

# Laboratoire de Chimie Physique – Matière et Rayonnement

*Philippe JONNARD*

*Activités de l'équipe*

*“Interfaces, Multimatériaux, Sources et  
Optiques X”*

*Sorbonne Universités, UPMC Univ Paris 06, LCPMR, Paris, France  
CNRS UMR 7614, LCPMR, Paris, France*



## Equipe IMSOX

### « Interfaces, Multimatériaux, Sources et Optiques X »

<https://lcpmr.cnrs.fr/content/interfaces-multimatériaux-sources-et-optique-x>

## Laboratoire de Chimie Physique - Matière et Rayonnement

### Département/UFR de Chimie

### Faculté des Sciences et Ingénierie

### Sorbonne Université

(fusion Paris VI – Paris IV au 1<sup>er</sup> janvier 2018)

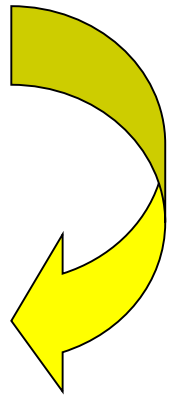
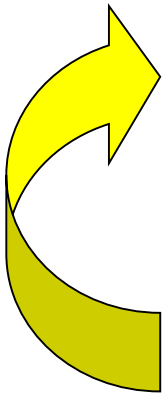


# Topics

## IMSOX team

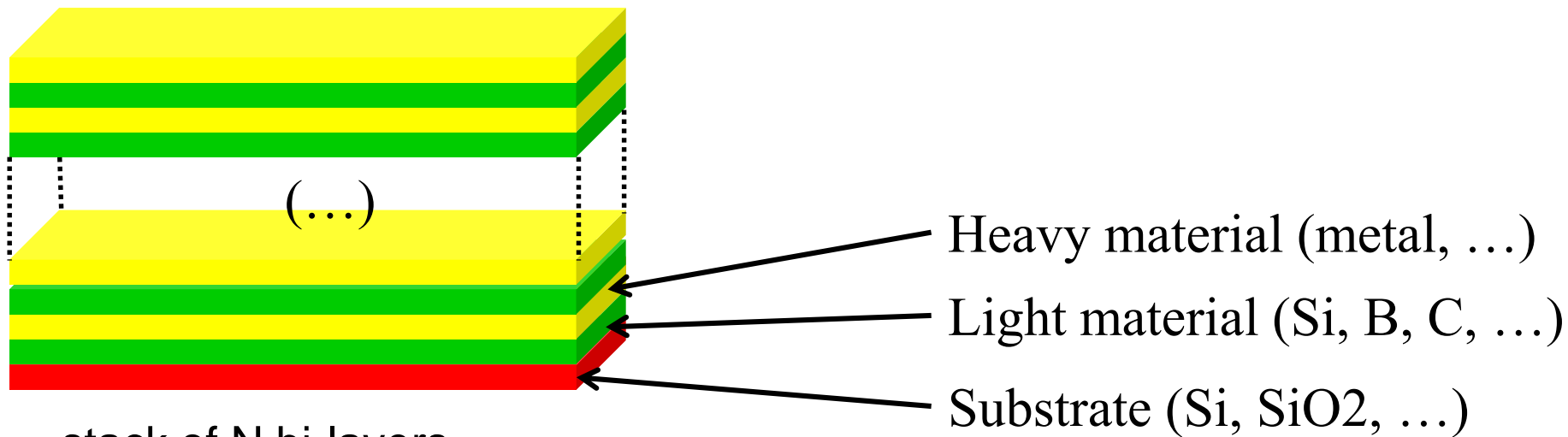
Characterization of  
nanometric multimaterials  
by x-ray spectroscopy and x-ray optics

Development of  
spectroscopic and optical devices  
for materials characterization



# Periodic multilayers for EUV and X-ray ranges

Extreme UV : 20 – 200 eV      0.6 – 6 nm  
Soft x-ray :    200 – 5000 eV    0.25 – 0.6 nm



stack of N bi-layers

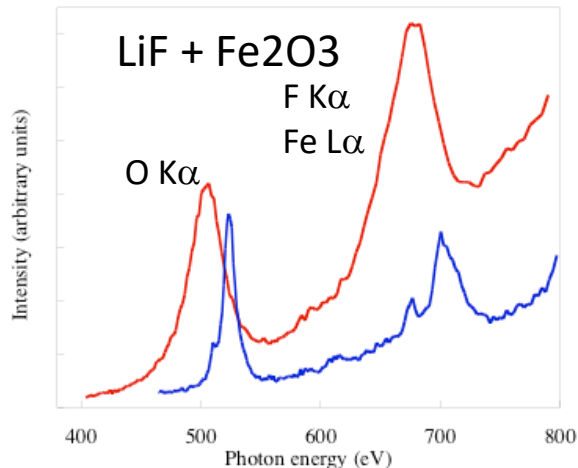
$\text{thickness\_light} + \text{thickness\_heavy} = \text{period } d \text{ of a few nm}$

↳ can diffract EUV and x-rays

**Bragg law :  $p\lambda = 2d \sin\theta$**

# Applications of multilayers

- Solar images from spatial telescopes
- Photolithography @ 13.5 nm
- Optical components for synchrotron beamlines
- Optical components for new x-ray sources (x-ray laser, high harmonic generation, ...)
- Optics for diffraction apparatus



X-ray emission spectroscopy

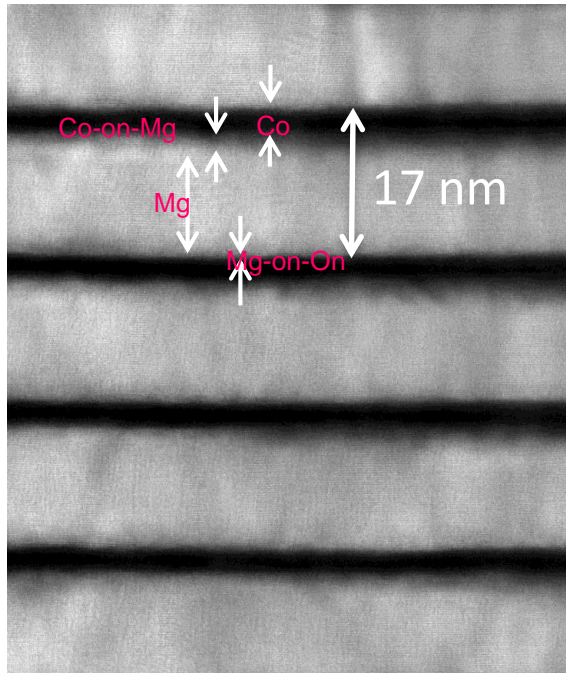


Imaging at a given wavelength

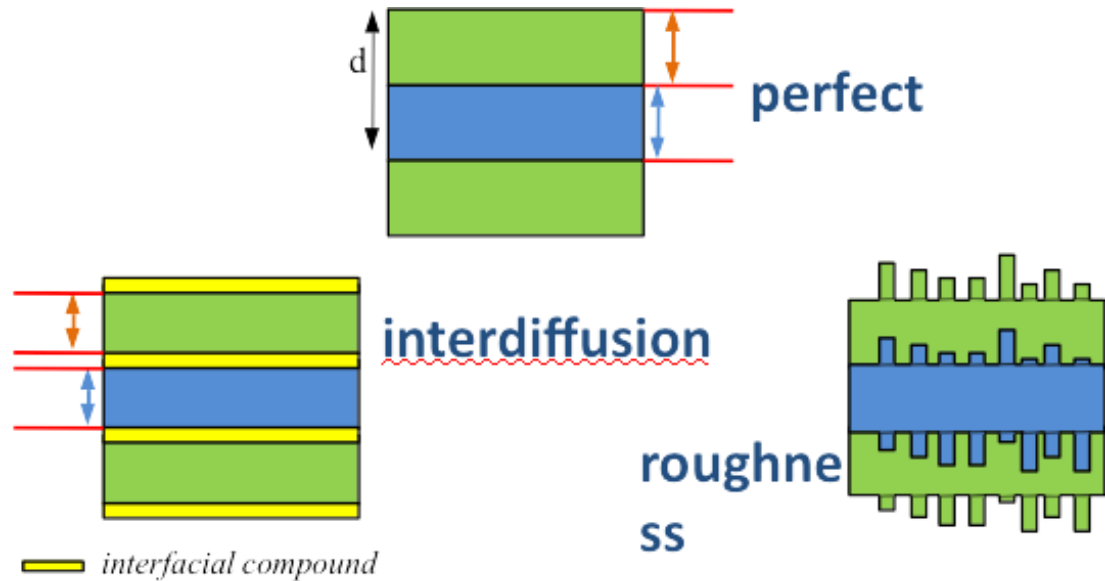


Photolithography  
@ 13.5 nm, 6.x nm

# Motivation and challenges



Co  
Mg  
Co  
Mg  
Co  
Mg

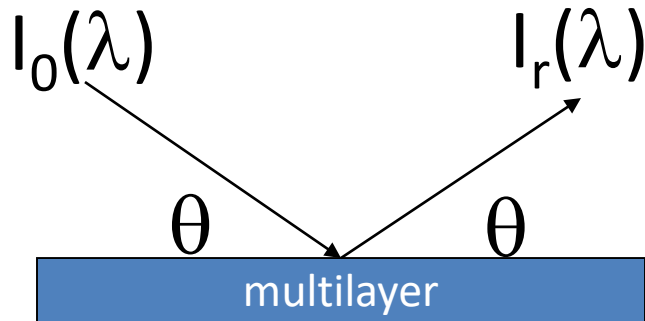


	Visible $\lambda=500\text{nm}$	EUV $\lambda=30.4\text{nm}$
d	$\sim 125\text{nm}$	Co_2.6nm/Mg_13.6nm
$\sigma$	$\sim 10\text{ nm}$	$\sim 0.5\text{-}0.8\text{nm}$

R multiplied by **DW factor**  
 $\exp(-2[2\pi \sigma \sin\theta / \lambda]^2)$   
 $\exp(-2[\pi \sigma / d]^2)$

Interface is the largest challenge for EUV multilayer!

# X-ray reflectivity

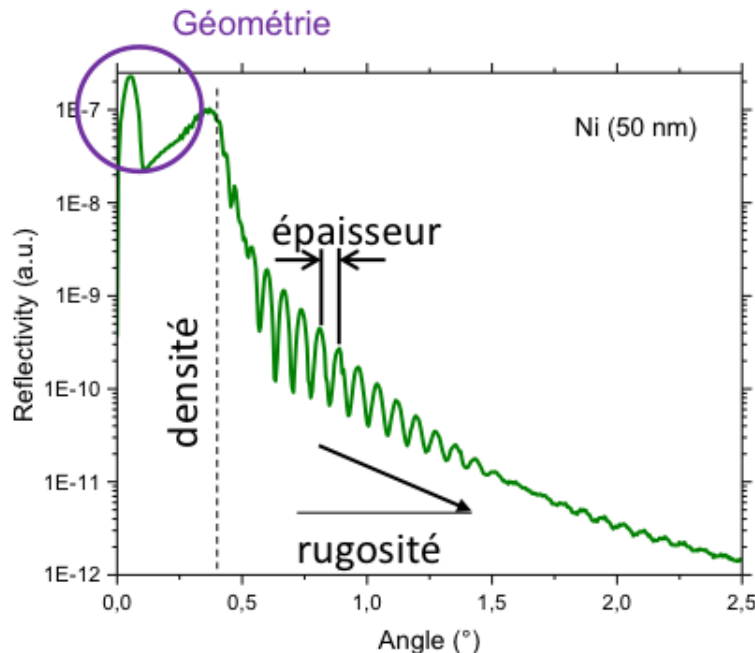


$$R_{\theta} = I_r(\lambda) / I_o(\lambda)$$

$$R_{\lambda} = I_r(\theta) / I_o(\theta)$$

$$2d \sin\theta = p \lambda$$

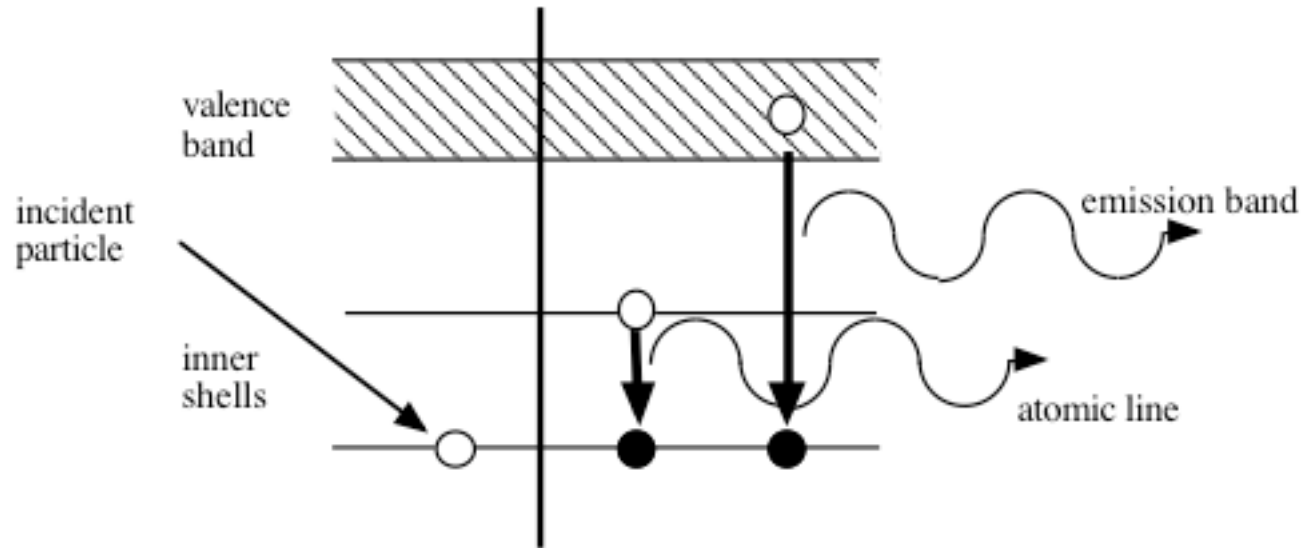
Bragg law



Determination of parameters  
of the stack

- thickness
- roughness
- density / optical index  
of the various layers

# X-ray emission spectroscopy



Observation of the energy distribution of the emitted radiation  
Information about the **chemical state of the emitting element**

Incoming beam

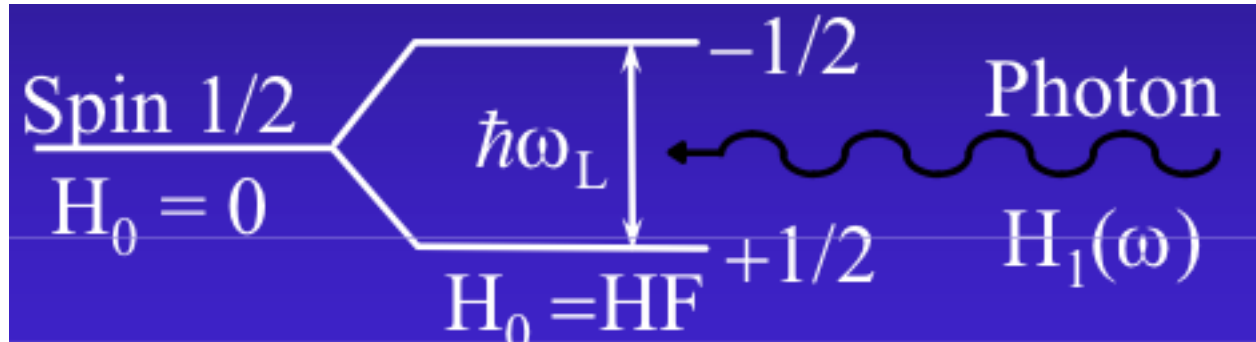
- **Electrons**
- Particles
- X-rays

Detection / dispersion

- **WDS : crystal spectrometer**
- EDS : Si(Li), SDD, bolometer



# NMR spectroscopy

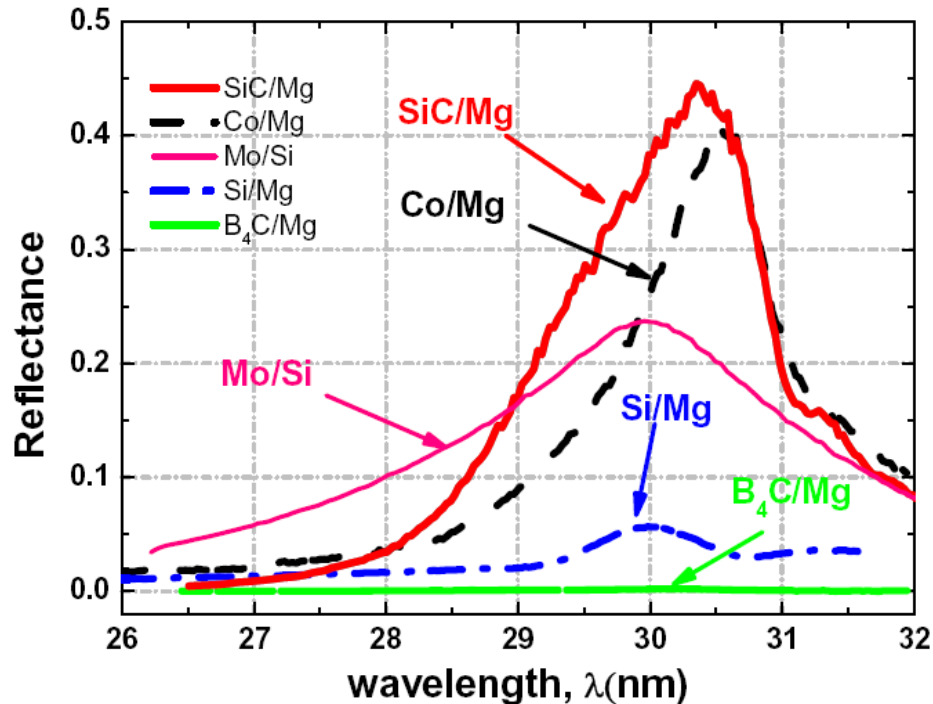


HF: hyperfine field

In ferromagnets, the magnetic field  $H_0$  is the field inside the material on the nuclei sites (20 T for Co nuclei in bulk Co)

The HF strength depends on the local symmetry and local chemical environment of the probed nuclei: nearest neighbour local structure and/or local chemical environment.

# Mg/Co multilayers (1)



- Design

Si / [Co (2.67 nm)/Mg (13.61 nm)]x30

- Fabrication

Deposition by DC-MS

Ultra-smooth Si substrates ( $\sigma \sim 0.3$  nm)

High purity sputtering targets

High purity sputtering gas

High precision deposition rates

- Measurement

High reflectivity: 40.3%

Narrow band-width: 1.32 nm

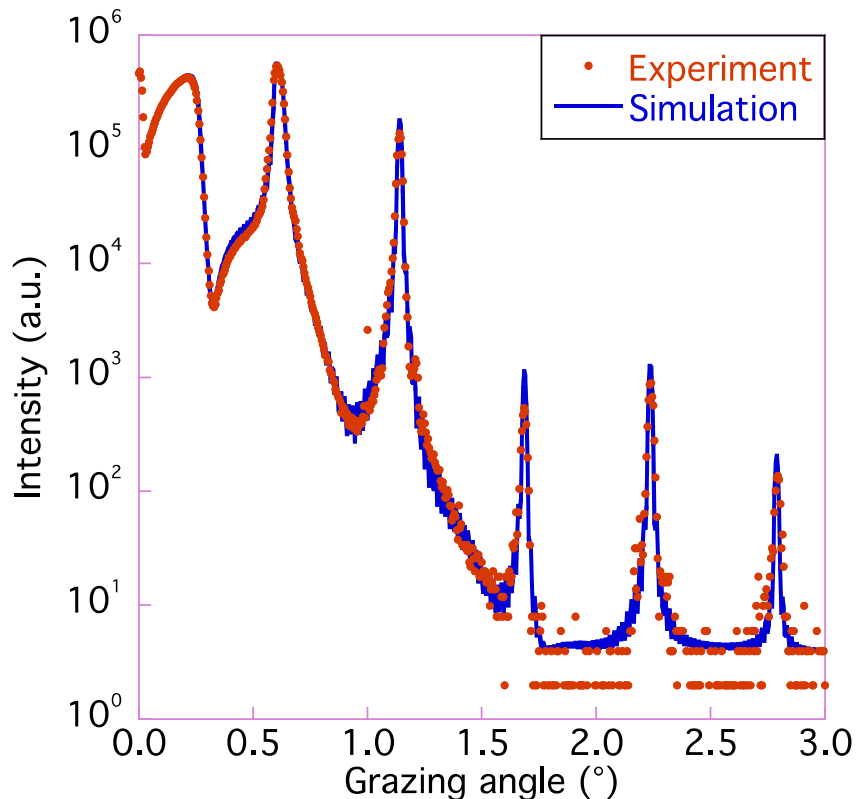
Co/Mg is a promising multilayer for EUV applications

# Mg/Co results (2)

## Design

Si substrate / [Co (2.55 nm)/Mg (14.45 nm)]x30/ B<sub>4</sub>C (3.5 nm)

B<sub>4</sub>C: capping layer to prevent oxidation



**R<sub>sim</sub> = 56.5% @ 25.2 nm (49.2 eV)**  
**45° s-pol**

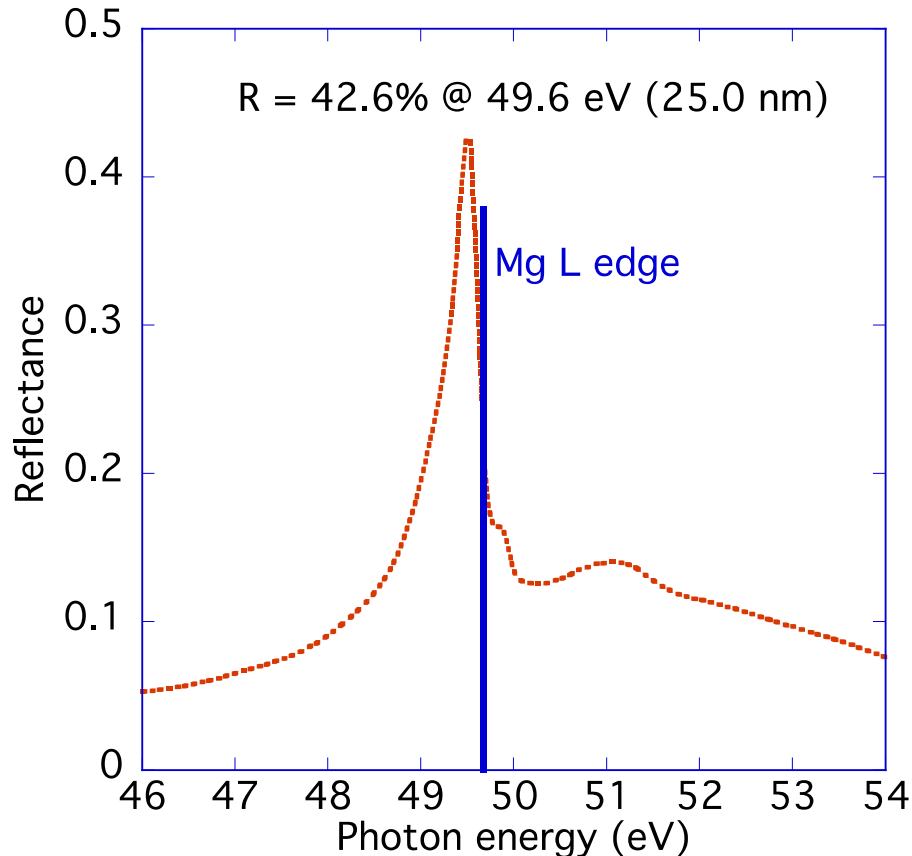
for perfect multilayer: without  
roughness or interdiffusion

## X-ray Reflectivity

- High structural quality
- Thickness close to the design
- Interfacial roughness 0.6 nm

# Mg/Co results (3)

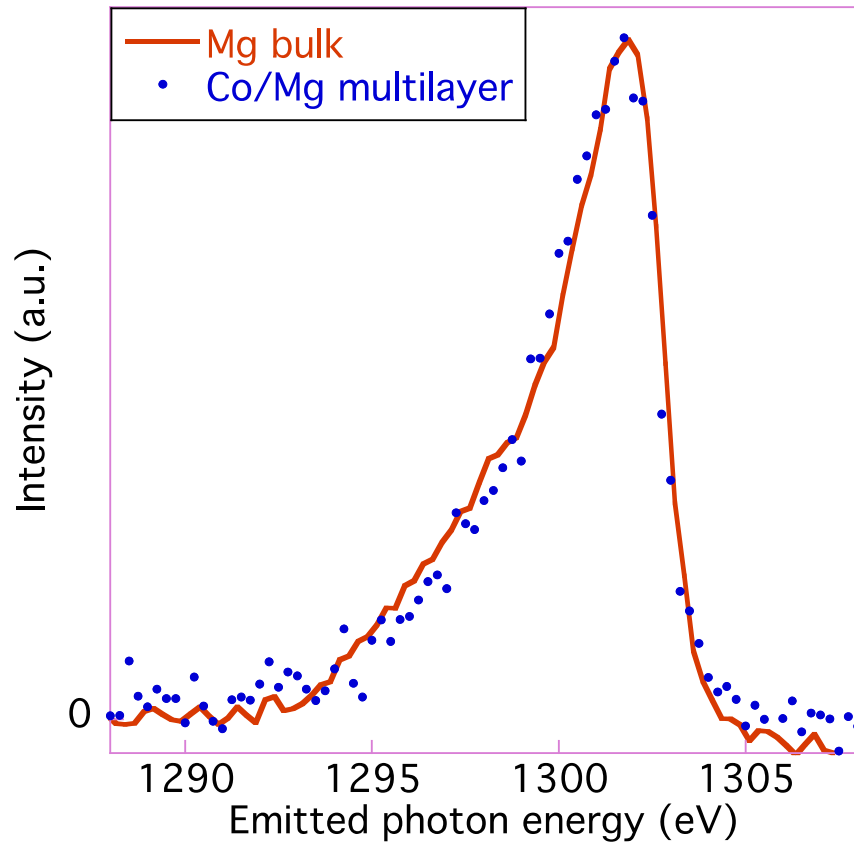
EUV reflectivity



- High reflectance
- 75% of the value simulated for perfect multilayer
- Asymmetrical peak owing to Mg L edge

# Mg/Co results (4)

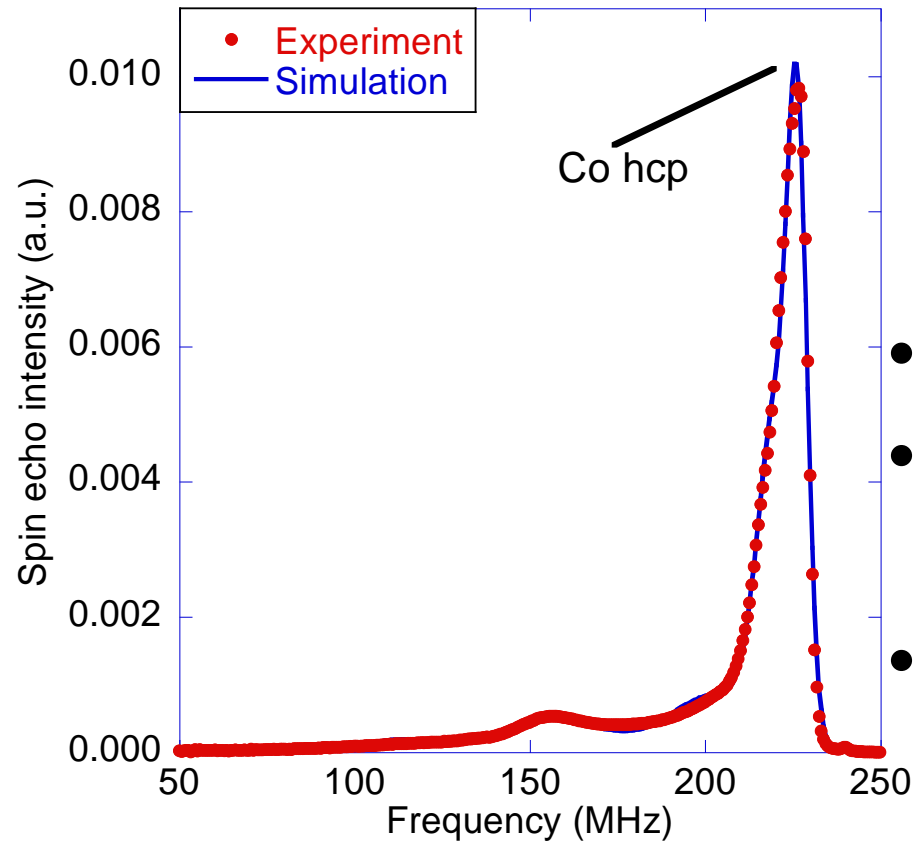
## X-ray Emission Spectroscopy



- Mg atoms as in pure Mg
- No interaction between Mg and Co layers

# Mg/Co results (5)

## Nuclear Magnetic Resonance Spectroscopy



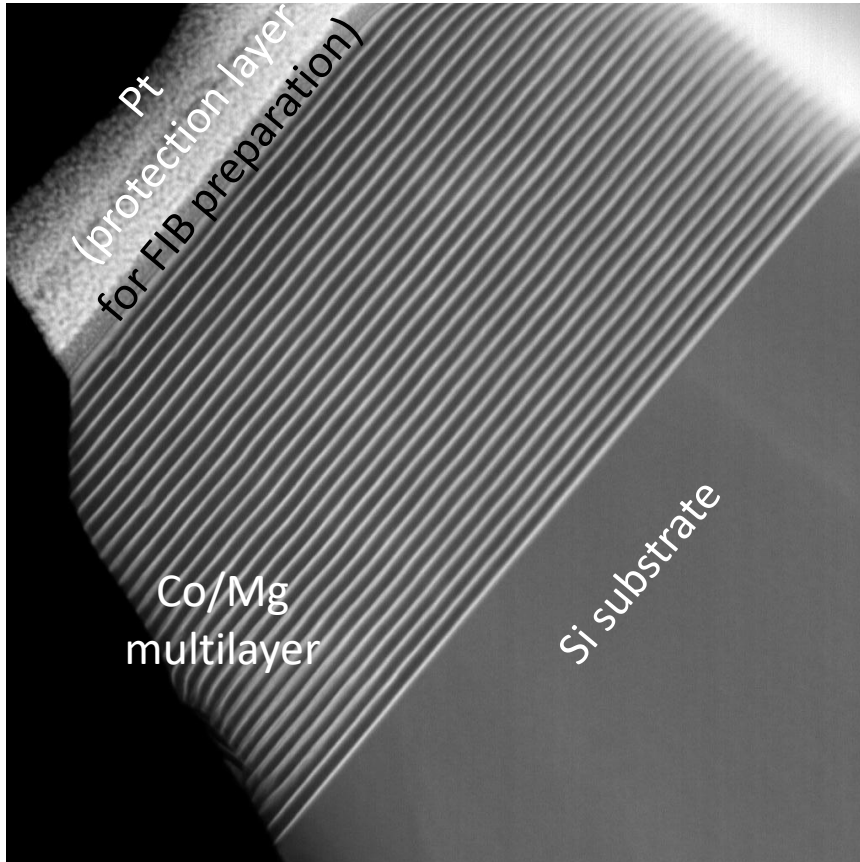
- Co atoms as in pure Co
- No interaction between Co and Mg layers
- Faint peak due to Co atoms in contact with the Mg layer

# Mg/Co results (6)

High-resolution images  
Co and Mg layers crystallized

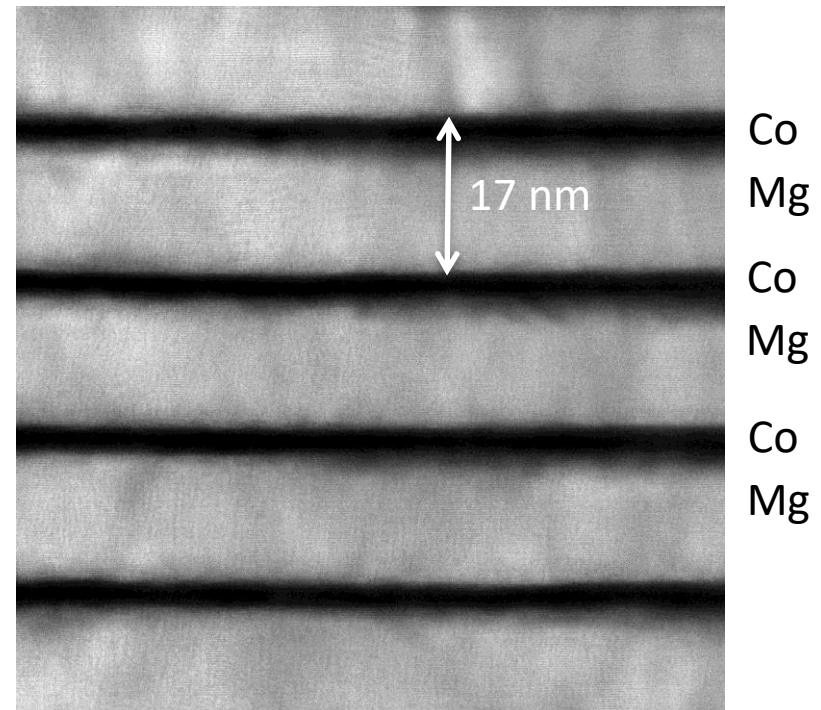
EELS

Abrupt interfaces



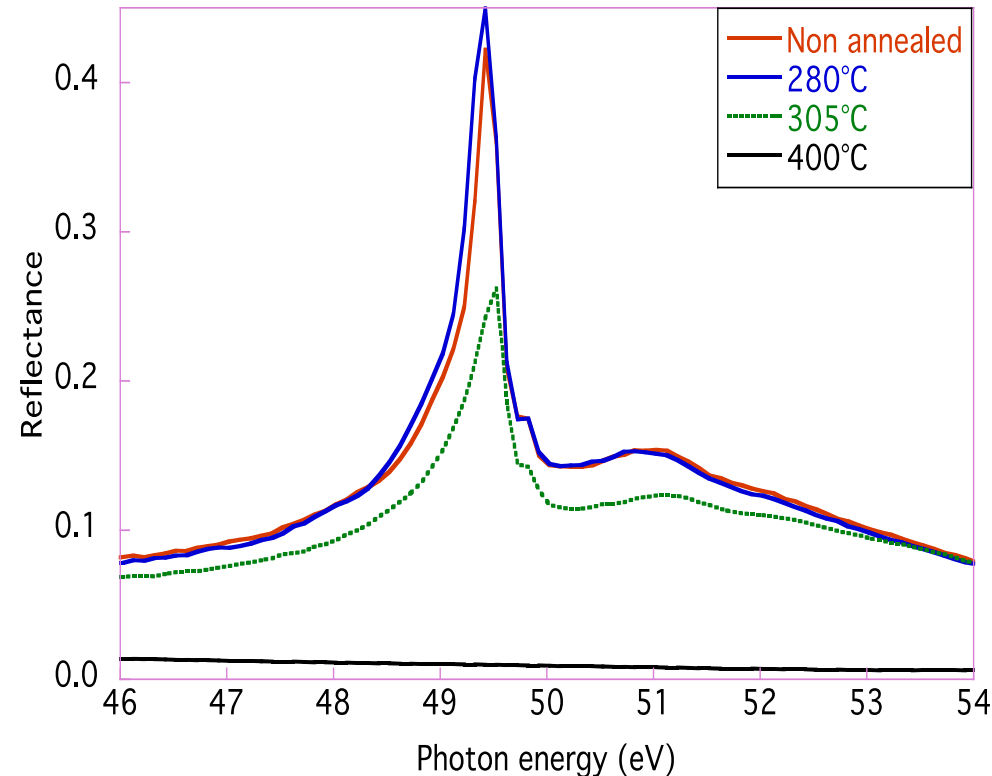
TEM 100 keV

Sample prepared by focused ion beam  
Thinning down to  $\approx 40$  nm



# Mg/Co results (annealing)

EUV reflectivity



- Stable up to 280° C
- R divided by 2 after 305° C
- No more reflectivity after 400° C



# Mg/Co results (annealing)

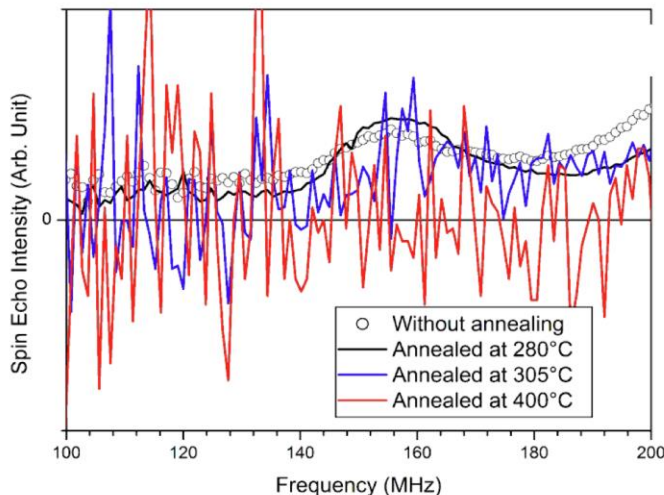
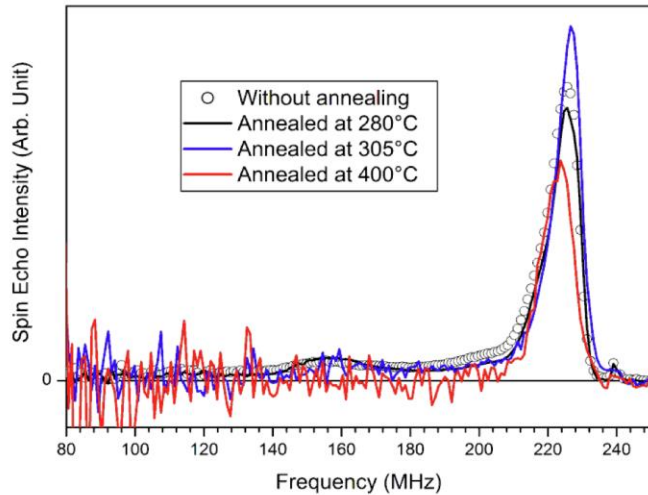
## Nuclear Magnetic Resonance Spectroscopy



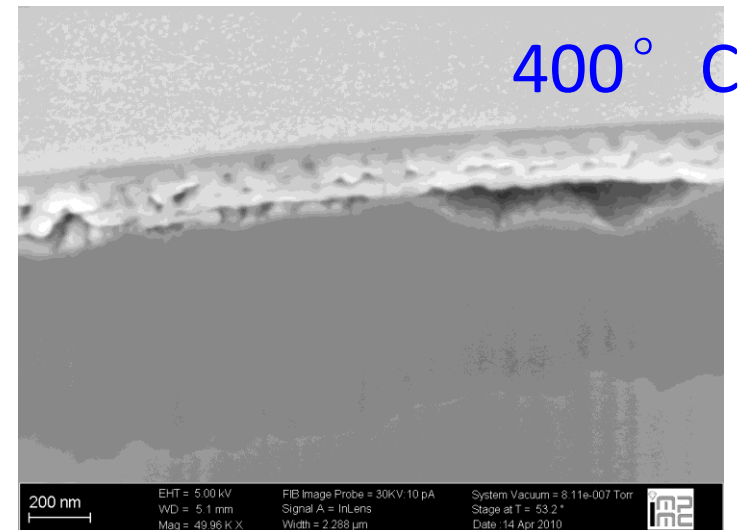
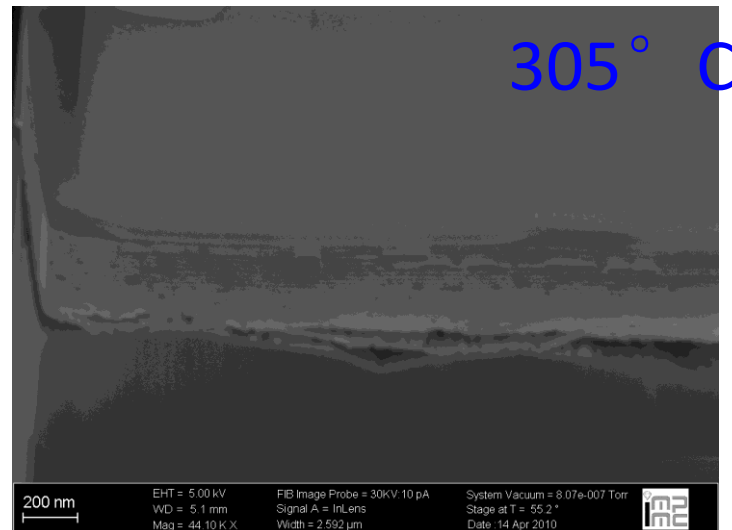
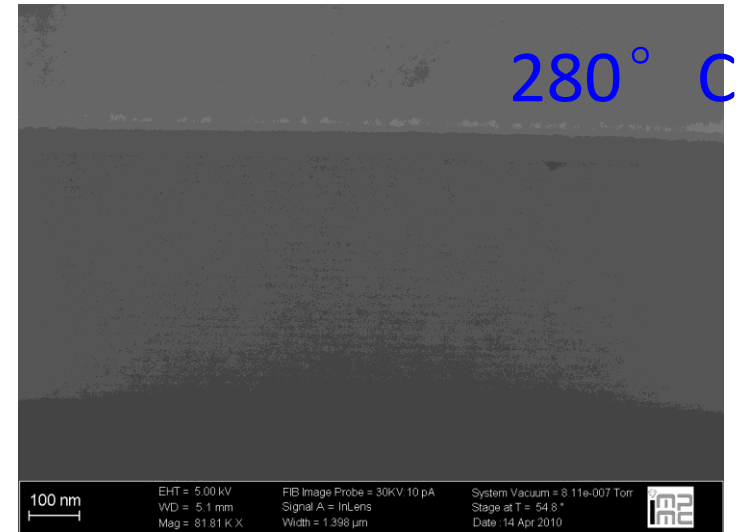
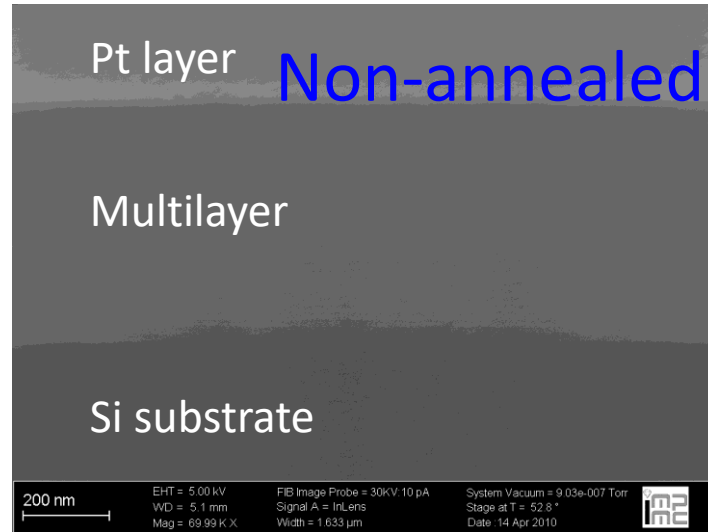
- Co atoms as in pure Co
- No more interfacial Co atoms

## XES

- Mg atoms as in pure Mg

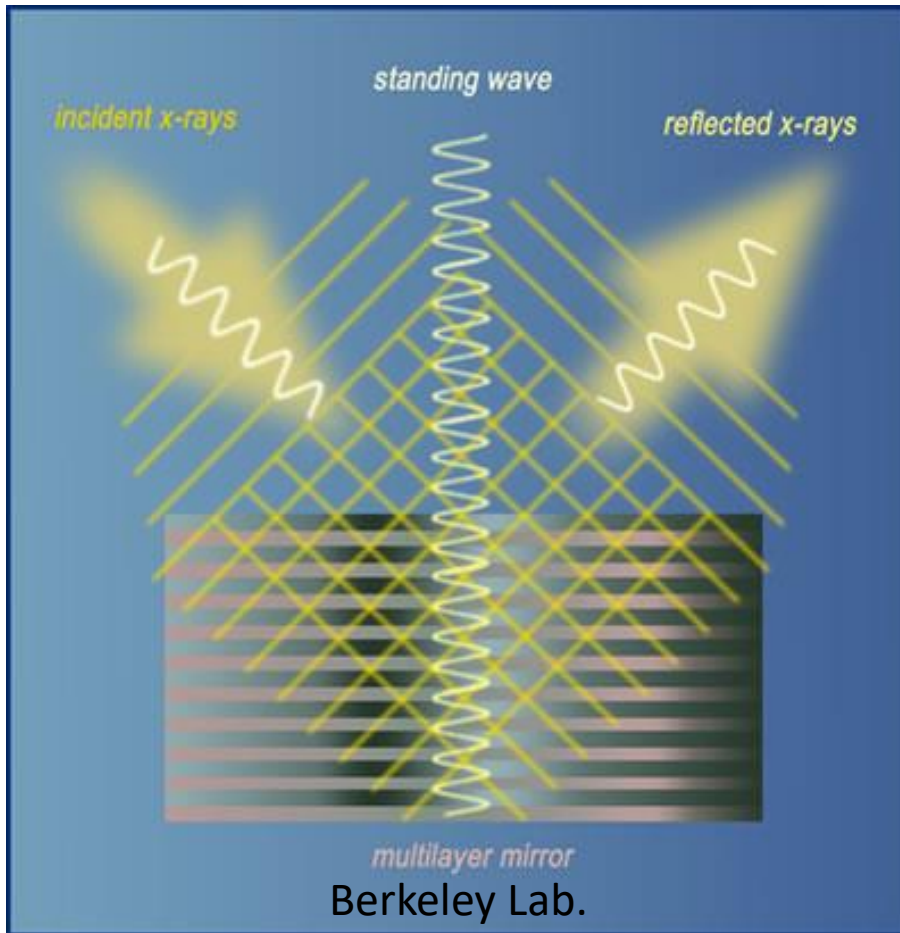


# Mg/Co results (annealing)



Mechanical deficiency due to Co clustering

# X-ray standing waves



In (or close to) **Bragg conditions**

- a strong standing wave develops inside and outside the multilayer
- having the period of the multilayer

## Generally used

- In **hard** x-ray range
- In **glancing incidence**
- With crystal or
- With multilayer (set of **bilayers**)

To probe

- thin layer on **top of the multilayer**
- **Interfaces of the multilayer** itself

By using

- Fluorescence or photoelectrons

## What we do

- In **soft** x-ray range
- In **glancing incidence and exit**
- With multilayer (set of **bilayers or trilayers**)

To probe

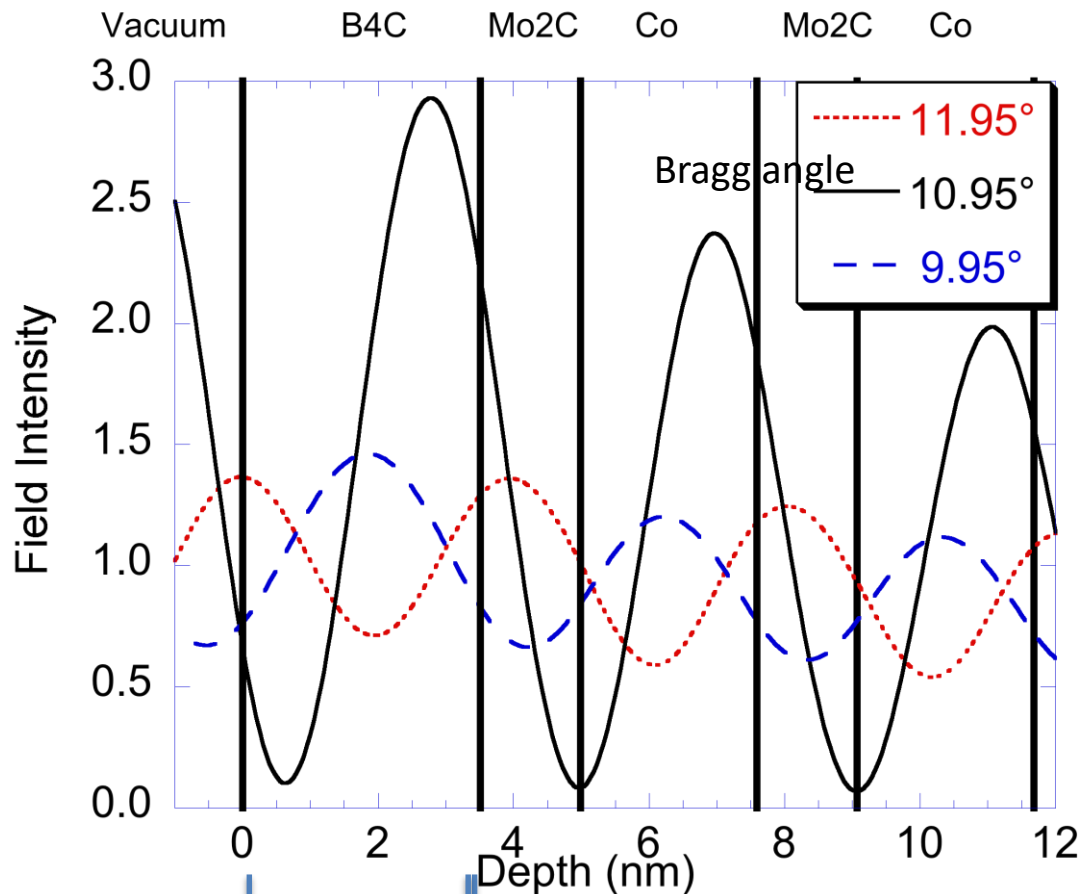
- **Interfaces of the multilayer itself**

By using

- **X-ray fluorescence**

# X-ray standing waves

## Depth distribution of the electric field



Rotate sample  
(change the wavelength)  
Change incident or detection angle  
↓  
Shift of the nodes and anti-nodes

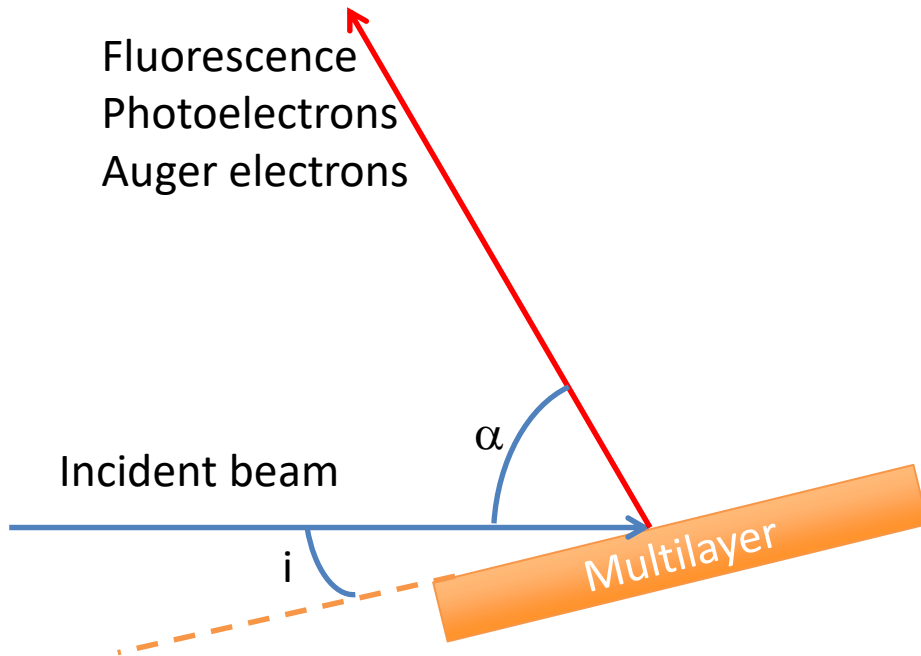
Analysis by

- XPS
- XRF
- AES

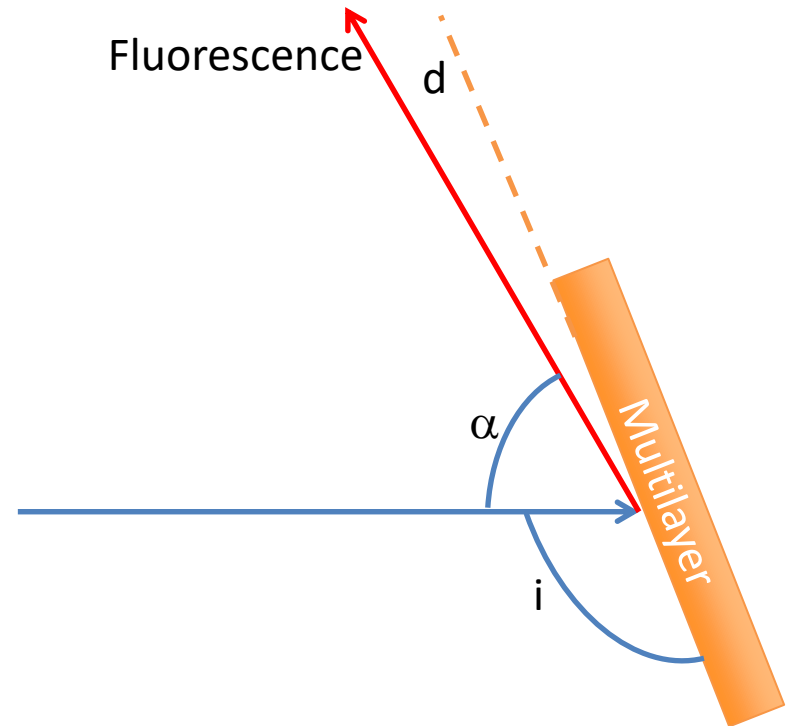
of a

- Multilayer
- Superficial material

# Two XSW modes



Glancing incidence mode  
**“Normal” or GI**



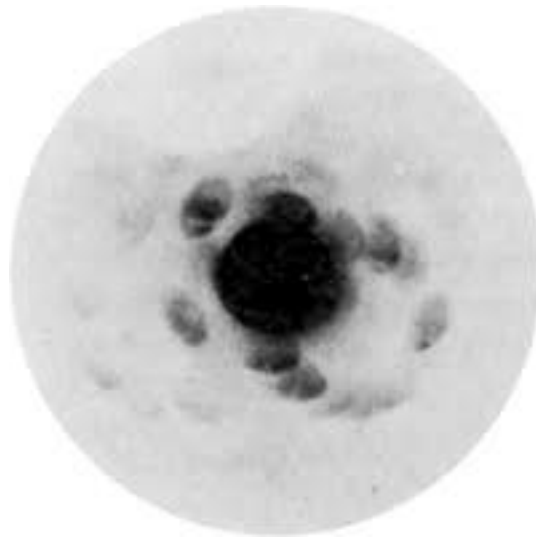
Glancing exit mode  
**“Kossel” or GE**

# A bit of history



## M. Von Laue

Nobel prize 1914 for his discovery of the x-ray diffraction by crystals



## First x-ray diffraction pattern

Hydrated copper sulfate

P1 triclinic

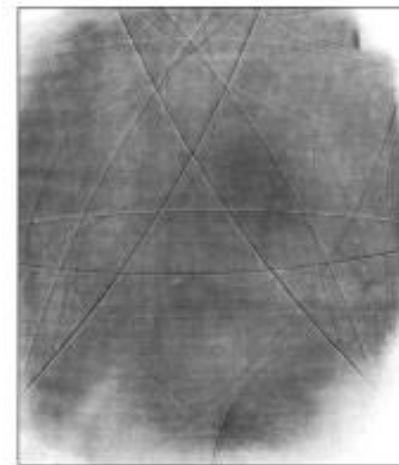
1912: von Laue, Friedrich, Knipping



## W. Kossel

1935

Diffraction of the fluorescence  
produced within the crystal  
by the crystal itself



Multilayer

Si substrate /

[Mg (5.1nm) / Co (2.6nm)]x30 /

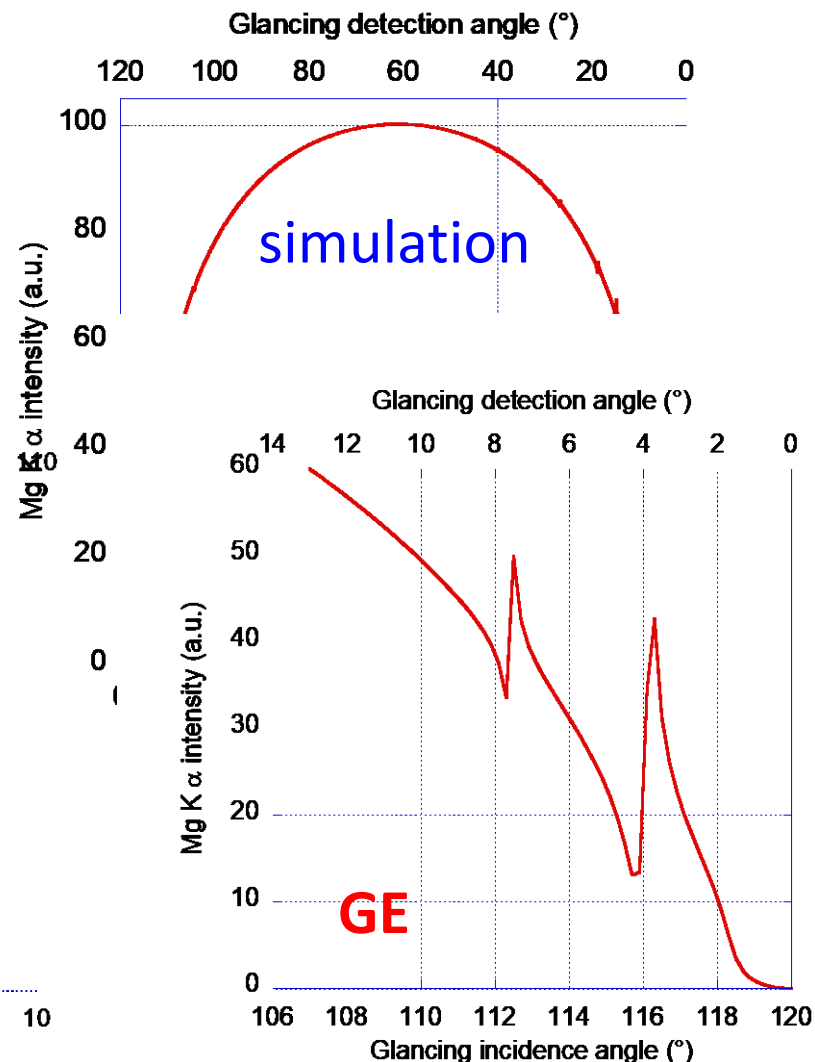
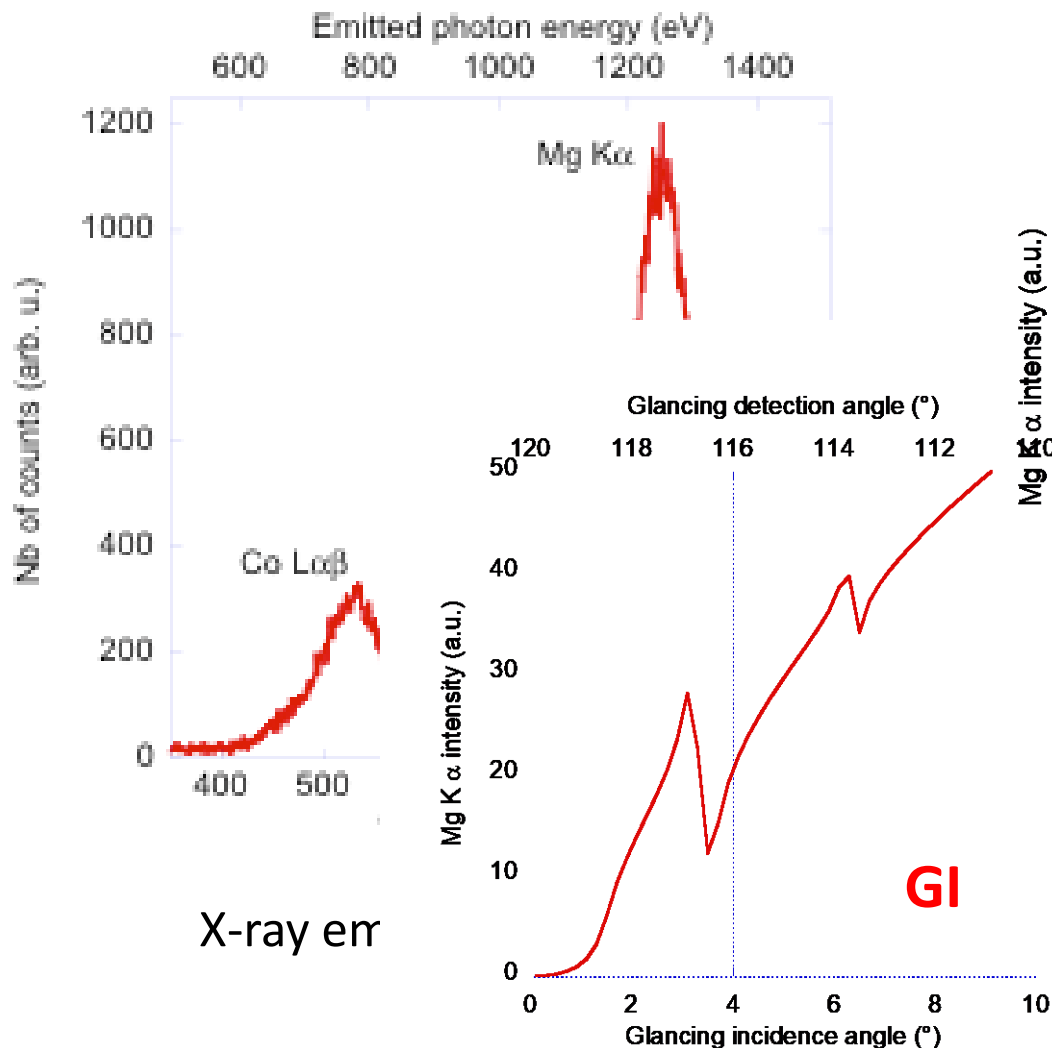
B4C (3.5nm) capping layer

# Mg/Co XSW - XRF

Incident radiation 1500eV; 0.827nm

Mg K $\alpha$  emission 1253.6eV; 0.989nm

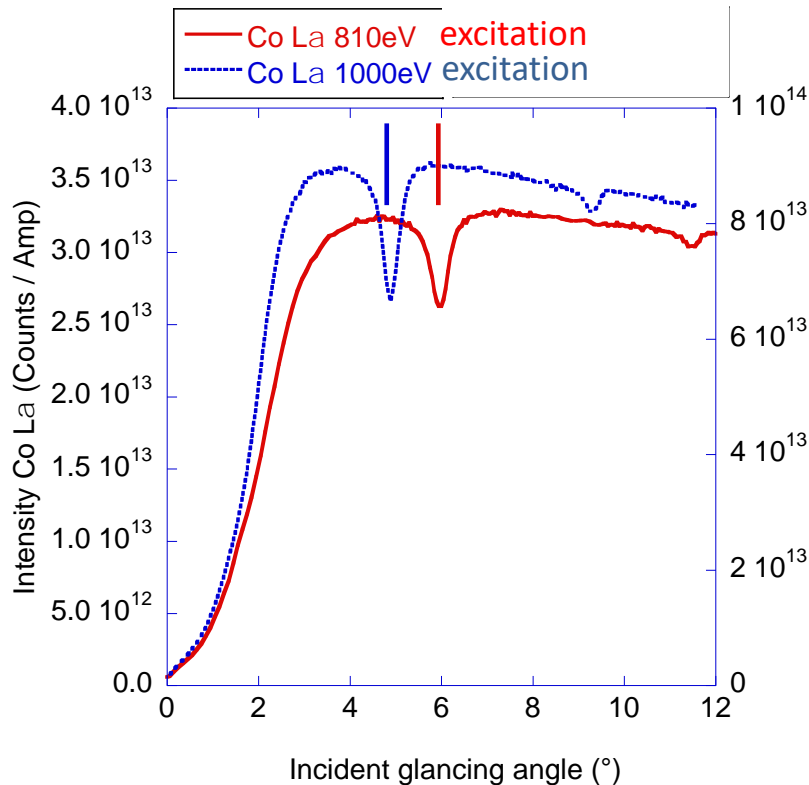
60° between incident and detection directions



# Fluorescence of Mg/Co multilayer

Si substrate / **[Mg (5.1nm) / Co (2.6nm)]x30** / B4C (3.5nm)

"Classic" - GIF mode

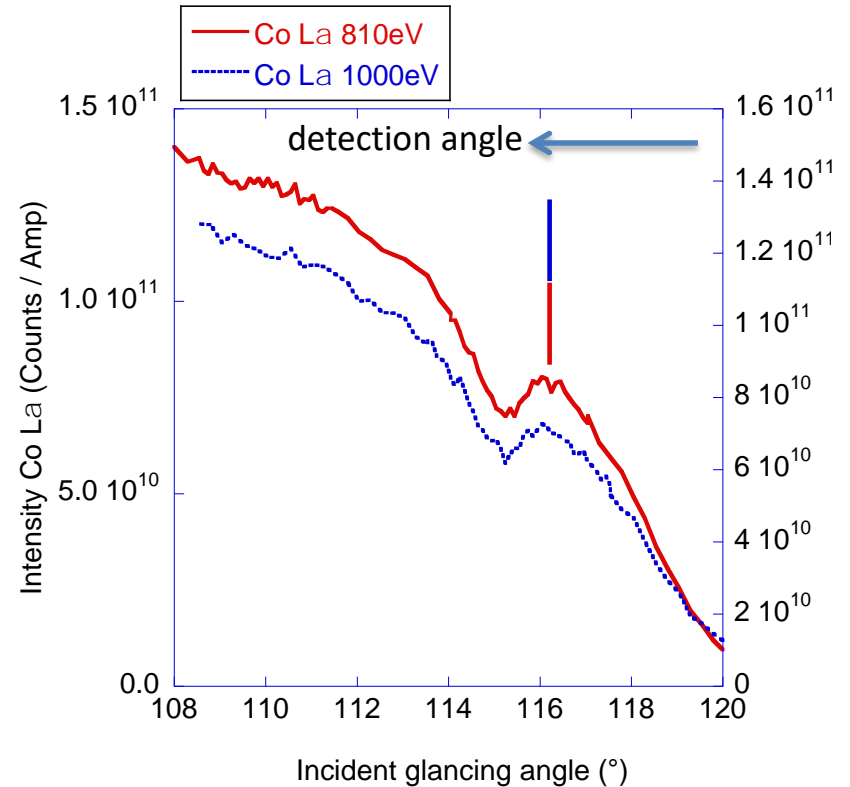


Features appear at Bragg angle  
of **incident** radiation



**Move** with energy  
of incident radiation

"Kossel" - GEF mode



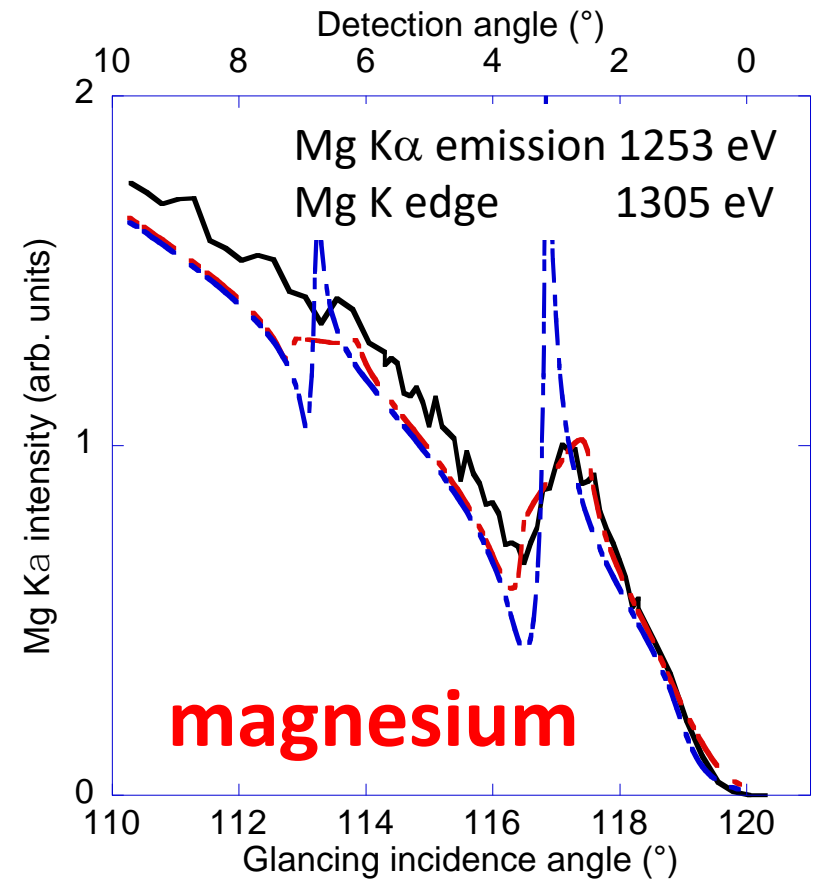
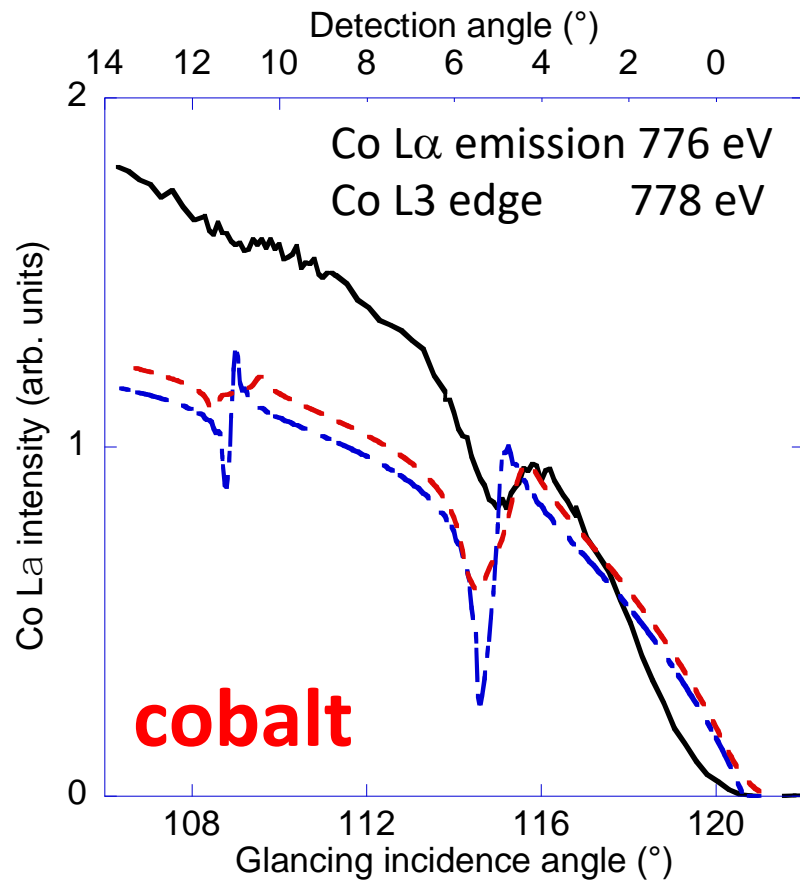
Features appear at Bragg angle  
of **emitted** radiation



**Do not move** with energy  
of incident radiation



# GE experiment-simulations Mg/Co



- abrupt interfaces
- Effect of the refractive indices

# Introduction of Zr into Mg/Co stack

- Makes the stack stable upon annealing
- Improves the reflectivity (optimization on the optical path within the stack)

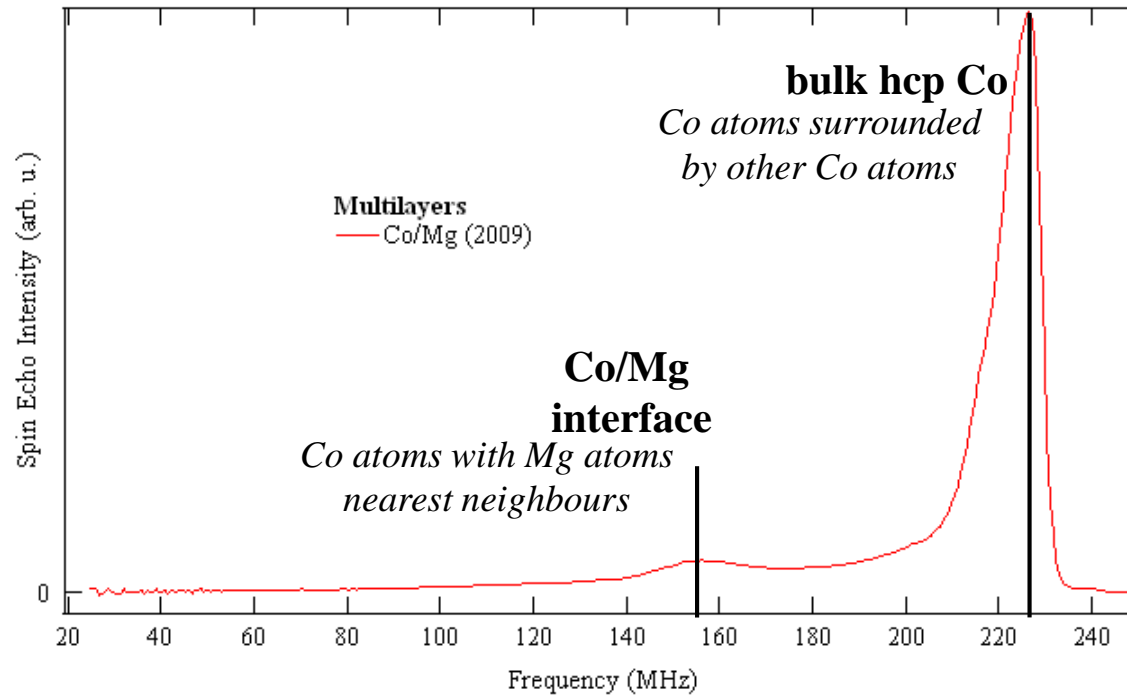
Si substrate / [Mg (5.45nm) / Co (2.55nm) / Zr (1.5nm)]x30 / B4C (3.5nm)

Si substrate / [Mg (5.45nm) / Zr (1.5nm) / Co (2.55nm)]x30 / B4C (3.5nm)

**Two different orders of the layers**

# NMR spectroscopy (1)

Probe of the nearest neighbour local structure around the Co atoms

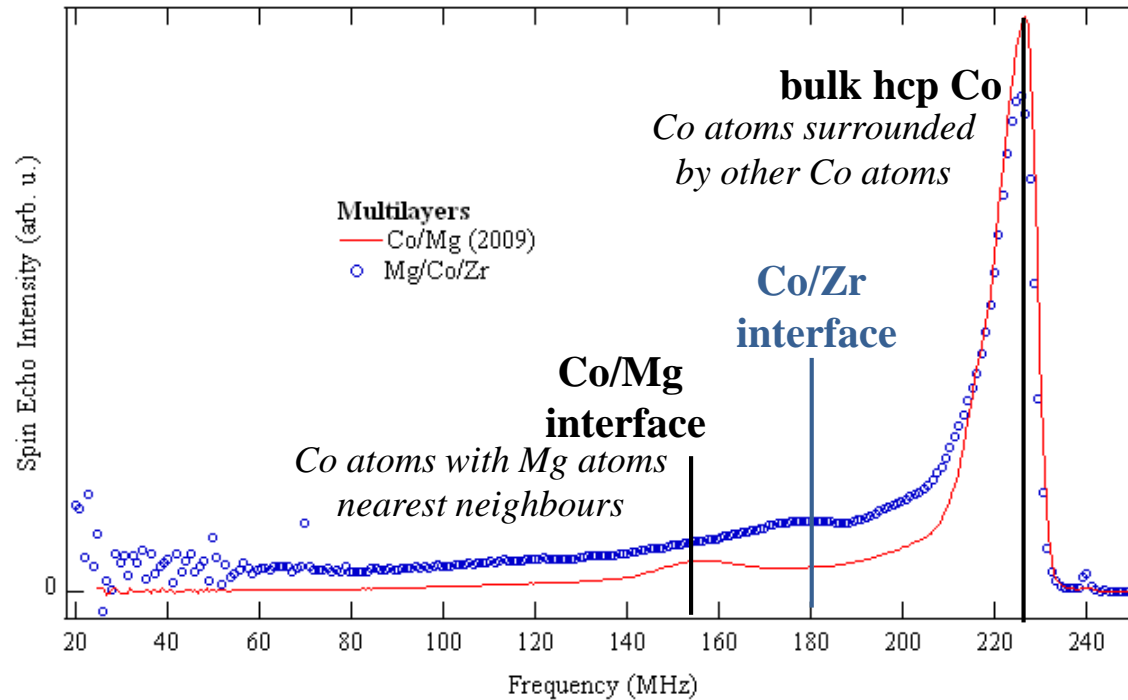


**Mg/Co**

well-defined layers and interfaces

# NMR spectroscopy (2)

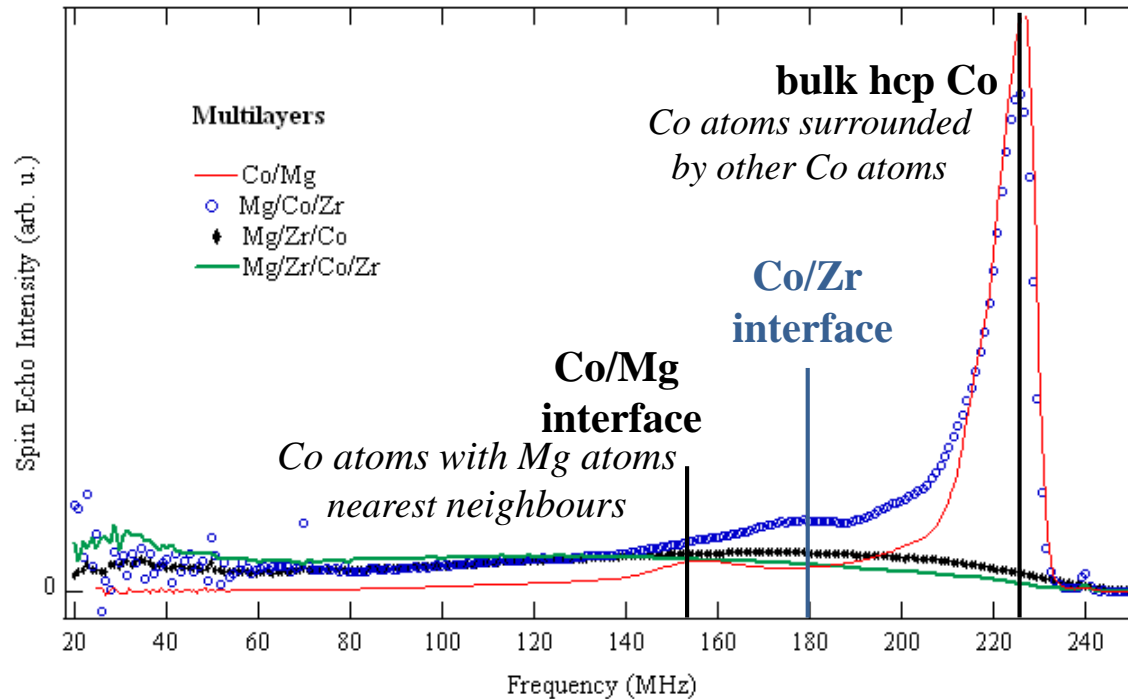
Probe of the nearest neighbour local structure around the Co atoms



**Mg/Co and Mg/Co/Zr**  
well-defined layers and interfaces

# NMR spectroscopy (3)

Probe of the nearest neighbour local structure around the Co atoms



**Mg/Co and Mg/Co/Zr**  
well-defined layers and interfaces

**Mg/Zr/Co and Mg/Zr/Co/Zr**  
**strong intermixing** between Co and Zr

**Mg/Co and Mg/Co/Zr**

**only geometrical roughness**

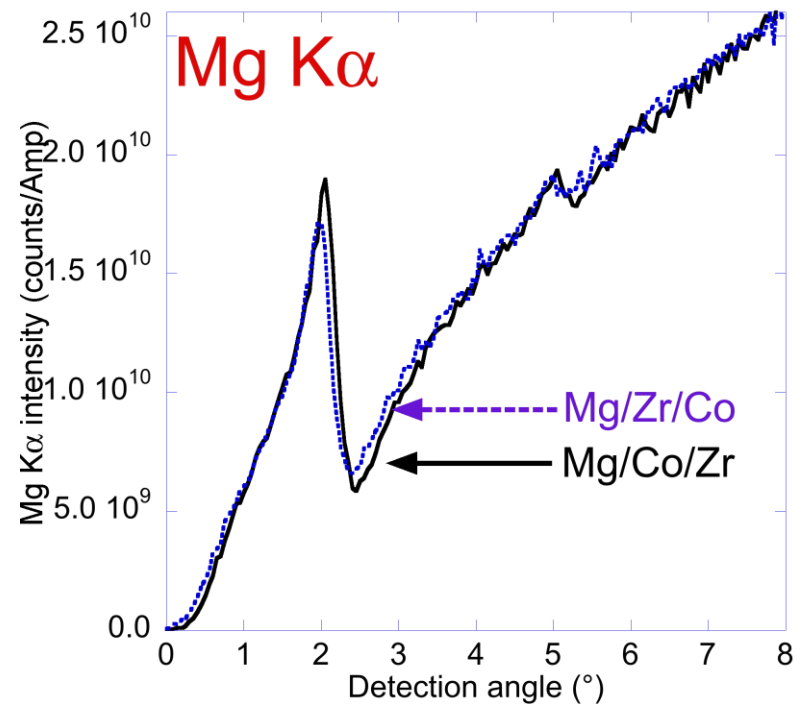
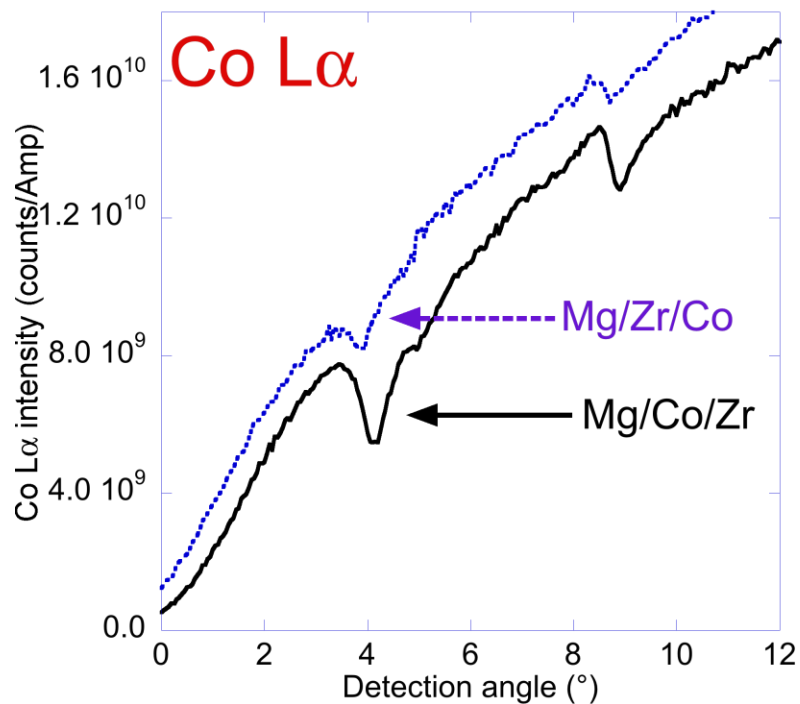
**Mg/Zr/Co and Mg/Zr/Co/Zr**

**reaction between Co and Zr**

**XES : Mg does not react**

# GE measurements – Mg-Co-Zr

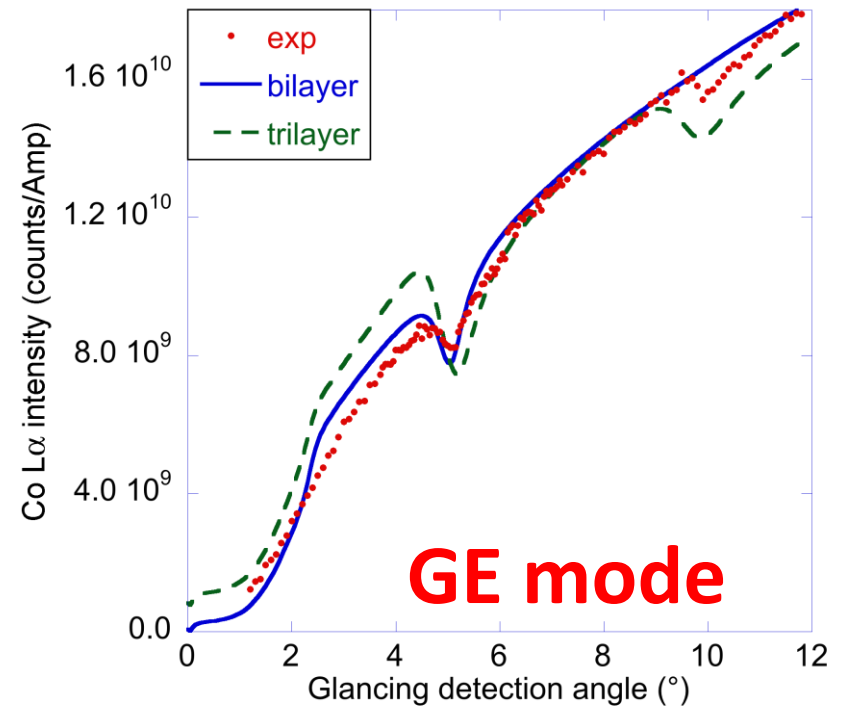
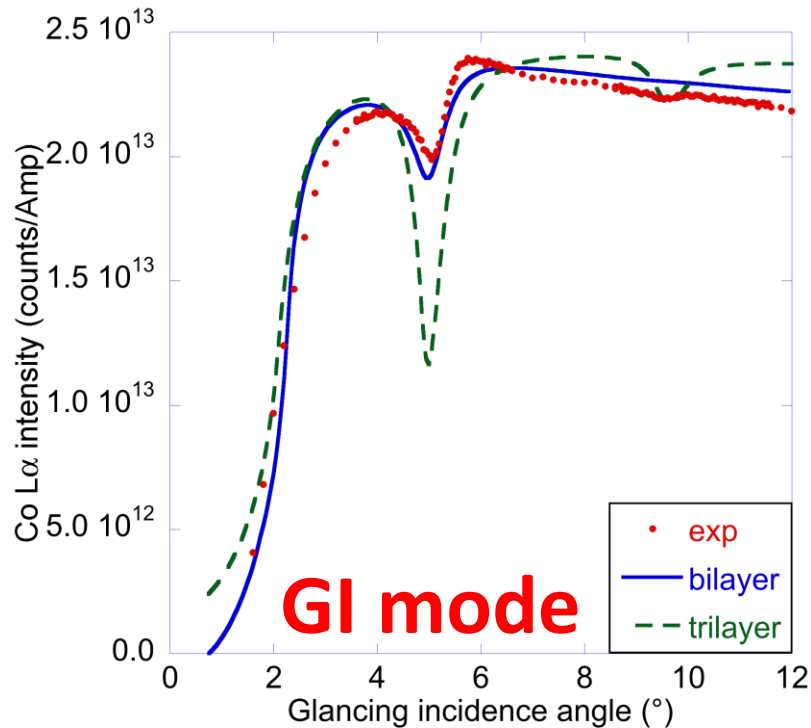
Different contrasts of the features for Co L emission depending on the sample



Same behavior in GI mode

# Simulations – Mg-Co-Zr

## Mg/Zr/Co – Co L emission



- Mg/Zr/Co described as Mg/Co<sub>4</sub>Zr
- Mg/Co/Zr trilayer with nominal parameters

# Mg-Co-Zr interfaces

From XRR, NMR, XES, XSW-XRF

- **Sharp Zr-on-Co interfaces** in Mg/Co/Zr
- **Mixing at Co-on-Zr interfaces** in Mg/Zr/Co

Surface free energy

- Co       $2.0 \text{ J.m}^{-2}$
- Zr       $1.6 \text{ J.m}^{-2}$



**Asymmetric behavior of**  
Zr-on-Co and Co-on-Zr interfaces



# **Diffraction de Kossel**

## **Caméra CCD**

# Pd/Y based periodic multilayers

- **Problem: the original design has bad optial performance**

- Grazing incident X-ray reflectometry (Cu K radiation 8048 eV)

**Low reflection, bad periodicity**

- Severe interdiffusion between Pd and Y layers.

- **Solution: Derivative systems**

- N<sub>2</sub> in the sputtering gas [1].

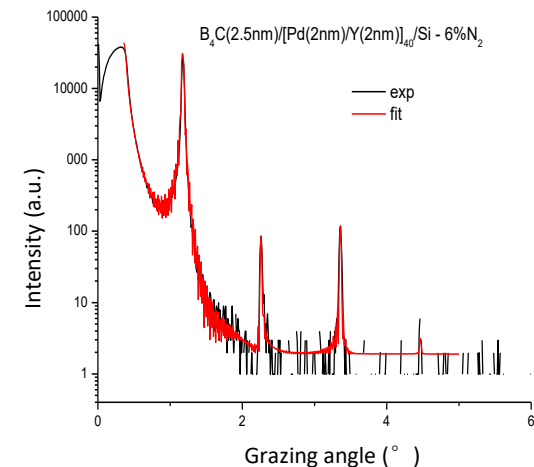
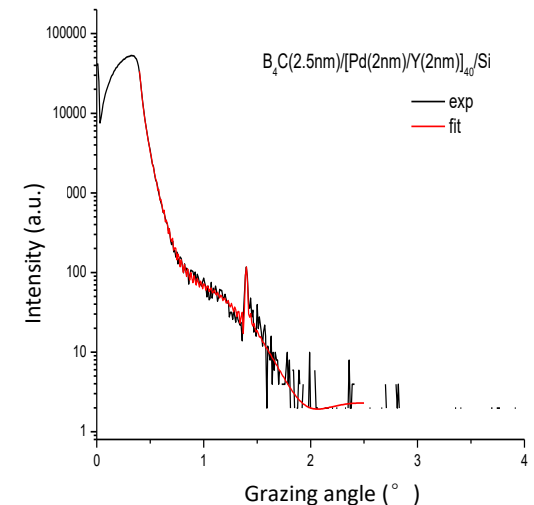
**0%**

**2%**

**6%**

- B<sub>4</sub>C barrier layers [2].

- **Pd-on-Y interfaces**
- **Y-on Pd interfaces**
- **all interfaces**

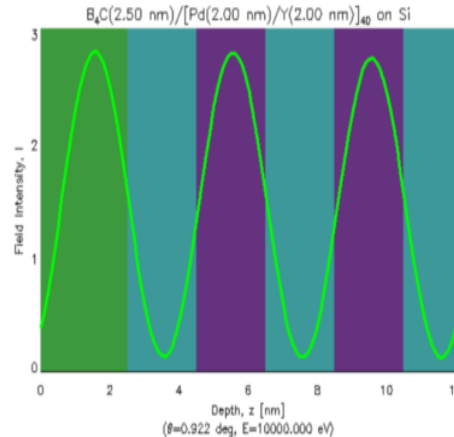


[1] Xu *et al.*, "Enhancement of soft X-ray reflectivity and interface stability in nitridated Pd/Y multilayer mirrors," Opt. Express. 23, 33018 (2015).

[2] Prasciolu *et al.*, "Thermal stability studies of short period Sc/Cr and Sc/B<sub>4</sub>C/Cr multilayers," Appl. Opt. 53(10), 2126 (2014).

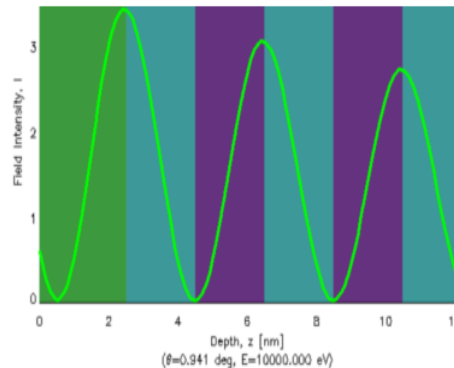
# Combine PIXE with Kossel diffraction

$\theta < \theta_{\text{Bragg}}$

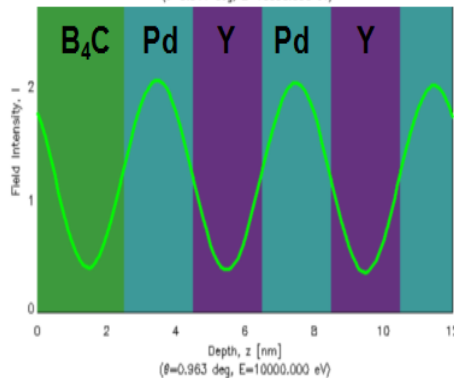


$$D = \frac{\lambda}{2 \sin \theta} = \frac{2\pi}{Q}$$

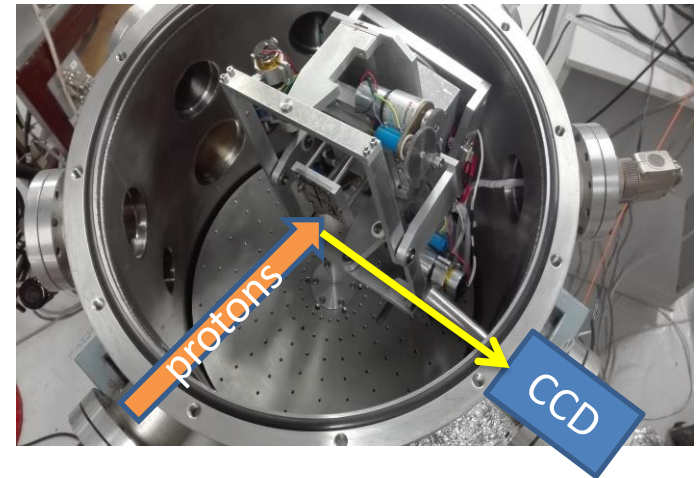
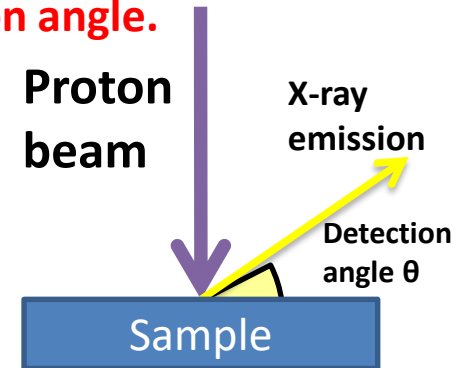
$\theta = \theta_{\text{Bragg}}$



$\theta > \theta_{\text{Bragg}}$



Measurement of X-ray emission intensity as a function of the detection angle.



# Energy dispersive CCD

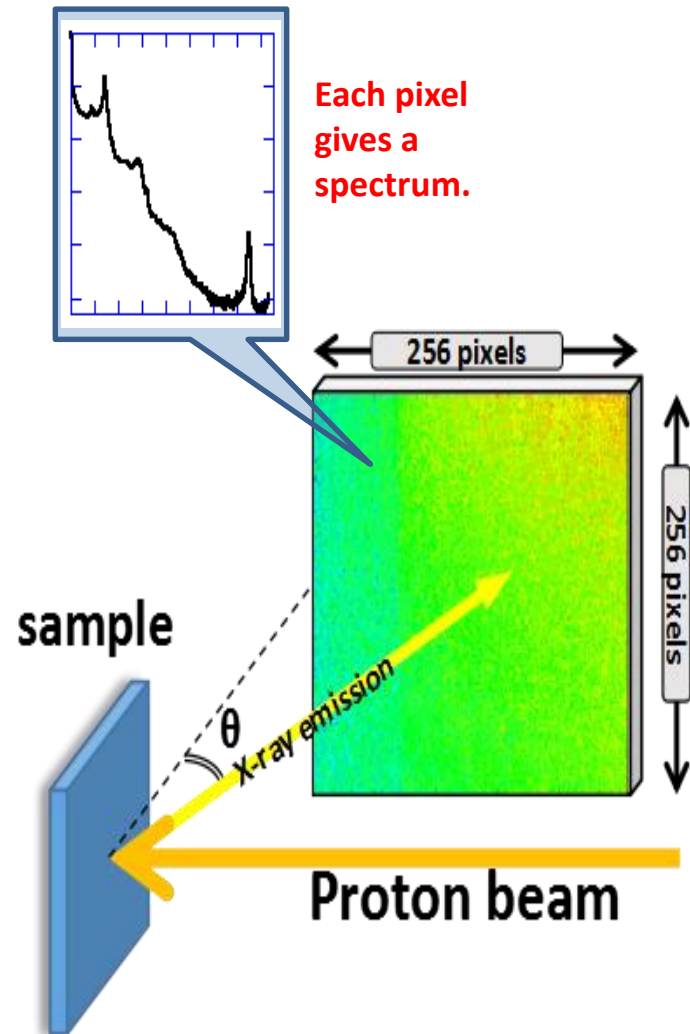
- Advantage: spatially resolved.

- Measurement of X-ray emission intensity in a squared area of about 13 x 13 mm.
- Native: 1024 x 1024 sensor array with 13 x 13  $\mu\text{m}$  pixels.
- Our selection: 256 x 256 of 52 x 52  $\mu\text{m}$ .

>>> compromise of angular/energy resolution

- No need to scan the angle.
- We place a 200  $\mu\text{m}$  beryllium film in front of the camera to filter the scattered protons. Protection of the camera.
- Acquisition time significantly reduced compared to SDD.

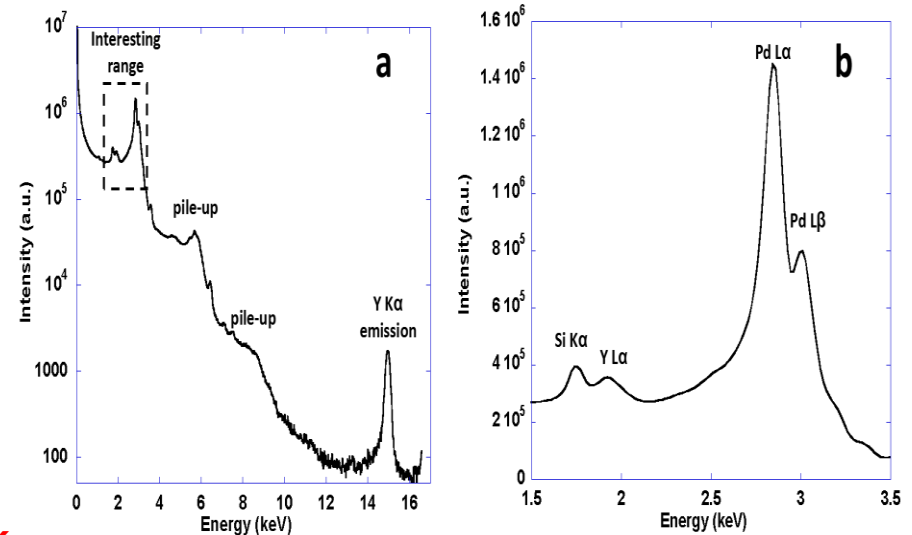
Days to 2 hours >>> potential of in-situ measurements  
(annealing test, oxidation test)



# X-ray emission spectrum

- $B_4C(2.5 \text{ nm})/[Pd(2 \text{ nm})/B_4C(2 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$
- Energy resolution is about 150 eV at 5.9 keV (Mn K $\alpha$ ).
- Pd L $\alpha$  L $\beta$ , Y L $\alpha$  K $\alpha$ , Si K $\alpha$  can be observed
- Pile up effect due to multiple photons detection
- Energy calibration of the spectrum is carried out with **Pd L $\alpha$  peak (2.838 keV)** and **Y K $\alpha$  peak (14.958 keV)**

- Y K $\alpha$  has too low intensity.
- Y L $\alpha$ , Si K $\alpha$  are in the low efficiency part of the X-ray camera.
- Pd L $\beta$  does not bring additional information
- **We measure Pd L $\alpha$  emission**

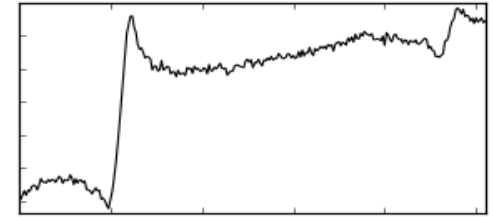


X-ray spectrum of Pd(2 nm)/ $B_4C$ (2 nm)/Y(2 nm) multilayer:

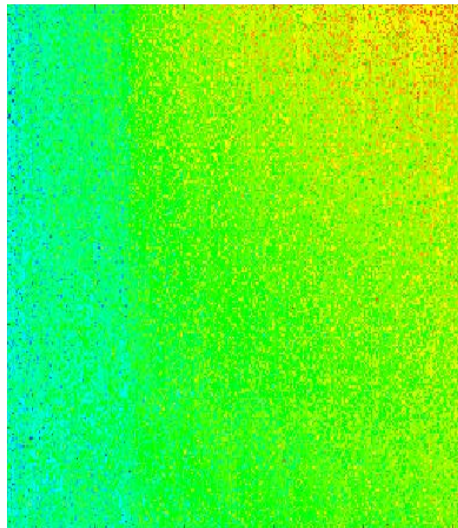
- a) overview (log scale)
- b) zoomed range of interest (linear scale).

# Kossel curves

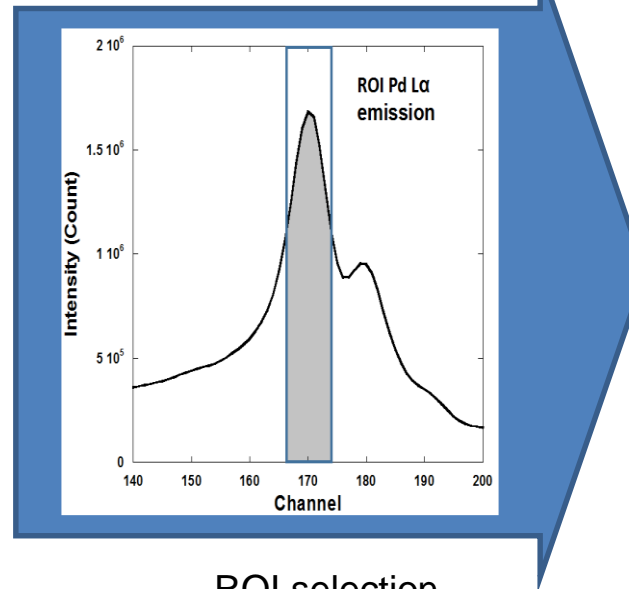
- The original image obtained by X-ray color camera contains the intensity of emitted photons of all energies.
- Kossel curve: the angular distribution of the characteristic X-ray emission.
- To get the Kossel curve of Pd L $\alpha$  emission, we need 3 steps:
  1. Select region of interest (ROI) on the spectrum.
  2. “Filter” the original image by applying ROI.
  3. Integrate the “filtered” image along the vertical pixels.



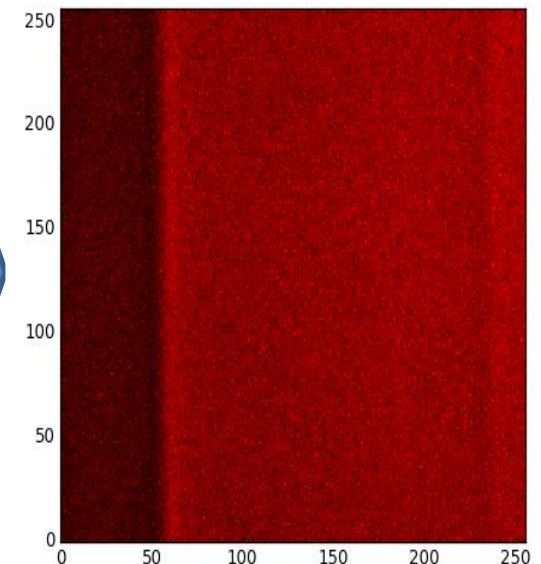
Integrate  
along the  
vertical  
pixels



Distribution of X-ray  
emission



ROI selection



Distribution of Pd L $\alpha$

# Calibration of detection angle

- Pixel of the detector - grazing exit angle

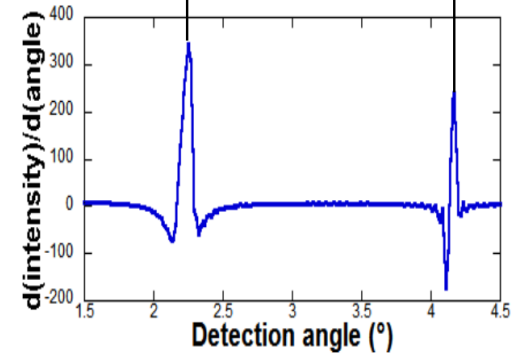
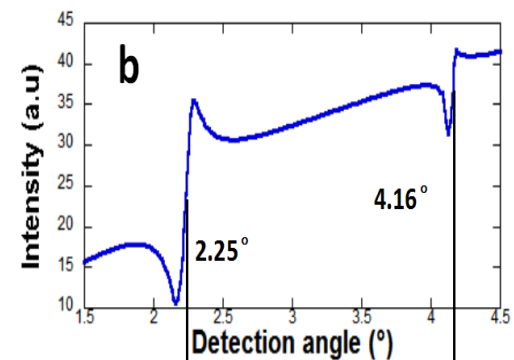
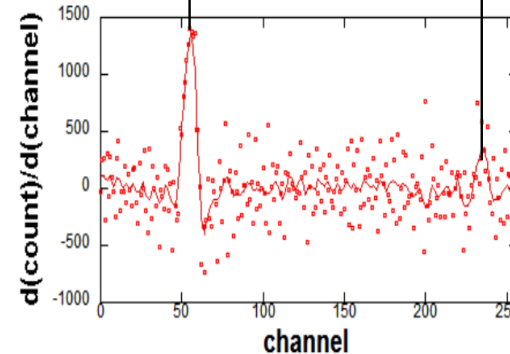
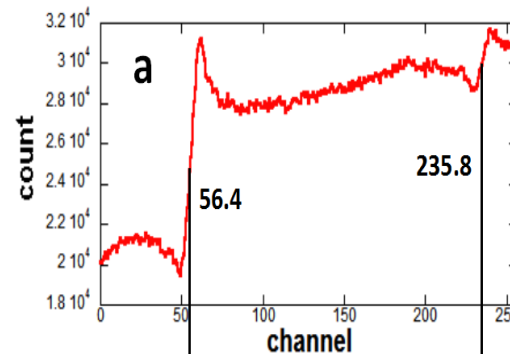
4-layer sample:  
 $B_4C(2.5 \text{ nm})/[B_4C(1 \text{ nm})/Pd(2 \text{ nm})/B_4C(1 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$

- 1st and 2nd order of Kossel oscillation

a) experimental curve in channel (pixel)

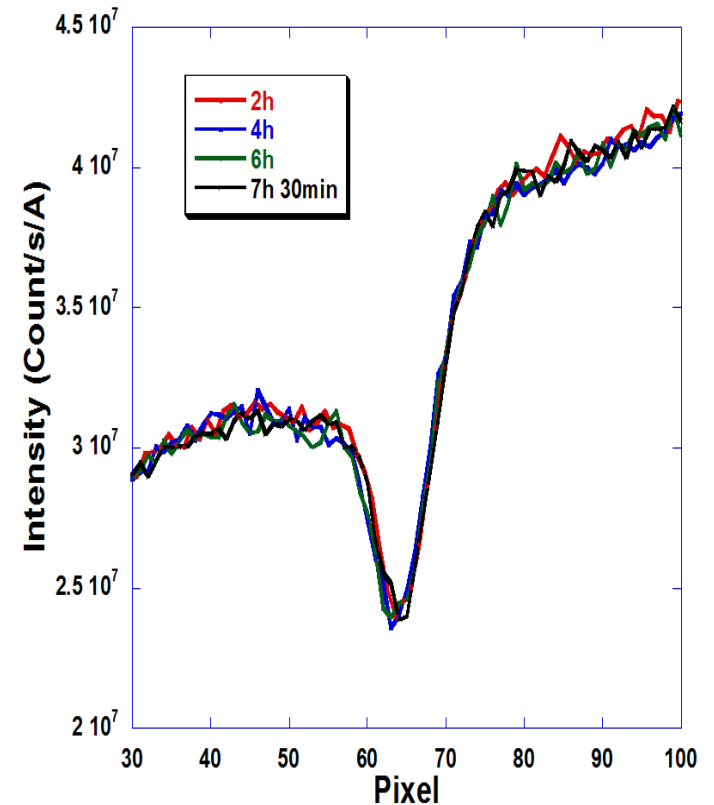
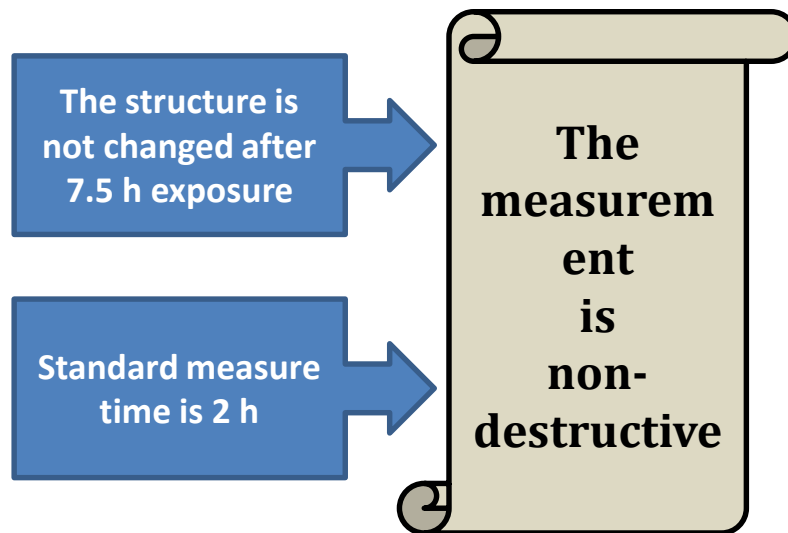
b) simulated curve in angle (degree)

- Precise values obtained from the derivatives of the curves



# Non-destructive test

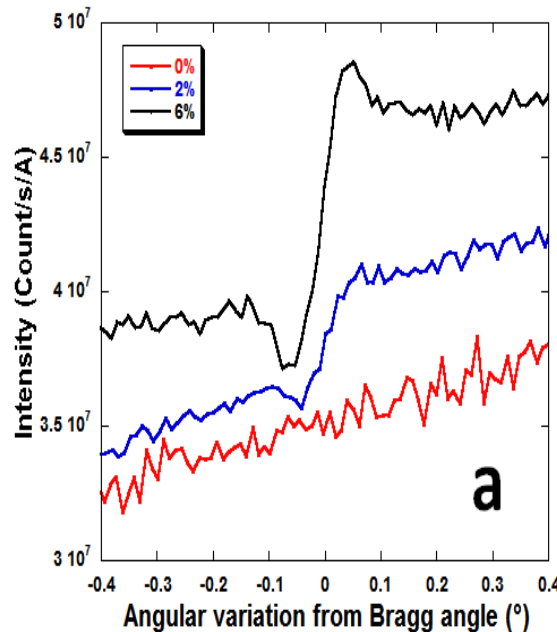
- $B_4C(2.5 \text{ nm})/[Pd(2 \text{ nm})/B_4C(2 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$
- Exposure under proton beam for 7.5 hours
- Kossel curve maintains its shape



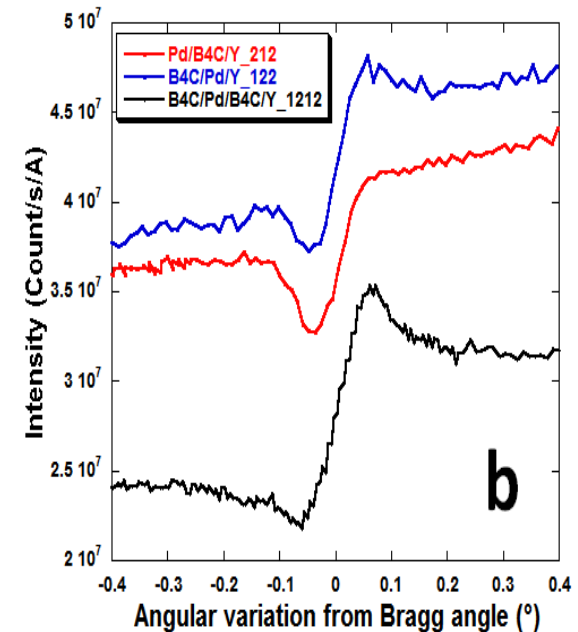


# Kossel curves of Pd La emission

- 2-hour acquisition time. Curve statistics can be further improved by increasing the acquisition time.
- Angles are adjusted to the Bragg angle, which is in most cases located in the center of the Kossel oscillation.
- The periodicity of the originally designed Pd/Y multilayer is totally compromised.
- Nitrogen reduces the interdiffusion.
- Kossel features can be distinguished for samples with different B<sub>4</sub>C barrier layers.  
**Structural sensitivity.**



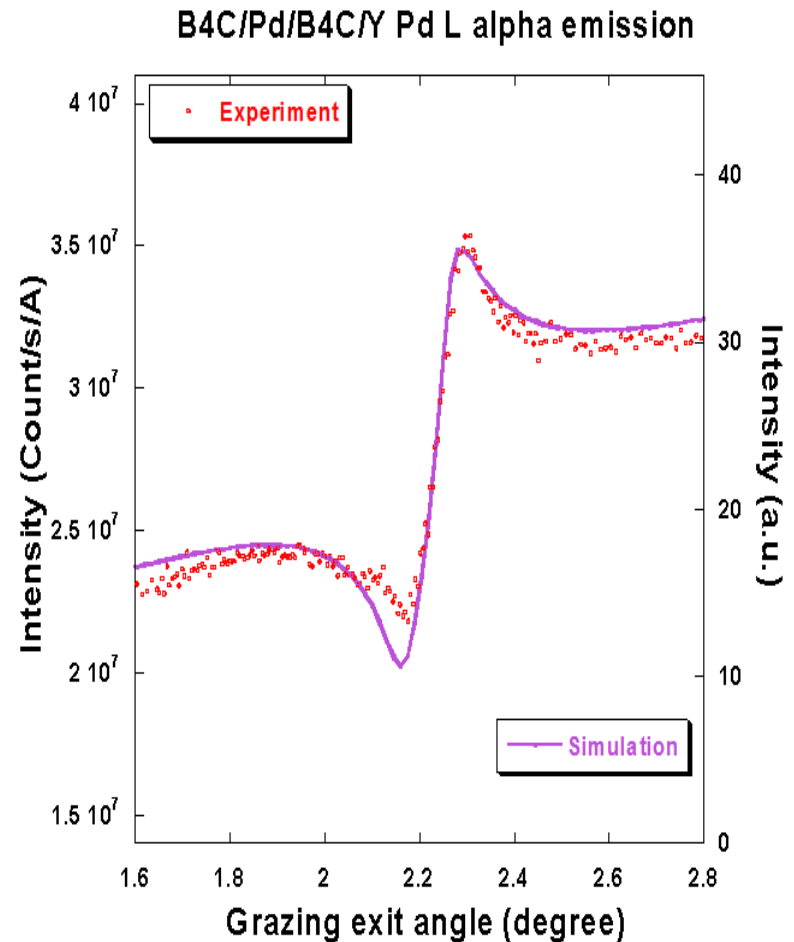
Kossel curves of the series of samples:  
a) Deposited with nitrogen in the sputtering gas.



Kossel curves of the series of samples:  
b) With B<sub>4</sub>C barrier layers. The notation gives multilayer structure and layer thickness respectively.

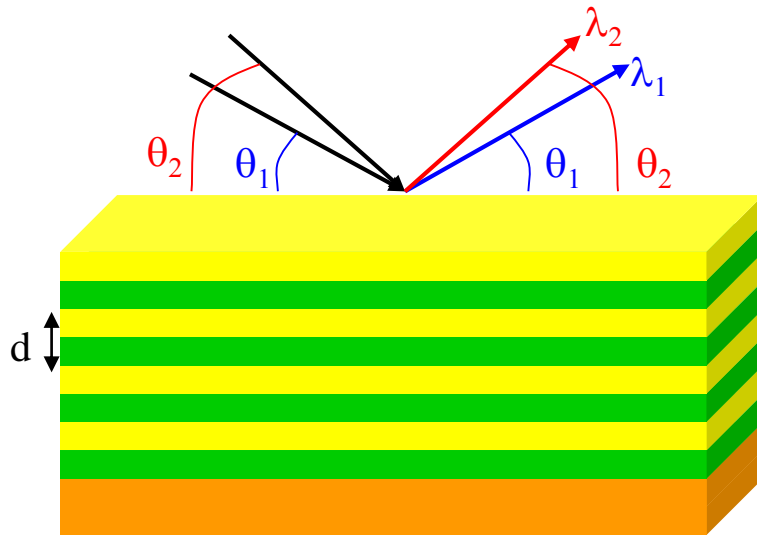
# Simulation

- Simulation of the PIXE-Kossel curve.
- Code for XRF-Kossel curve.
- Approach.
- Uniform ionization.
- Still not perfect due to background.
- Improvement needed.



**Multicouches gravées**

## Multilayer mirror (MM)



$d$ : multilayer period

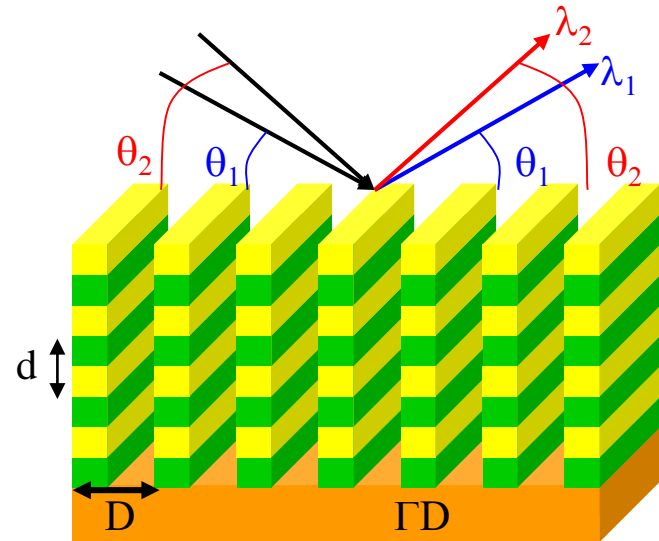
**Bad spectral resolution**

**Owing to large diffraction pattern**

**1D periodical structure** used  
at the 1<sup>st</sup> (2<sup>nd</sup>) diffraction order

Bragg law  
 $2d \sin\theta = n\lambda$

## Etched mirror (EM)



$d$ : multilayer period

$D$ : grating period

$\Gamma D$ : grating line width

$1 - \Gamma D$ : grating line spacing

**Calculations:**  $D = 1 \mu\text{m}$   $\Gamma = 0.35$

**2D periodical structure** used:

- at the 0<sup>th</sup> order of the grating
- at the 1<sup>st</sup> (2<sup>nd</sup>) diffraction order

Bragg law  
 $2d \sin\theta = n\lambda$

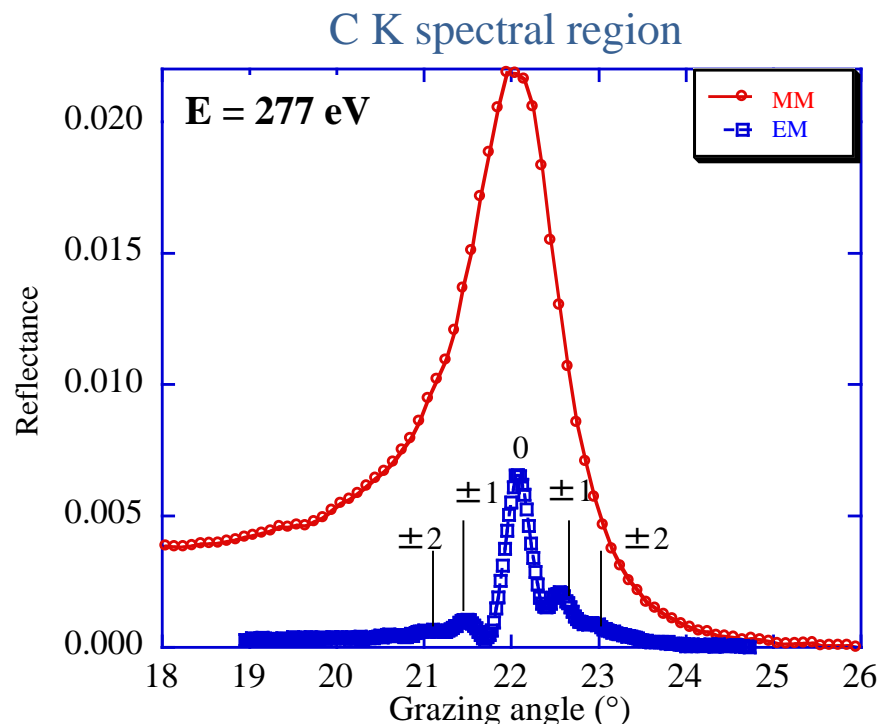
~~grating law~~

# Reflectivity curves: comparison MM/EM



**MM:**  
continuous profile

**EM:**  
oscillations due to  
the coupling with  
the grating orders  
(0,  $\pm 1$ ,  $\pm 2$  ...)



Grating period  
 $1 \mu\text{m}$  to  $0.2 \mu\text{m}$

		MM	EM	ratio MM/EM
C K region	<b>R (%)</b>	2.2	0.65	3.4
	<b><math>L_{1/2}</math> (°)</b>	1.4	0.34	4.1

$R$ : peak reflectivity

$L_{1/2}$ : width at half maximum

## Decrease of R for EM:

- $\Gamma_{\text{exp}} = 0.20 \neq \Gamma_{\text{theo}} (0.35)$
- annealing during  $\text{SiO}_2$  deposition

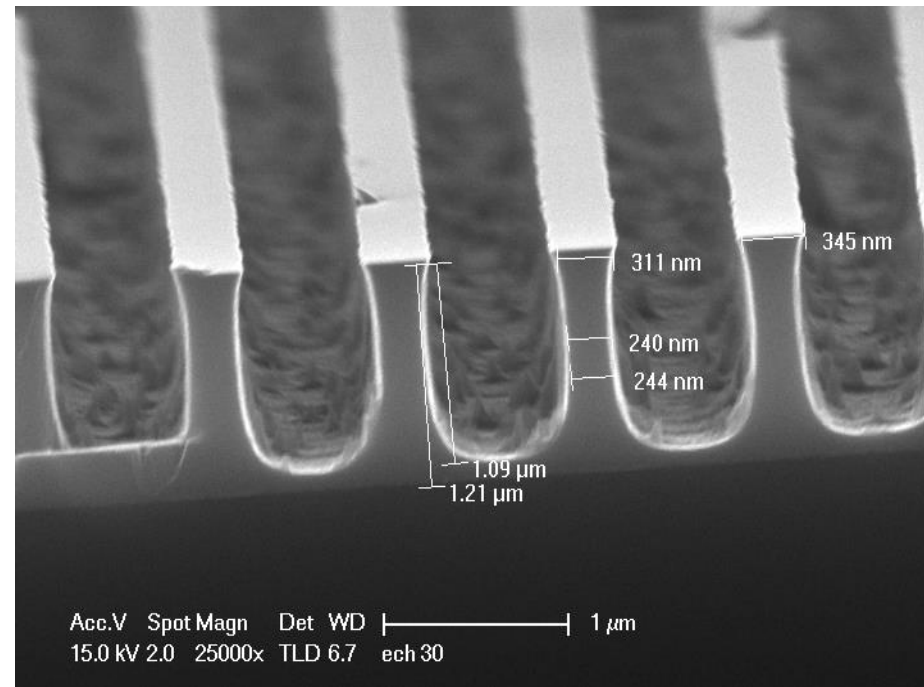
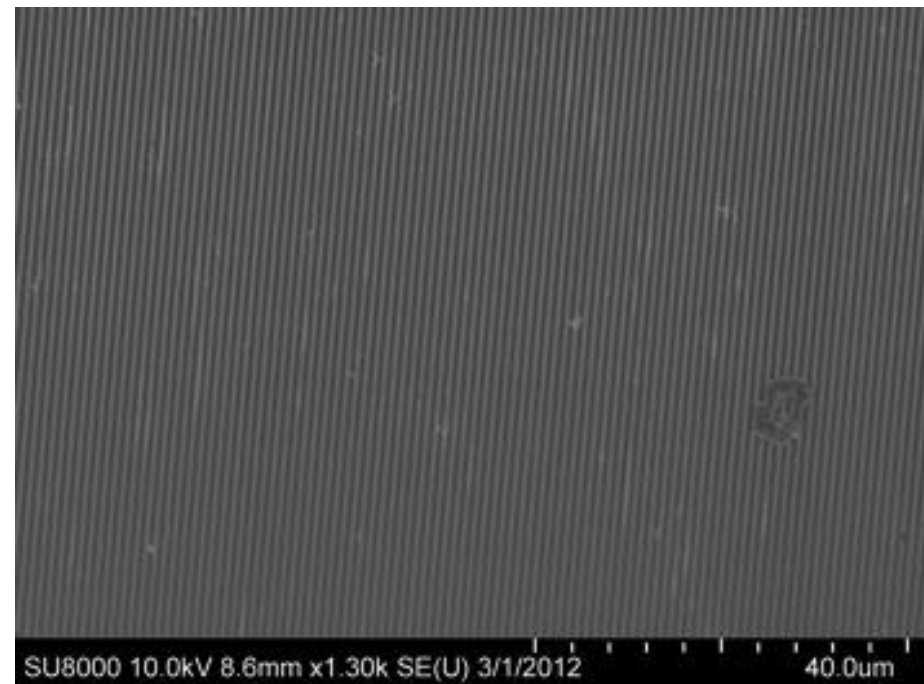
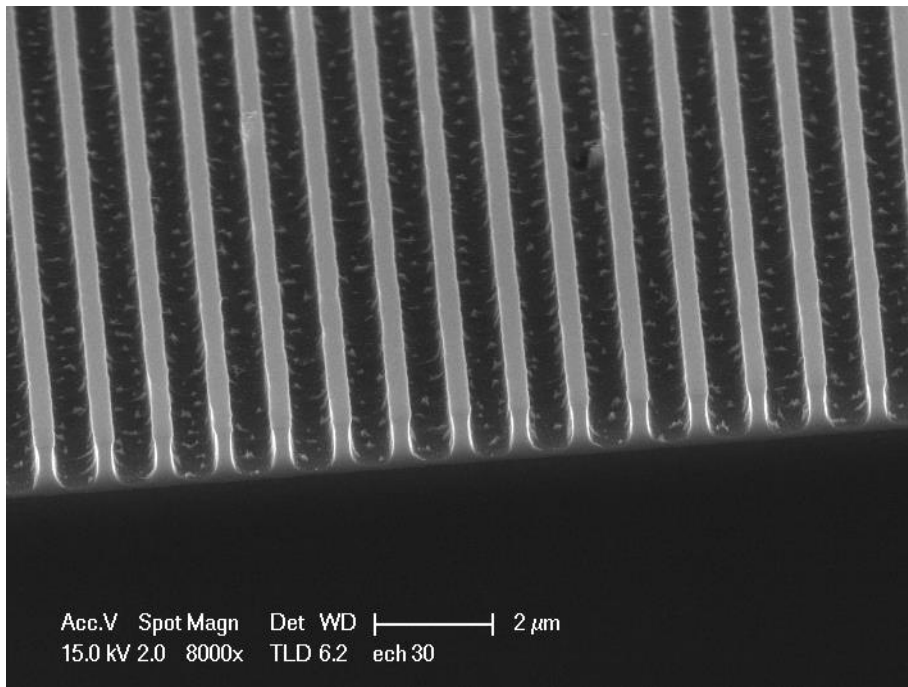
**Decrease of  $L_{1/2}$  for EM:**  
strong in the C K region

# Etching process

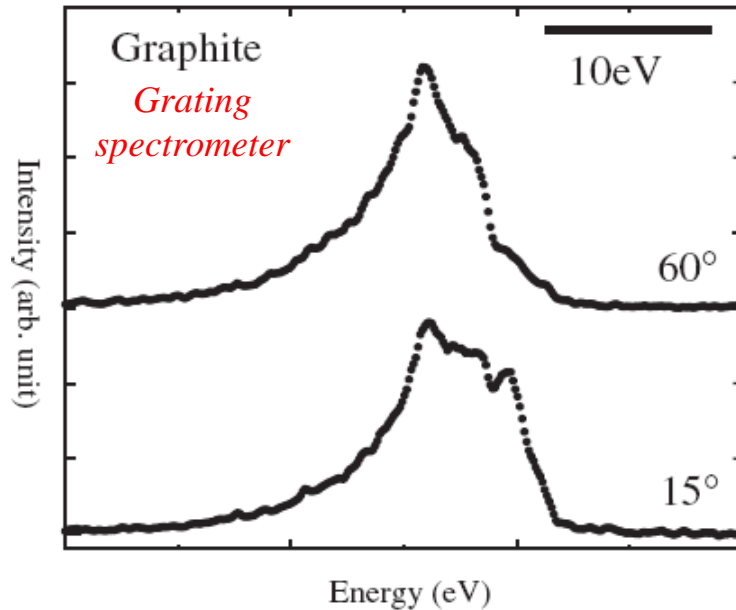
Scanning electronic microscopy images

## Aspect ratio:

- aimed 300:1200
- experimental ~ 310:1210

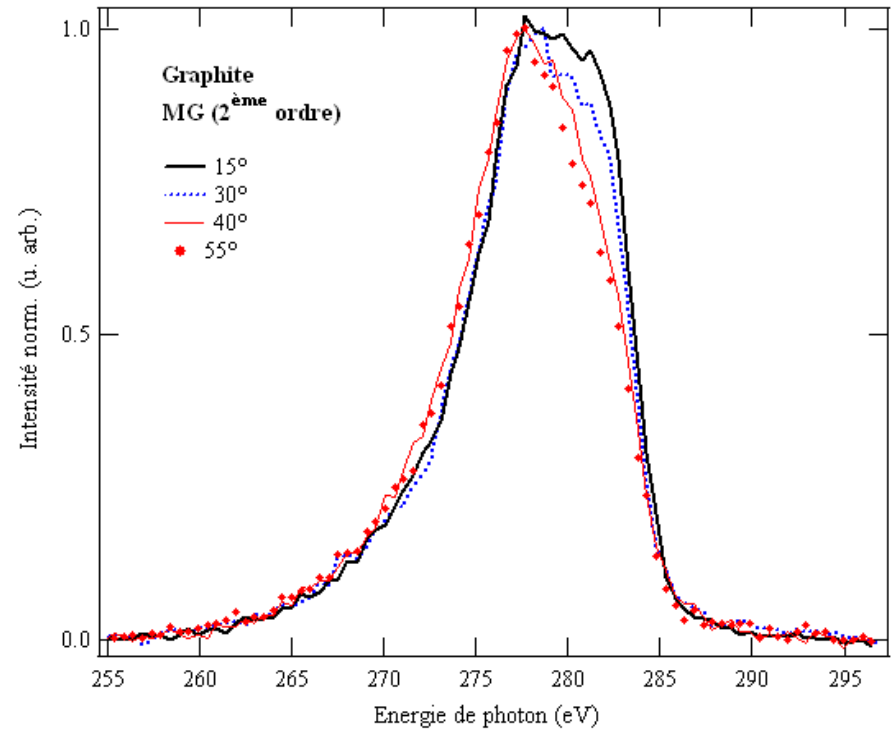


# Example of an etched multilayer in a curve-crystal spectrometer: C K $\alpha$ emission band of graphite



M. Terauchi *et al.*  
*Journal of Electron Microscopy.* 1–11 (2010)  
doi:10.1093/jmicro/dfq010

$\theta$  angle entre la direction d'émission  
et le plan (0001) du graphite



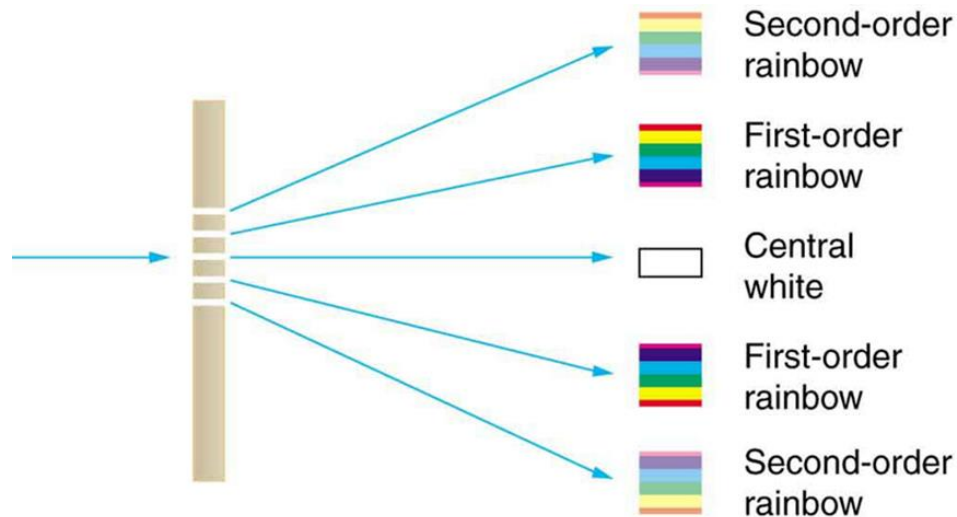
**anisotropic graphite crystal**



**anisotropic emission band**

# **Réseau de diffraction en transmission**

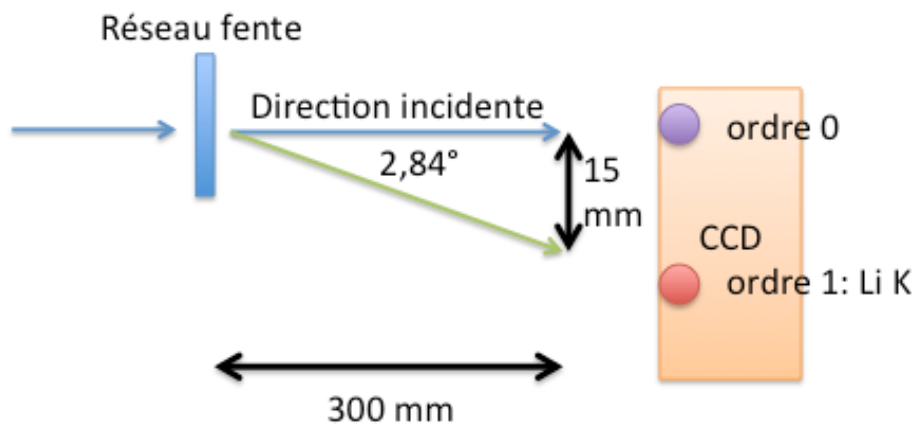




$$d(\sin \theta_i + \sin \theta_m) = m\lambda.$$

Theta = incidence angle

$$d \sin \theta_m = m\lambda.$$



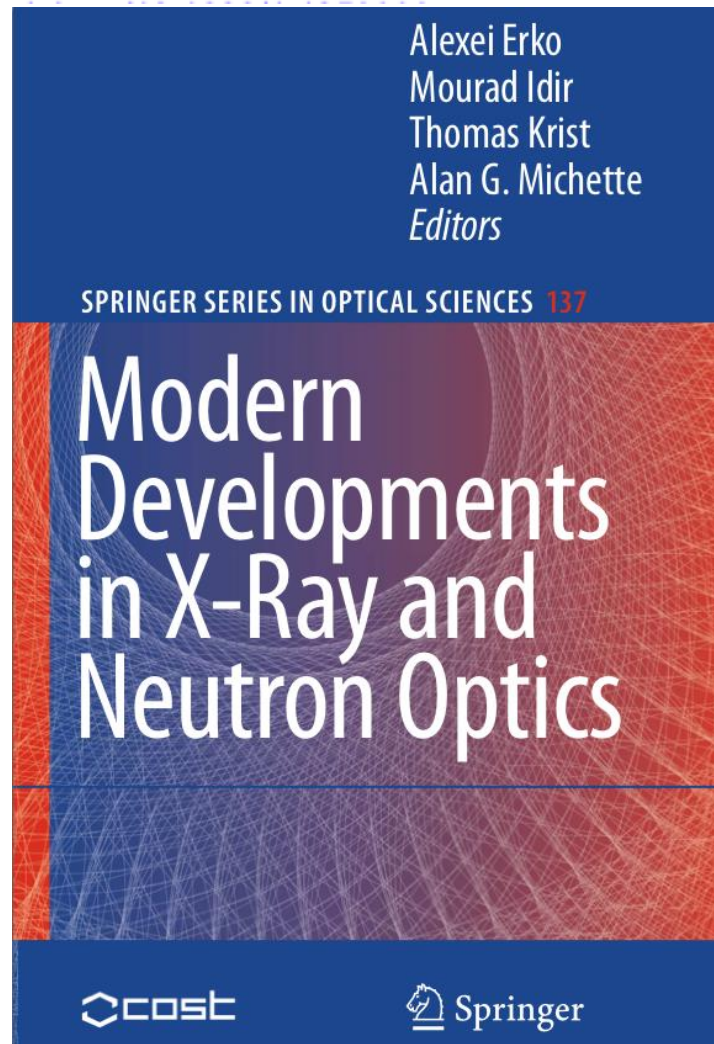
# **Tracé de rayons**

## **Spectromètre Johann**

## RAY-UI: A powerful and extensible user interface for RAY

P. Baumgärtel<sup>\*</sup>, M. Witt, J. Baensch, M. Fabarius, A. Erko, F. Schäfers, and H. Schirmacher

Citation: [AIP Conference Proceedings](#) **1741**, 040016 (2016); doi: 10.1063/1.4952888



Johann  
InSb (111)

$R = 500$  mm  
Si Ka = 1740 eV

