Nanopowder crystallite sizes and shapes from diffraction experiments

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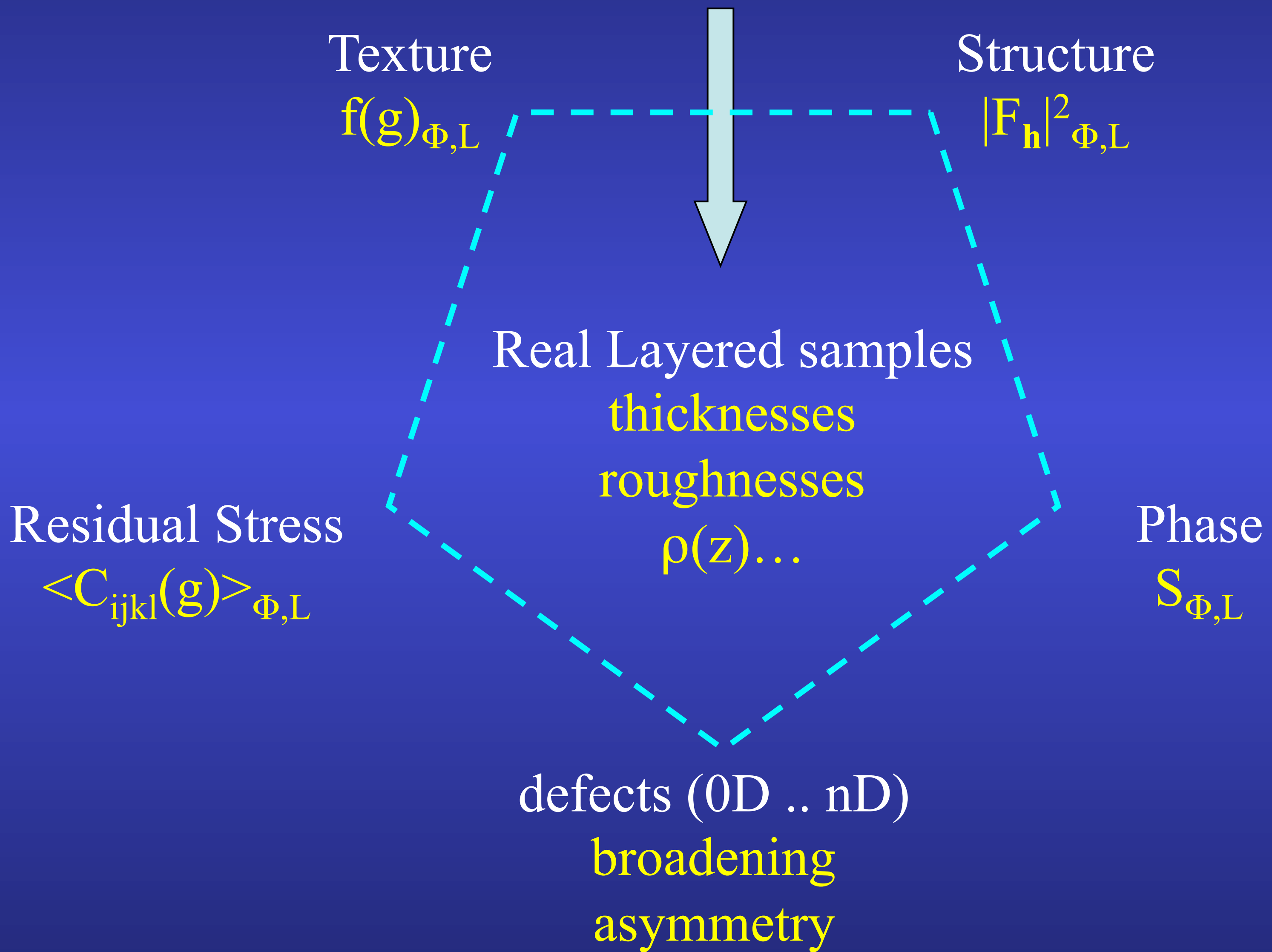
Diffraction "sees"



Line Broadening causes

- Instrumental broadening

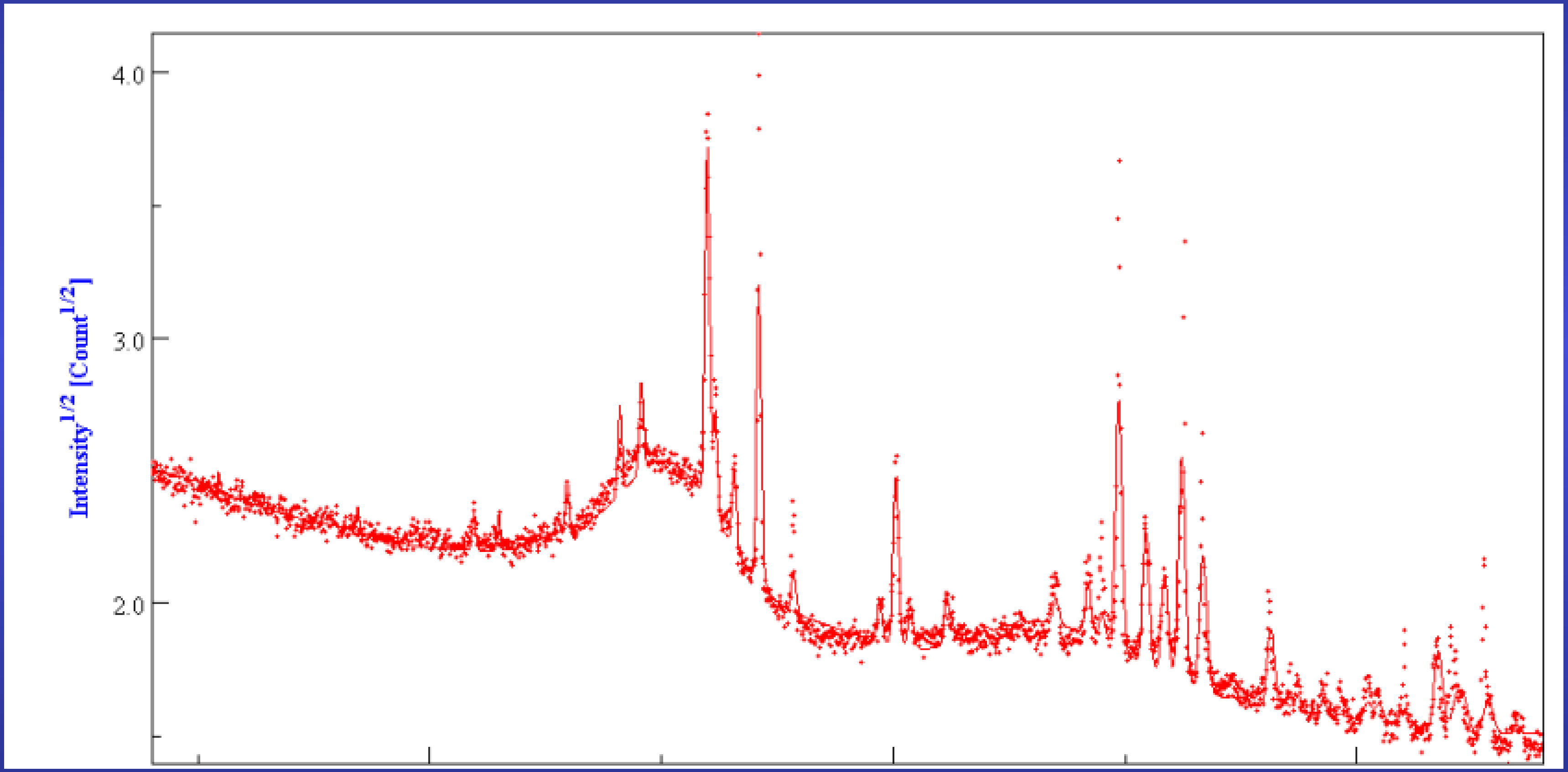
- Finite size of the crystals
  acts like a Fourier truncation: size broadening

- Imperfection of the periodicity
  due to d_h variations inside crystals: microstrain effect

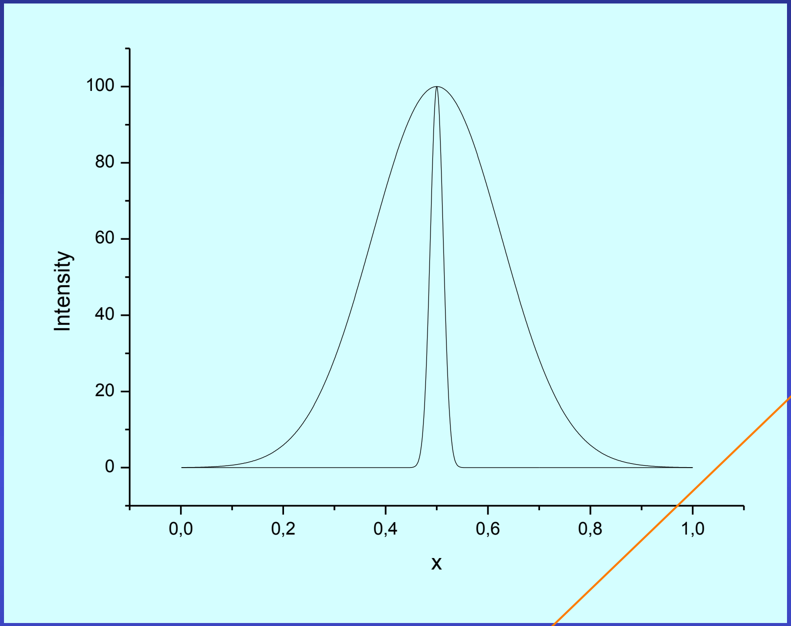
- Generally: 0D, 1D, 2D, 3D defects

- All quantities are average values over the probed volume
  electrons, x-rays, neutrons: complementary
  distributions: mean values depend on distributions' shapes

Irradiated Fluorapatites



Instrumental broadening



$$g(x) = g_{\lambda}(x) \otimes g_{g}(x)$$

Energy dispersion

Geometrical aberrations

$$h(x) = f(x) \otimes g(x) + b(x) = b(x) + \int_{-\infty}^{+\infty} f(y) g(x - y) dy$$

Measured profile

Sample contribution

Background

Back on diffraction expression

$$A_{\vec{h}} = F_{\vec{h}} T_{\vec{a}\vec{b}\vec{c}}(\vec{h})$$

$$T_{\vec{a}\vec{b}\vec{c}}(\vec{h}) = \frac{\sin[\pi(n+1)\vec{a}.\vec{h}]}{\sin[\pi\vec{a}.\vec{h}]} \frac{\sin[\pi(p+1)\vec{b}.\vec{h}]}{\sin[\pi\vec{b}.\vec{h}]} \frac{\sin[\pi(q+1)\vec{c}.\vec{h}]}{\sin[\pi\vec{c}.\vec{h}]}$$

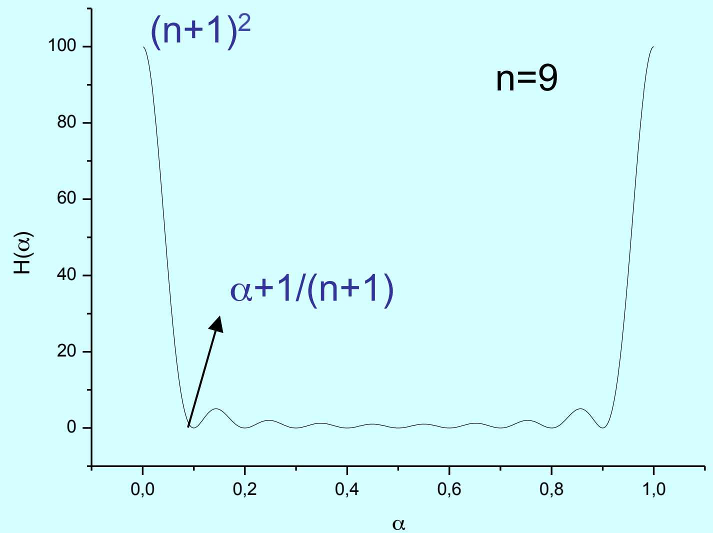
$A_{\vec{h}}$: scattered amplitude

$F_{\vec{h}}$: structure factor

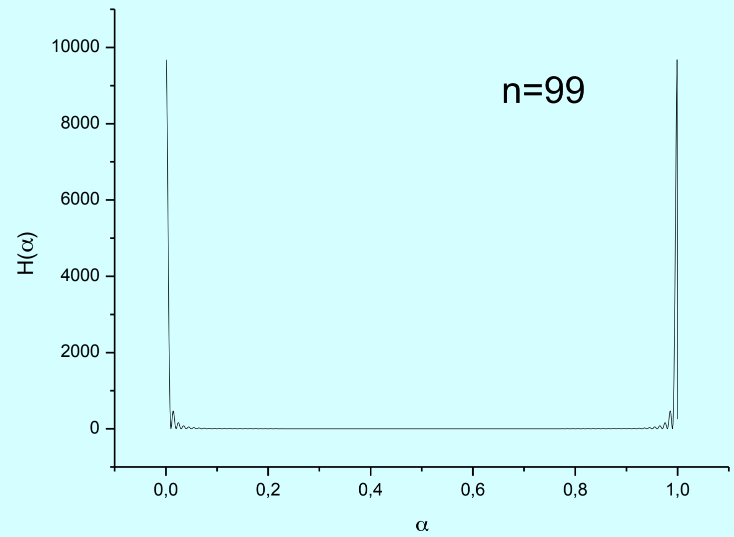
$T_{\vec{a}\vec{b}\vec{c}}(\vec{h})$: interference function

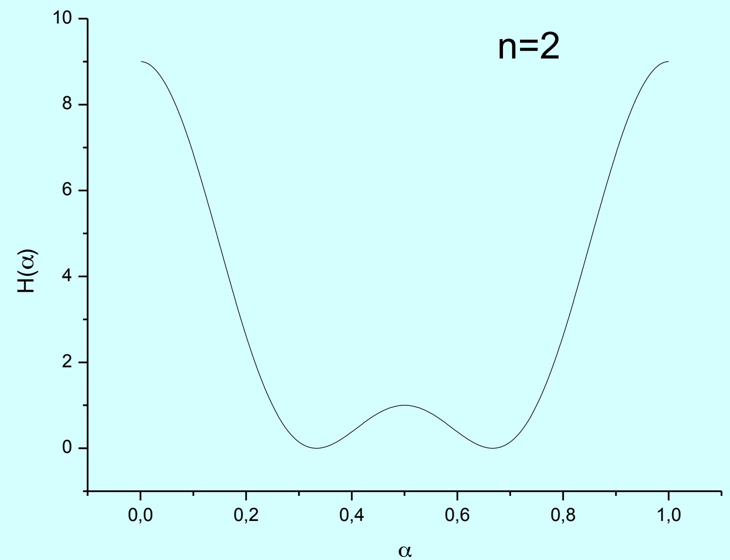
n, p, q : number of periods in the $\vec{a}$, $\vec{b}$, $\vec{c}$ directions

$$H(\alpha) = \frac{\sin^2[\pi(n+1)\alpha]}{\sin^2[\pi\alpha]}$$



$$\text{infinite crystal}: \left| \begin{array}{l} \vec{a}.\vec{h} = h \\ \vec{b}.\vec{h} = k \\ \vec{c}.\vec{h} = l \end{array} \right.$$



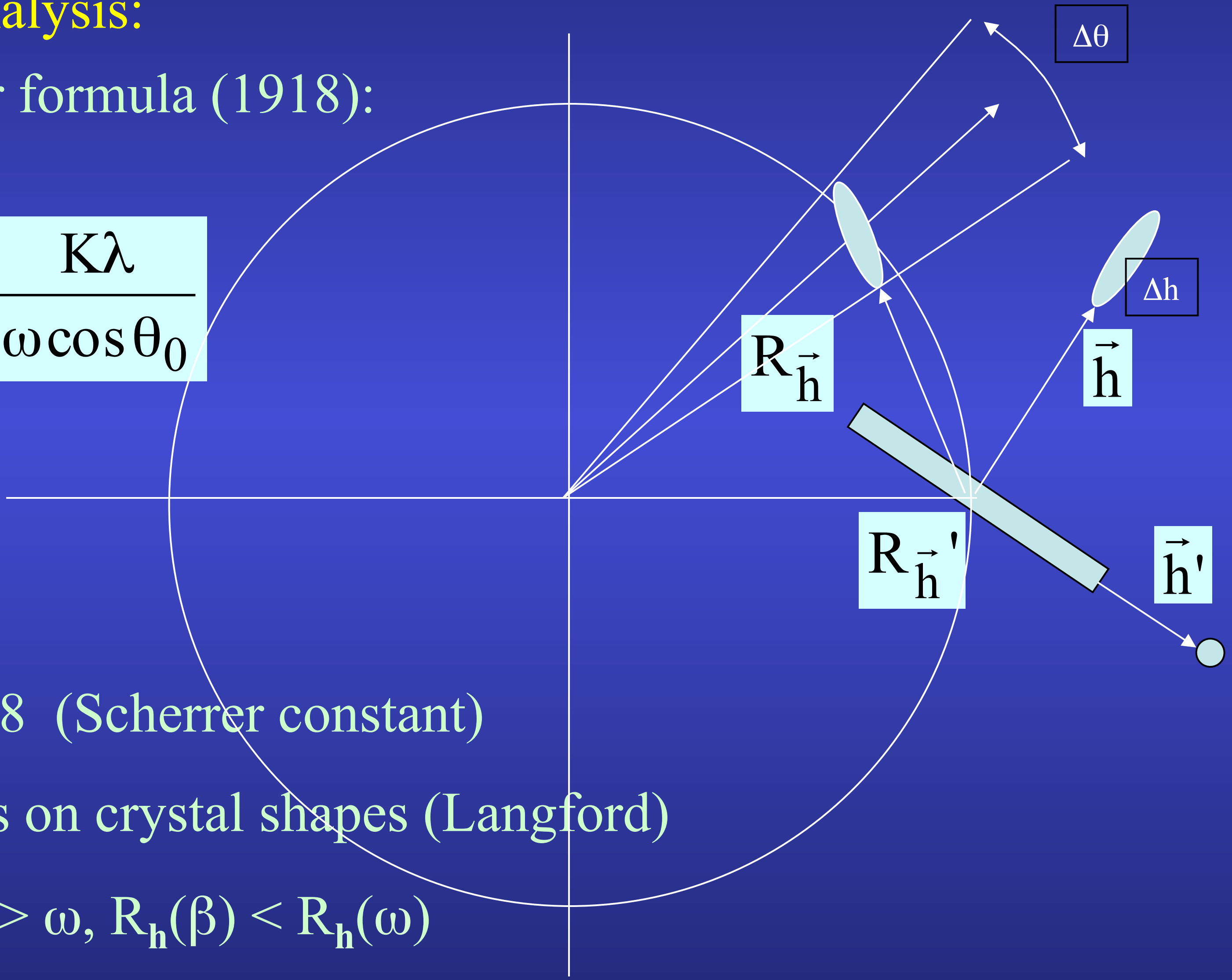


Crystallite's size-shape effect

Scherrer analysis:

Scherrer formula (1918):

$$R_{\vec{h}} = \frac{K\lambda}{\omega \cos\theta_0}$$



K= 0.888 (Scherrer constant)

Depends on crystal shapes (Langford)

Since $\beta > \omega$, $R_{\mathbf{h}}(\beta) < R_{\mathbf{h}}(\omega)$

After Scherrer analysis …

Williamson-Hall (1949)

Warren-Averback-Bertaut (1952)

Whole-Pattern analysis: Langford (1978), de Keijser (1982), Balzar et Ledbetter (1982) …

But deconvolution of contributions (Stokes 1948) !

Rietveld (1969): convolution !

More infos: http://www.ecole.ensicaen.fr/~chateign/formation/course/Classical_Microstructure.pdf

Rietveld: extended to lots of spectra

$$y_c(\mathbf{y}_S,\theta,\eta) = y_b(\mathbf{y}_S,\theta,\eta) + I_0 \sum_{i=1}^{N_L} \sum_{\Phi=1}^{N_\Phi} \frac{\nu_{i\Phi}}{V_{c\Phi}^2} \sum_h Lp(\theta) j_{\Phi h} |F_{\Phi h}|^2 \Omega_{\Phi h}(\mathbf{y}_S,\theta,\eta) P_{\Phi h}(\mathbf{y}_S,\theta,\eta) A_{i\Phi}(\mathbf{y}_S,\theta,\eta)$$

Texture:

$$P_h(\mathbf{y}_S) = \int_{\tilde{\varphi}} f(g,\tilde{\varphi}) d\tilde{\varphi}$$

E-WIMV, components …

Strain-Stress:

$$\langle S \rangle_{geo}^{-1} = \left[\prod_{m=1}^{N} S_m^{\nu_m}\right]^{-1} = \prod_{m=1}^{N} S_m^{-\nu_m} = \prod_{m=1}^{N} \left(S_m^{-1}\right)^{\nu_m} = \left\langle S^{-1} \right\rangle_{geo} = \langle C \rangle_{geo}$$

Geometric mean, Voigt, Reuss, Hill …

Layering:

$$C_\chi^{top\ film} = g_1\left(1-\exp\left(-\mu T g_2/\cos\chi\right)\right)/\left(1-\exp\left(-2\mu T/\sin\omega\cos\chi\right)\right)$$

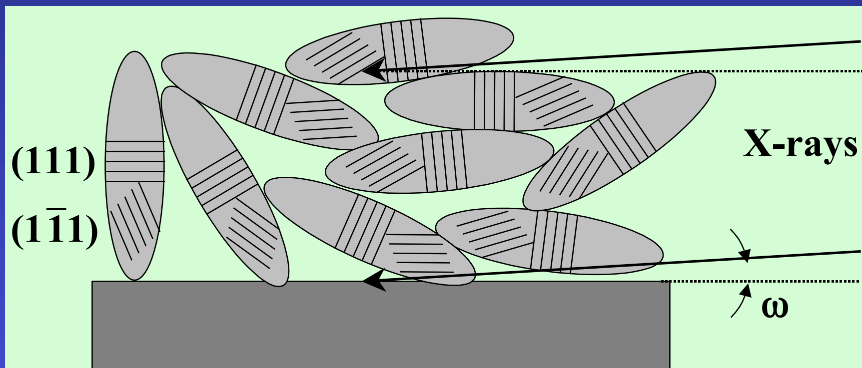
XRR:

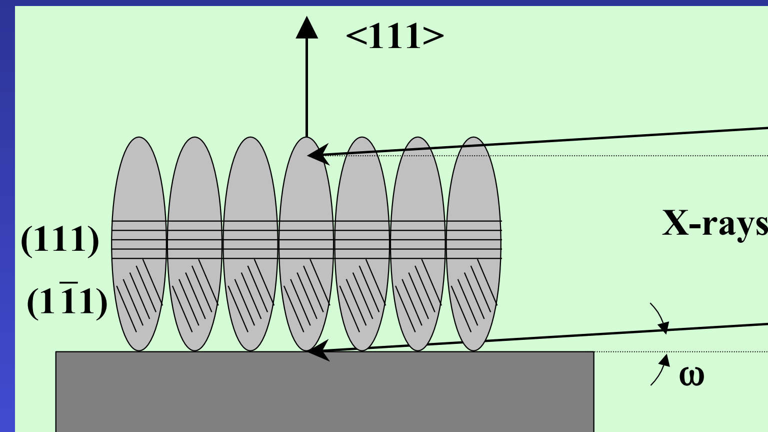
Parrat, DWBA, EDP …

XRF, PDF …

Popa Line Broadening model

Crystallite sizes, shapes, μstrains, distributions





- Texture helps the "real" mean shape determination

$$\left\langle R_{\vec{h}} \right\rangle = \sum_{\ell=0}^{L} \sum_{m=0}^{\ell} R_\ell^m K_\ell^m(\chi,\varphi)$$

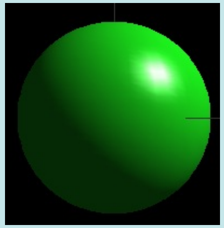
Symetrised spherical harmonics

$$K_\ell^m(\chi,\varphi) = P_\ell^m(\cos\chi)\cos(m\varphi) + P_\ell^m(\cos\chi)\sin(m\varphi)$$

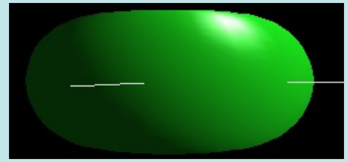
$$<R_{\mathbf{h}}> = R_0 + R_1P_2^0(x) + R_2P_2^1(x)\cos\varphi + R_3P_2^1(x)\sin\varphi + R_4P_2^2(x)\cos2\varphi + R_5P_2^2(x)\sin2\varphi + \ldots$$

$$<\varepsilon_{\mathbf{h}}^2>E_{\mathbf{h}}^4 = E_1h^4 + E_2k^4 + E_3\ell^4 + 2E_4h^2k^2 + 2E_5\ell^2k^2 + 2E_6h^2\ell^2 + 4E_7h^3k + 4E_8h^3\ell + 4E_9k^3h + 4E_{10}k^3\ell + 4E_{11}\ell^3h + 4E_{12}\ell^3k + 4E_{13}h^2k\ell + 4E_{14}k^2h\ell + 4E_{15}\ell^2kh$$

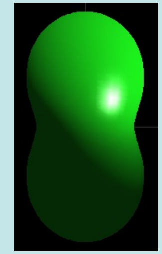
$\bar{1}$



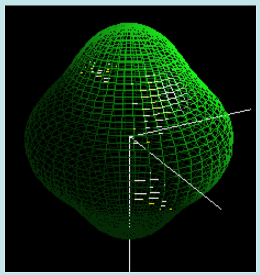
R_0



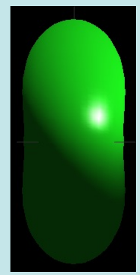
R_0, $R_1 < 0$



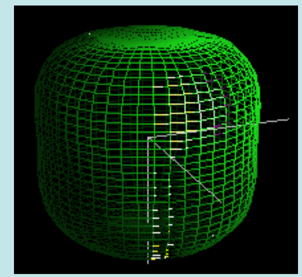
R_0, $R_1 > 0$



R_0, $R_6 > 0$

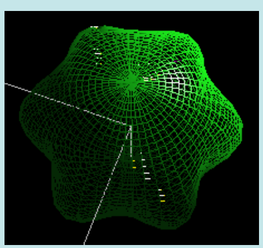


R_0,
R_2 and $R_6 > 0$

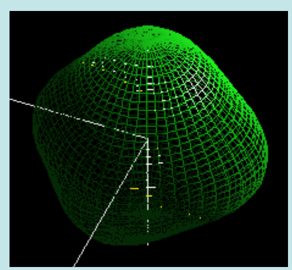


R_0, $R_6 < 0$

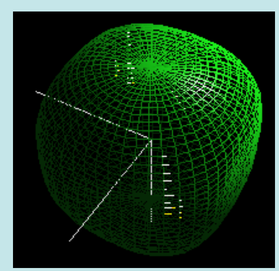
6/m



R_0, $R_4 > 0$



R_0, $R_1 > 0$

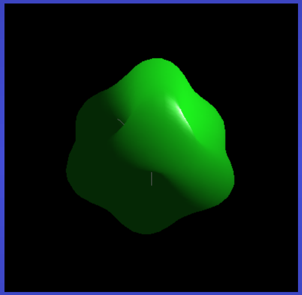


R_0, $R_1 < 0$

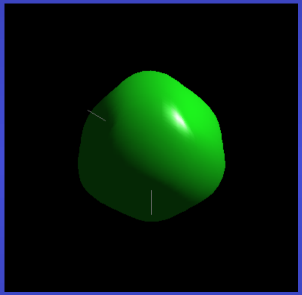
m3m

Gold thin films

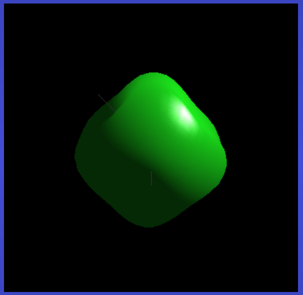
Crystallite size (Å) along	Film thickness					
	10nm	**15nm**	**20nm**	**25nm**	**35nm**	**40nm**
[111]	176	153	725	254	343	379
[200]	64	103	457	173	321	386
[202]	148	140	658	234	337	381



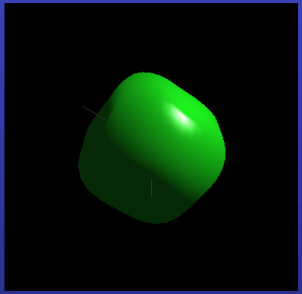
10 nm



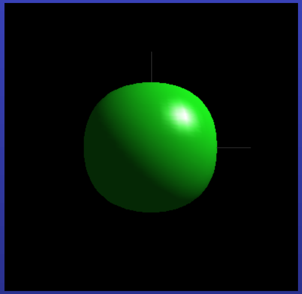
15 nm



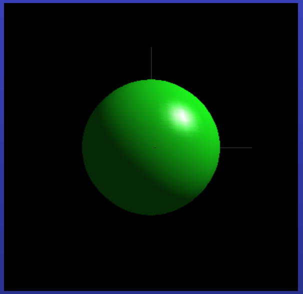
20 nm



25 nm

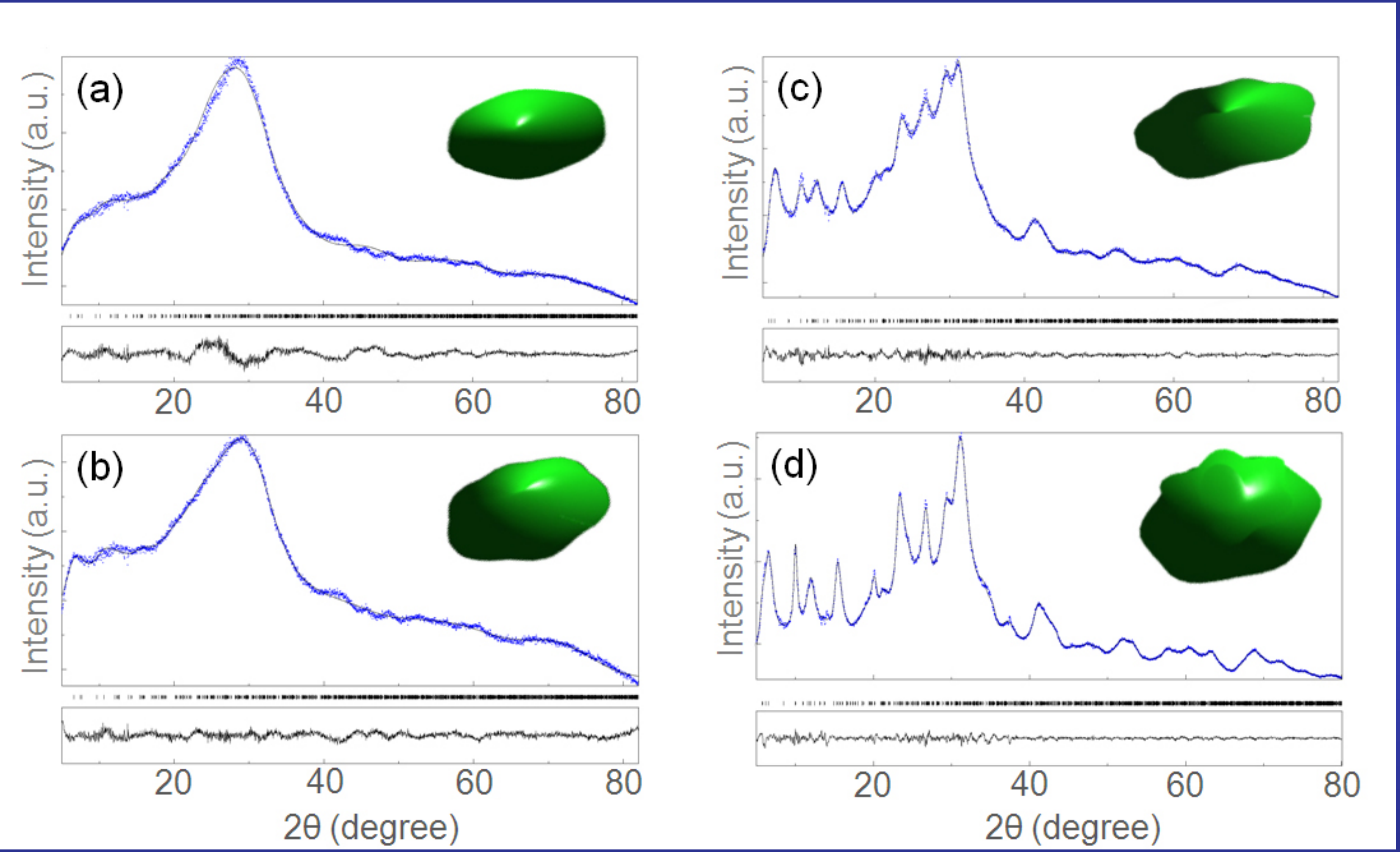


35 nm



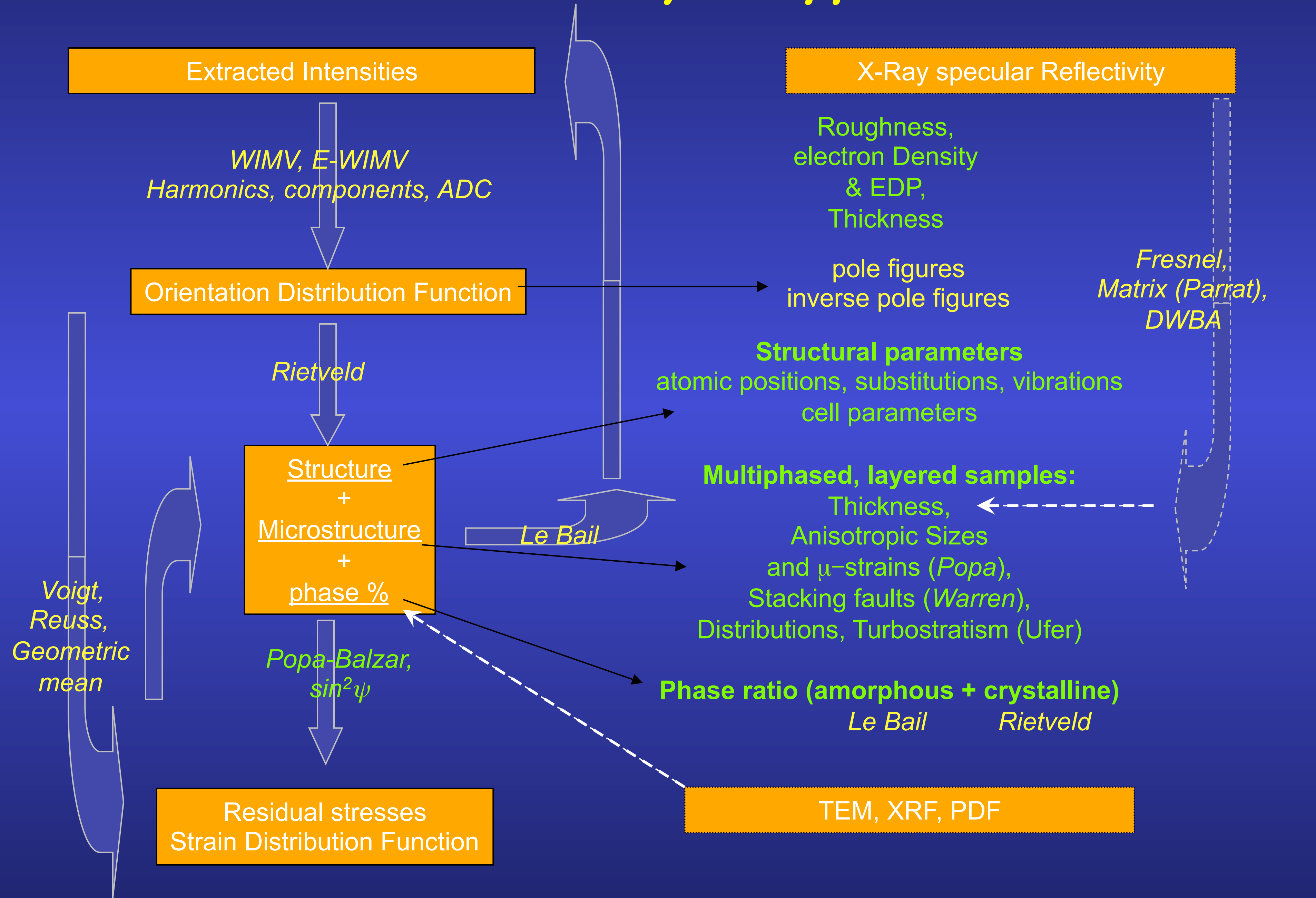
40 nm

EMT nanocrystalline zeolite

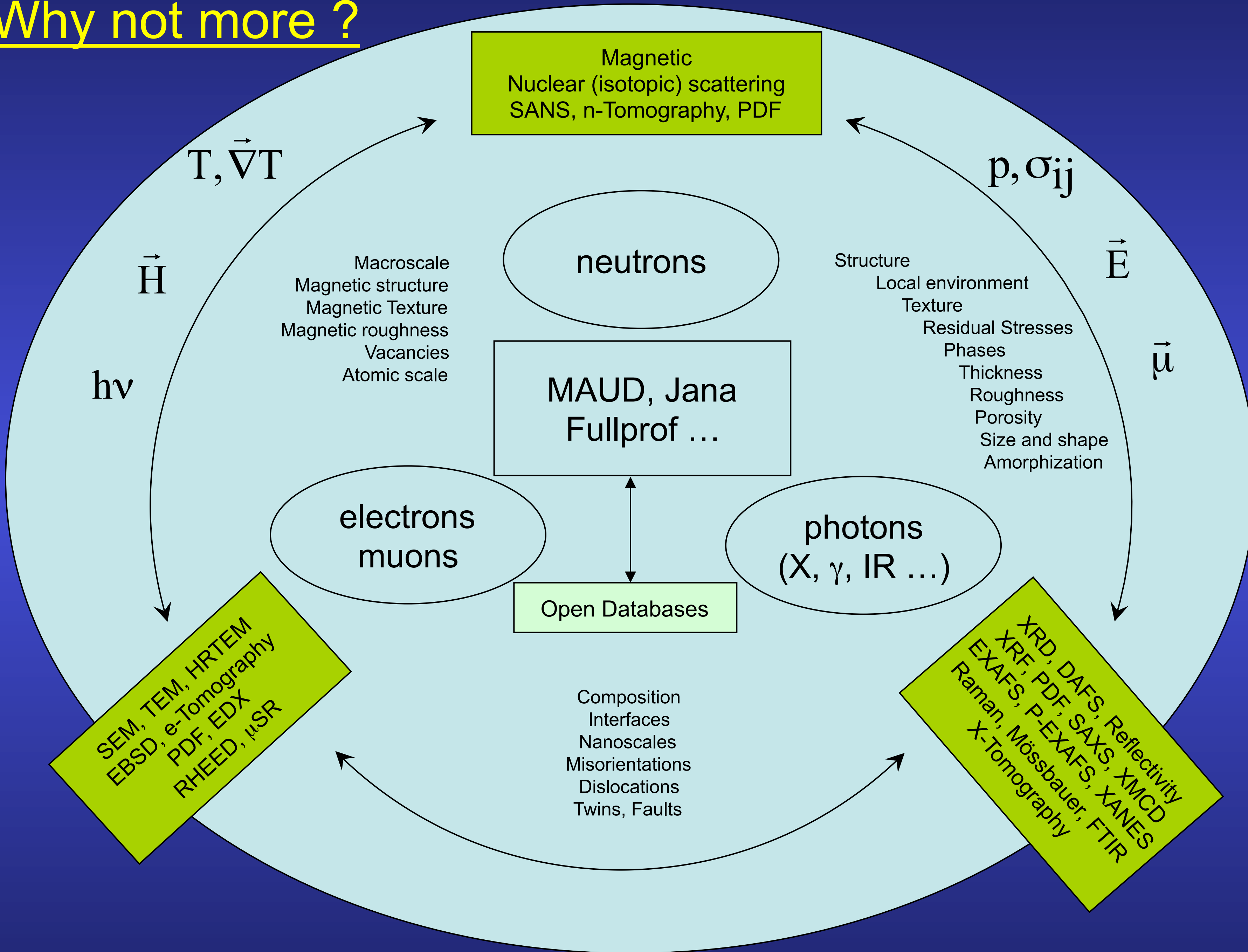


Ng, Chateigner, Valtchev, Mintova: *Science* **335** (2012) 70

Combined Analysis approach



Why not more ?



Magnetic
Nuclear (isotopic) scattering
SANS, n-Tomography, PDF
$T, \vec{\nabla}T$
p, σ_{ij}
$\vec{H}$
$\vec{E}$
$h\nu$
$\vec{\mu}$
neutrons
Macroscale
Magnetic structure
Magnetic Texture
Magnetic roughness
Vacancies
Atomic scale
Structure
Local environment
Texture
Residual Stresses
Phases
Thickness
Roughness
Porosity
Size and shape
Amorphization
MAUD, Jana
Fullprof …
electrons
muons
photons
(X, γ, IR …)
Open Databases
SEM, TEM, HRTEM
EBSD, e-Tomography
PDF, EDX
RHEED, μSR
XRD, DAFS, Reflectivity
XRF, PDF, SAXS, XMCD
EXAFS, P-EXAFS, XANES
Raman, Mössbauer, FTIR
X-Tomography
Composition
Interfaces
Nanoscales
Misorientations
Dislocations
Twins, Faults

Combined Analysis Workshop in Caen:

3rd - 7th July 2017 !

www.ecole.ensicaen.fr/~chateign/formation/

Thanks !