A tool for GIXRF/XRR simulation and data analysis

Vakula N.I., Leani J.J., Migliori A., Bogovac M., Padilla-Alvarez R., Kaiser R.B. and Karydas A.G.

IAEA
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Introduction

Motivation:

The IAEA has developed a beamline end-station facility that it is currently installed at the newly developed XRF beamline of Elettra Sincrotrone Trieste, Italy

The end-station called Ultra High Vacuum Chamber (UHVC) is a multipurpose facility for applying simultaneously various complementary and advanced variants of X-Ray Spectrometry (XRS) techniques, including:

- Total Reflection X-ray Fluorescence Analysis (**TXRF**)
- Grazing Incidence/Exit XRF analysis (**GIXRF- GEXRF**)
- Near Edge X-ray Absorption Fine Structure (**NEXAFS**)
- X-ray Reflectometry (**XRR**)

➢ The current development of GIXRF/XRR simulations/analysis tool aims at assisting end-users in data processing and interpretation

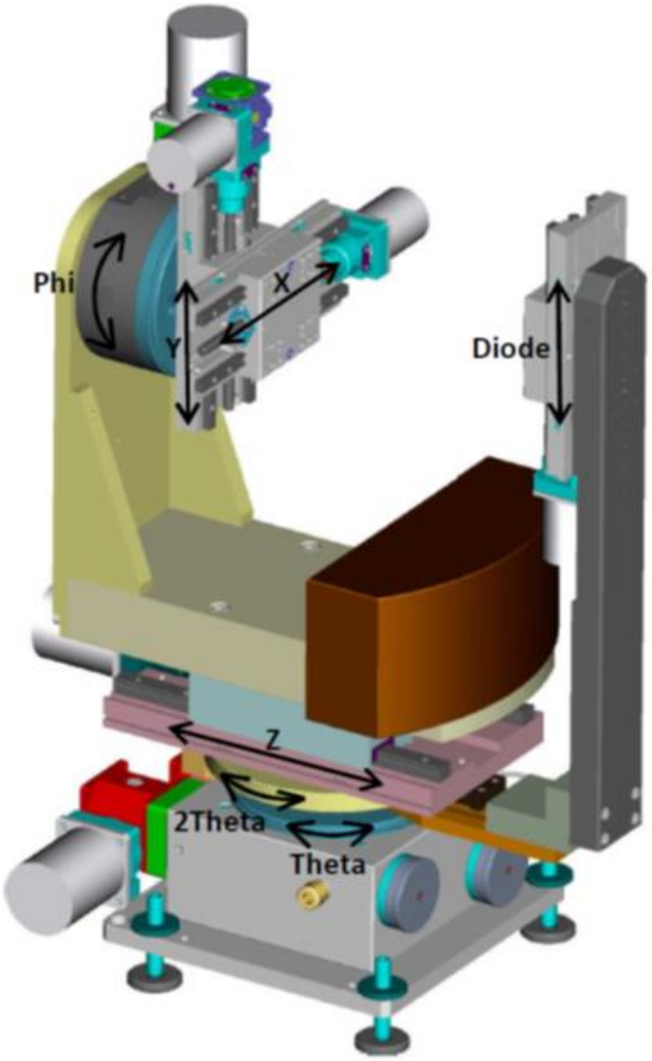
UHVC Instrumentation: 7-Axis Sample Manipulator

The sample manipulator includes:
Four (4) linear stages (‘X’, ‘Y’, ‘Z’, ‘Diode’)
Three (3) goniometers (‘Theta/2Theta’, ’Phi’)

Aiming at moving the sample to be investigated in various directions/ orientations with respect to the exciting X-ray beam or with respect to the detectors.

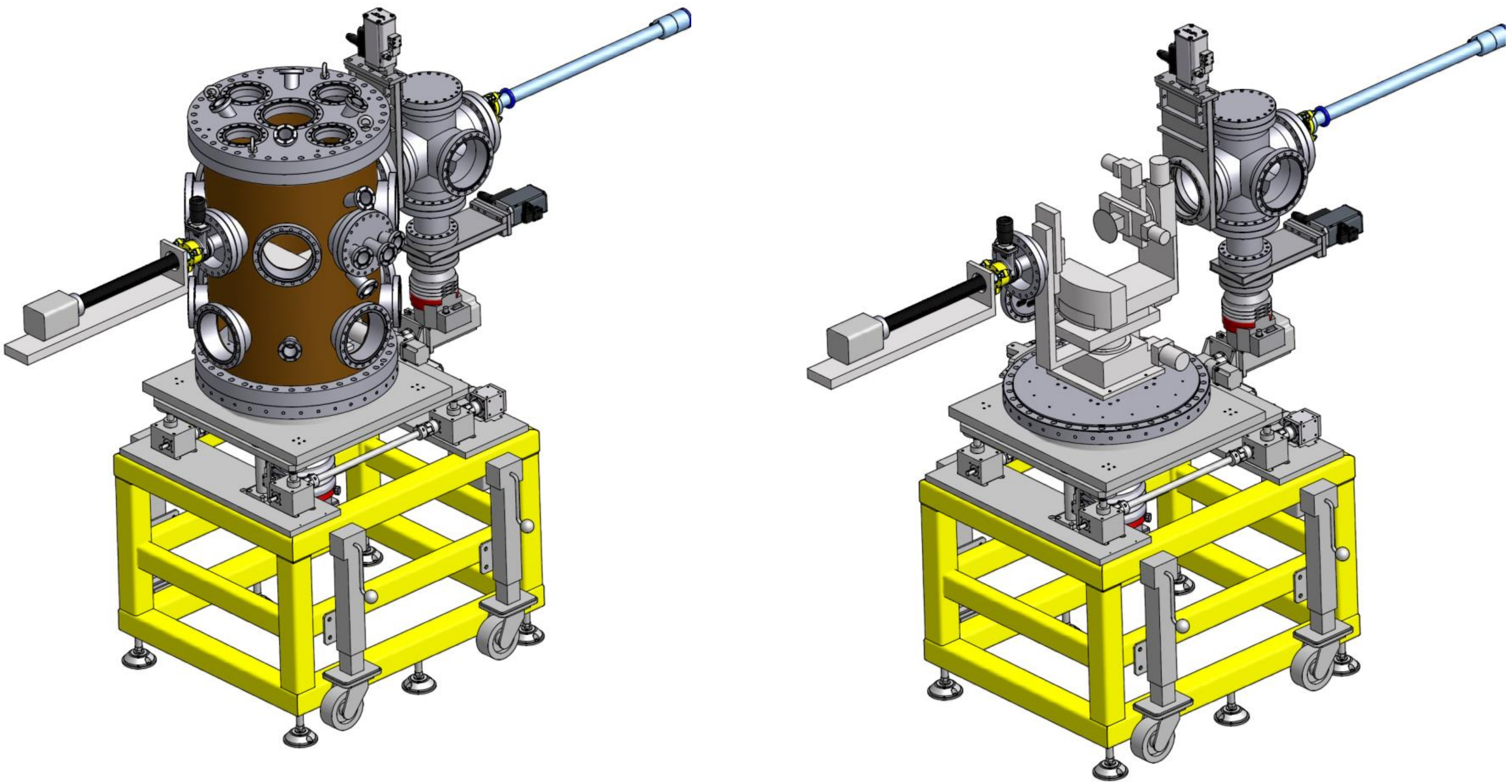
X-ray Detectors:
Ultra Thin Window (UTW) Bruker Silicon Drift detector ($30\ mm^2$, FWHM 130 eV @ Mn-Ka), photodiodes and other beam monitoring devices

A high performance x-ray tube was mounted on a flange of the UHVC allowing to use this end-station as a standalone device



The ‘Theta’ axis would provide an accuracy better than 0.15mrad in the range of -5-110 degrees

The IAEA integrated XRS end station



The IAEA Ultra High Vacuum Chamber (UHVC) is based on a prototype design by Physikalisch - Technische Bundesanstalt (PTB, Berlin)* with the assistance of the the Technical University of Berlin (TUB)

***Janin Lubeck et *al*, A novel instrument for quantitative nanoanalytics involving complementary X-ray methodologies, Rev. Scientif. Instrum. 84 (2013) 045106-7**

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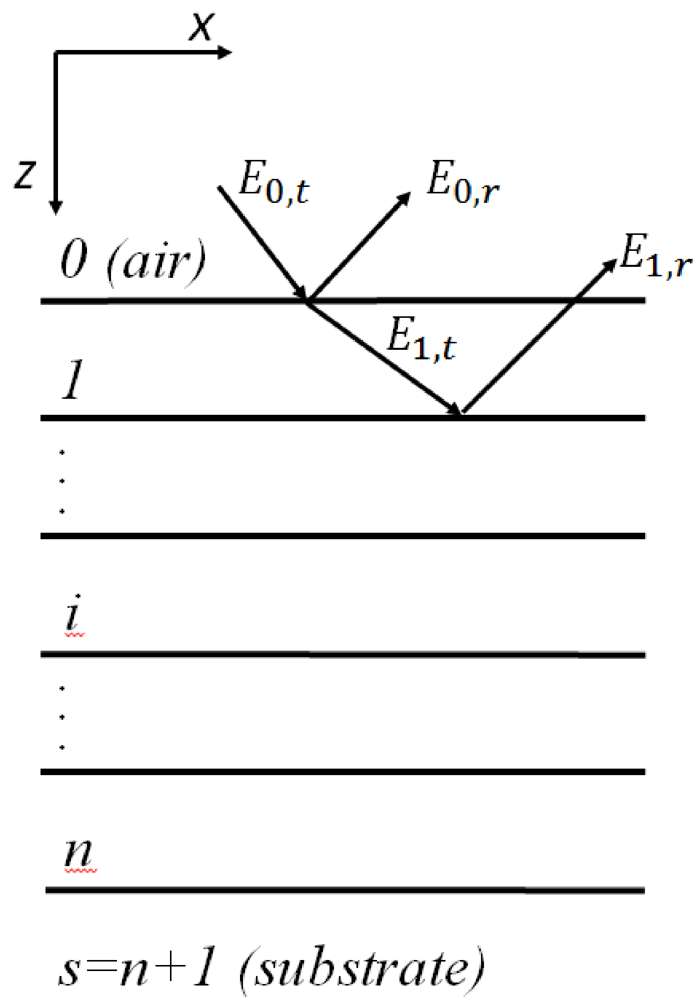
XRF Beamline@ Elettra Sincrotrone, Trieste

Energy Range (excitation)	2000 - 14000 eV
Beam size (at exit slits)	250 µm (hor) X 50 µm (vert)
Beam divergence (at exit slits)	0.15 mrad
Flux @5.5 keV (2 GeV) or 7 keV (2.4 GeV)	5 10^9 ph/s (theory)
Monochromator	Si (111), InSb, Multilayers
Resolving power	DE/E: 1.5 10^{-4} (Si(111))
Source	Bending Magnet

XRF Beamline team: D. Eichert, W. Jark, L. Luhl
Diane.Eichert@Elettra.eu

Elettra Sincrotrone Trieste

Theory (Parratt's formalism)



Schematic diagram for stratified media

$$E_j(r) = E_j exp\left[i\left(w \times t - \vec{k}_j \overrightarrow{\times r}\right)\right]$$

$$k_{j,x} = \frac{2\pi}{\lambda} cos\theta \qquad k_{j,z} = \frac{2\pi}{\lambda}\left(\varepsilon_j - cos^2\theta\right)^{1/2}$$

$$\varepsilon_j = n_j^2 \approx 1 - 2\delta_j - i2\beta_j$$

n_j - refractive index can be calculated directly from **Xraylib**:

float **Refractive_Index_Re**(const char compound[], float E, float density)
float **Refractive_Index_Im**(const char compound[], float E, float density)

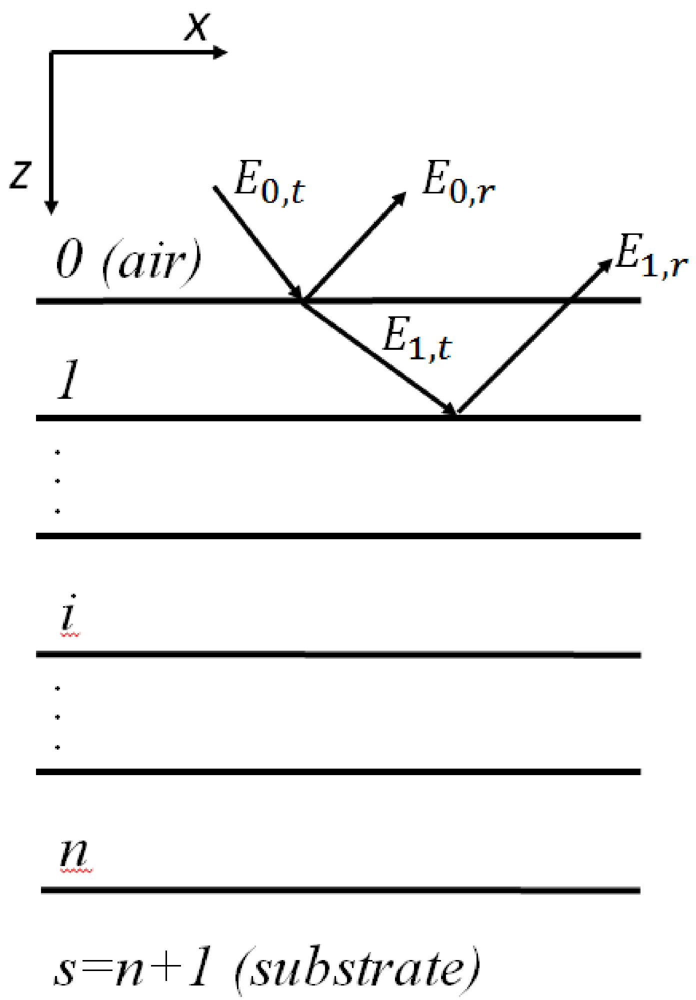
The sign convention is IMPORTANT!

Fresnel coefficients for each interface:

$$r_j = \frac{k_{j,z} - k_{j+1,z}}{k_{j,z} + k_{j+1,z}}$$

$$t_j = \frac{2k_{j,z}}{k_{j,z} + k_{j+1,z}}$$

Theory (Parratt's formalism)



Schematic diagram for stratified media

Recursive method:
The transmitted (E_j^t) and reflected (E_j^r) field amplitudes at the top of layer *j*

$$E_j^r = a_j^2 X_j E_j^t$$

$$E_{j+1}^t = \frac{a_j E_j^t t_j}{1 + a_{j+1}^2 X_{j+1} r_j}$$

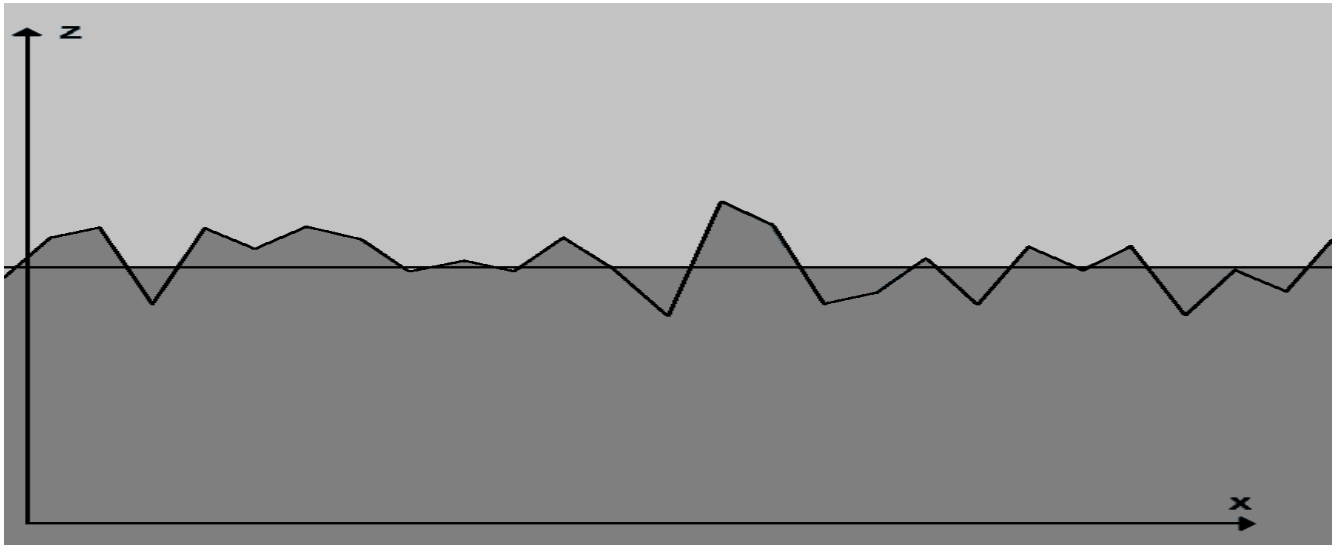
$$X_j = \frac{\left(r_j + a_{j+1}^2 X_{j+1}\right)}{1 + a_{j+1}^2 X_{j+1} r_j}$$

$$a_j = \exp(-ik_{j,z} d_j)$$

The **reflectivity** (***R***) is found from:

$$R(\theta) = \left|\frac{E_0^r}{E_0^t}\right|^2$$

Roughness: how to deal with imperfect surfaces?



Debye-Waller approximation: $\tilde{r}_j = r_j S_j$, where $S_j = exp\left[-2\sigma_j^2 k_{j,z} k_{j+1,z}\right]$

Appliccable only to small roughness values (0-2 nm)

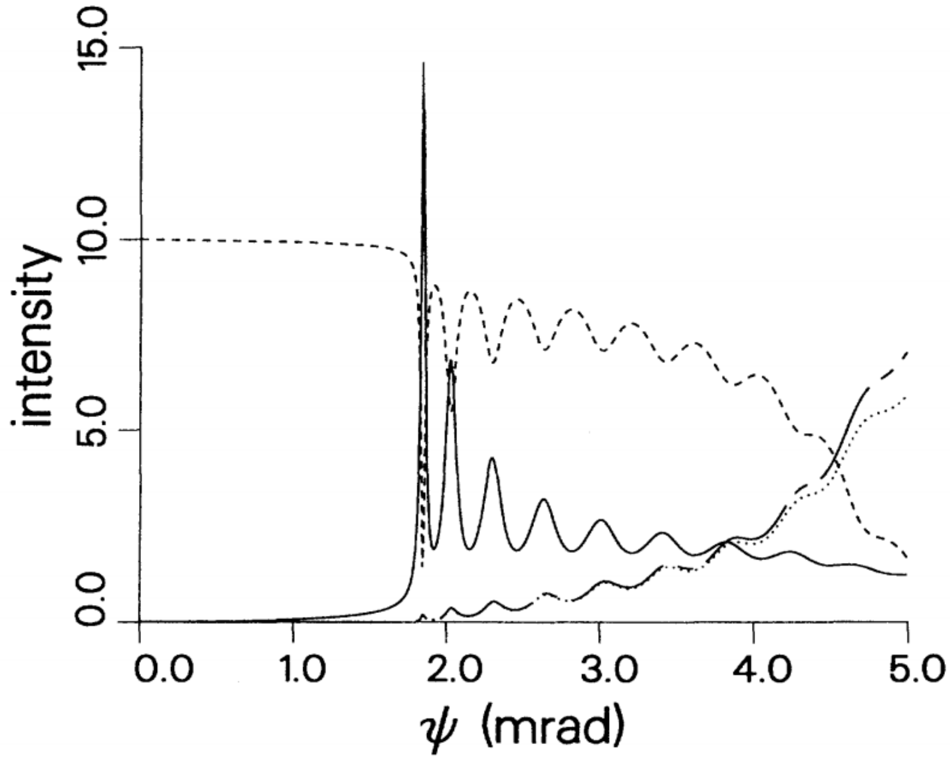
Nevot-Croce approximation: $\tilde{r}_j = r_j S_j$ and $\tilde{t}_j = t_j T_j$, $where\ T_j = \frac{exp\left[\sigma_j^2 (k_{j,z} - k_{j+1,z})^2\right]}{2}$

GIXRF

Fluorescence intensity: element *x*

$$I_x(\theta) = \sum_i \left(exp\left[-\sum_{j<i} \frac{\left(\mu/\rho\right)_{j,E} \rho_j d_j}{sin\varphi} \right] \cdot I_{i,x}(\theta) \right)$$

$$I_{j,x}(\theta) = I_0 G S_{x,E_0} \varepsilon_{det} T_{air} \int_0^{d_j} c_x(z) \frac{\left|E_j^r + E_j^t\right|^2}{\left|E_j^t\right|^2} \, exp\left(-\left[\frac{\left(\mu/\rho\right)_E}{sin\varphi} \right] \rho z \right) dz$$



D.K.G. de Boer, *PRB*, **44**, 1991, 498

Fitting: Differential evolution

Differential Evolution is an heuristic optimizer developed by Rainer Storn and Kenneth Price

Storn, R.; Price, K. , *Journal of Global Optimization* **11**, 1997, 341–359

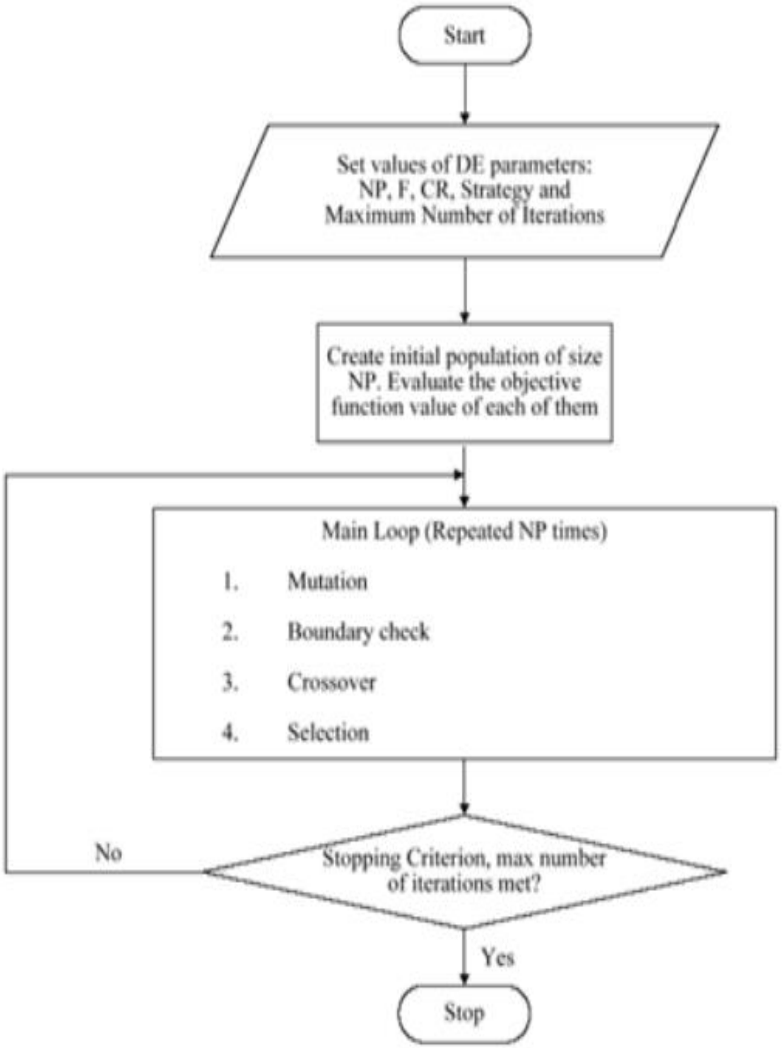
GIXRF/XRR data:

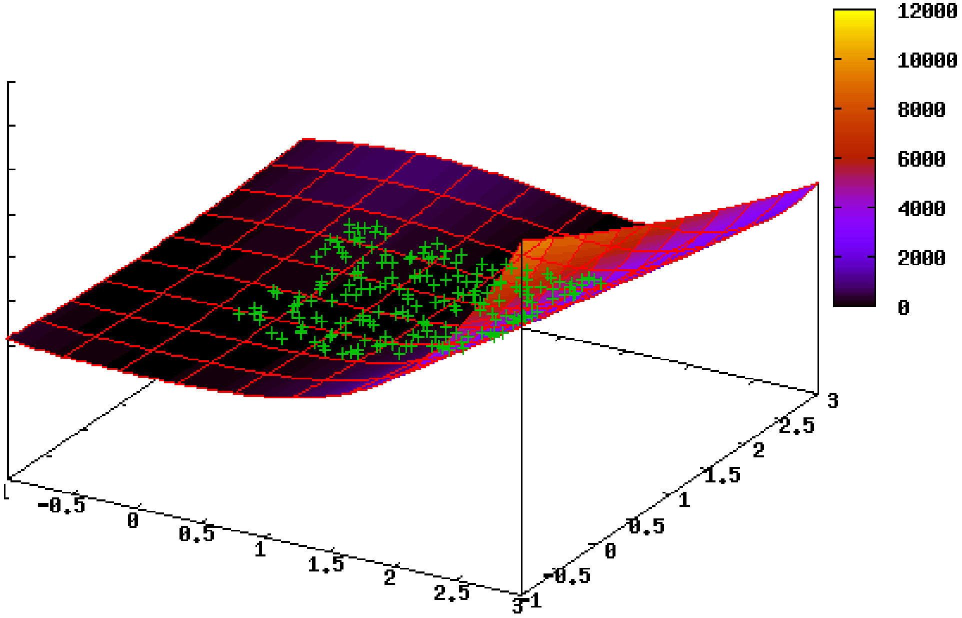
- Many parameters to fit
- Many local minima

Genetic algorithms:

- Allow to find the global minimum
- No need to know derivatives
- The convergence could be unstable (might need more than one run)

Fitting: Differential evolution

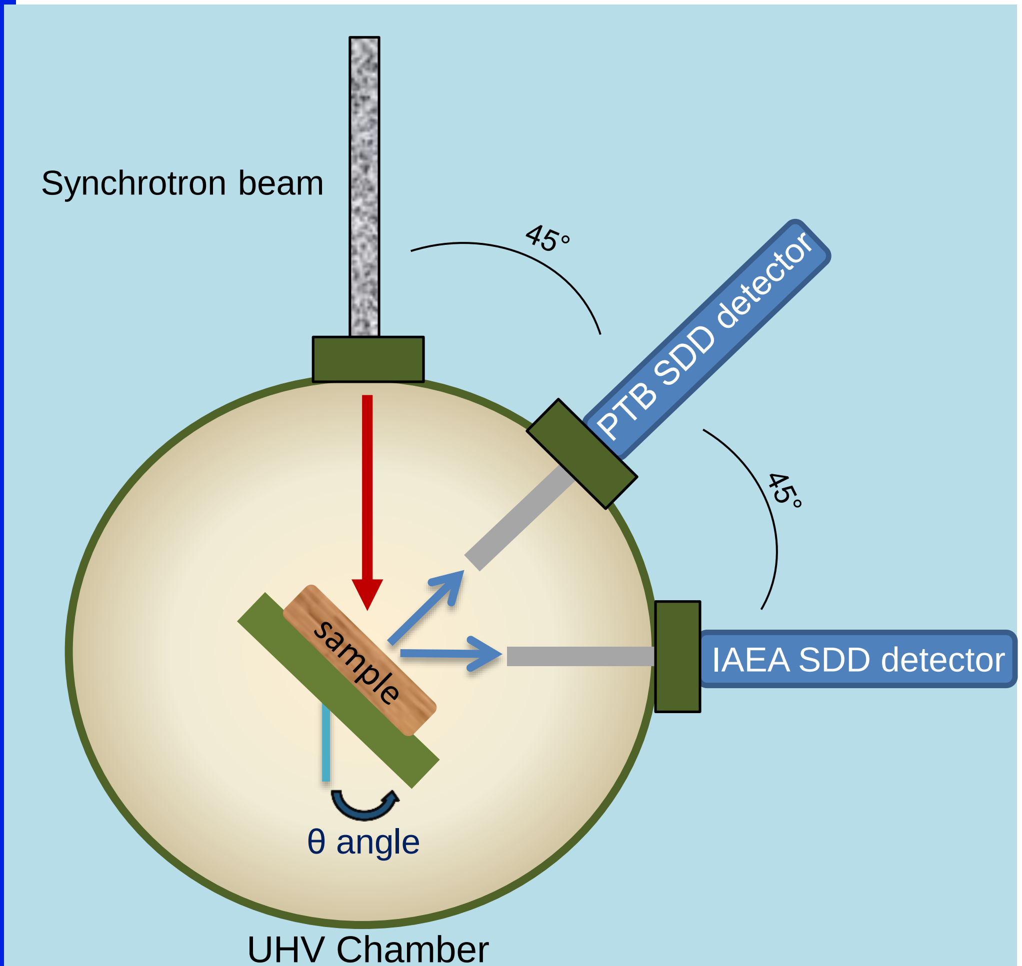




Flow chart of a DE algorithm

1st phase of commissioning at PTB, May-August 2013

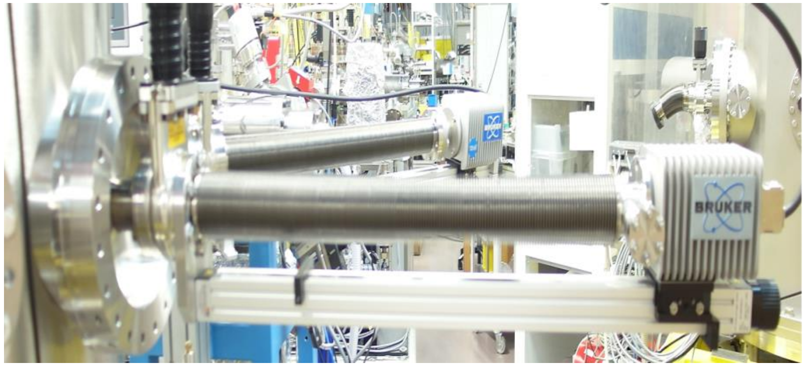
- First measurements and alignment tests at the PGM beamline of BESSY II
- Experimental setup



Measurements at conventional XRF geometry and GI conditions (scan of θ angle from 0^{o} to $10\ ^{o}$).

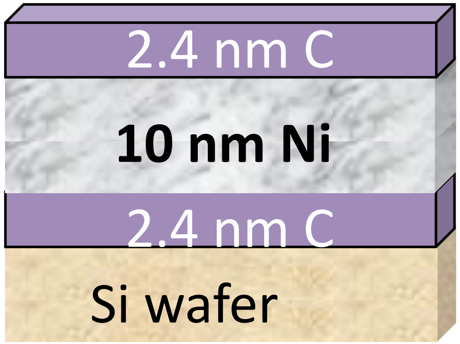
Distance sample-detector ~ 5 cm.

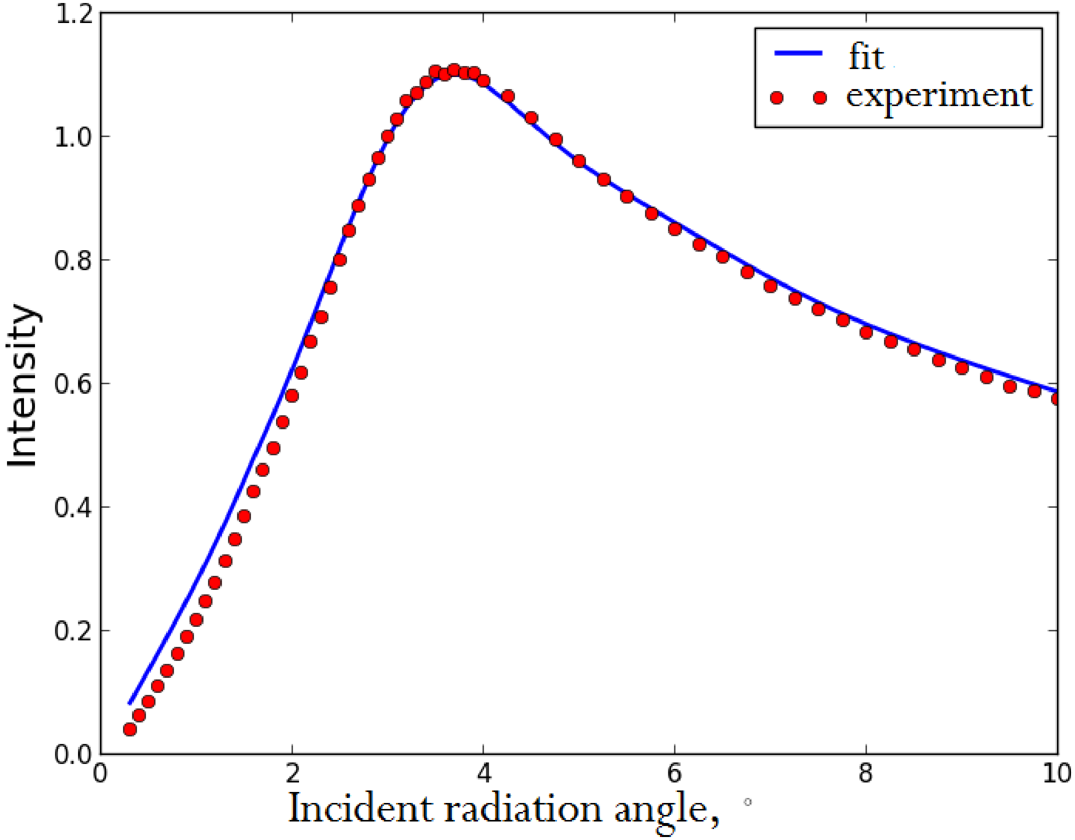
Incident photon energy **1060 eV**



1st phase of commissioning at PTB, May-August 2013

Analysis of stratified nano-structured samples (August 2013)

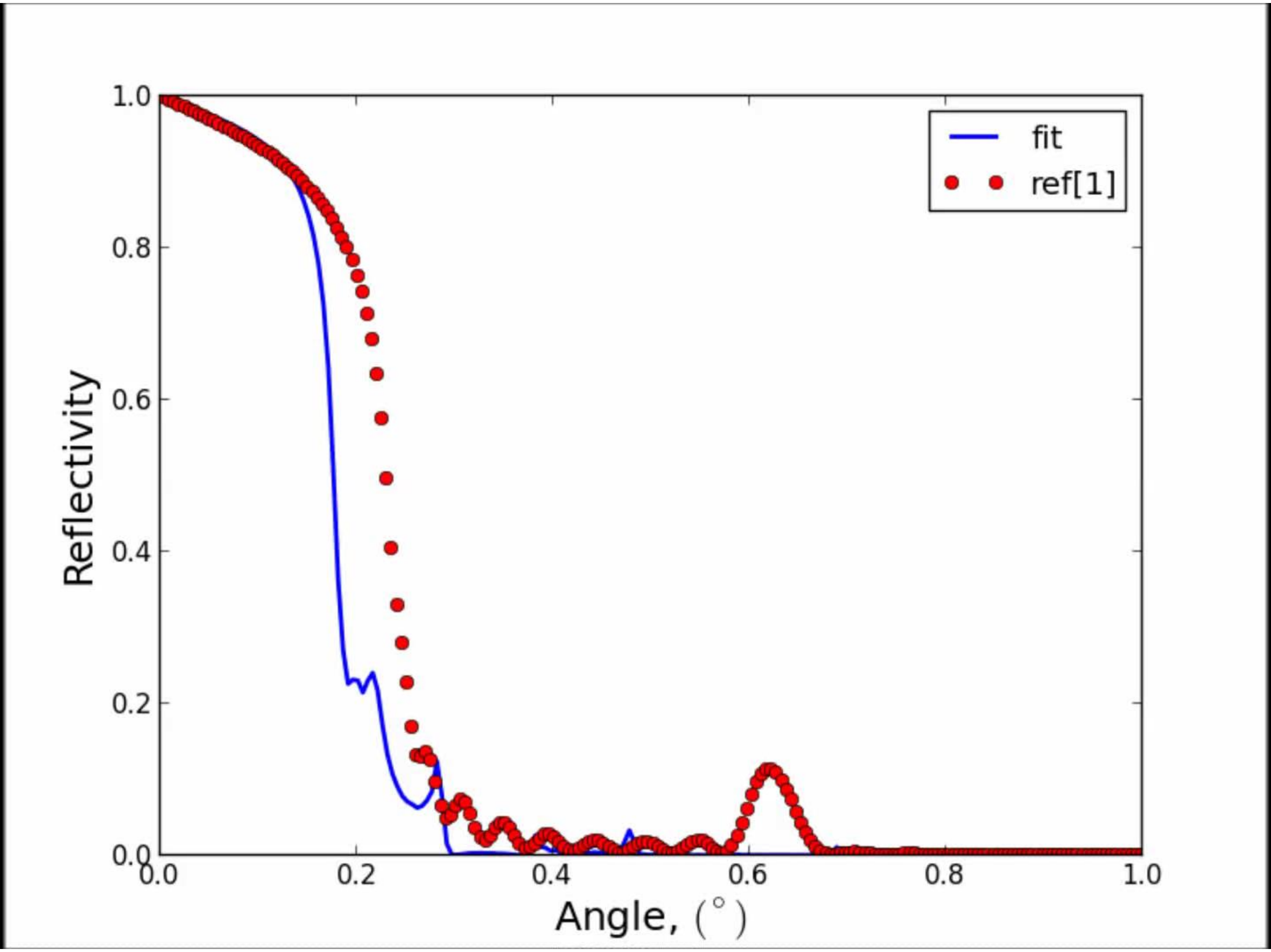




Ni-L line intensity vs incident SR angle (experiment + theory)

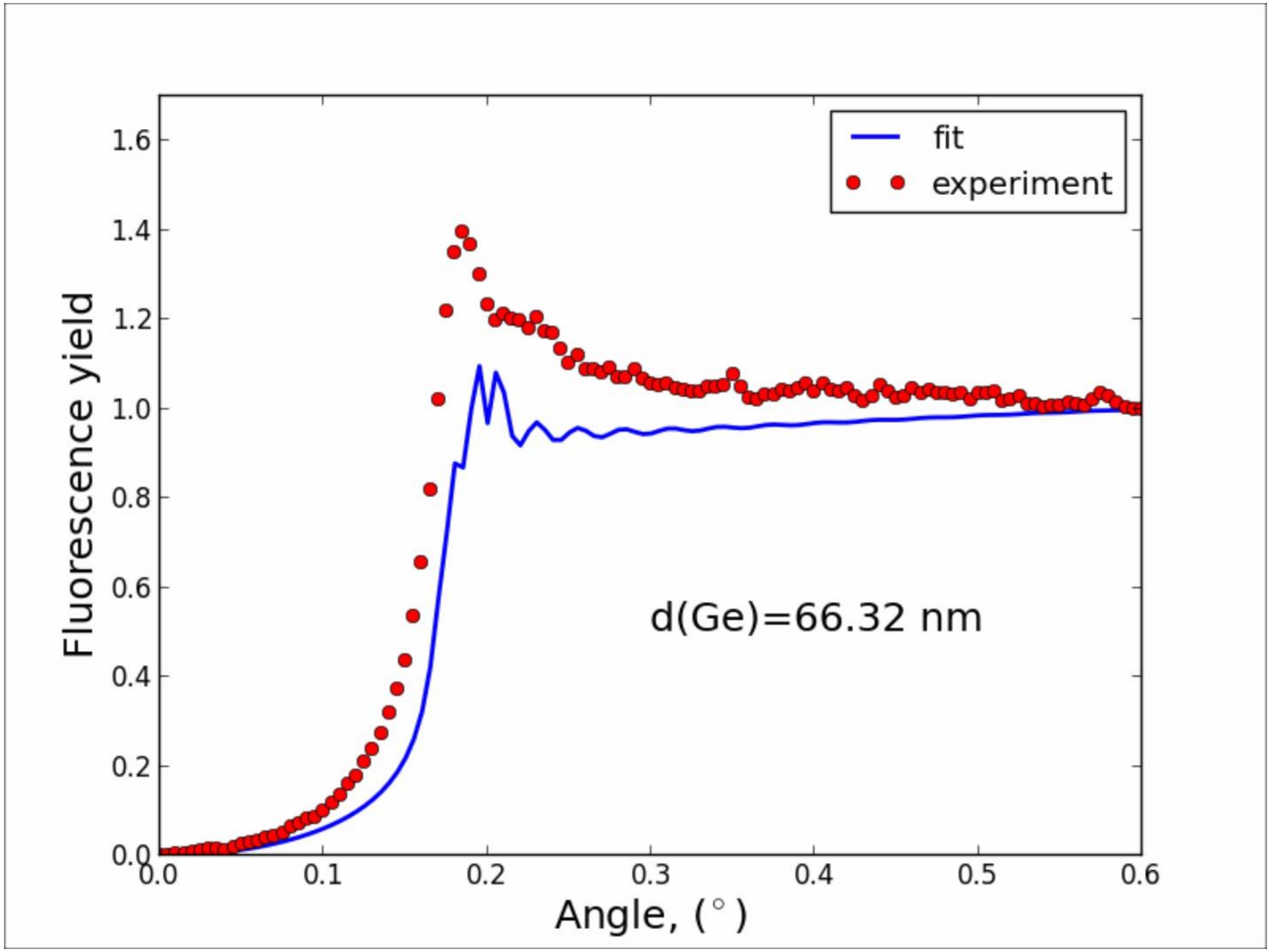
(Preliminary results: first GI experiment)

Relectivity ([Au(2 nm)/Co(1.5 nm)]$_{20}$/Si @ 17.4 keV)



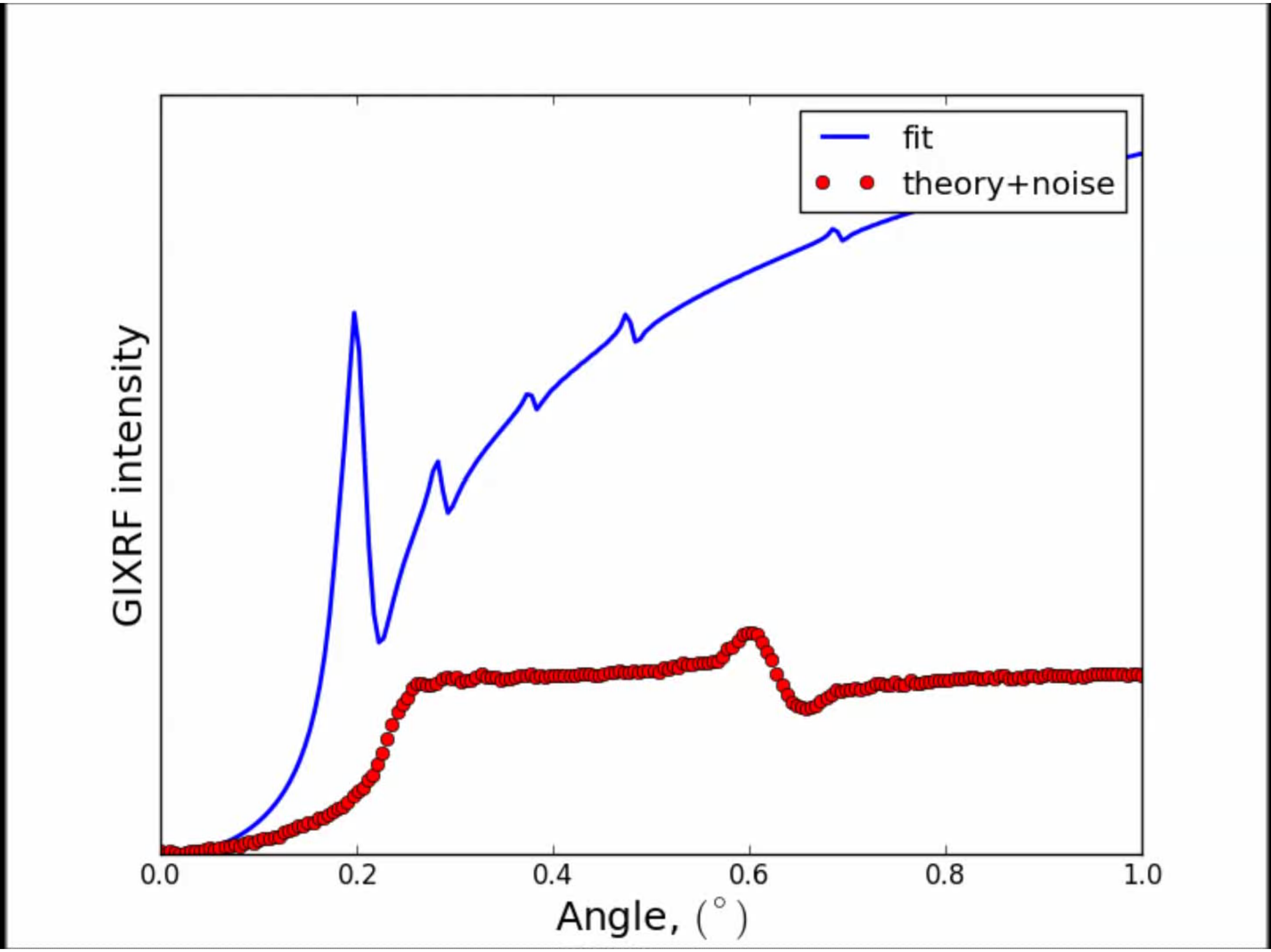
[1] D.K.G. de Boer, *PRB*, **44**, 1991, 498

Example Ge(29 nm)/Si at 15.2 keV



M. Krämer, PhD thesis

Example ([Au(2 nm)/Co(1.5 nm)]$_{20}$/Si @ 17.4 keV)



Remarks

- We used Parratt's recursive algorithm to calculate GIXRF/XRR intensities and DE to fit the experimental data. This allowed us to characterize the first measurements obtained with the new UHVC end-station of IAEA-Elettra

- The results showed an acceptable agreement with the experiment. Further improvements are under development

Thank you for your attention!