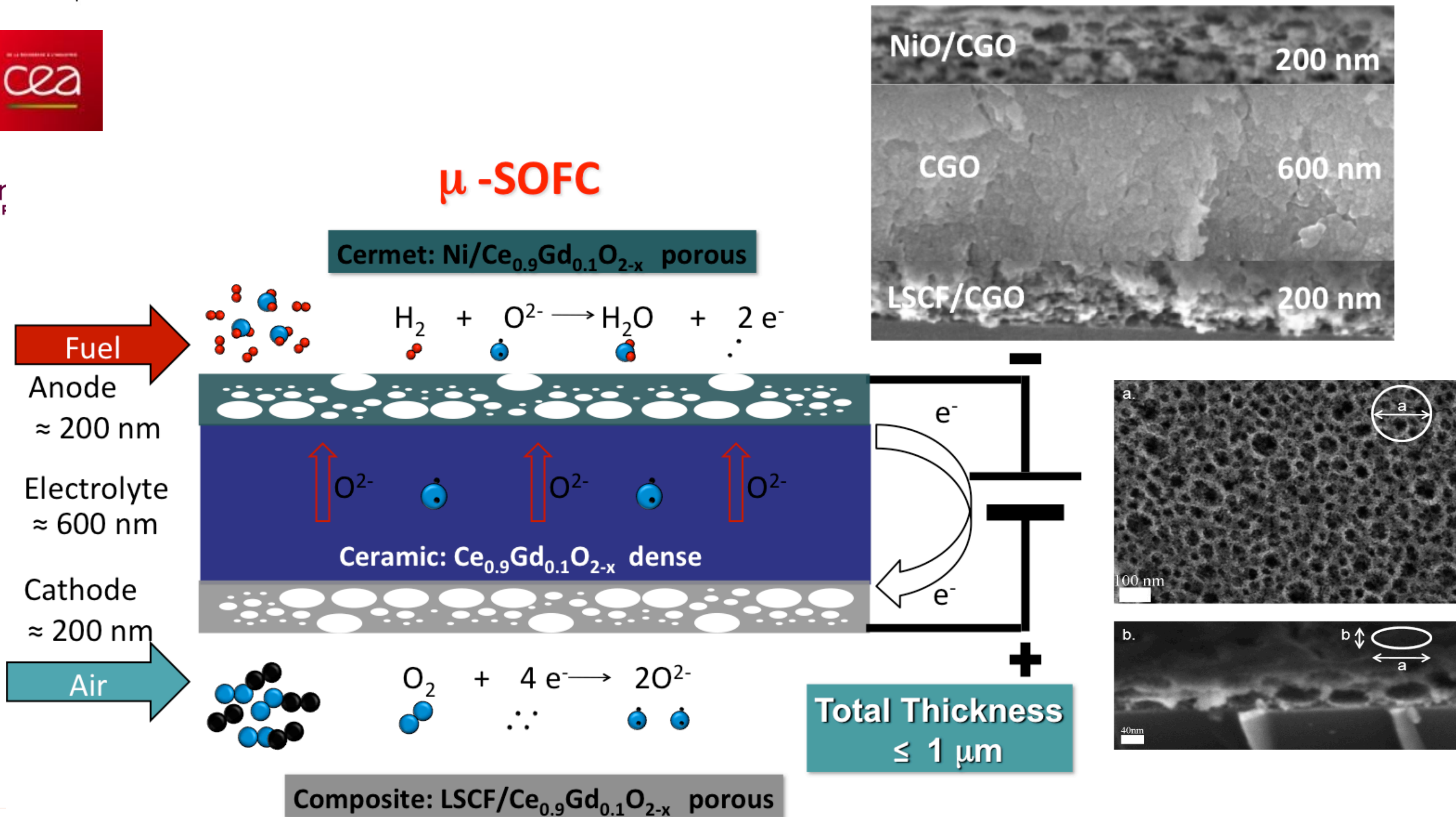
- **Fourier syntheses derived from the observed diffracted intensities indexed in the Fd3m space group**

How to reconcile LRO & SRO?

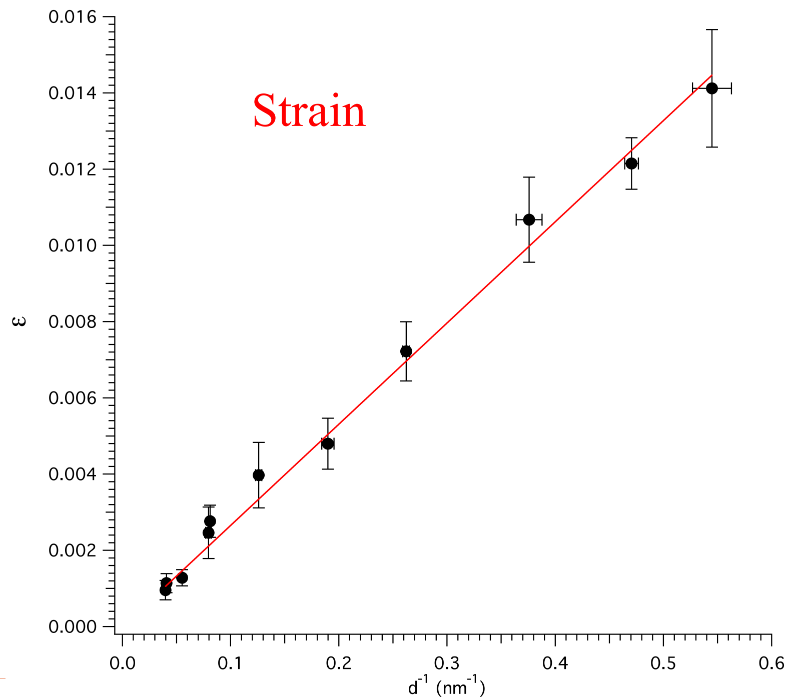


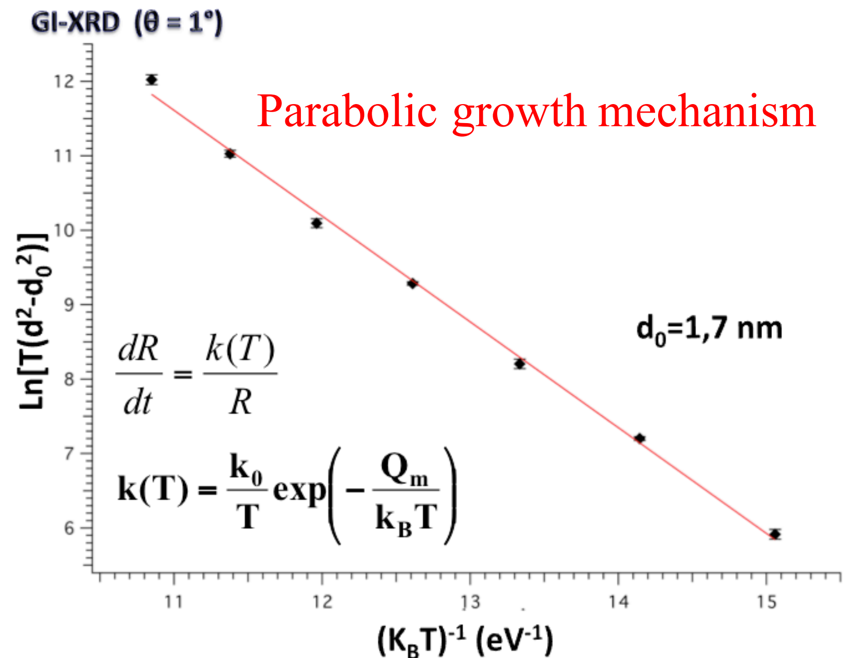
- **Ion irradiation produces changes in the structures of spinels:**
  - **At the atomic scale:**
    - ✓ Cations are interchanged as in the thermal picture
    - ✓ The local structure consists of octahedra and tetrahedra
    - ✓ The "true" space group is unchanged
  - **The existence of extended defects produces**
    - ✓ A broadening of (ooo) peaks
    - ✓ An apparent symmetry change to the Fm3m (a' =a/2)
- **Antiphase domain boundaries?**
  - **Formed during the ordering of a material that goes through an order-disorder transformation**
  - **The fundamental peaks are not affected**
  - **The superstructure peaks are broadened**
    - ✓ the broadening of superstructure peaks varies with *hkl*

Mesoporous ceria layers (coarsening)



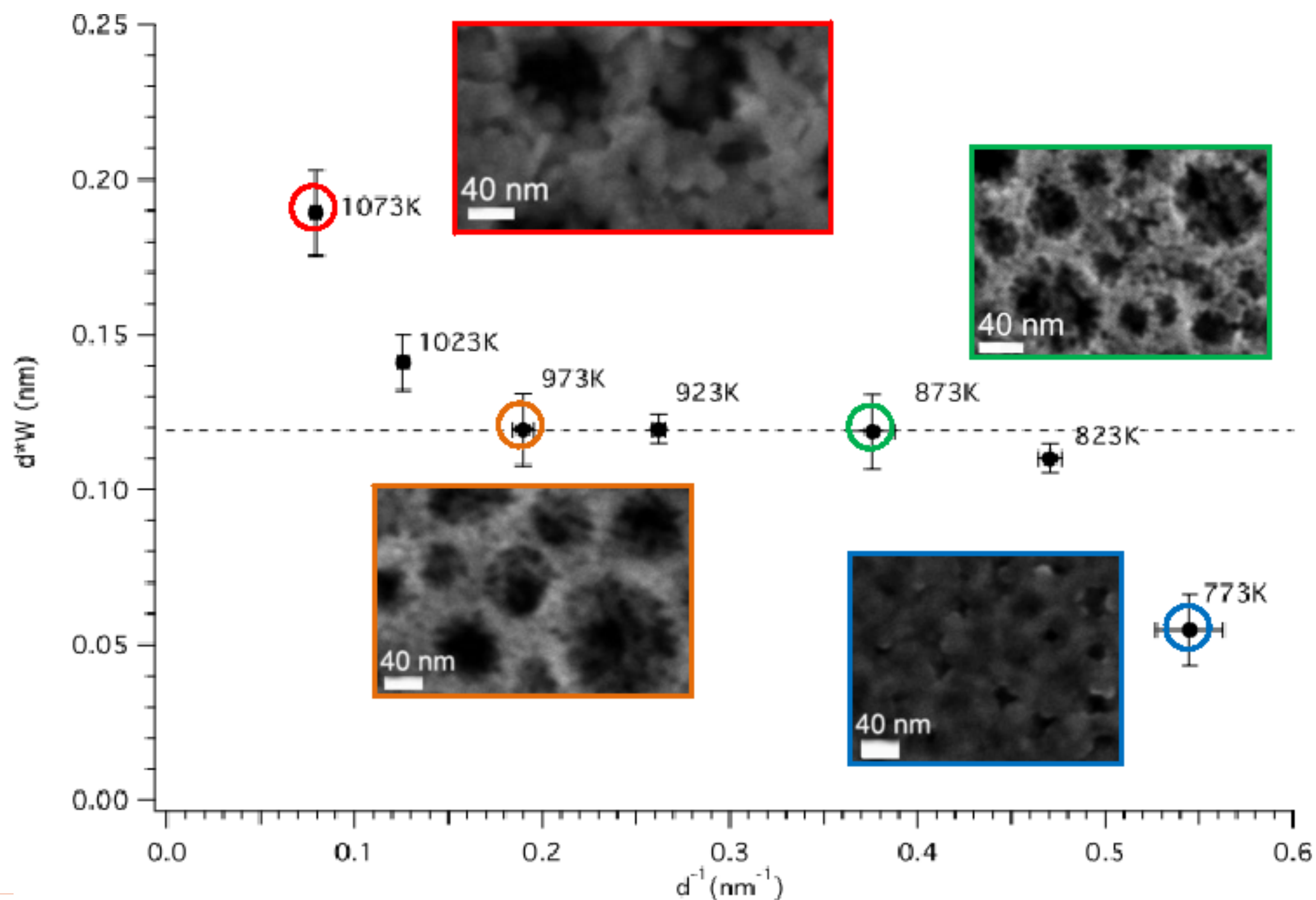
Finite crystallite size and lattice strain in nanocrystalline ceria



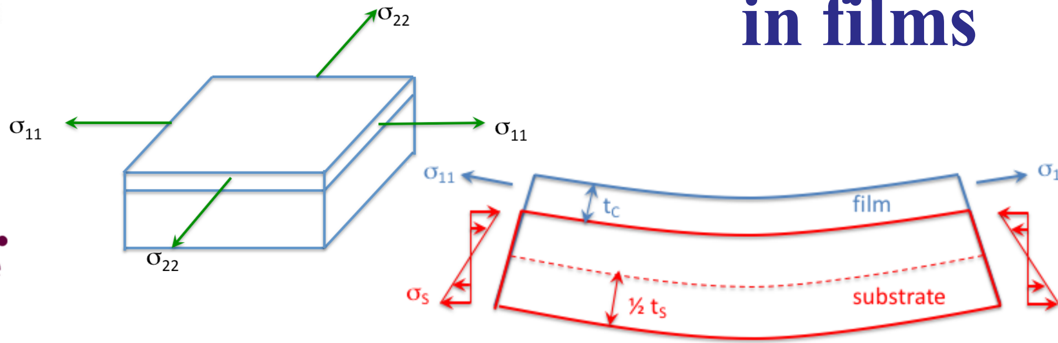


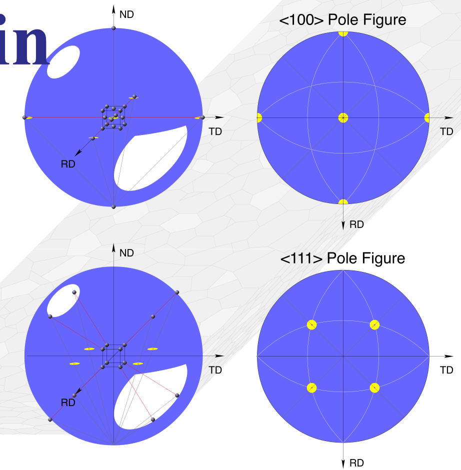
J. Phys Chem C 116 7658-7663 (2012)

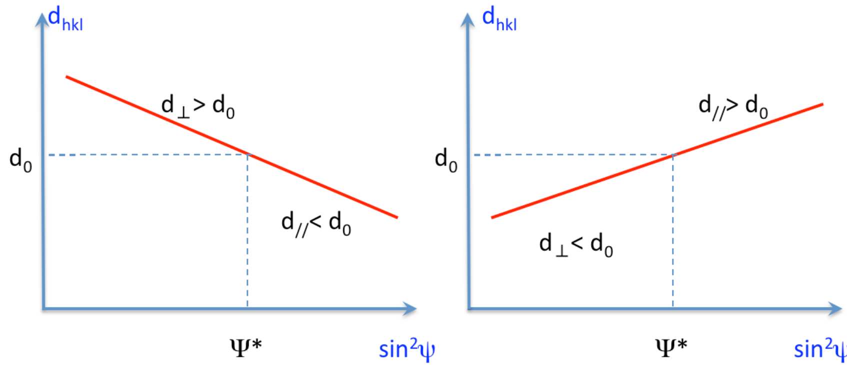
Monitoring the particle contacts in mesoporous ceria as a function of the annealing T



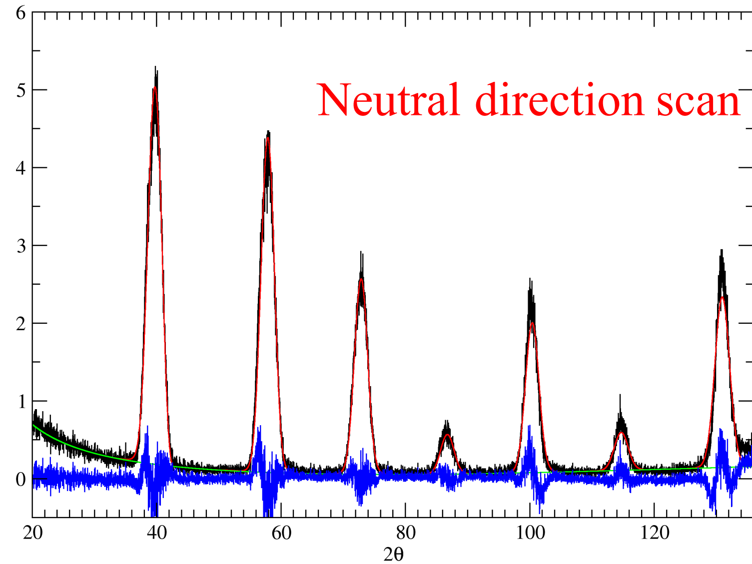
Inhomogeneous strain in films







But the regular ψ-scan method unfortunately probes a volume that changes as a function of ψ, averaging out the strain in the film, and preventing a mapping of the local strain



Measuring the local strain in glancing geometry

$$\psi = \alpha - \theta(hkl)$$

ψ angle should be re-encoded in glancing geometry

$$\tau = \frac{\sin\alpha \sin(2\theta - \alpha)}{\mu\left[\sin\alpha + \sin(2\theta - \alpha)\right]}$$

The depth τ probed by X-rays is a now a function of the impinging angle

$$\langle\epsilon_{\varphi\psi}\rangle = \frac{\int_0^t \epsilon_{\varphi\psi}(z)\exp\left(-\frac{z}{\tau}\right)dz}{\int_0^t \exp\left(-\frac{z}{\tau}\right)dz}$$

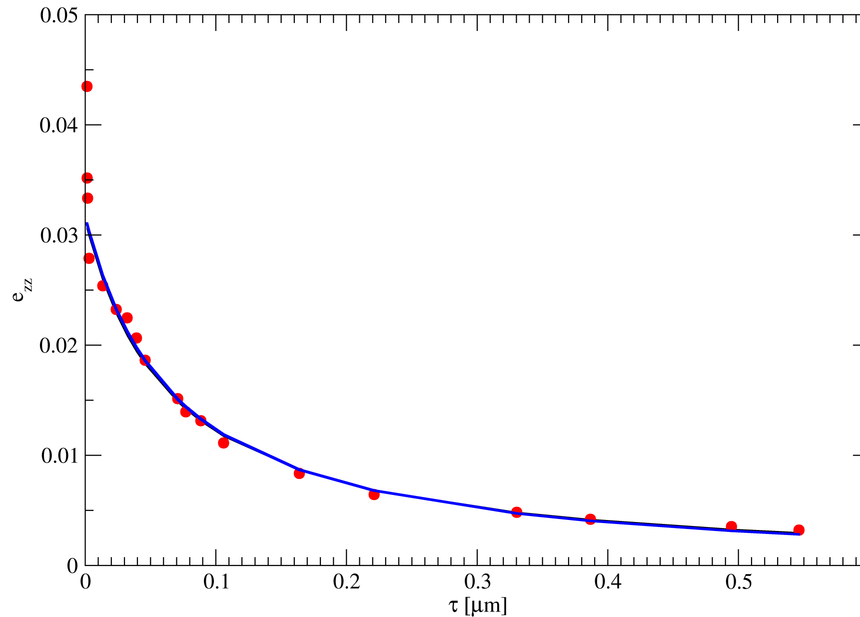
The average strain in a film of thickness t is still averaged by the way we measure (Fredholm's integral)

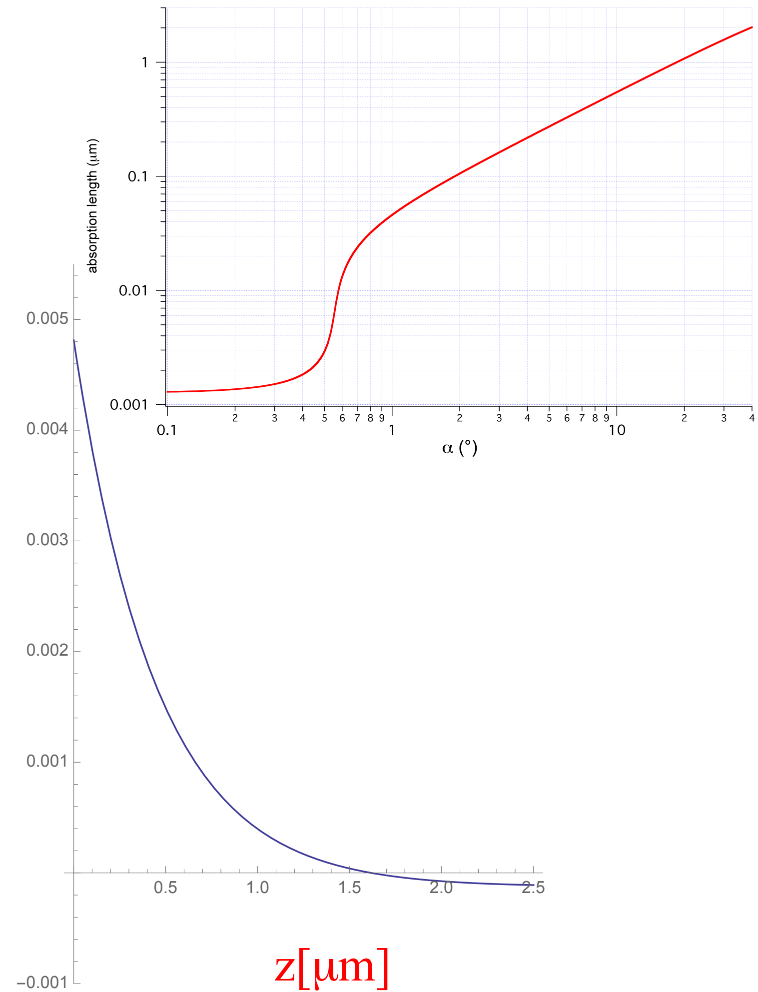
$$\langle\epsilon_{\varphi\psi}\rangle = \frac{1}{\tau}\int_0^\infty \epsilon_{\varphi\psi}(z)\exp\left(-\frac{z}{\tau}\right)dz = \frac{1}{\tau}\mathcal{L}\left(\epsilon_{\varphi\psi}(z), \frac{1}{\tau}\right)$$

$$\epsilon_{\varphi\psi}(z) = \mathcal{L}^{-1}\left(\tau\langle\epsilon_{\varphi\psi}\rangle, z\right)$$

If t is larger than the probed depth τ the Fredholm's integral becomes a Laplace transform that can be inverted, thus providing the value of the local strain at each value z in the film

Glancing geometry: asymmetric impinging beam on a W film





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Conclusion

- GAXRD & materials modelling - global approach to understand complex systems :
  - Elementary mechanisms
  - Chemistry, crystal structure
  - (Meso) Microstructures
- Understand the property changes
- Point out the key issues to design new/better materials for advanced technologies