UNIVERSITAS ATHESINA STUDIORUM

Elettra Sincrotrone Trieste

Design and management of a XRPD Beamline for Line Profile Analysis: a realistic ray-tracing approach

Luca Rebuffi, Elettra-Sincrotrone Trieste (ITA)

Introduction: Scientific Case

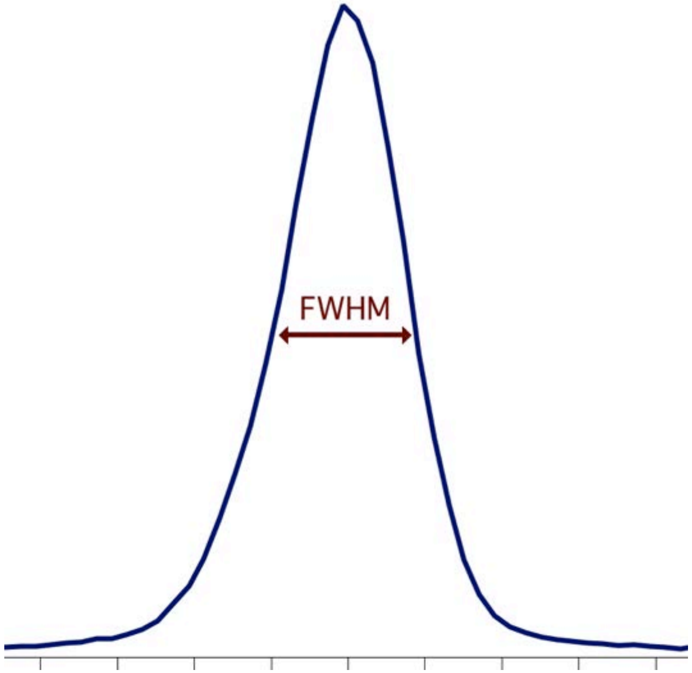
- ✓ Synchrotron Radiation X-Ray Powder Diffraction (SR-XRPD) is one of the main tools in the study of nanomaterials.

- ✓ The modern approach to Nanomaterials, Line Profile Analysis (LPA), requires a complete control of the diffracted signal

THE OPTICS AND GENERAL SET-UP OF THE BEAMLINE:

INSTRUMENTAL PROFILE FUNCTION (IPF)

Introduction: Scientific Case



An experimental Powder Diffraction profile shows **Peaks Broadening**

FROM THE SAMPLE:

- ✓ Crystalline Domains Size Distribution
- ✓ Lattice Strain (Defects)
- ✓ …

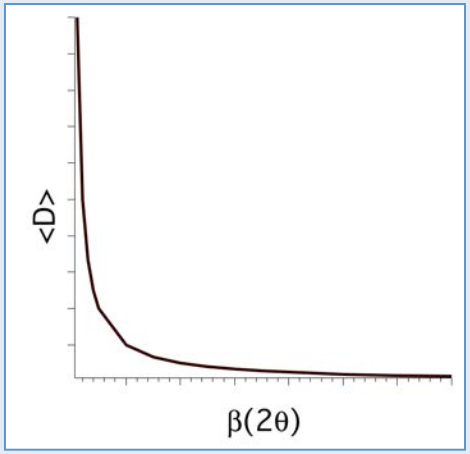
FROM THE INSTRUMENT:

- ✓ Photon Source
- ✓ Optical Setup & Layout
- ✓ Optical Elements Quality

Introduction: Scientific Case

- ✓ Crystallite Size and Measured Integral Breadth ➔ Scherrer's Formula:

$$\beta(2\theta) = \frac{K_\beta \lambda}{\langle D \rangle \cos\theta}$$



BUT

- ✓ Measured Integral Breadth contains the contribution of the

  Instrumental Profile in terms of Divergence and Aberrations:

- ✓ Error on $\langle D \rangle$ is large when β is small, i.e. when the instrumental

  broadening becomes the main feature

Introduction: Scientific Case

INSTRUMENTAL PROFILE FUNCTION CALCULATION IS A

GENERAL ISSUE

IN ALL SPECTROSCOPY TECHNIQUES

$$h(\varepsilon) = \int_{-\infty}^{\infty} g(\eta) f(\varepsilon - \eta)\, \mathrm{d}\eta.$$

Klug, H. & Alexander, L., "X-ray Diffraction Procedure for Polycrystalline and Amorphous Materials", New York: John Wiley (1974).

The proposed approach can be easily extended to a wide number of experimental techniques.

Direct applications will include catalysts, heavily deformed materials and other nanocrystalline systems.

Introduction: Layout of the Presentation

Characterization of optical components for powder diffraction beamlines, to properly calibrate and adjust all component to deliver the beam under the best possible conditions.

Examples of nanostructured materials “at the limit”, where the Instrumental Profile Function is the main feature

Development of a realistic beamlines and powder diffraction experiments simulation/modeling tools based on ray-tracing algorithms, to properly handle and predict the Instrumental Profile Function.

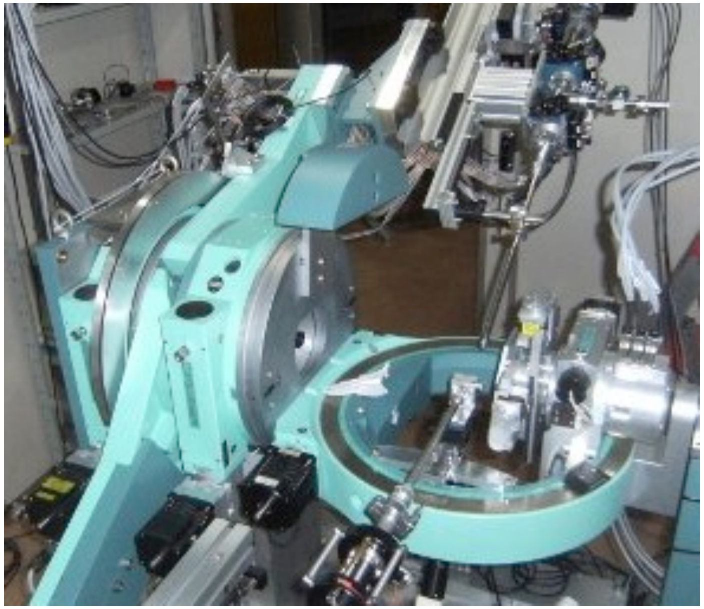
Characterization of a XRPD beamline

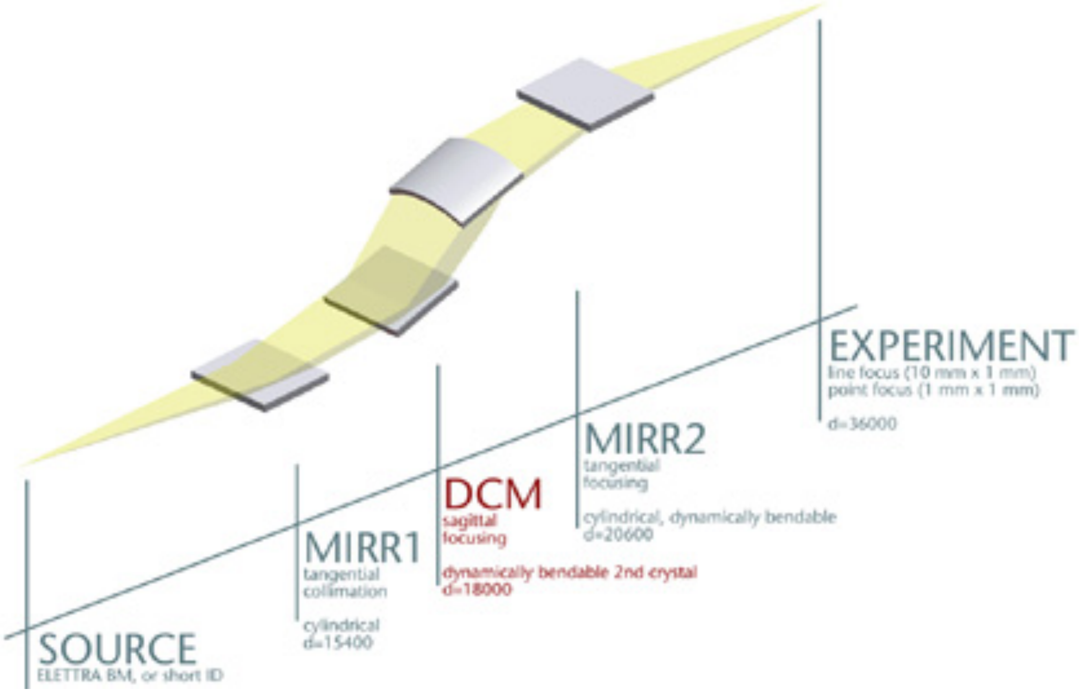
Characterization of a XRPD beamline

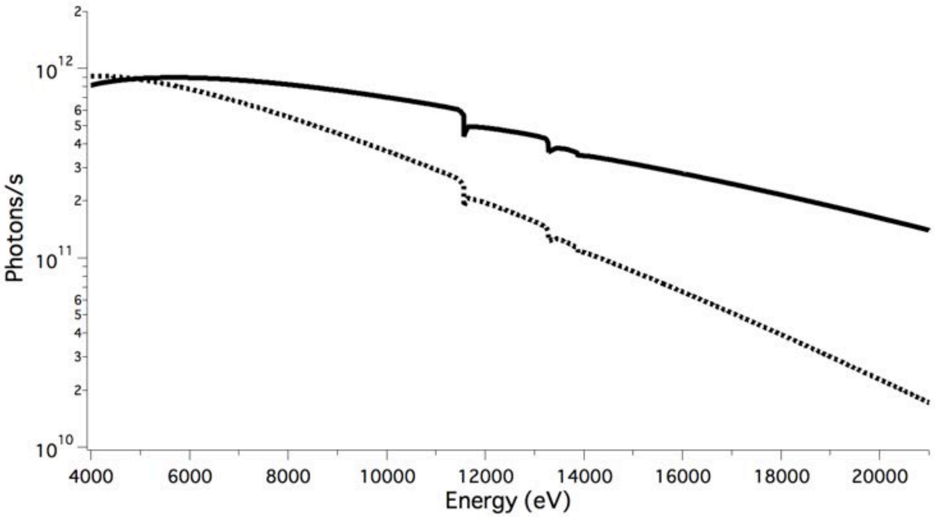
MCX at Elettra-Sincrotrone Trieste

Beamline optical layout (36 meters) :

- ✓ Electron Beam Energy 2 GeV
- ✓ Bending Magnet with C.E 3.2 keV
- ✓ Vertically collimating mirror
- ✓ D.C.M., Si(111), sagitally bendable 2nd crystal
- ✓ Vertically focusing mirror
- ✓ 2 horizontal slits

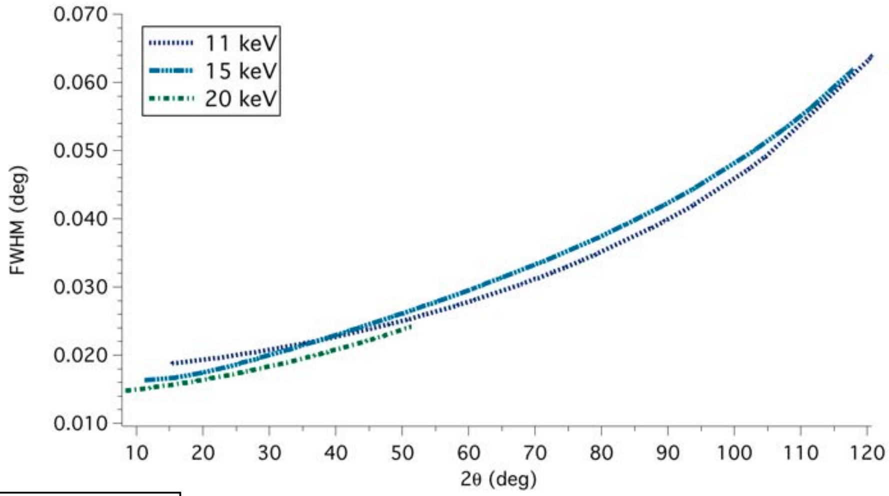


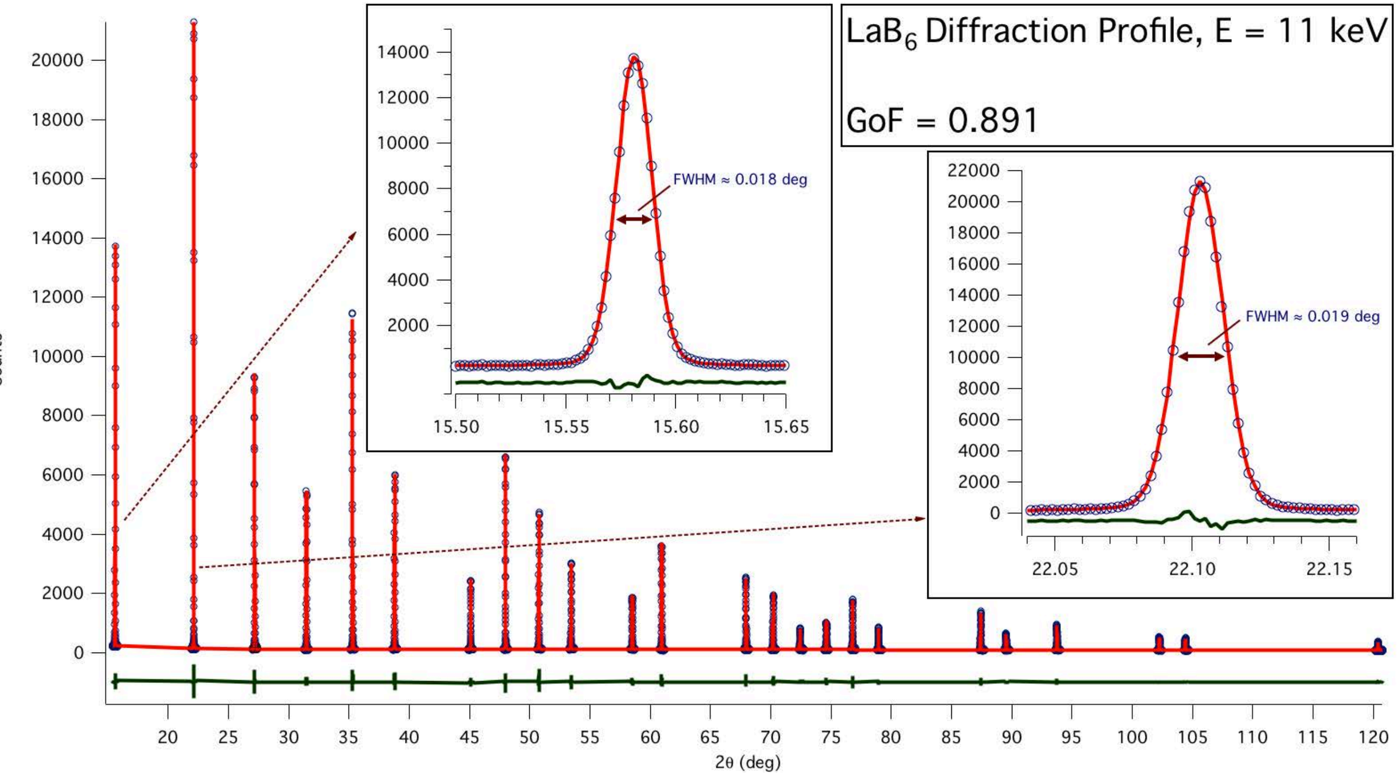




Characterization of a XRPD beamline

Parameterization of the Instrumental Profile Function through LPA of NIST 660a SRM LaB_6: Peak profiles as Pseudo-Voigt curves





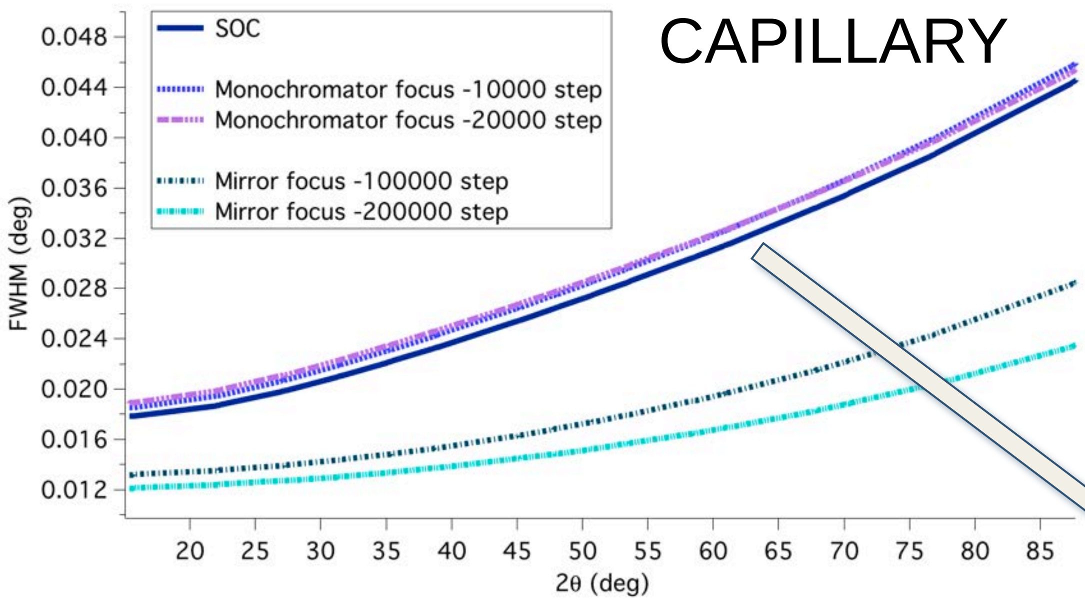
Caglioti's equation is used for the FWHM:

$$FWHM(\theta) = \sqrt{W + V \tan\theta + U \tan^2\theta}$$

Characterization of a XRPD beamline

Elettra Sincrotrone Trieste

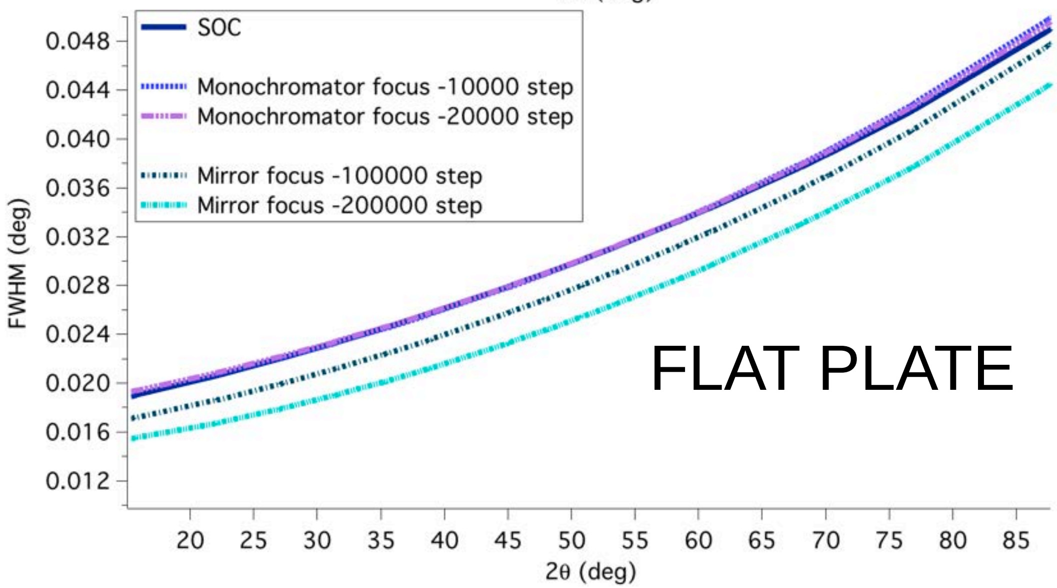
CAPILLARY



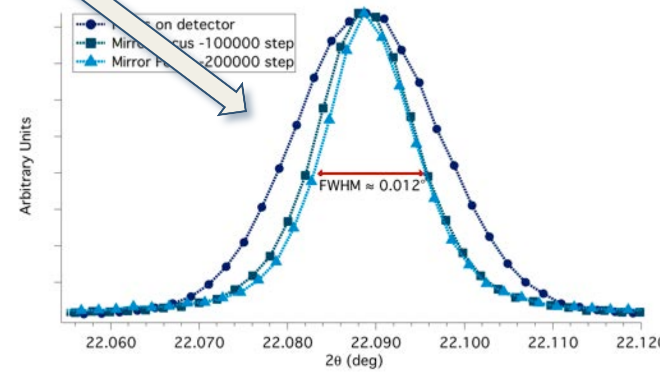
Optical characterization of the IPF:

Best Flux (SOC)

Narrowest peak profile



FLAT PLATE

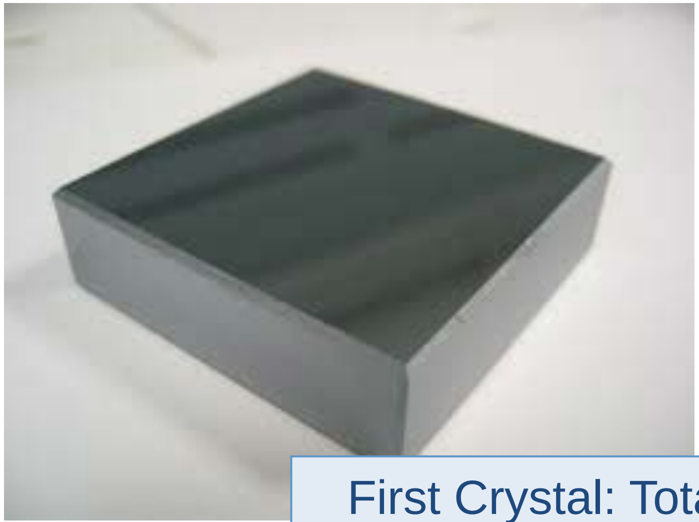


L. Rebuffi, J.R. Plaisier, M. Abdellatief, A. Lausi and P. Scardi, “MCX: a Synchrotron Radiation Beamline for X-ray Diffraction Line Profile Analysis”, Z. Anorg. Allg. Chem. (2014), doi: 10.1002/zaac.201400163

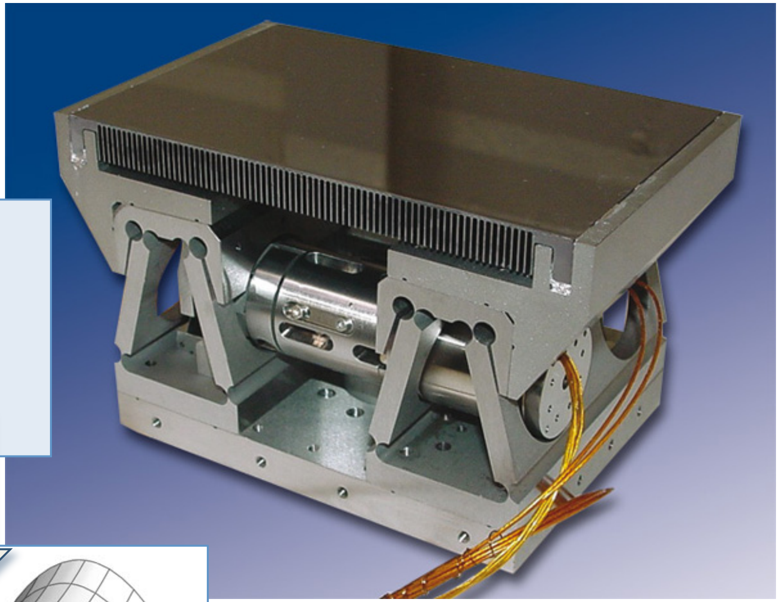
Characterization of a XRPD beamline

Elettra
Sincrotrone
Trieste

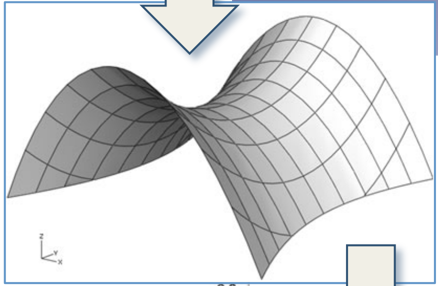
DCM : Thermo-Mechanical Characterization

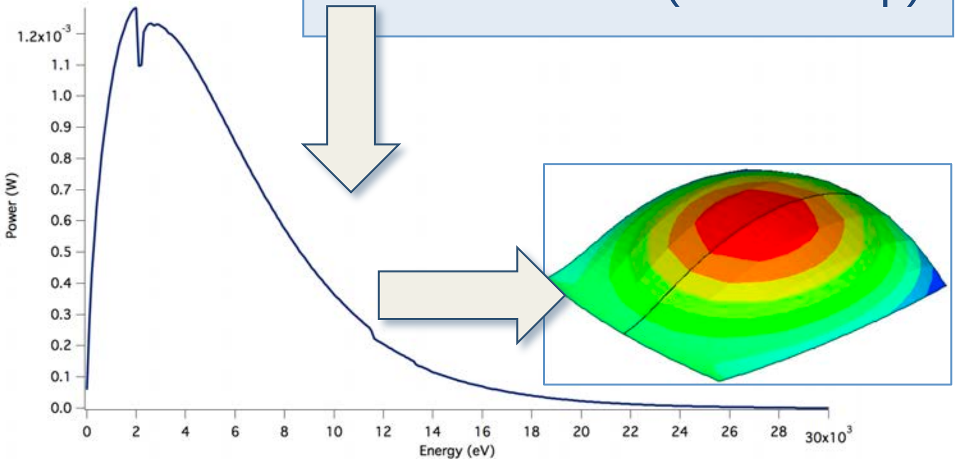


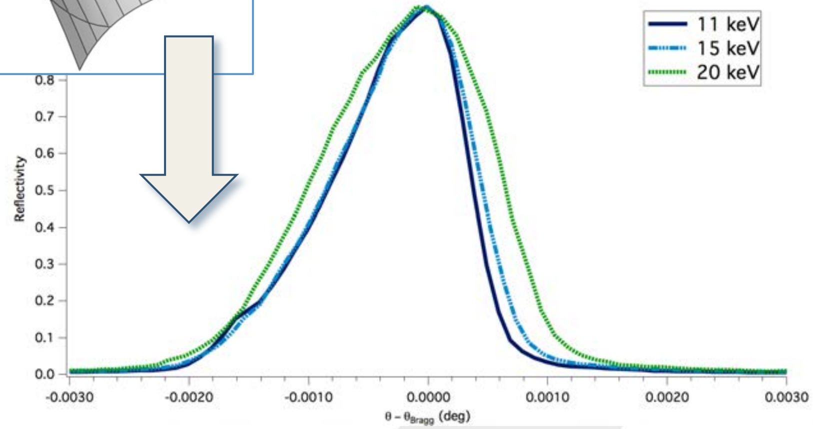
Second Crystal: Diffraction Profiles to analyze mechanical aberrations



First Crystal: Total Power Absorbed to analyze thermal issues (heat bump)

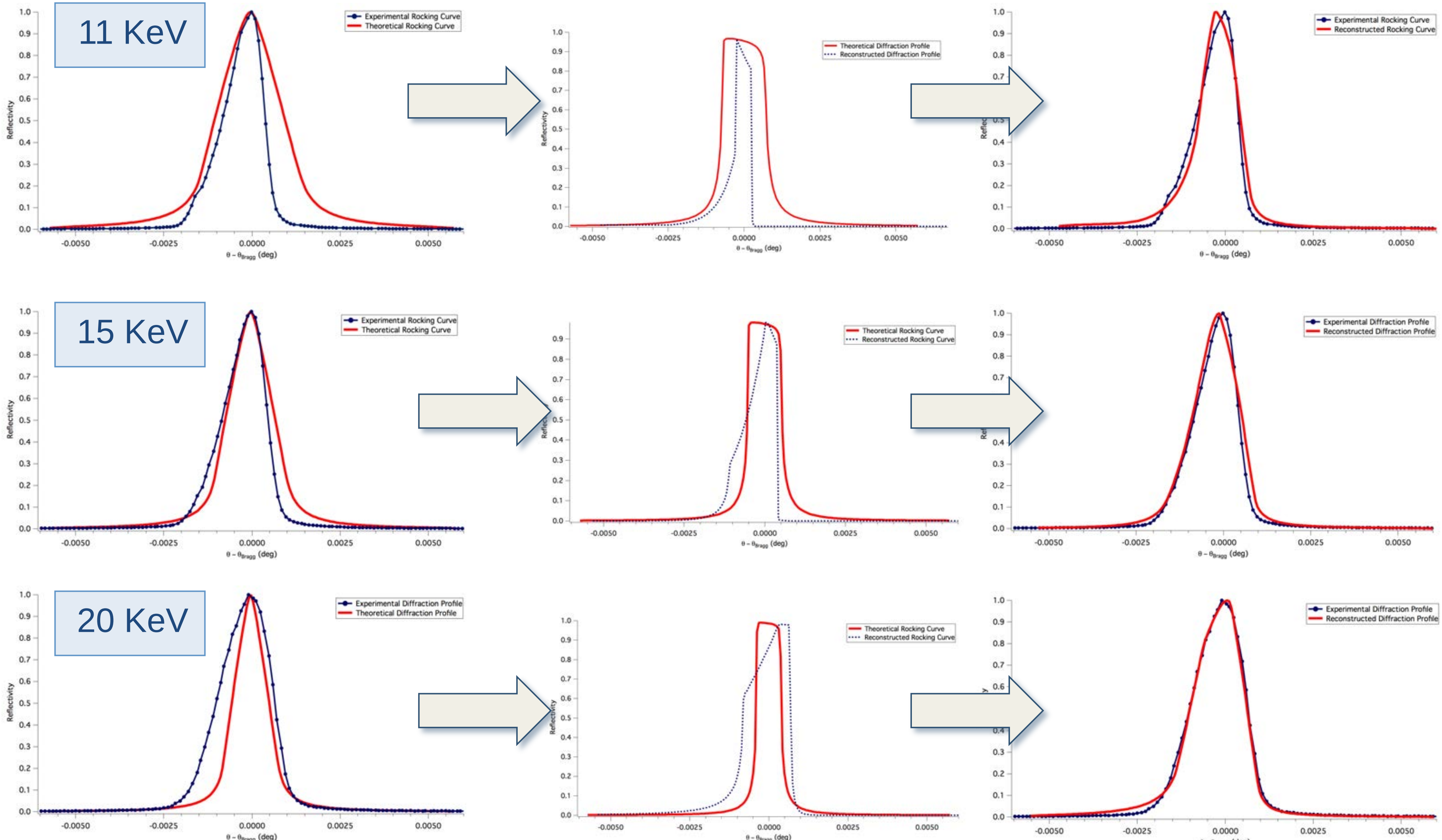






Characterization of a XRPD beamline

DCM : Second Crystal experimental Rocking Curve reconstruction



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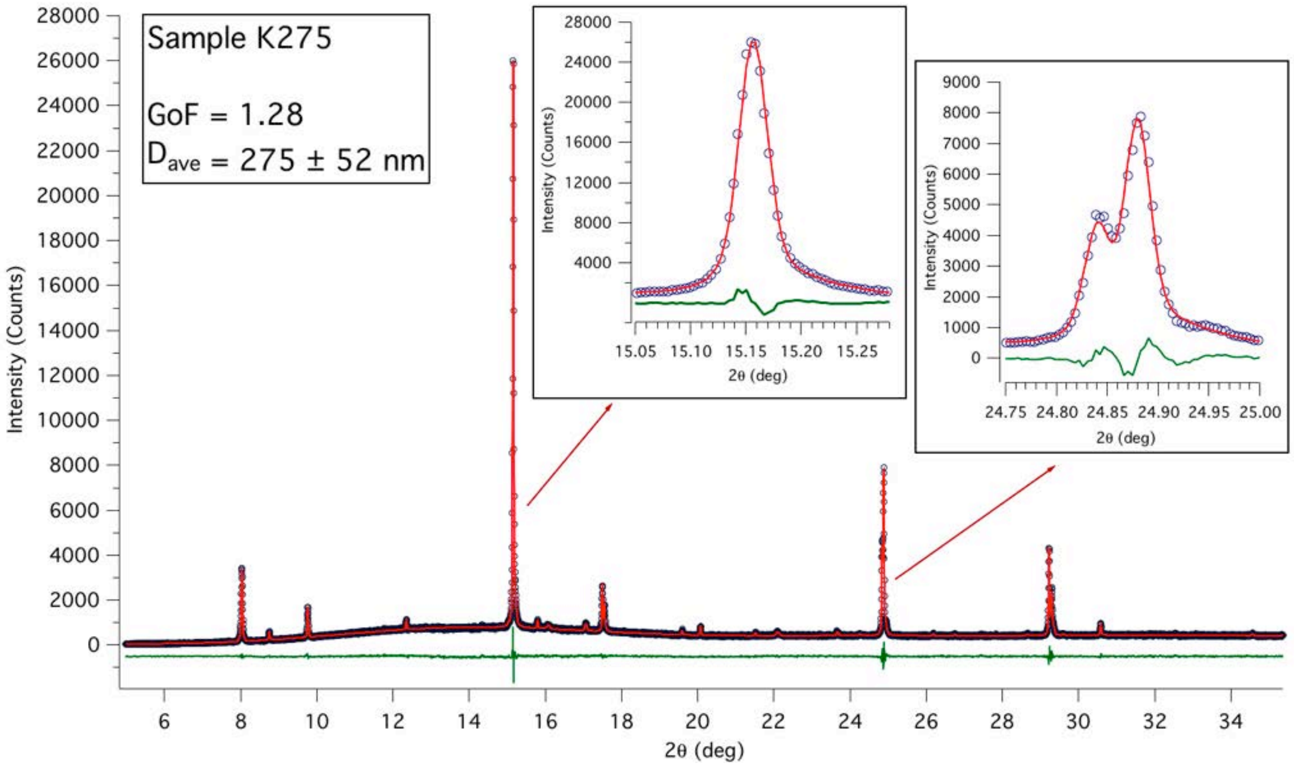
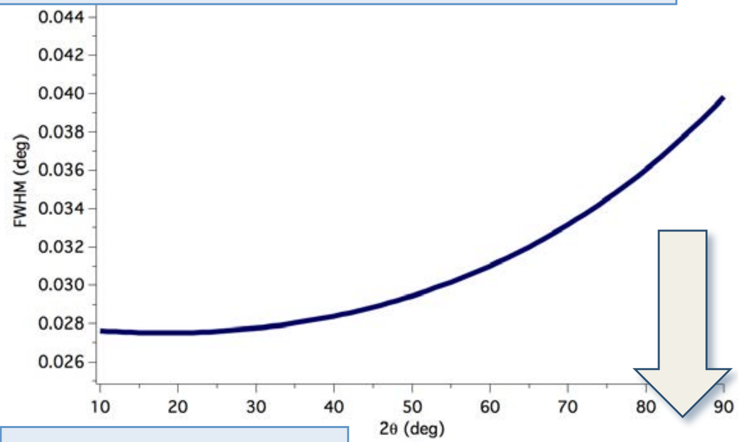
Examples of nanostructured materials with large crystalline domains

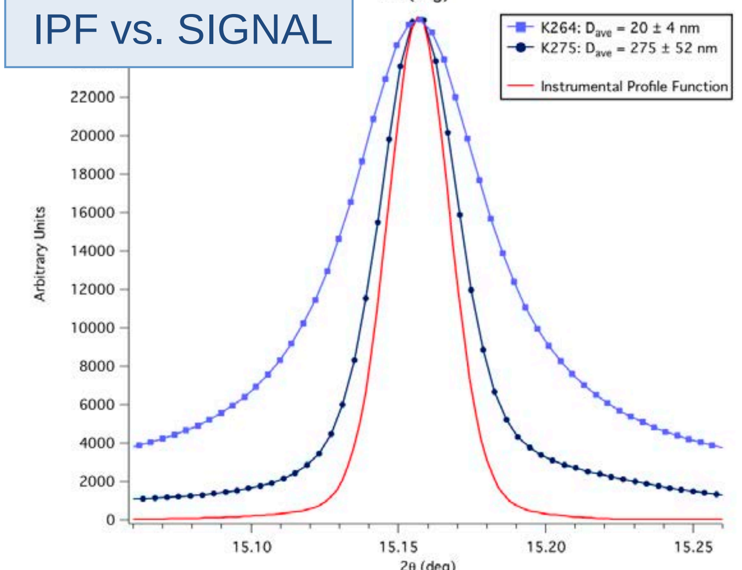
Nanomaterials “at the limit”: Kesterite

KESTERITE MICROSTRUCTURE STUDIED AT ELETTRA MCX BEAMLINE:
AN EXAMPLE OF NANOSTRUCTURED MATERIAL WITH LARGE CRYSTALLINE DOMAINS ($\langle D \rangle$ ≈ 250 nm)



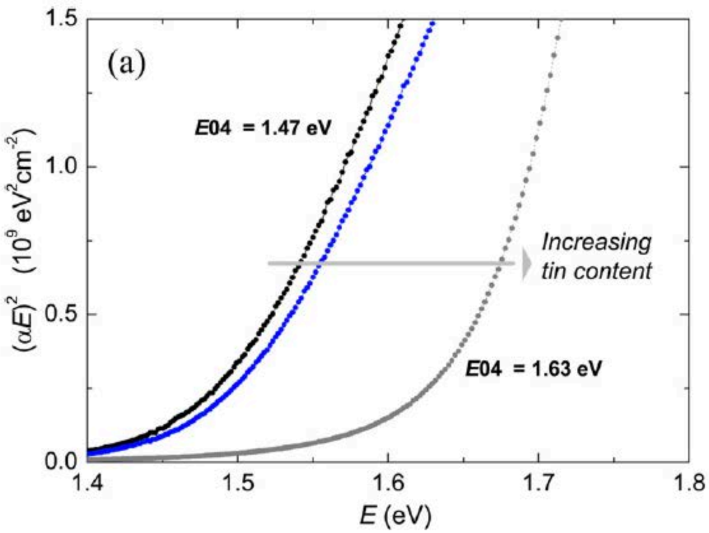


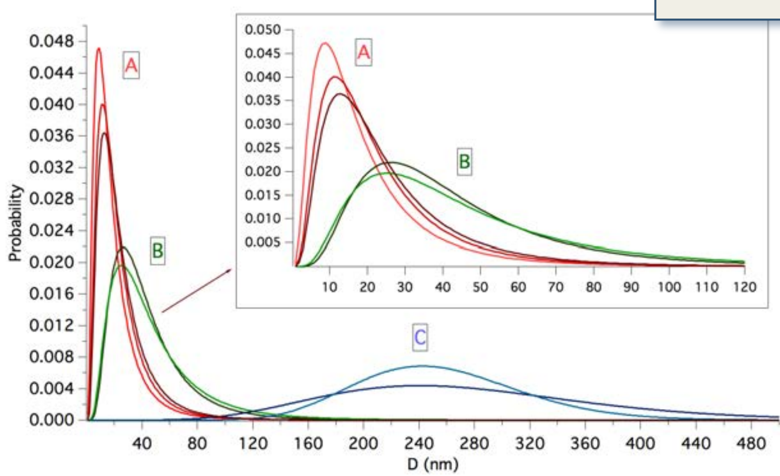
IPF vs. SIGNAL

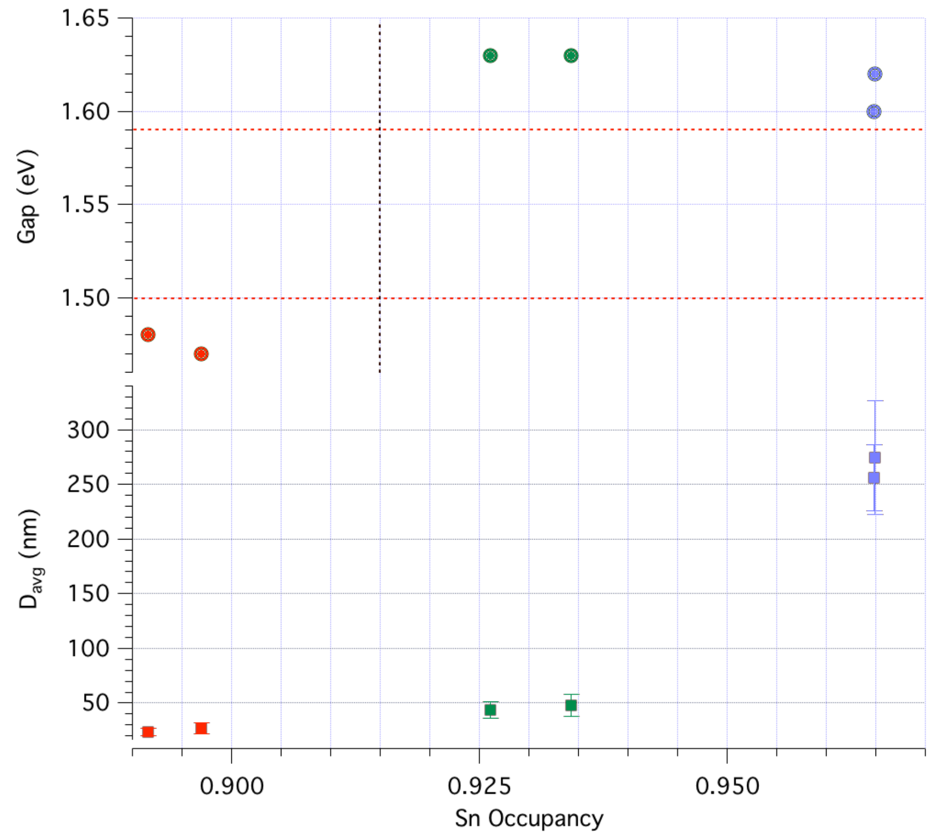


FILMS OF Cu_2ZnSnS_4 ON A GLASS SUBSTRATE:
FLAT PLATE CONFIGURATION, BEAM ENERGY = 15 keV

Nanomaterials "at the limit": Kesterite





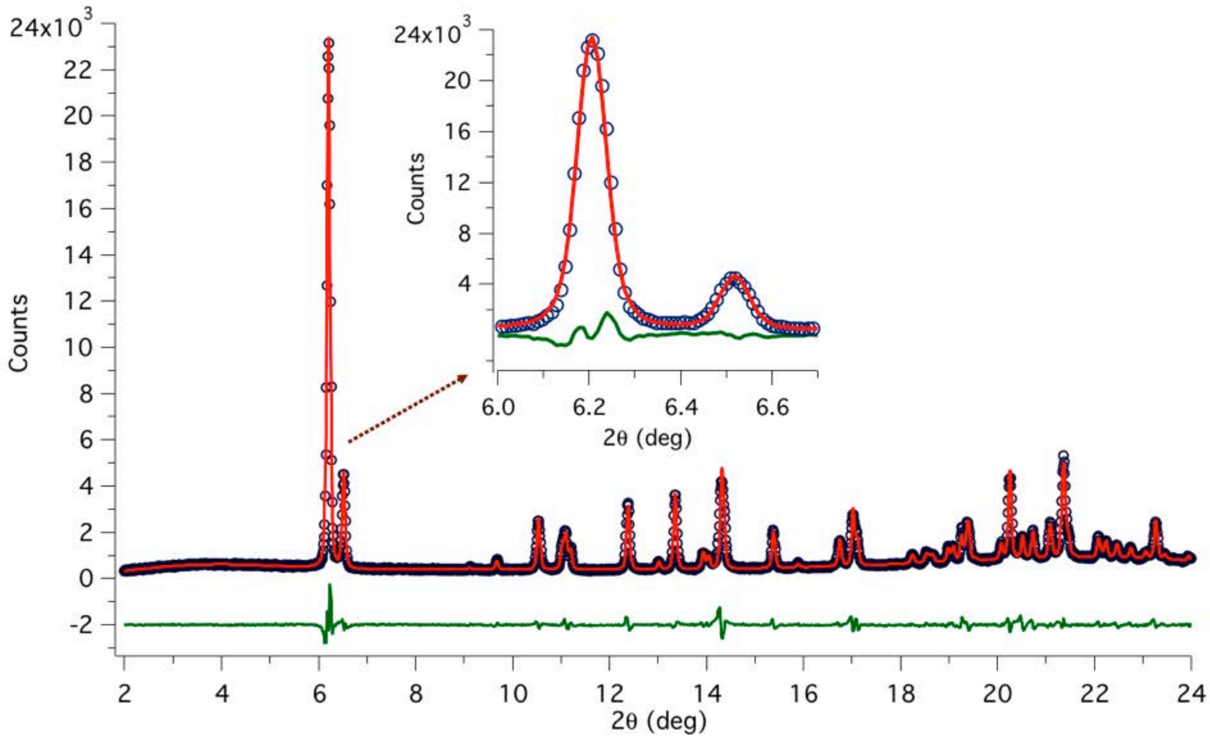


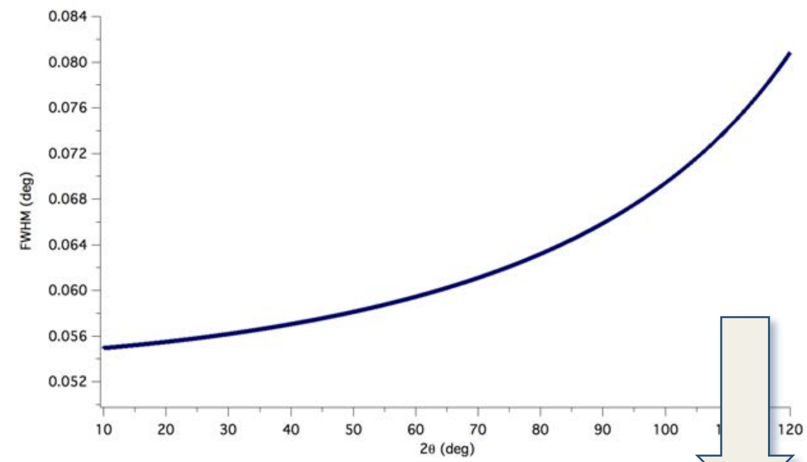
CORRELATION BETWEEN Sn CONTENT (Occupancy), CRYSTALLINE DOMAIN SIZE DISTRIBUTION AND OPTICAL PROPERTIES (Energy Gap)

C. Malerba, C. L. Azanza Ricardo, M. Valentini, F. Biccari, M. Müller, L. Rebuffi, E. Esposito, P. Mangiapane, P. Scardi, and A. Mittiga, "Stoichiometry effect on Cu_2ZnSnS_4 thin films morphological and optical properties", J. Renewable Sustainable Energy (2014), 6, 011404

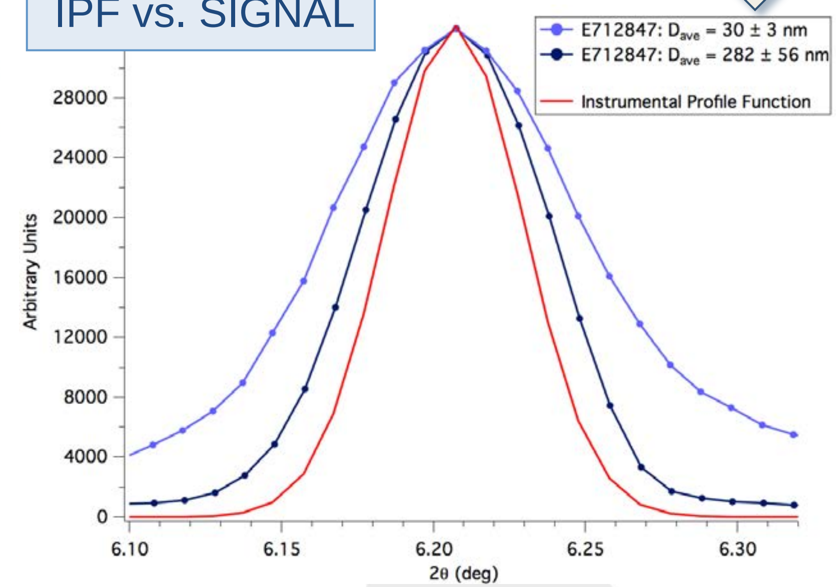
Nanomaterials “at the limit”: Efavirenz

ANTI-HIV DRUG EFAVIRENZ MICROSTRUCTURE STUDIED AT ELETTRA MCX BEAMLINE, AGAIN WITH LARGE CRYSTALLINE DOMAINS ($\langle D \rangle$ ≈ 300 nm)





IPF vs. SIGNAL

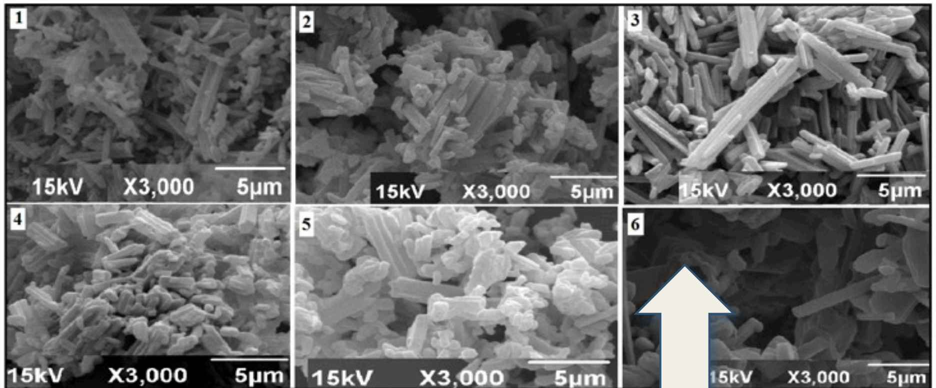


MICRONIZED POWDER:

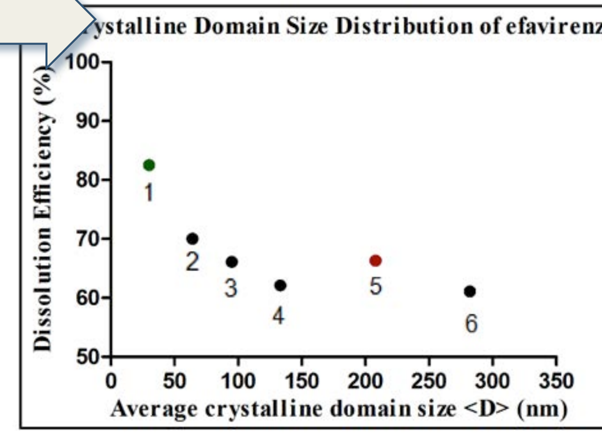
CAPILLARY CONFIGURATION, BEAM ENERGY = 8 keV

(ORGANIC MATERIAL)

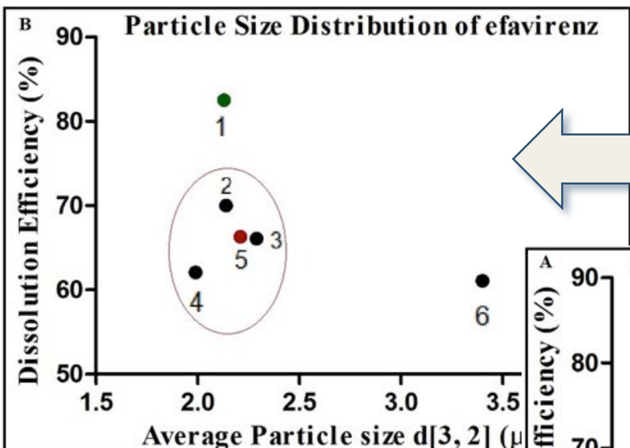
Nanomaterials “at the limit”: Efavirenz

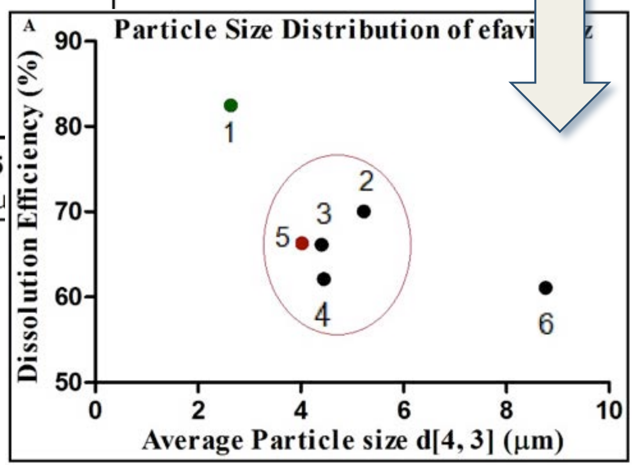


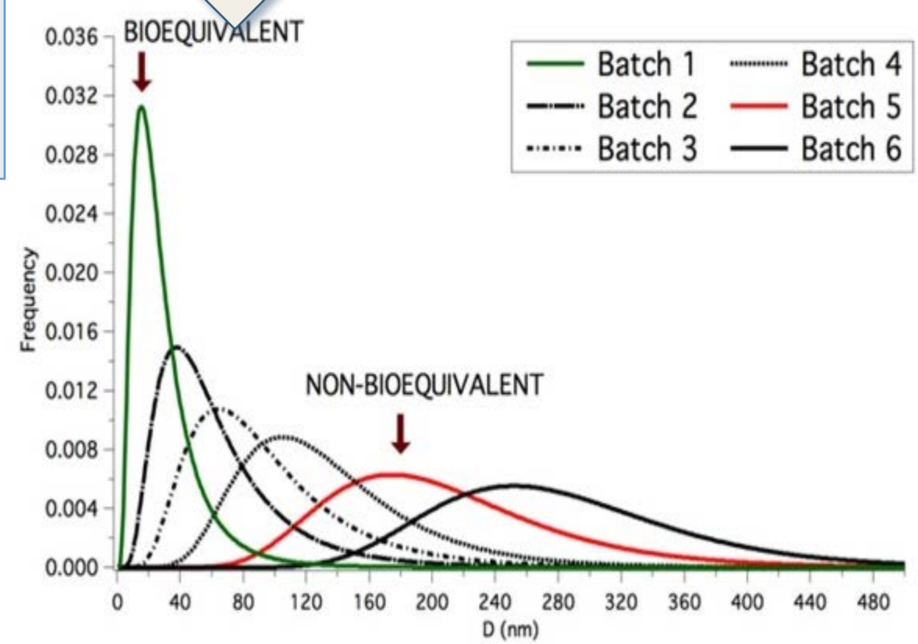
XRPD AND LPA: CORRELATION BETWEEN CRISTALLINE DOMAIN SIZE AND BIOAVAILABILITY



NO CORRELATION BETWEEN PARTICLE SIZE AND BIOAVAILABILITY







C. Fandaruff, M.A. Segatto Silva, D.C. Galindo Bedor, D. Pereira de Santana, H.V. Antunes Rocha, L. Rebuffi, C.L. Azanza Ricardo, P. Scardi and S.L. Cuffini, “Correlation between crystalline microstructure and bioequivalence in Anti-HIV Drug Efavirenz”, Eur. J. Pharm. Biopharm. 91 (2015), 52–5, doi: 10.1016/j.ejpb.2015.01.020

Understanding the Instrumental Profile:
a realistic ray-tracing approach

A realistic ray-tracing approach

MATHEMATICAL DESCRIPTION OF THE INSTRUMENTAL BROADENING

OPTICAL ORIGIN OF THE DIFFRACTED BEAM DIVERGENCE:

- ✓ G. CAGLIOTI et al. (1958)
- ✓ T.M. SABINE (1987)

OPTICAL ABERRATIONS EFFECTS:

- ✓ A.D. ZUEV (2006,2008)
- ✓ R.W. CHEARY et al. (2004)

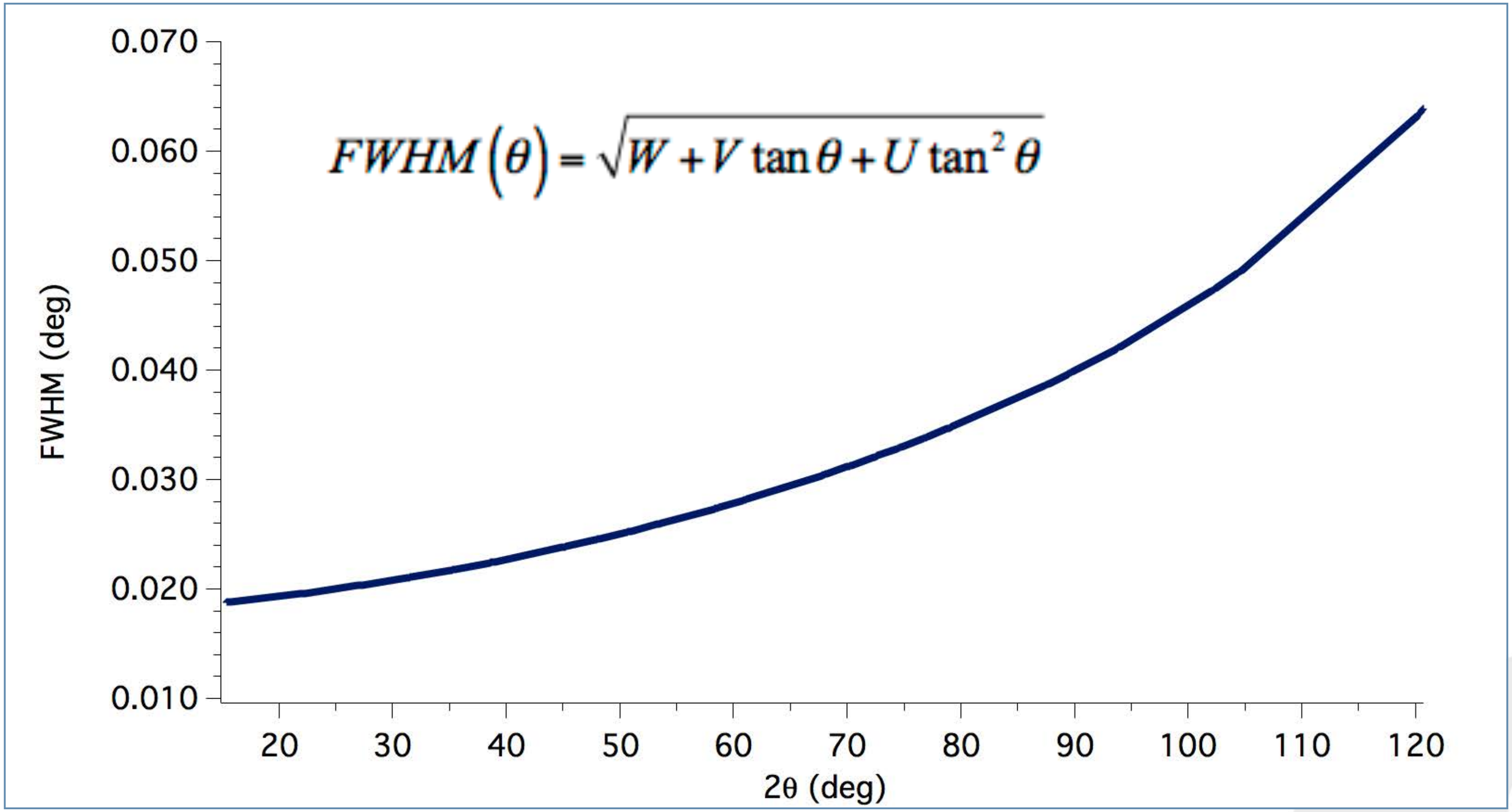
THE OPTICAL NATURE OF THE INSTRUMENTAL PROFILE SUGGESTS A RAY-TRACING SIMULATION APPROACH

M.Leoni, U. Welzel, P. Scardi, “Polycapillary Optics for Materials Science Studies: Instrumental Effects and Their Correction”, J. Res. Natl. Inst. Stand. Technol., 109, 27-48 (2004)

P. Scardi, L. Lutterotti, P. Maistrelli, "Experimental Determination of the Instrumental Broadening in the Bragg-Brentano Geometry," Powder Diffr. 9, 180-186 (1994)

A realistic ray-tracing approach

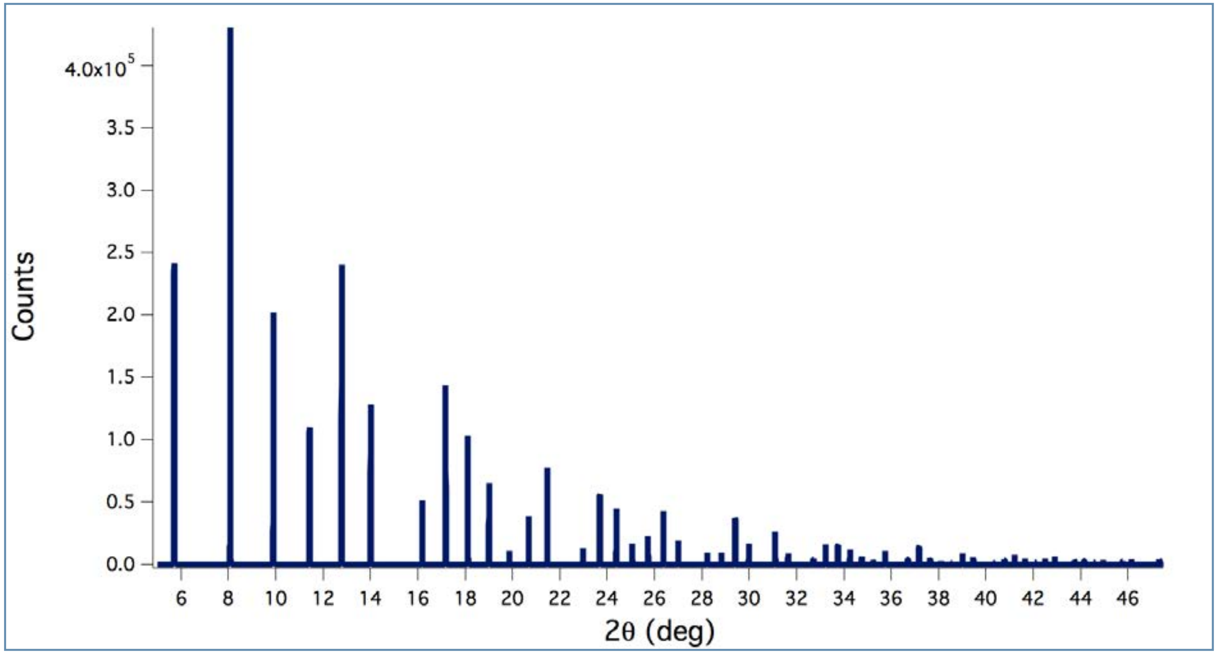
INSTRUMENTAL PROFILE FUNCTION IS USUALLY REPRESENTED AND PARAMETRIZED WITH THE CAGLIOTI'S EQUATION FOR THE FULL WIDTH HALF MAXIMUM OF THE INSTRUMENTAL PEAK PROFILE, REPRESENTED AS PSEUDO-VOIGT CURVES



A realistic ray-tracing approach

Experimental Instrumental Profile Function characterization

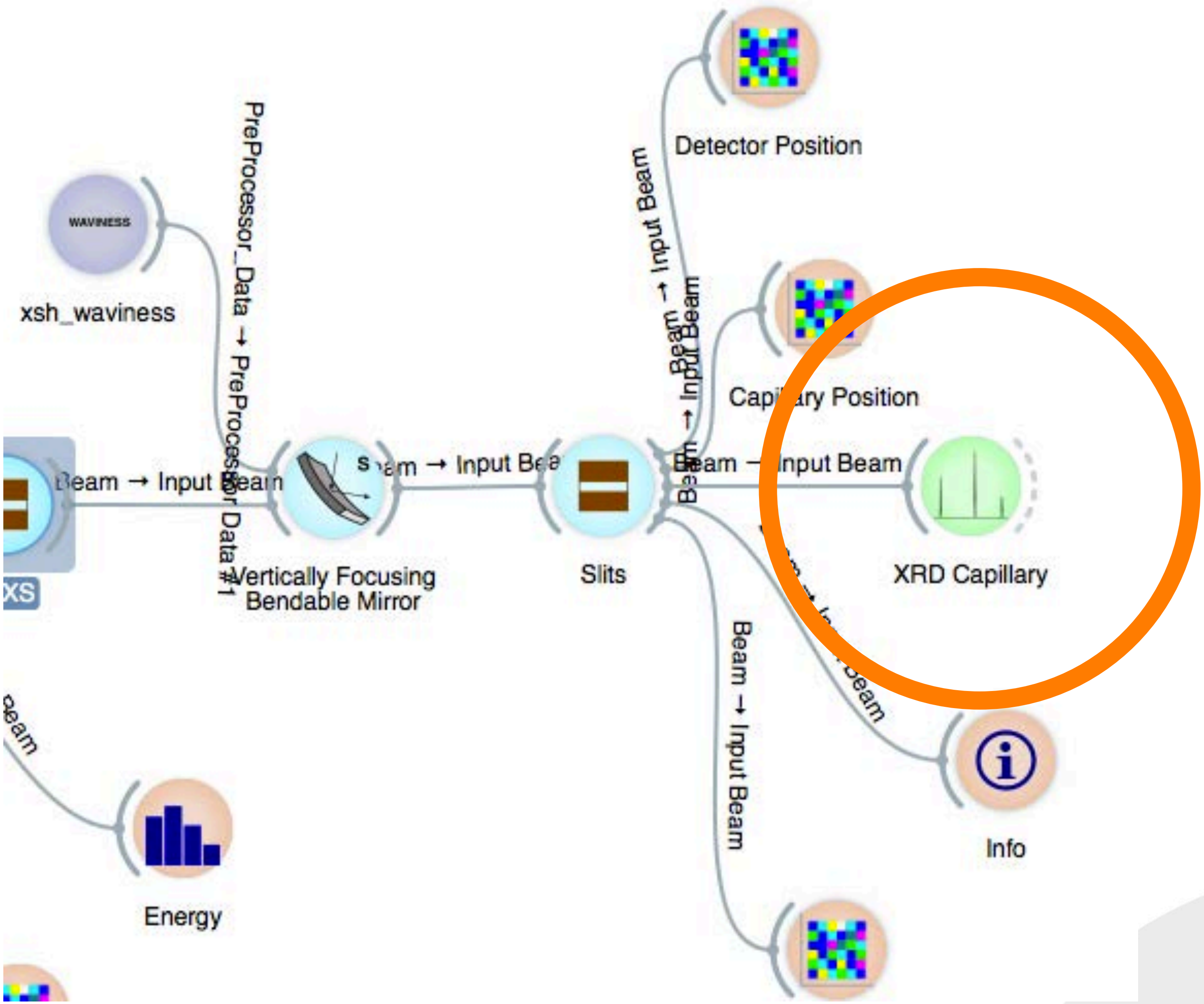
It can be obtained analyzing the diffraction pattern from a sample of LaB_6 a standard reference material produced by NIST



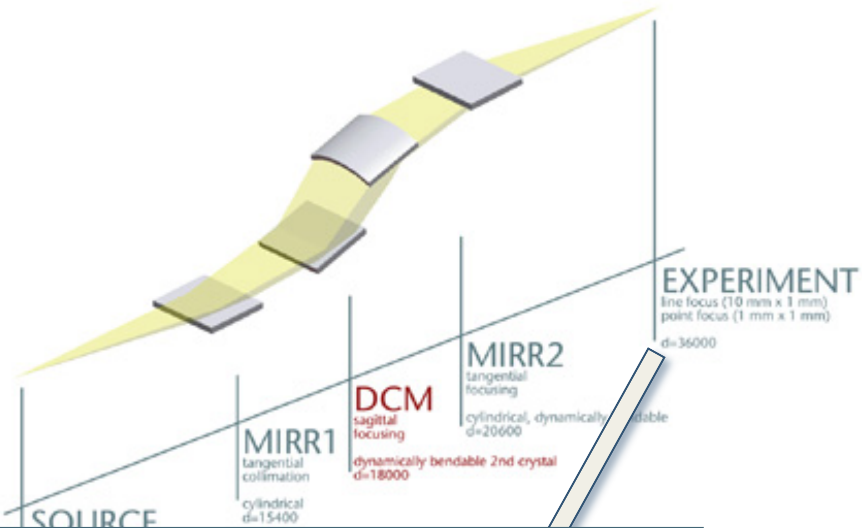
A realistic approach starts from the simulation of the interaction of the SHADOW photon beam with a capillary filled by such a standard reference material

L. Rebuffi, J.R. Plaisier, M. Abdellatief, A. Lausi, P. Scardi, “MCX: a Synchrotron Radiation Beamline for X-ray Diffraction Line Profile Analysis”, Z. anorg. allg. Chem. (2014), doi: 10.1002/zaac.201400163

XRPD ray-tracing simulation widget

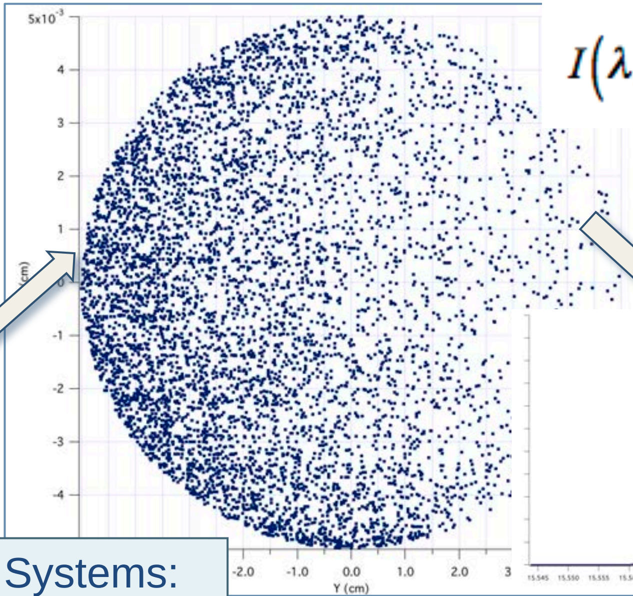


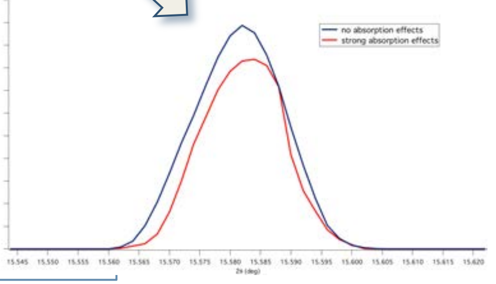
Ray-Tracing of LaB_6 (NIST 660a) Profile



X-ray Absorption Effects

$$I(\lambda,x) = I_0 \exp\left[-\mu(\lambda)\rho x\right]$$



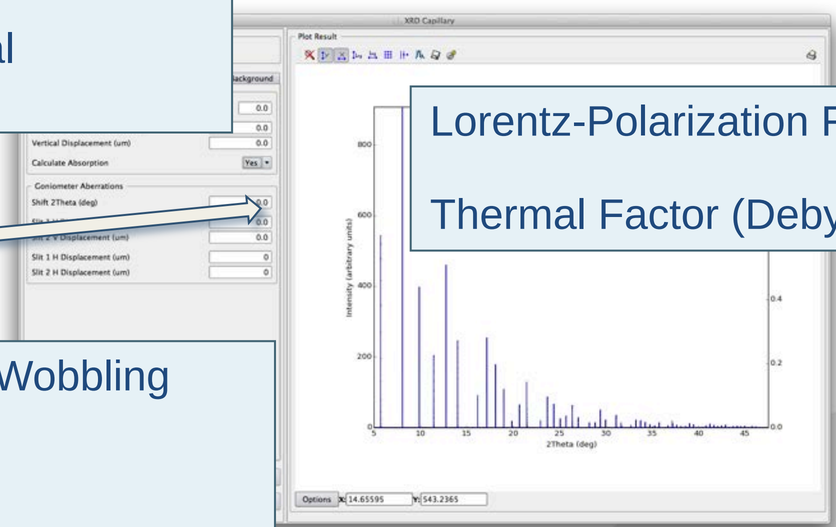


Ray-Tracing of Diffraction SHADOW Beam taking into account:

- Beam divergence
- Energy Distribution

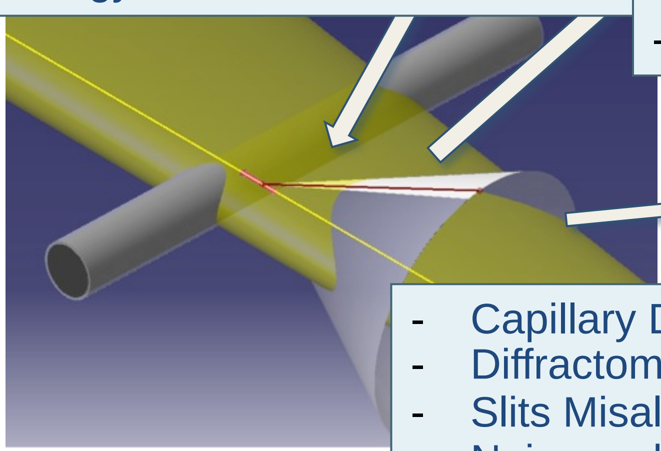
Different Detection Systems:

- Slits
- Analyzer Crystal
- Area Detector



Lorentz-Polarization Factor

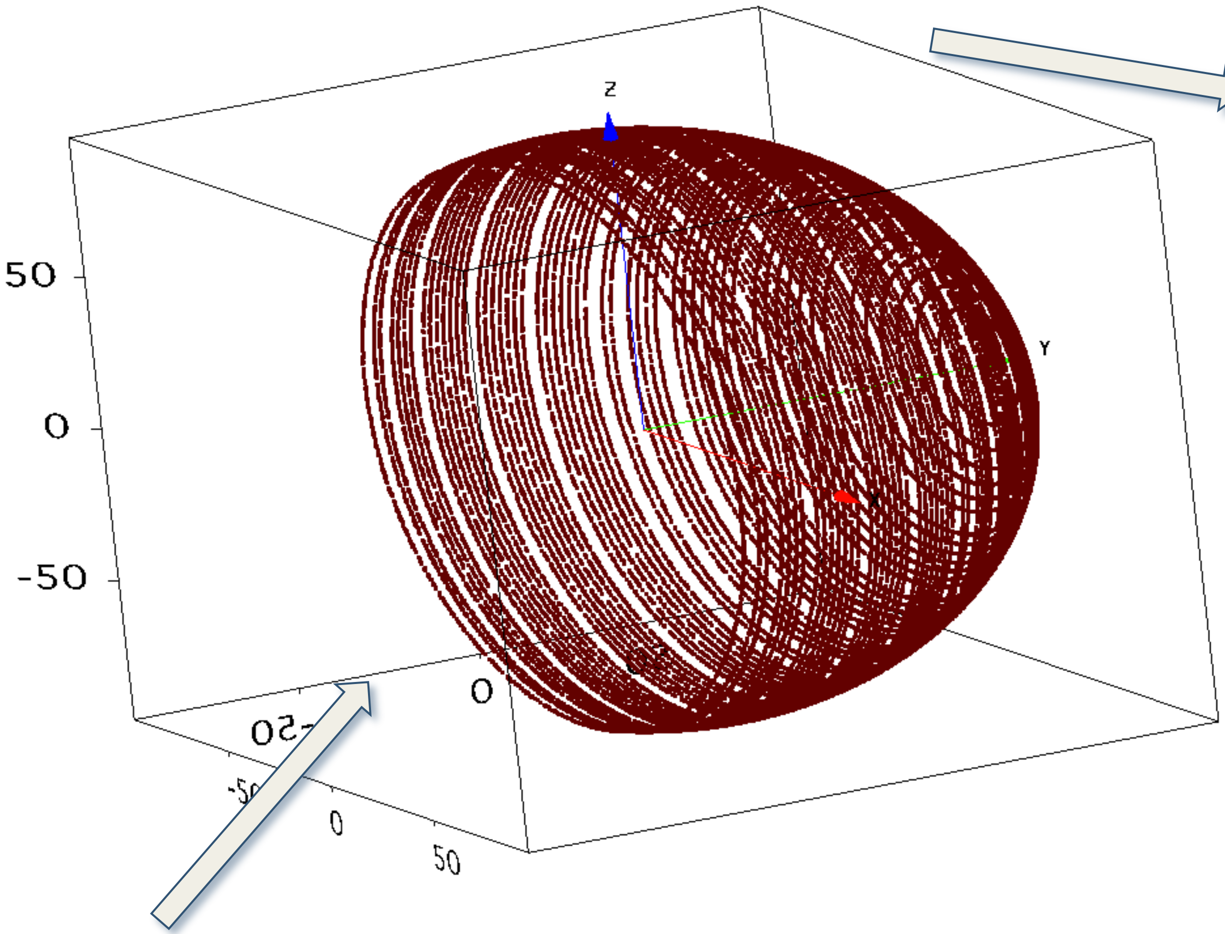
Thermal Factor (Debye-Waller)



- Capillary Displacement and Wobbling
- Diffractometer Misalignment
- Slits Misalignment
- Noise and Background

L. Rebuffi, P. Scardi and M. Sanchez del Rio, “Design and management of a powder diffraction beamline for Line Profile Analysis: a realistic ray-tracing approach”, Powder Diffraction (2014) accepted for publication.

Undertanding IPF

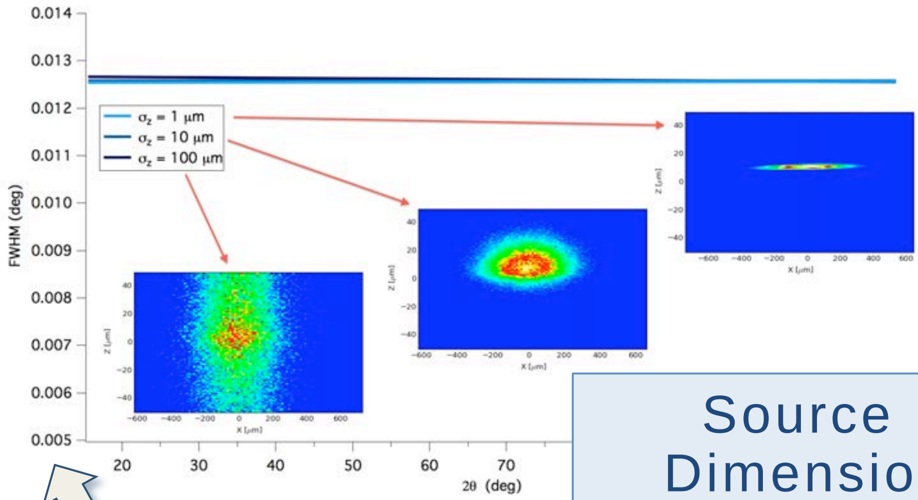


Debye Rings generated as SHADOW rays

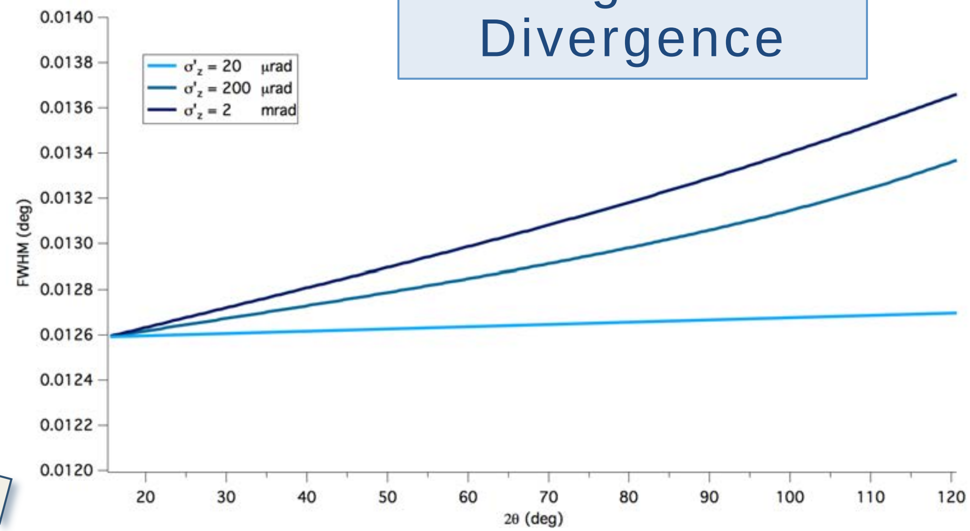
Thanks to SHADOW approach and capabilities it will be possible to study the different elements contributing to the IPF separately, like:

- Beam size
- Beam divergence
- ΔE/E of monochromator (and slits)
- Capillary size
- Diffractometer geometry and optical setup
- Sample material

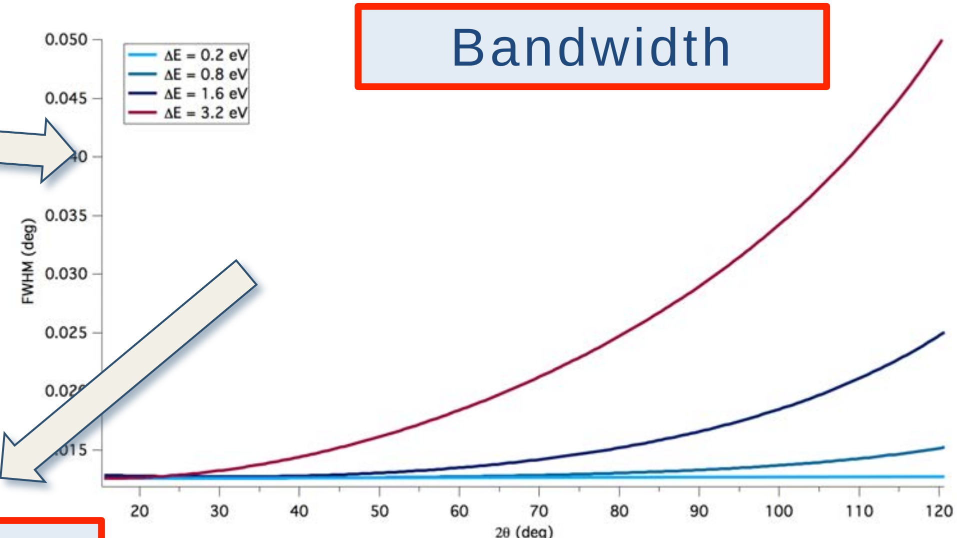
Understanding IPF



Source Dimension



Angular Divergence



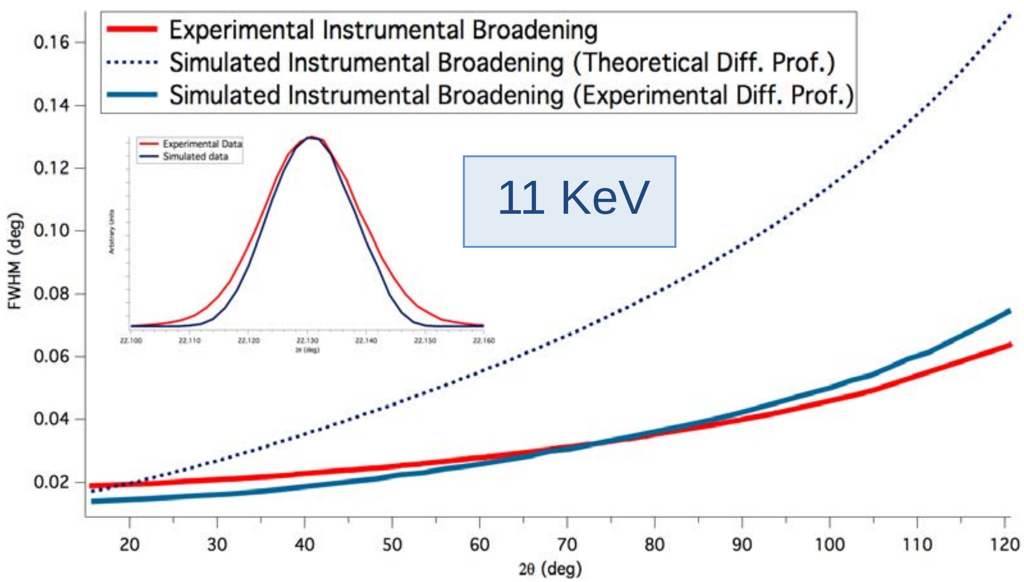
Bandwidth

With the ray-tracing approach and using SHADOW features it was possible to study independently single contributions to IPF

MCX @ Elettra: DCM diffraction profile plays a key role

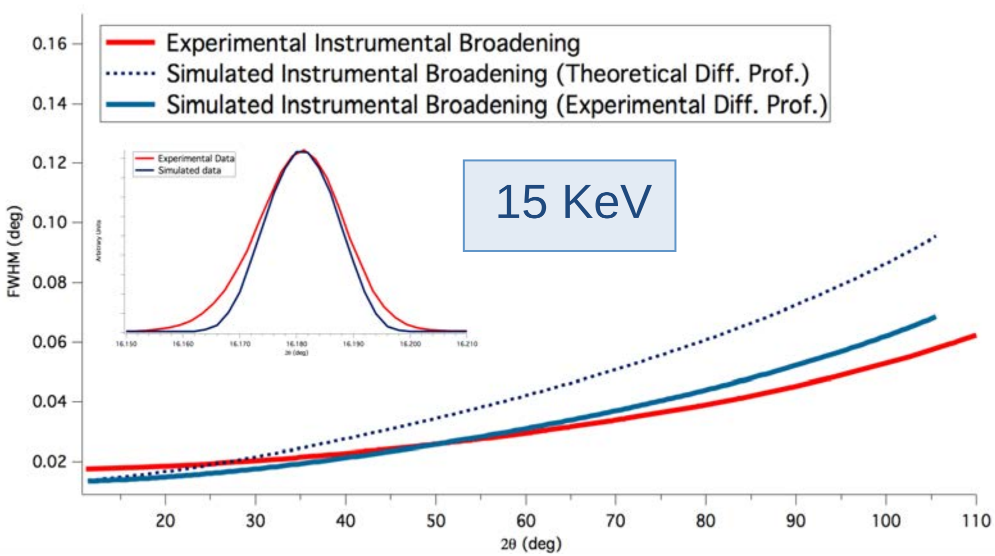
Understanding IPF: MCX @ Elettra

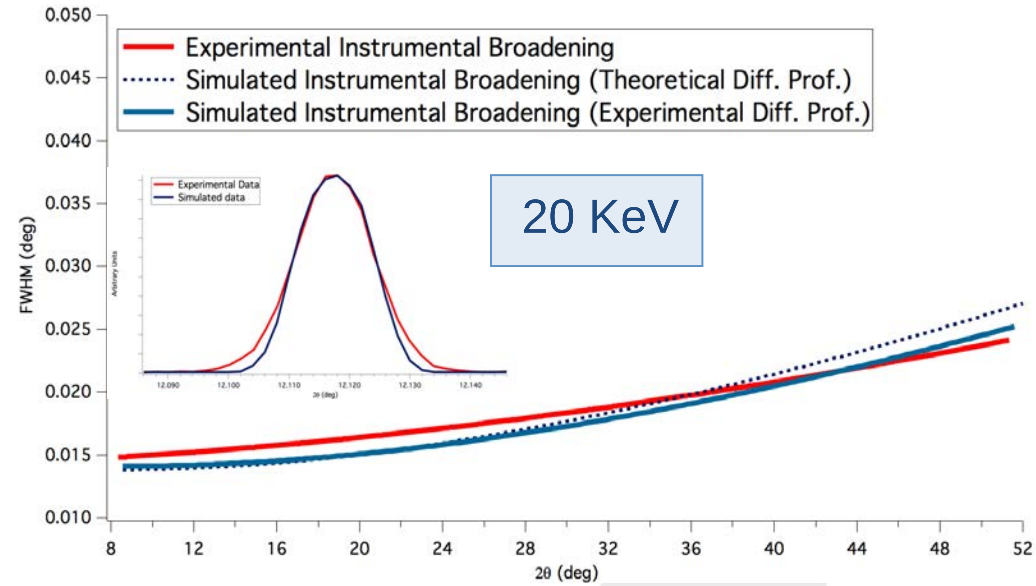
Elettra Sincrotrone Trieste



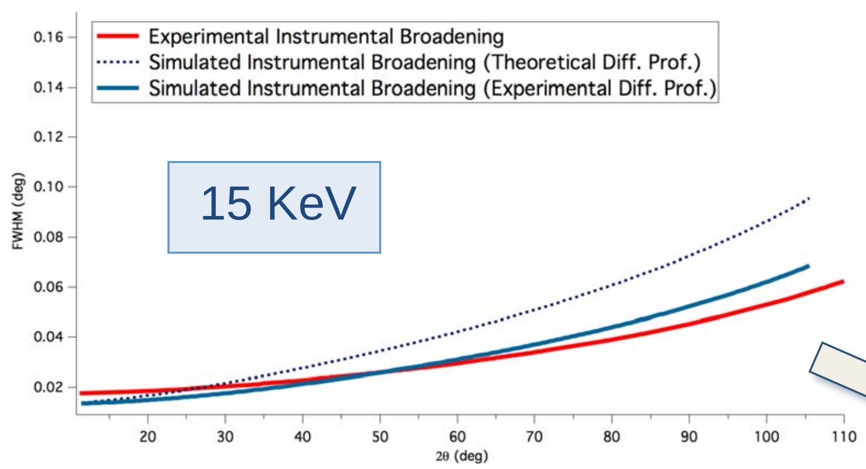
MCX @ Elettra: DCM diffraction profile plays a key role

Only reconstructed experimental rocking curves lead to a satisfactory reproducibility of IPF





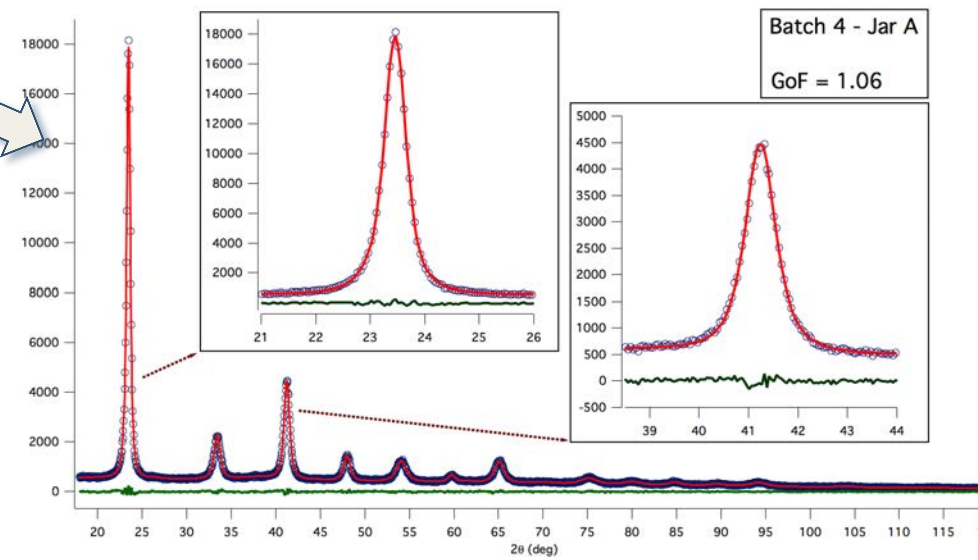
Quality of the Simulation: LPA of FeMo



15 KeV

LPA of FeMo XPRD patterns from MCX @ Elettra with

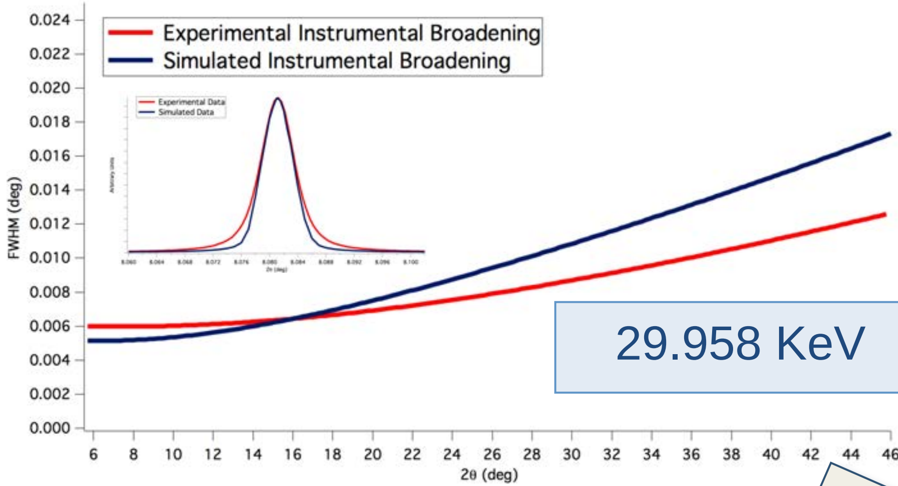
Simulated Instrumental FWHM(θ)



	Parameter	WPPM with experimental IPF	WPPM with simulated IPF
Size	$\langle D \rangle$	9.3(8) nm	9.4(8) nm
	s.d.	5.9(9) nm	5.7(9) nm
	$\langle D \rangle_S$	10.2(9) nm	10.3(9) nm
	$\langle D \rangle_V$	10.9(9) nm	11.0(9) nm
Strain	ρ	4.5(4) 10^{16} m^{-2}	4.7(3) 10^{16} m^{-2}
	R_e	4.3(4) nm	4.1(4) nm
	f_E	0.54(3)	0.54(3)

FULL AGREEMENT

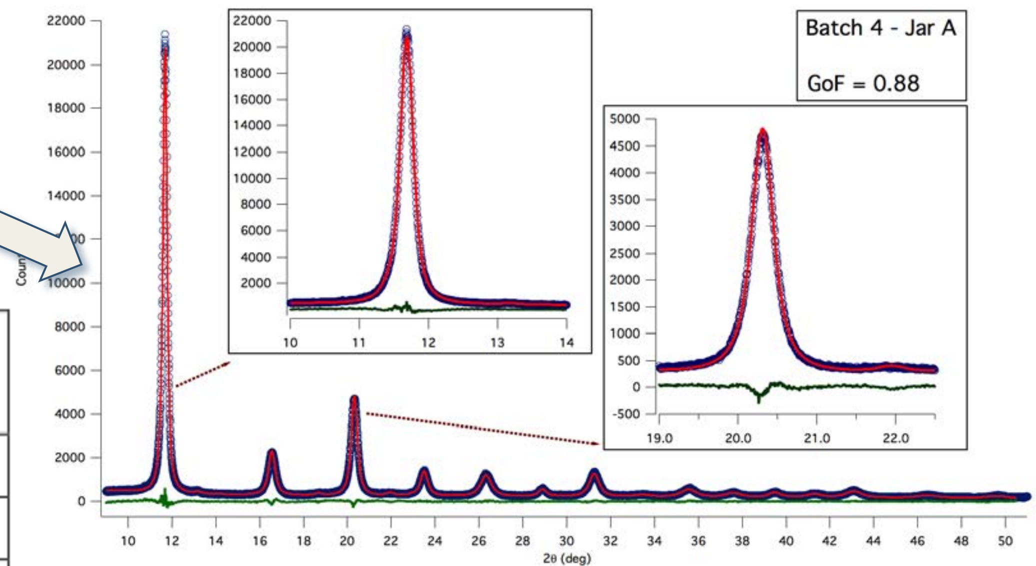
Realistic IPF Simulation: 11BM @ APS



29.958 KeV

LPA of FeMo XPRD patterns from 11BM @ APS with

Simulated Instrumental FWHM(θ)



	Parameter	WPPM with experimental IPF	WPPM with simulated IPF
Size	*<D>*	9.2(3) nm	9.3(3) nm
	s.d.	5.7(4) nm	5.6(3) nm
	<D>$_S$	10.1(3) nm	10.2(3) nm
	<D>$_V$	10.8(3) nm	10.8(3) nm
Strain	ρ	6.8(1) 10^{16} m^{-2}	7.4(2) 10^{16} m^{-2}
	R_e	2.0(1) nm	1.8(1) nm
	f_E	0.70(1)	0.71(1)

FULL AGREEMENT

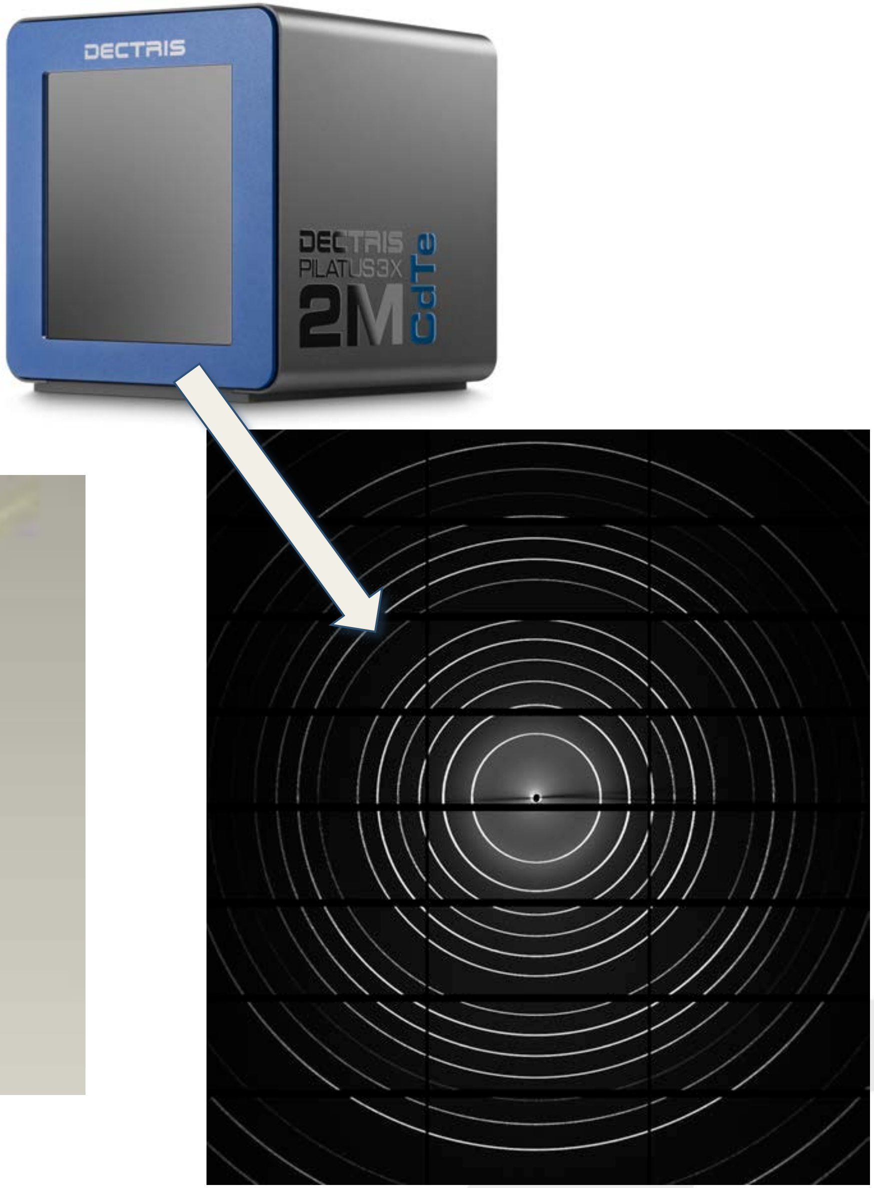
Elettra Sincrotrone Trieste

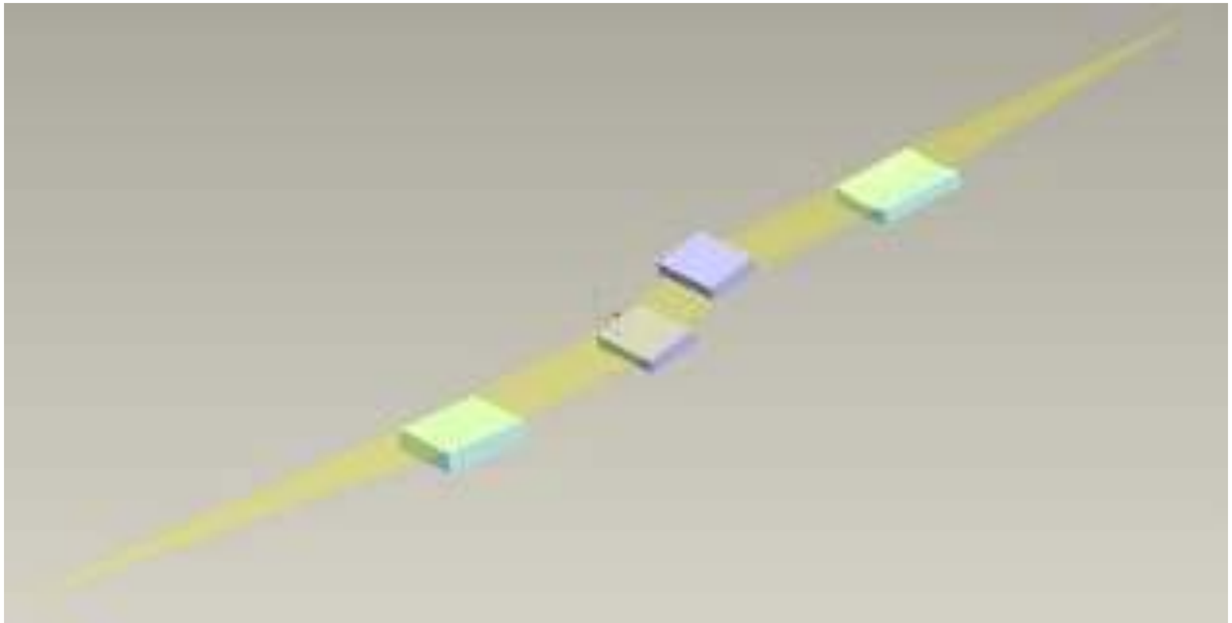
2D Detectors: XRD1 @ Elettra

XRD1at Elettra-Sincrotrone Trieste

Beamline optical layout (36 meters) :

- ✓ Electron Beam Energy 2 GeV
- ✓ NdBFe Multipole Wiggler with C.E 4.7 keV
- ✓ Vertically collimating mirror
- ✓ D.C.M., Si(111)
- ✓ Vertically/Horizontally focusing mirror (Thorus)
- ✓ Pilatus 2M Area Detector



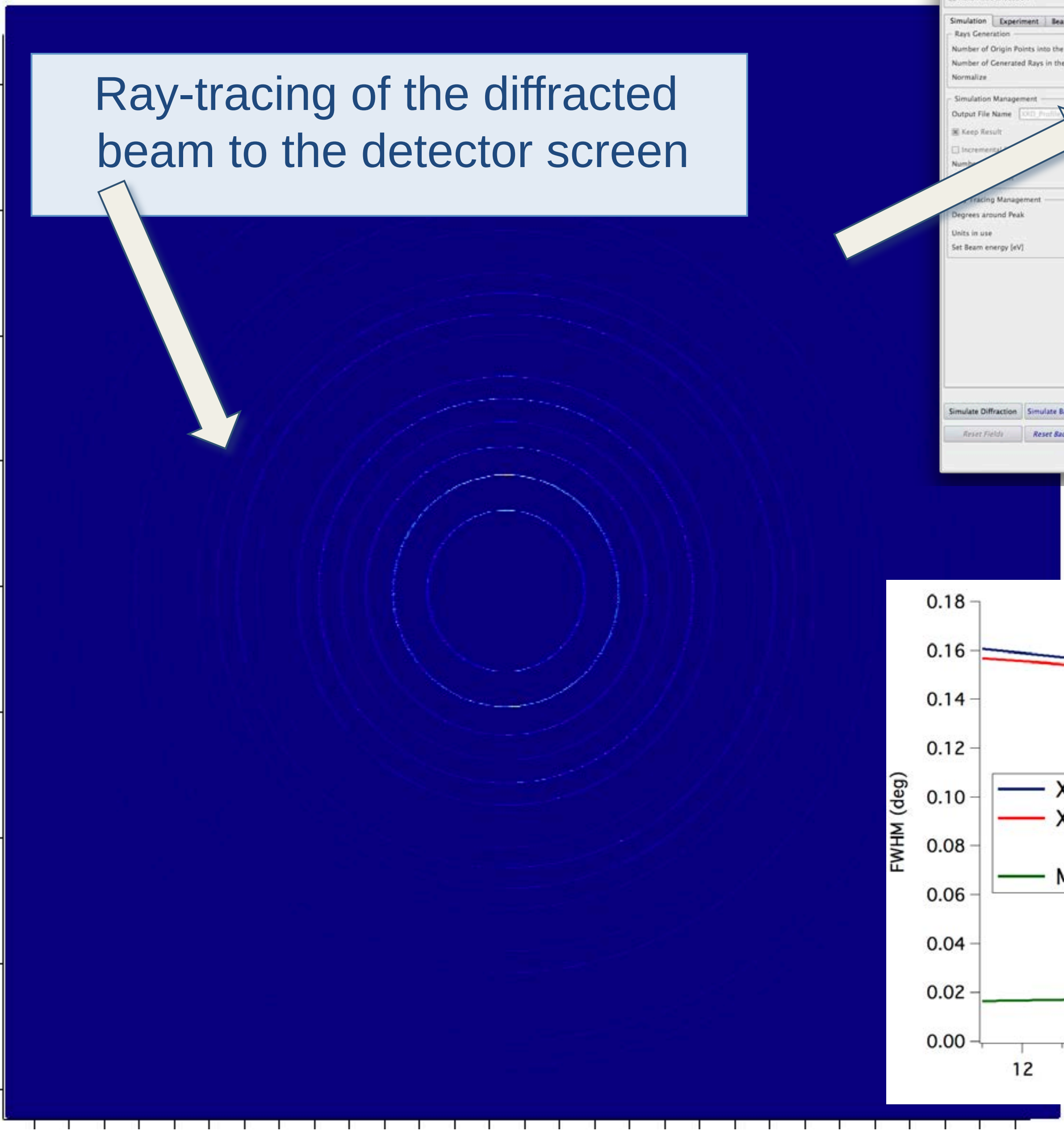


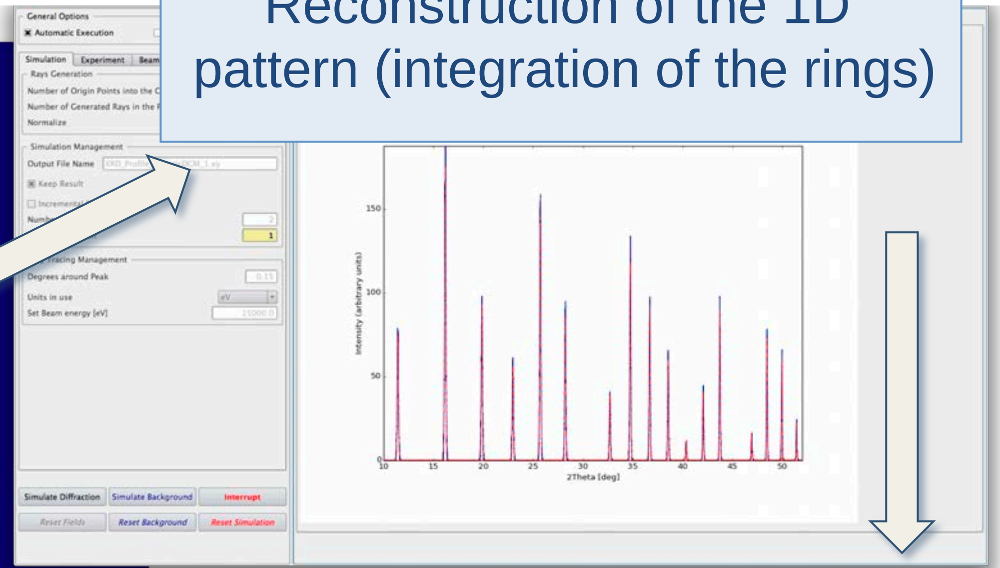
2D Detectors: XRD1 @ Elettra

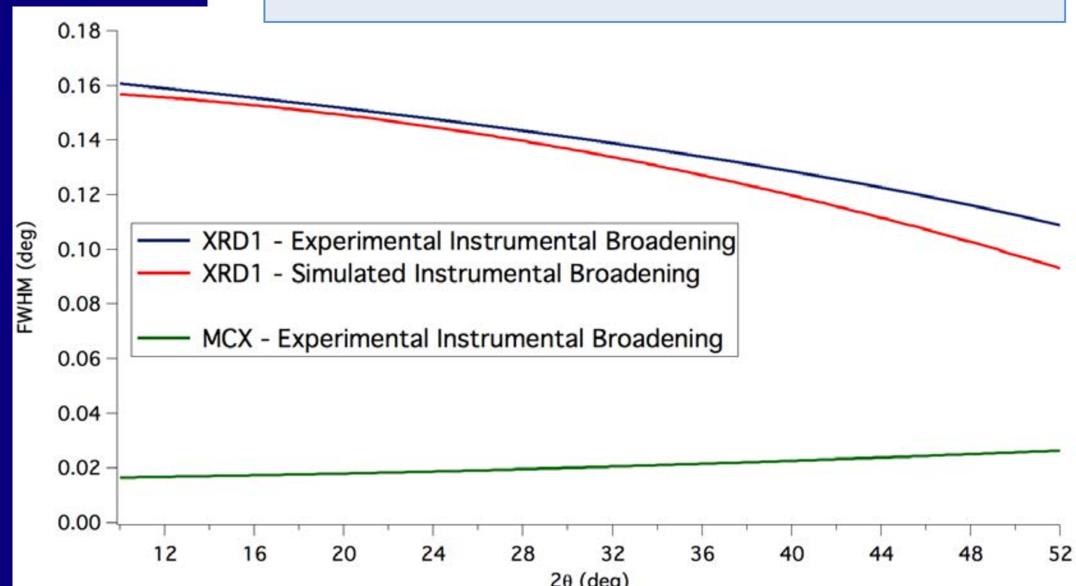
Ray-tracing of the diffracted beam to the detector screen

Reconstruction of the 1D pattern (integration of the rings)

Calculation of the I.P.F.







Thank you!

Elettra
Sincrotrone
Trieste

www.elettra.eu