

# Laboratoire de Chimie Physique – Matière et Rayonnement

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***Kossel diffraction combined to  
proton induced x-ray emission  
for the study of  
multilayers of nanometer thickness***

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IMSOX team

« 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



# Outline

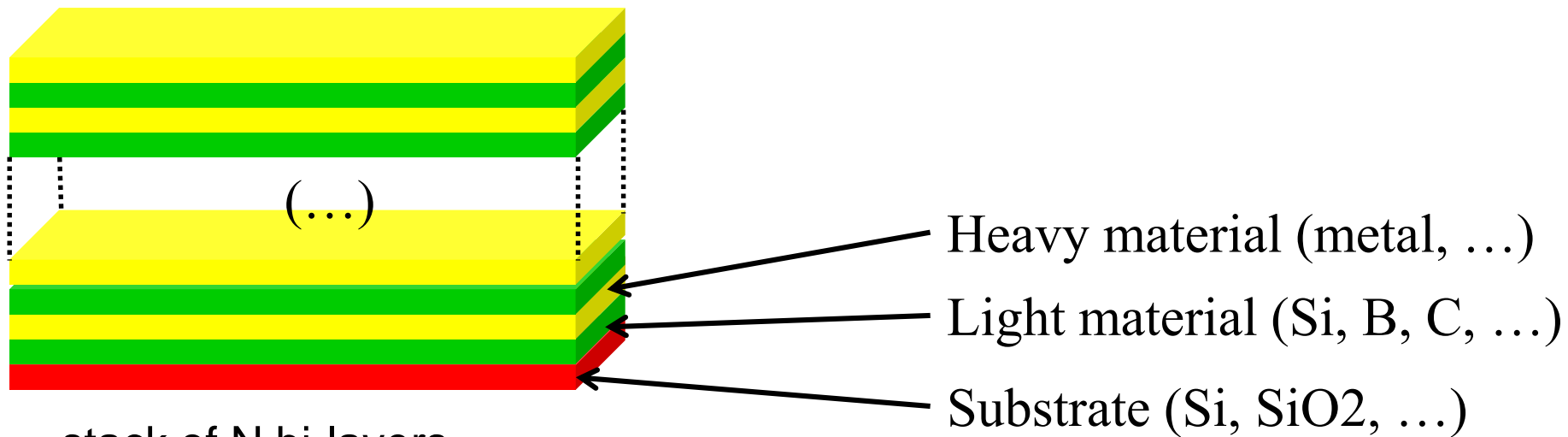
- Periodic multilayers
- XRR and PIXE techniques
- Standing waves and Kossel diffraction
  - Method
  - History
  - Example : XRF Kossel
- PIXE – Kossel combination
- Conclusion

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# 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

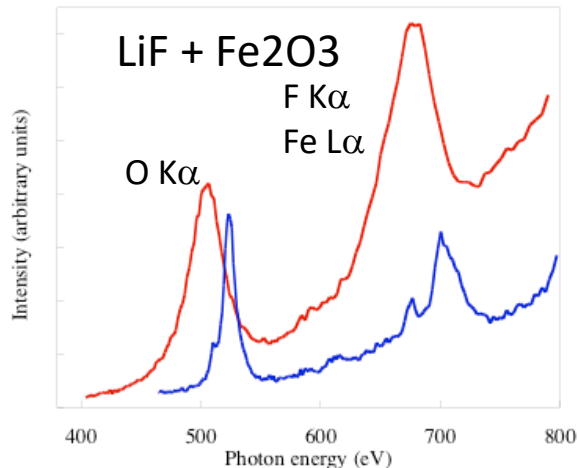
thickness<sub>light</sub> + thickness<sub>heavy</sub> = period d of a few nm

↳ 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

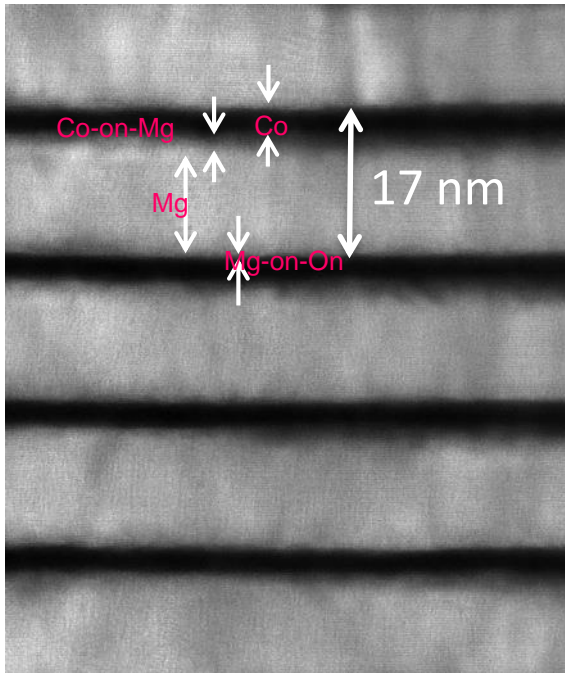


Imaging at a given wavelength

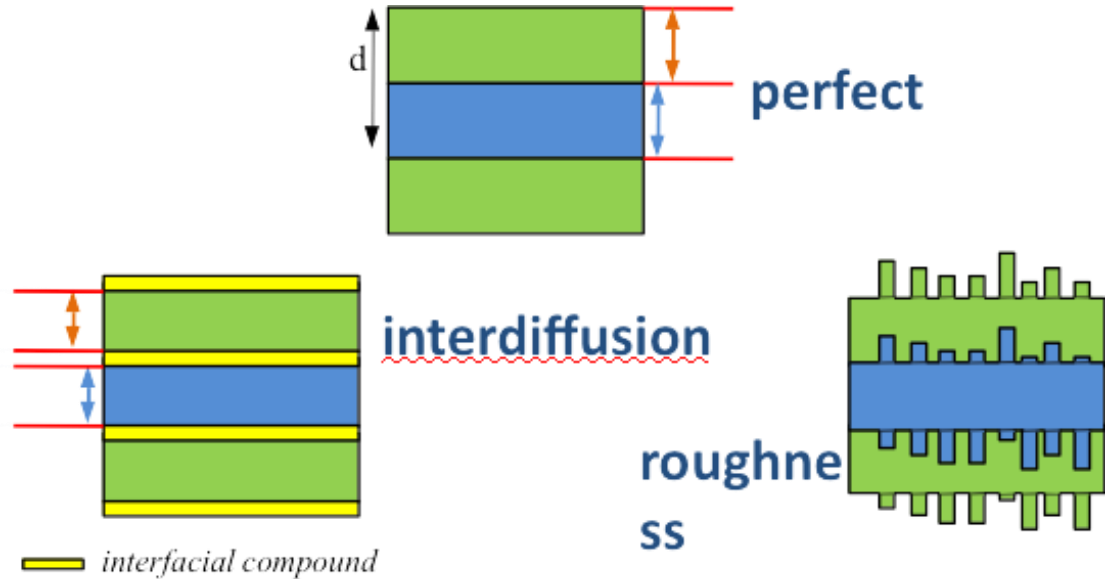


Photolithography  
@ 13.5 nm, 6.x nm

# Motivation and challenges



Co  
Mg  
Co  
Mg  
Co  
Mg



interfacial compound

roughness

|          | Visible<br>$\lambda=500\text{nm}$ | EUV<br>$\lambda=30.4\text{nm}$ |
|----------|-----------------------------------|--------------------------------|
| 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  
 $\exp(-2[2\pi \sigma \sin\theta / \lambda]^2)$   
 $\exp(-2[\pi \sigma / d]^2)$

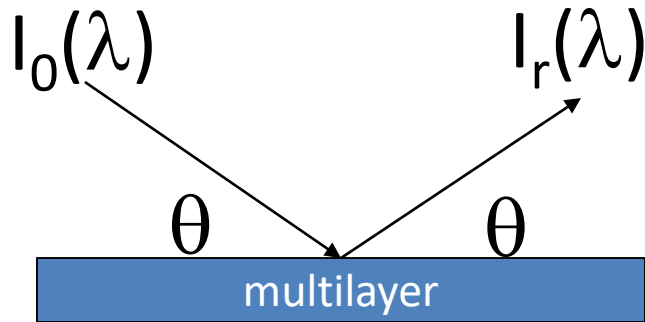
Interface is the largest challenge for EUV multilayer!

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# X-ray reflectivity



$$R_{\theta} = I_r(\lambda) / I_0(\lambda)$$

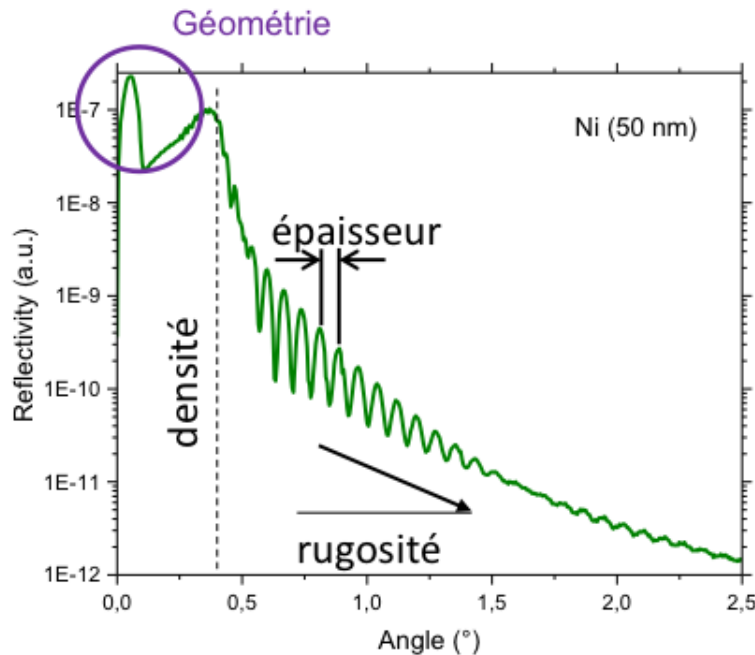
$$R_{\lambda} = I_r(\theta) / I_0(\theta)$$

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

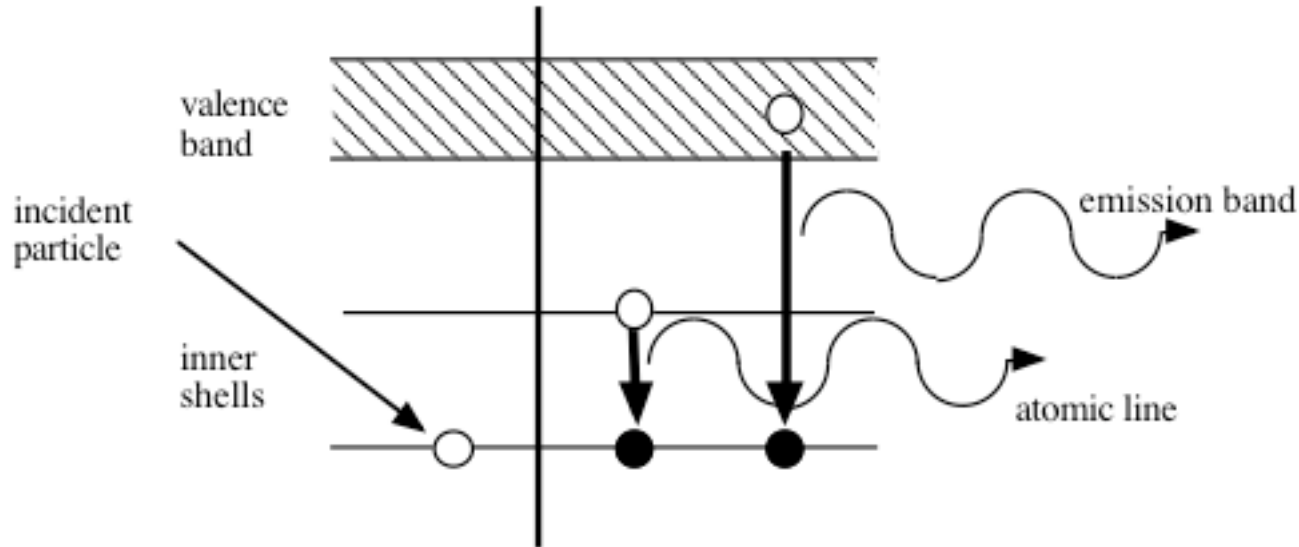
Bragg law

Determination of parameters  
of the stack

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



# X-ray emission spectroscopy



Observation of the **intensity** and **energy** distribution of the emitted radiation

Information about the **number (concentration)** and **chemical state** of the emitting elements

Incoming beam

- Electrons (EPMA)
- **Particles (PIXE)**
- X-rays (XRF)

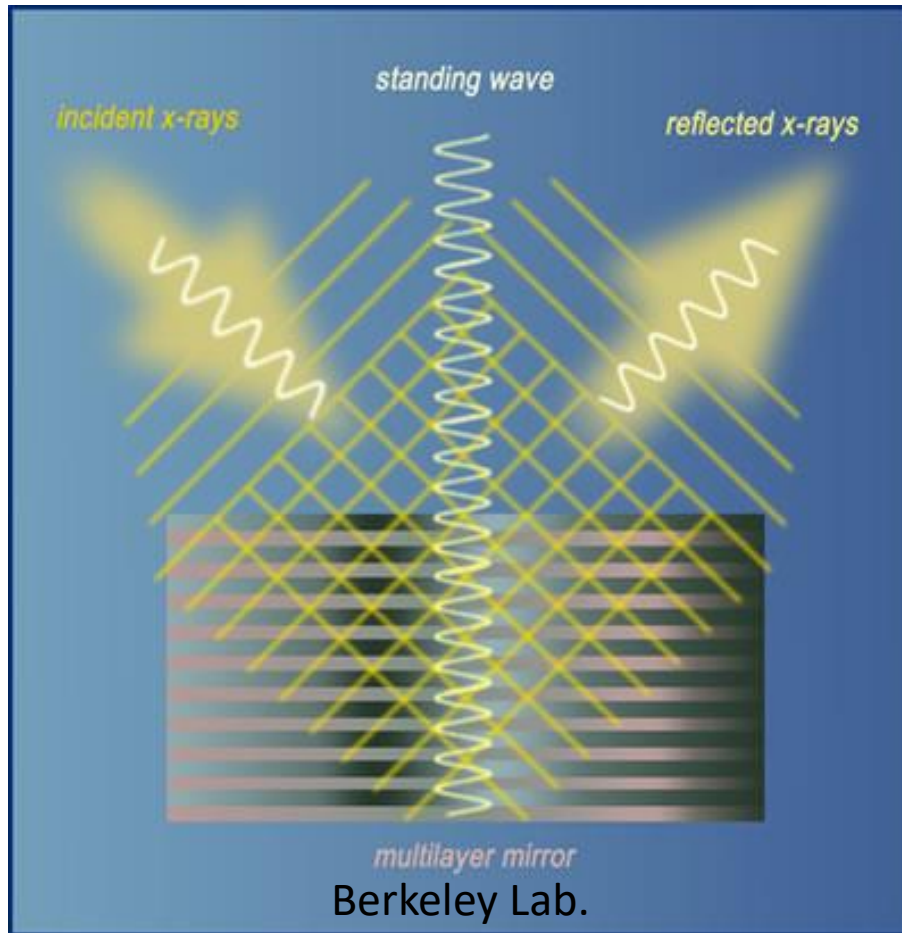
Detection / dispersion

- WDS : crystal spectrometer
- **EDS : Si(Li), SDD, bolometer, energy dispersive CCD camera**

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# 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

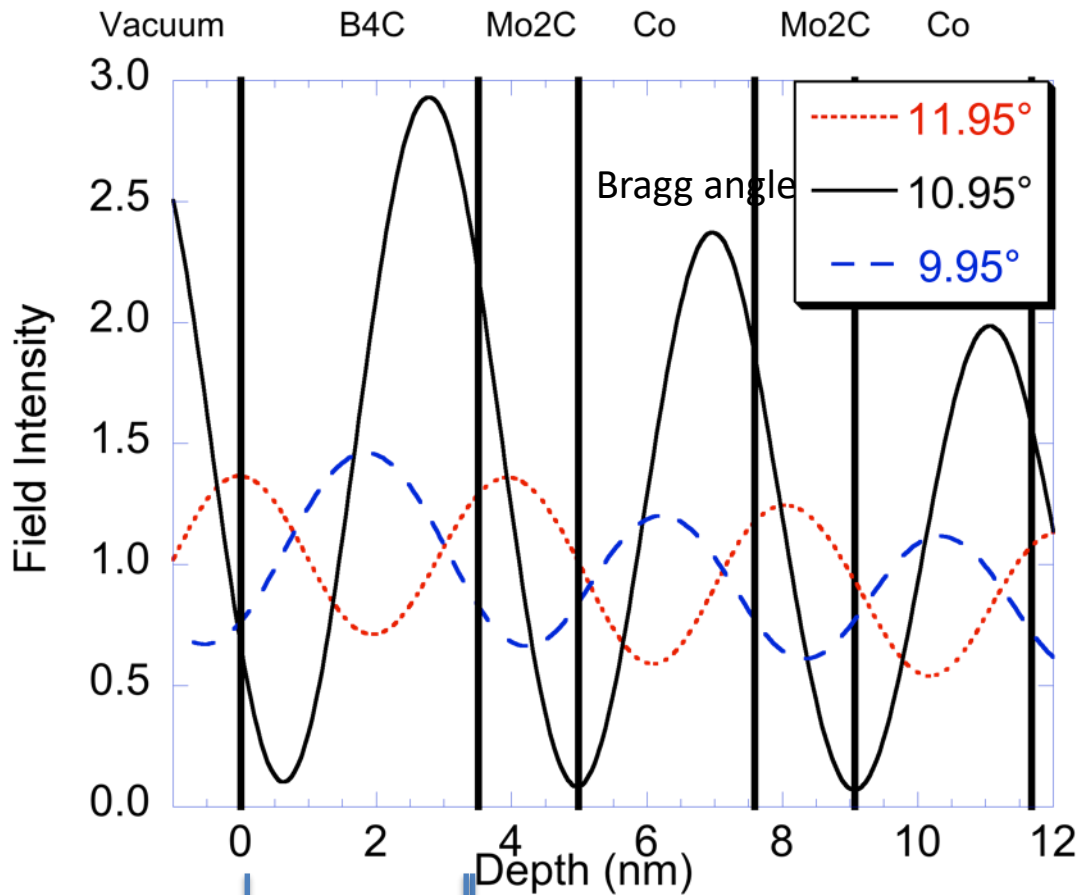
- **Interfaces of the multilayer itself**

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 maxima

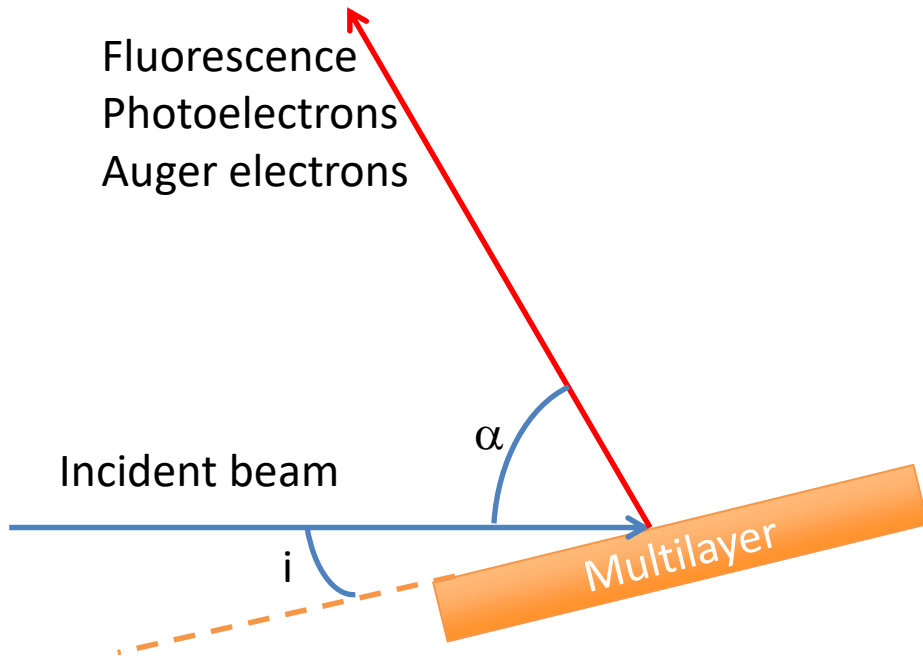
Analysis by

- XPS
- XRF
- AES

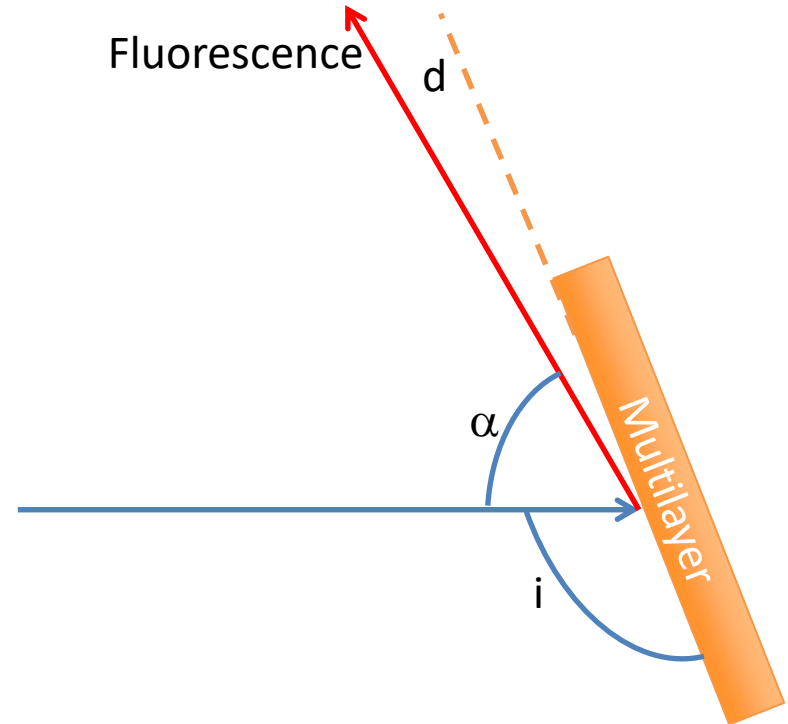
of a

- Multilayer
- Superficial material

# Two XSW modes



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



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

# Outline

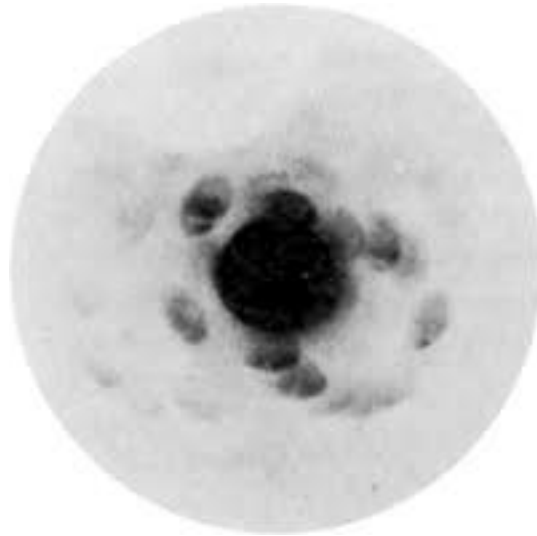
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# A bit of history



## 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

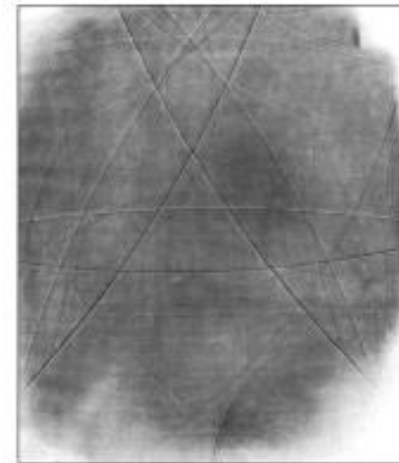
1912: von Laue, Friedrich, Knipping



## W. Kossel

1935

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





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# Multilayer

Si substrate /

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

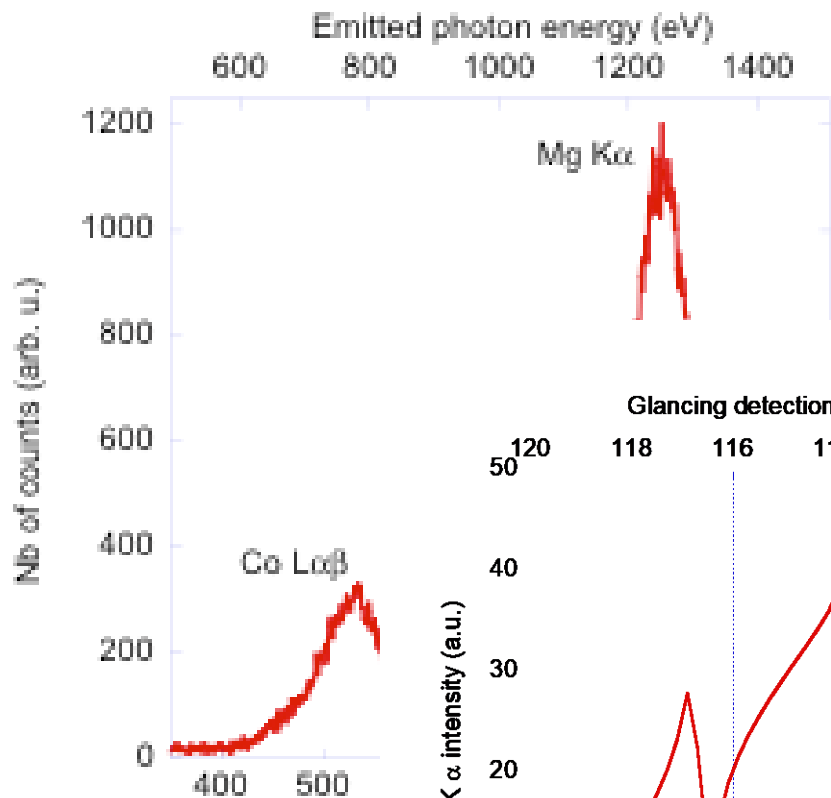
B4C (3.5nm) capping layer

# Mg/Co XSW - XRF

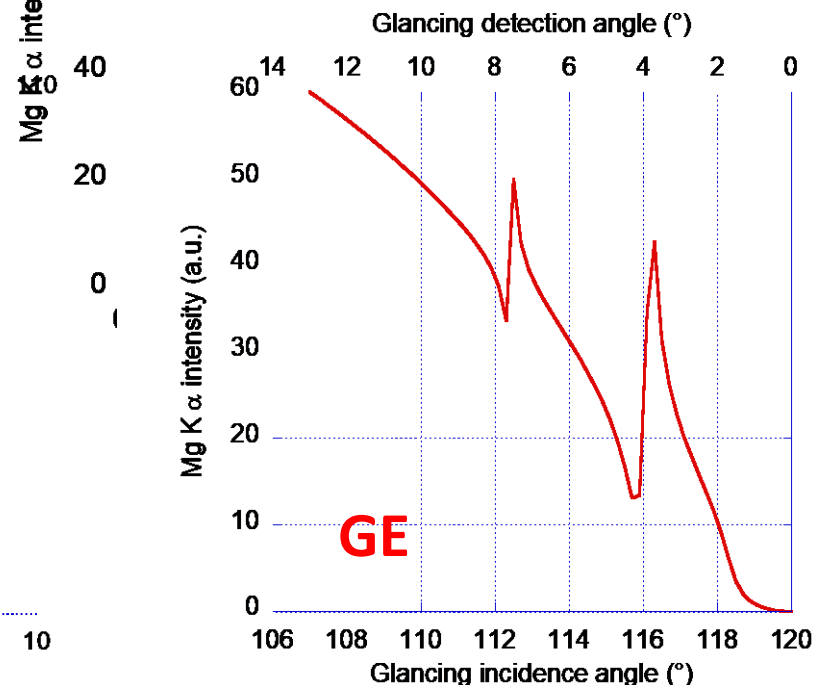
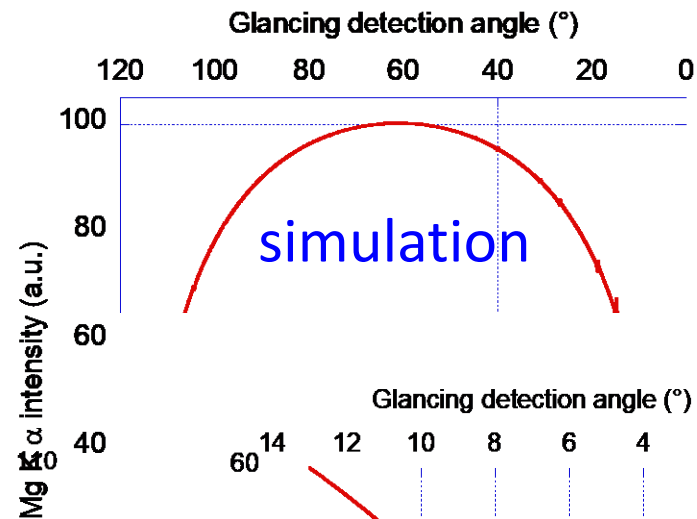
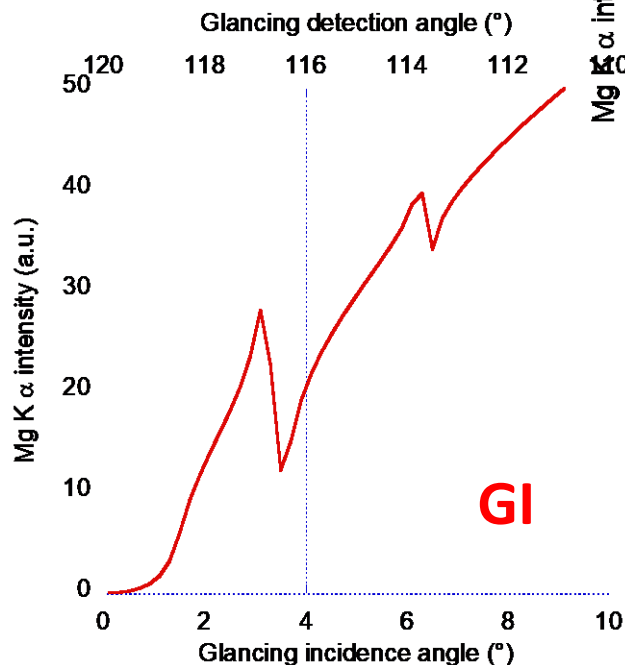
Incident radiation 1500eV; 0.827nm

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

60° between incident and detection directions



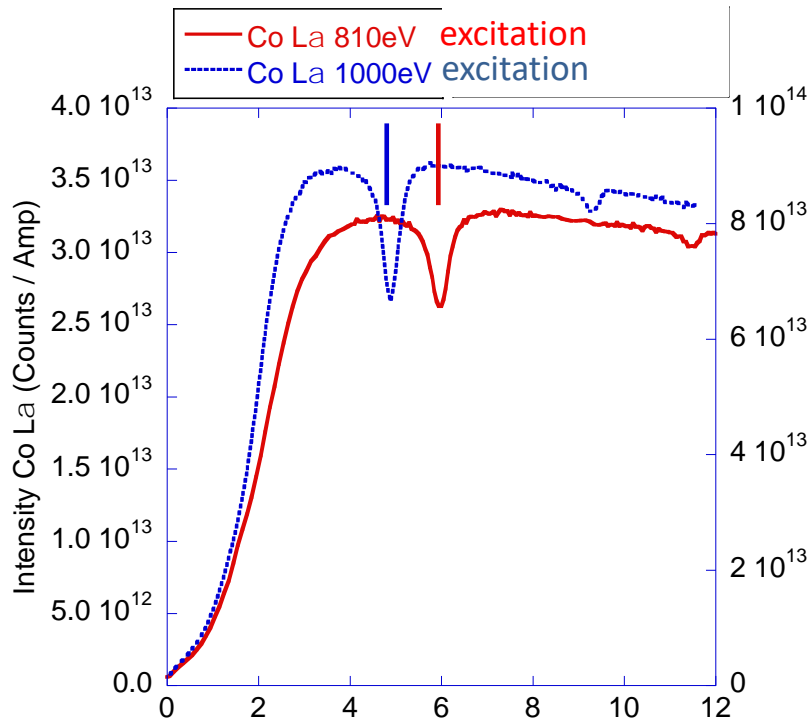
X-ray em



# Fluorescence of Mg/Co multilayer

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

"Classic" - GIF mode



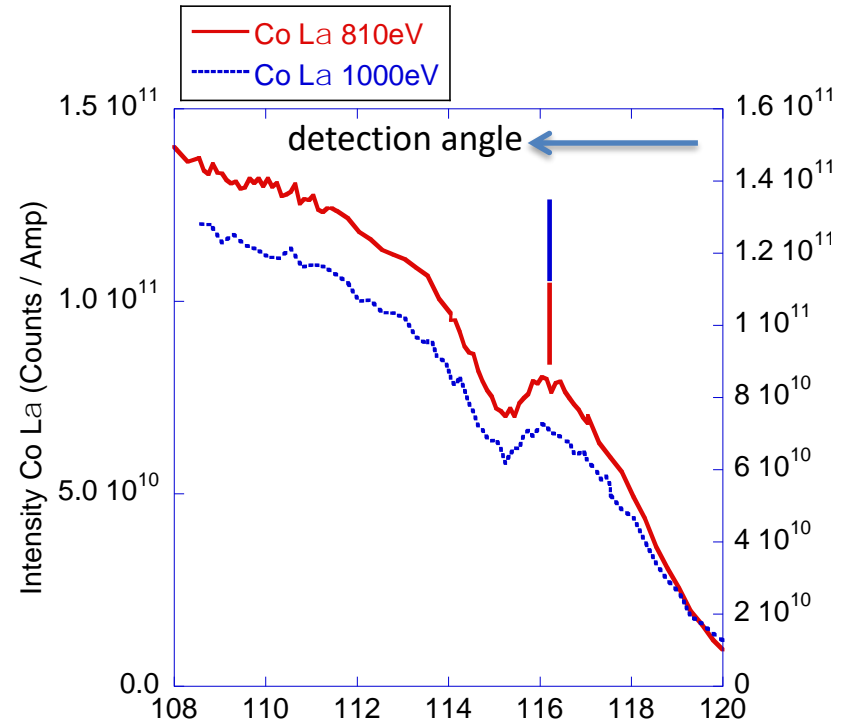
Incident glancing angle (°)

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



**Move** with energy of incident radiation

"Kossel" - GEF mode



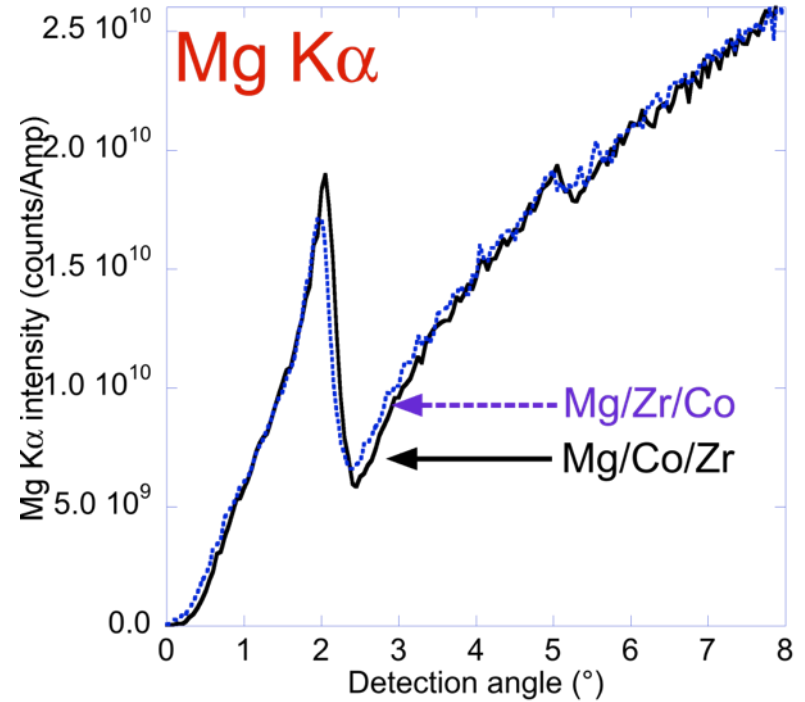
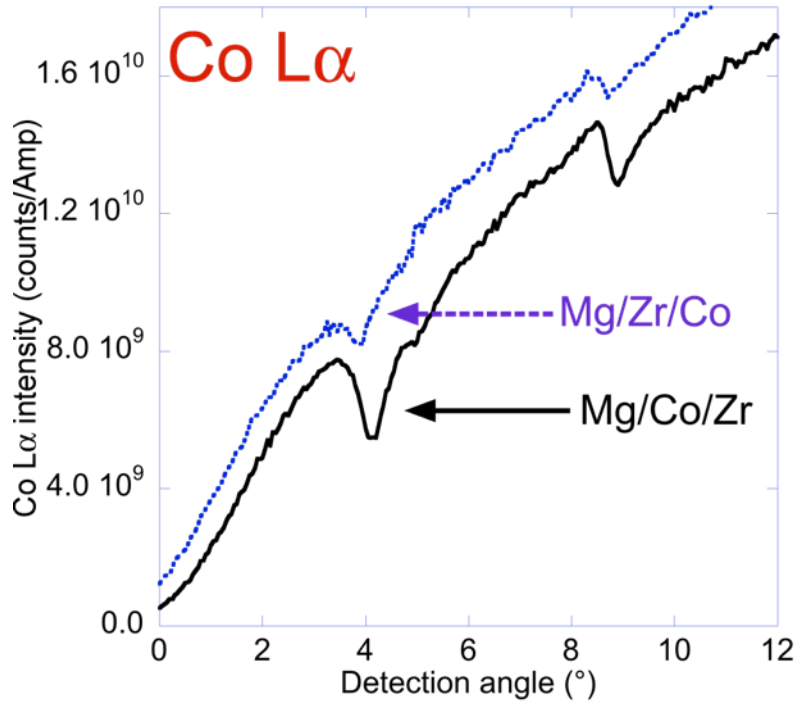
Incident glancing angle (°)

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



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

# GE experiment-simulations Mg/Co/Zr



Mg/Co/Zr  
TRI-LAYER

Mg/ZrxCoy  
BI-LAYER

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# Pd/Y based periodic multilayers

## ● Problem: the original design has bad optical performance

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

**Low reflection, bad periodicity**

- Severe interdiffusion between Pd and Y layers.

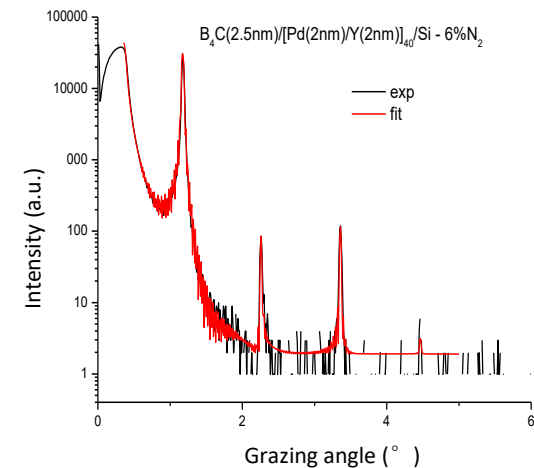
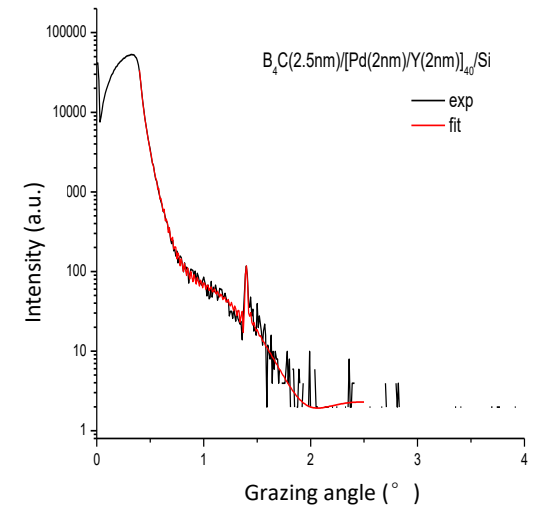
## ● Solution: Derivative systems

- 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).

# Particle Induced X-ray Emission

- Particle Induced X-ray Emission (PIXE)

- Ionization: particle generated core-hole.
- X-ray emission (fluorescence).

- SAFIR platform in SU

- Système d'Analyse par Faisceaux d'Ions Rapides  
(Analysis System using fast ions).
- Van de Graaff accelerator of positive ions.
- 2 MeV proton beam, ionization of Pd L shells.

- Advantages of protons

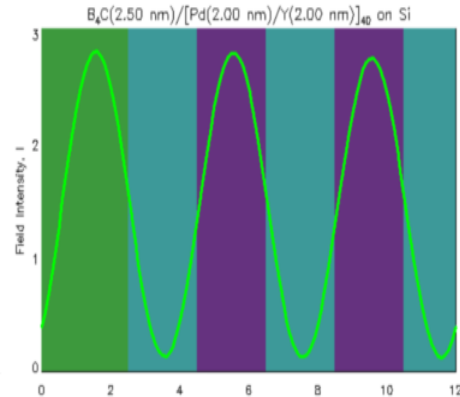
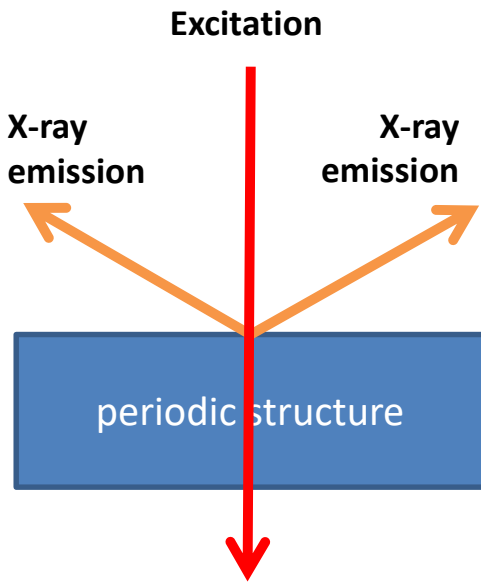
- Low scattering.
- Low Bremsstrahlung.
- Low energy loss (0.5% after penetrating the multilayer).
- Uniform ionization cross section.



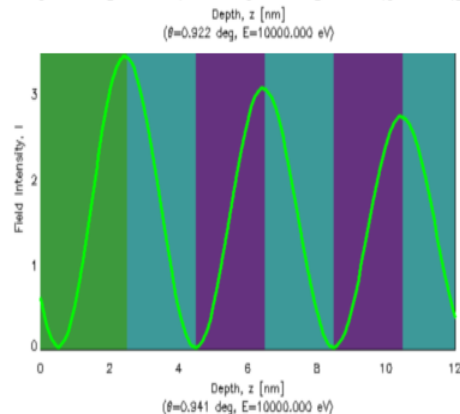
Accelerator in SAFIR

# Combine PIXE with Kossel diffraction

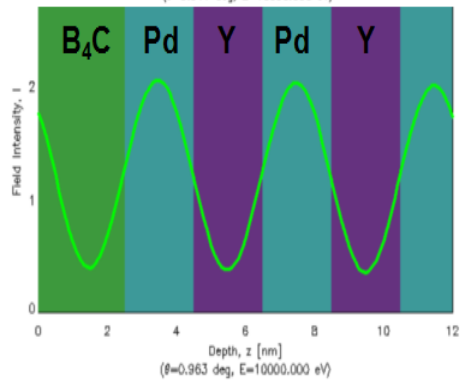
$$D = \frac{\lambda}{2 \sin \theta} = \frac{2\pi}{Q}$$



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

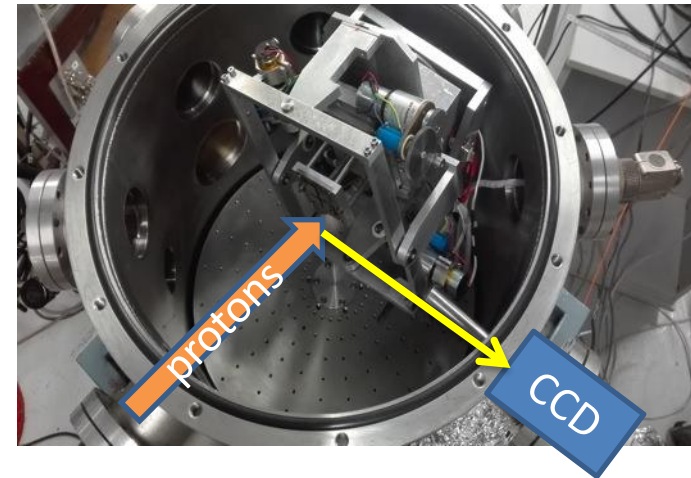
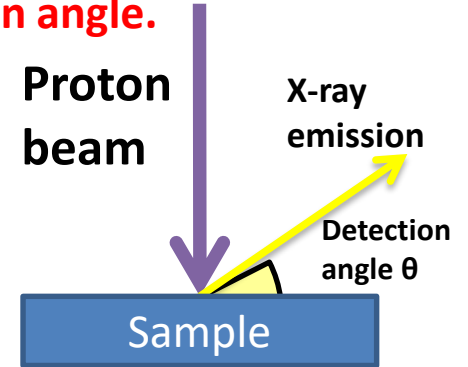


$\theta = \theta_{\text{Bragg}}$



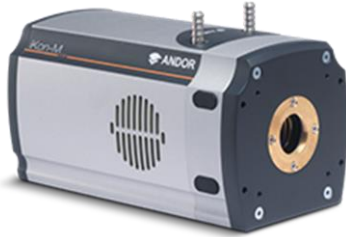
$\theta > \theta_{\text{Bragg}}$

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





# Energy dispersive CCD



## Andor Ikon-M CCD

~150 eV resolution @5.4 keV

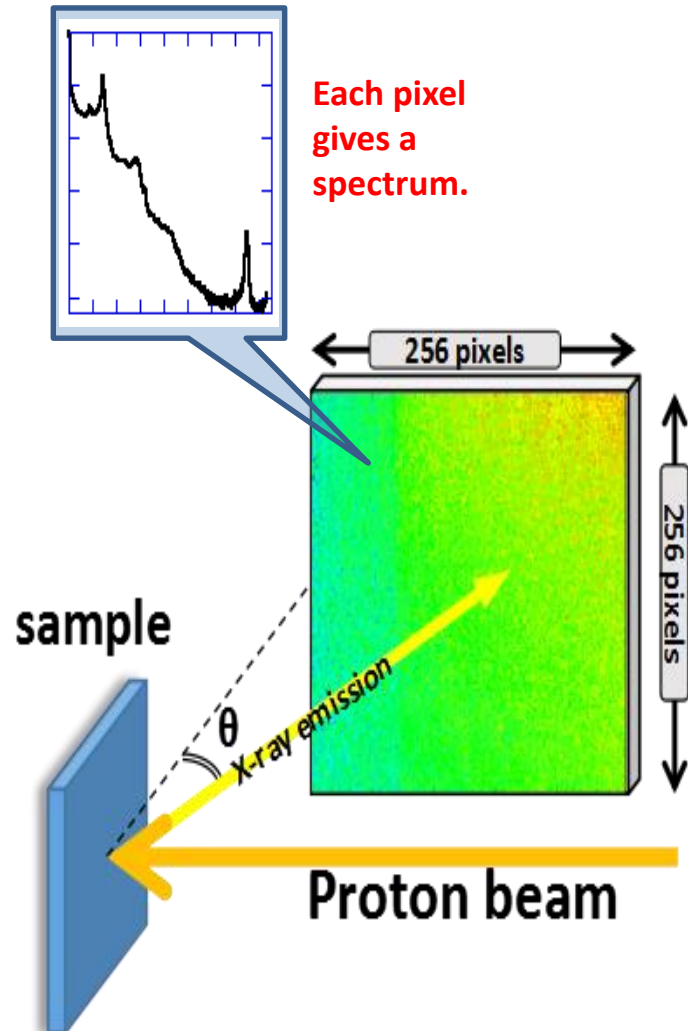
- **Advantage: spatially resolved.**

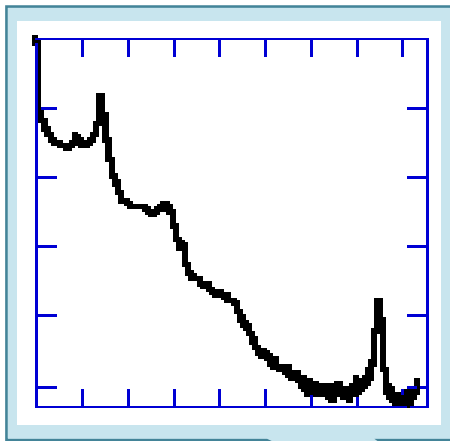
- Measurement of X-ray emission intensity in a squared area of about 13 x 13 mm.
- Native: 1024 x 1024 sensor array with 13 x 13  $\mu\text{m}$  pixels.
- Our selection: 256 x 256 of 52 x 52  $\mu\text{m}$ .

>>> **compromise of angular/energy resolution**

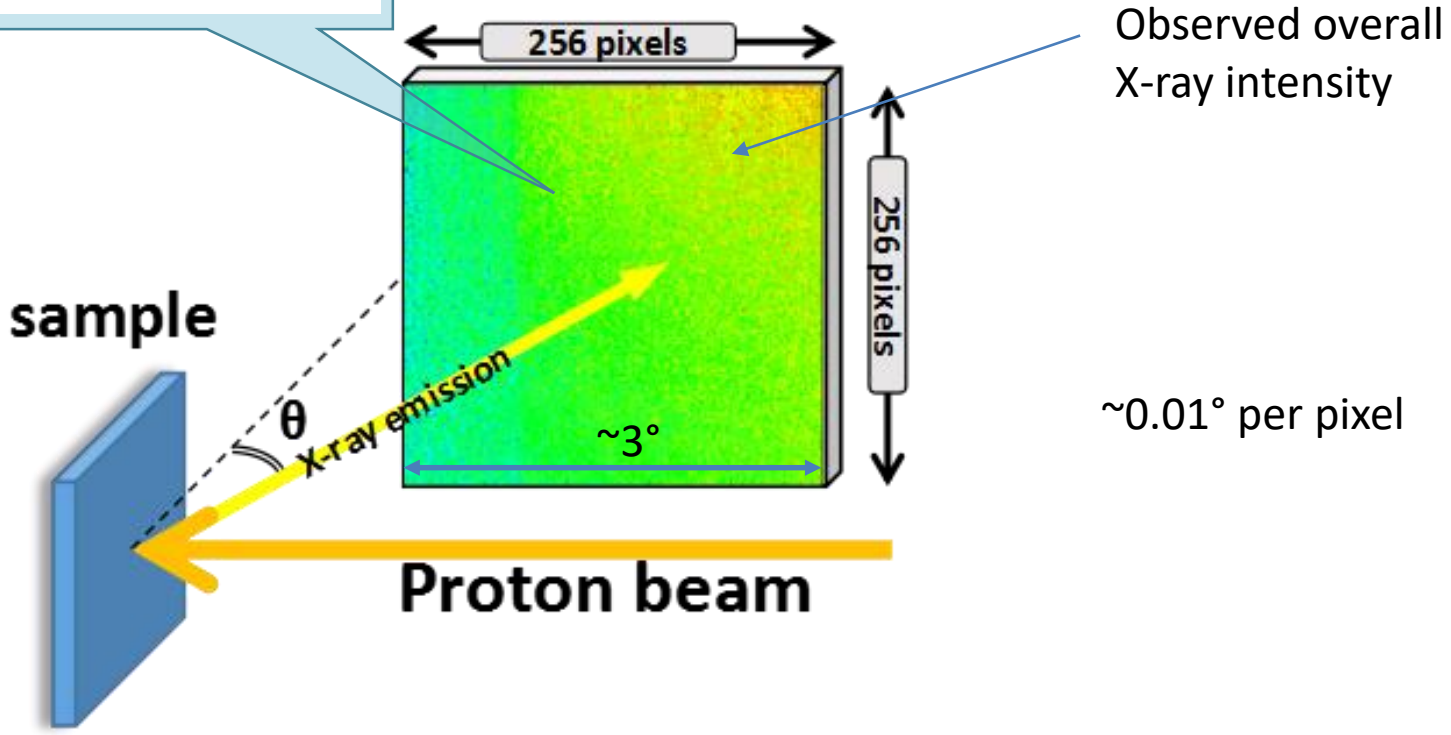
- No need to scan the angle.
- We place a 200  $\mu\text{m}$  beryllium film in front of the camera to filter the scattered protons. **Protection of the camera.**
- Acquisition time significantly reduced compared to SDD.

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





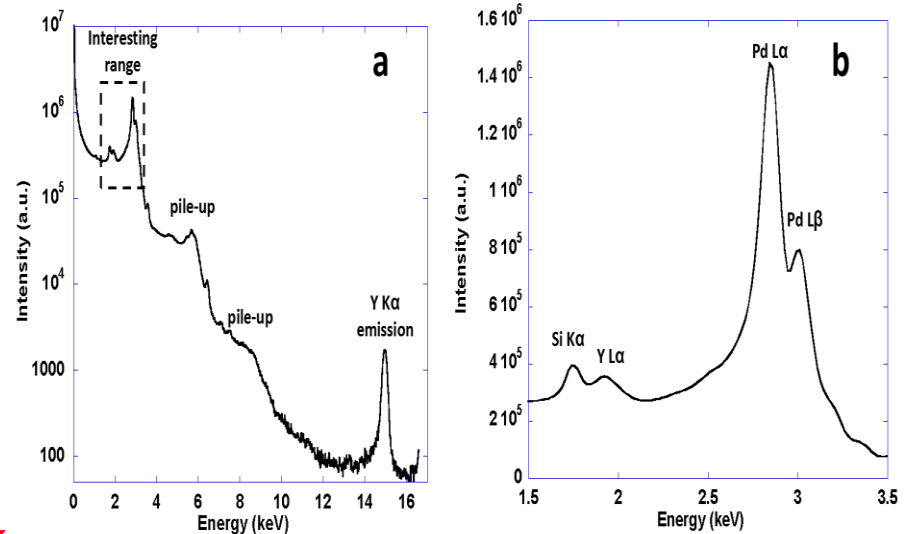
Pd 2nm  
Y 2nm } 40 periods  
4nm period



# 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)

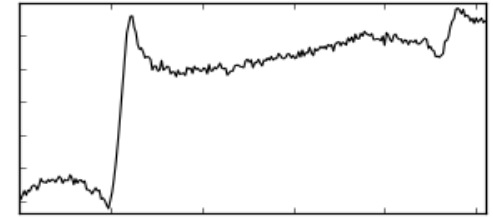
- Y  $K\alpha$  has too low intensity.
- Y  $L\alpha$ , Si  $K\alpha$  are in the low efficiency part of the X-ray camera.
- Pd  $L\beta$  does not bring additional information
- **We measure Pd  $L\alpha$  emission**



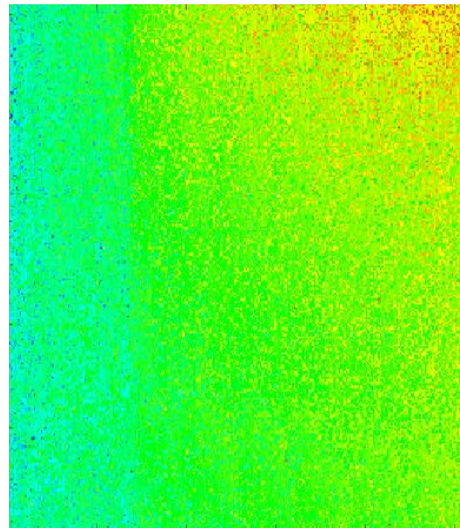
X-ray spectrum of Pd(2 nm)/ $B_4C$ (2 nm)/Y(2 nm) multilayer:  
a) overview (log scale)  
b) zoomed range of interest (linear scale).

# Kossel curves

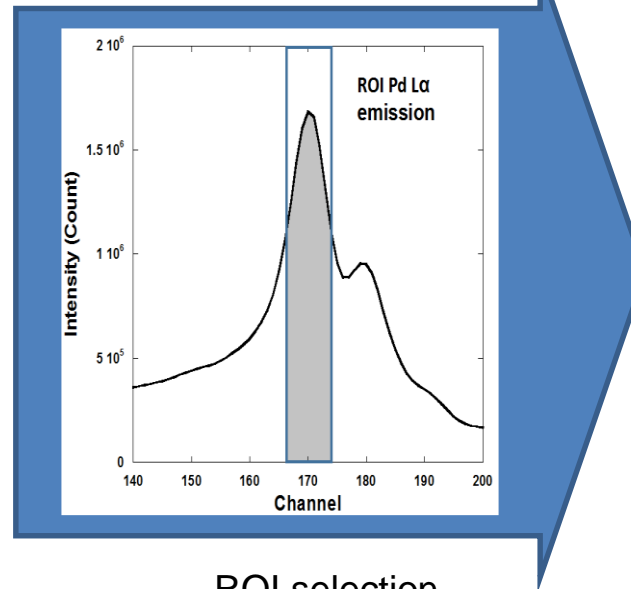
- The original image obtained by X-ray color camera contains the intensity of emitted photons of all energies.
- Kossel curve: the angular distribution of the characteristic X-ray emission.
- To get the Kossel curve of Pd L $\alpha$  emission, we need 3 steps:
  1. Select region of interest (ROI) on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



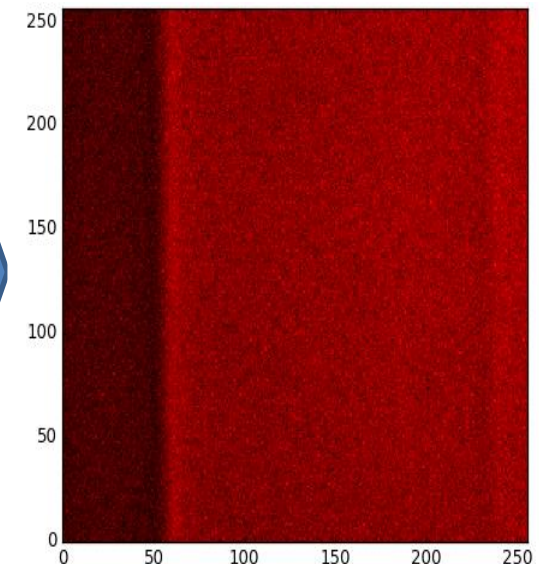
Integrate  
along the  
vertical  
pixels



Distribution of X-ray  
emission



ROI selection



Distribution of Pd L $\alpha$

# Calibration of detection angle

- Pixel of the detector - grazing exit angle

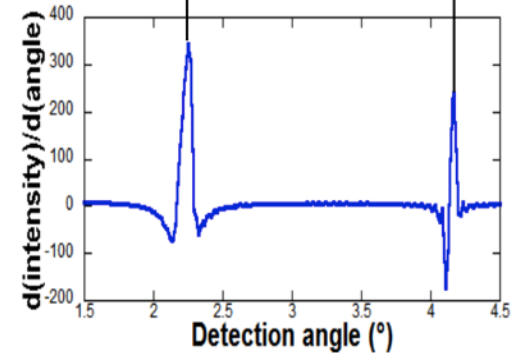
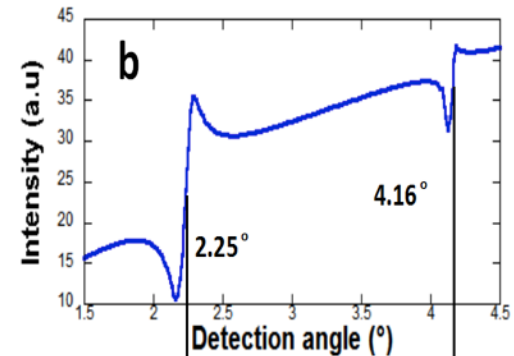
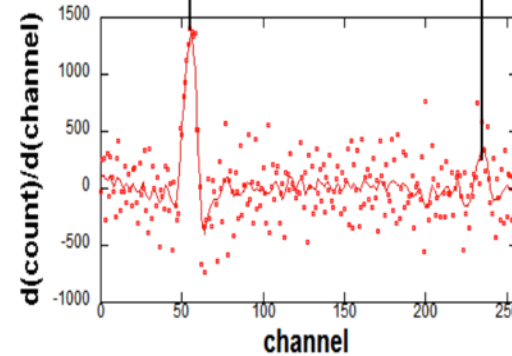
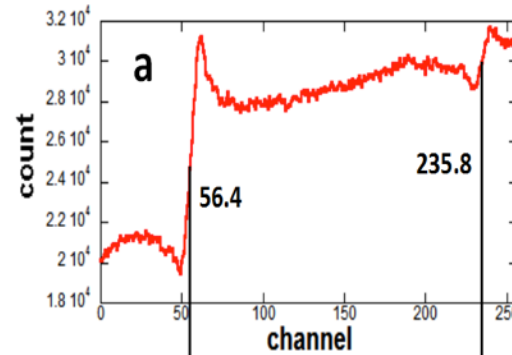
- 4-layer sample:  
 $B_4C(2.5 \text{ nm})/[B_4C(1 \text{ nm})/Pd(2 \text{ nm})/B_4C(1 \text{ nm})/Y(2 \text{ nm})]_{x40}/Si$

- 1st and 2nd order of Kossel oscillation

- a) experimental curve in channel (pixel)

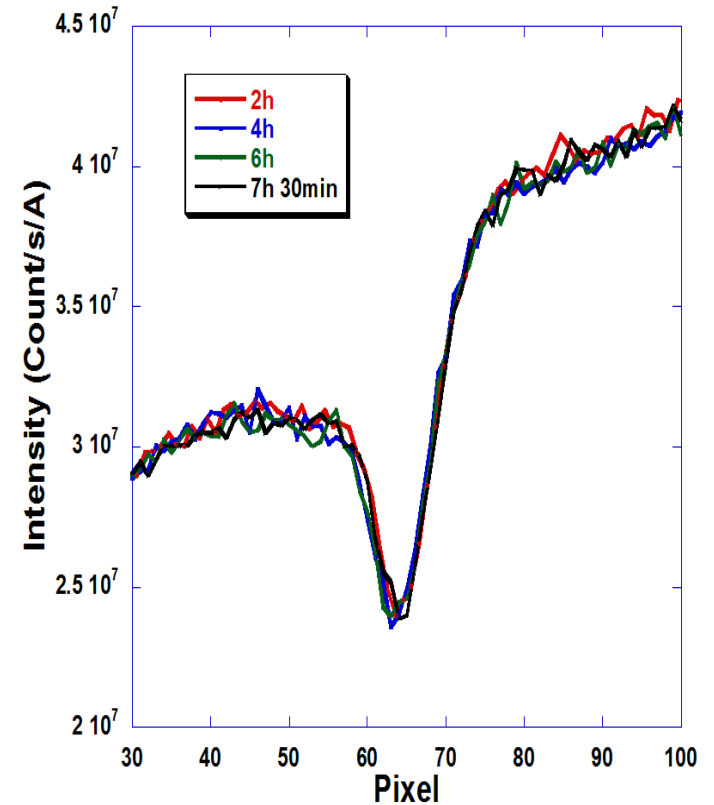
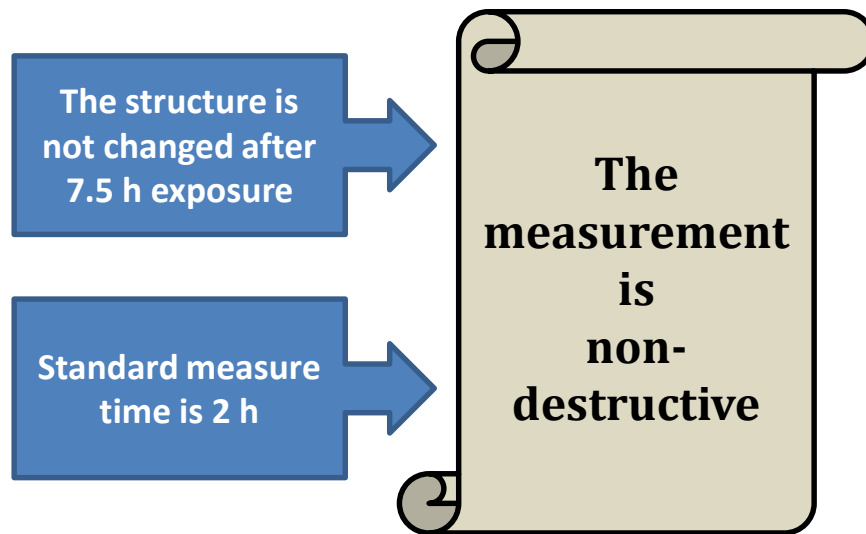
- b) simulated curve in angle (degree)

- 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

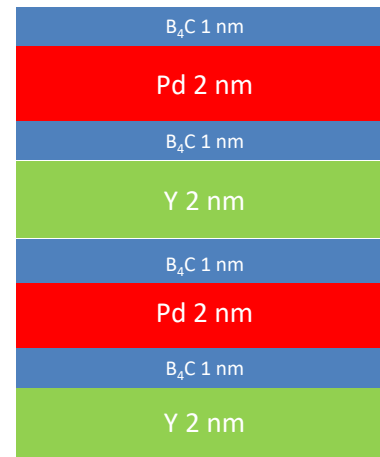
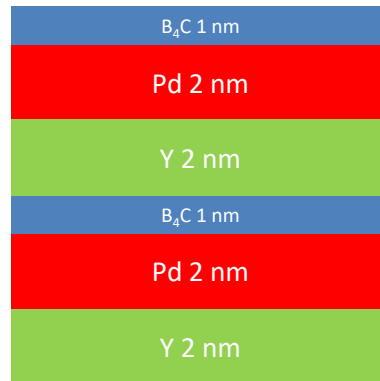
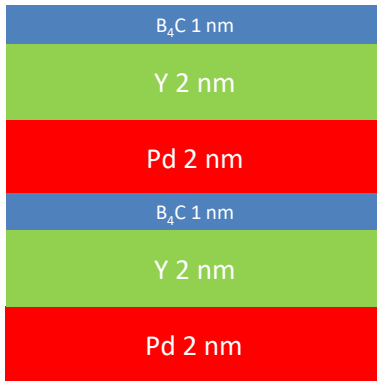


# First observations of multilayer structure

It is known that Pd and Y intermix easily during magnetron sputtering, and thus need stabilising

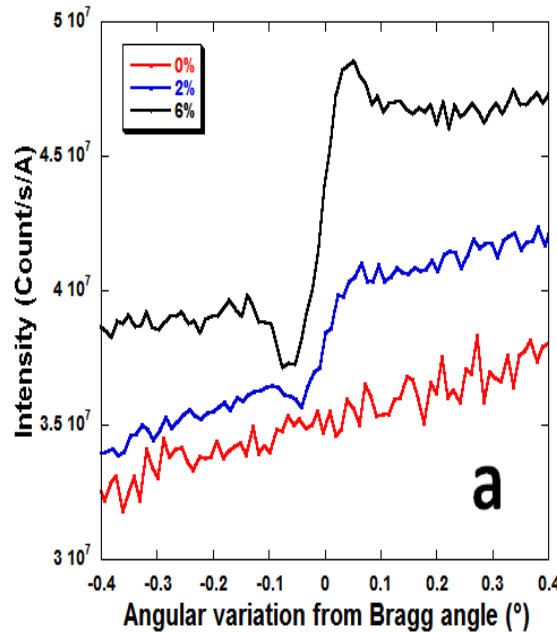
Strategies :

- Introduce  $N_2$  into the plasma during growth – 0%, 2%, 6%
- Use 1 nm  $B_4C$  buffer layers

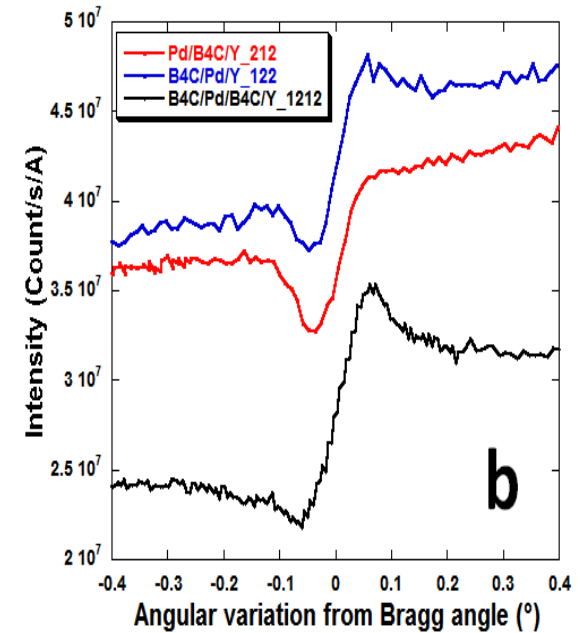


# Kossel curves of Pd La emission

- 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.

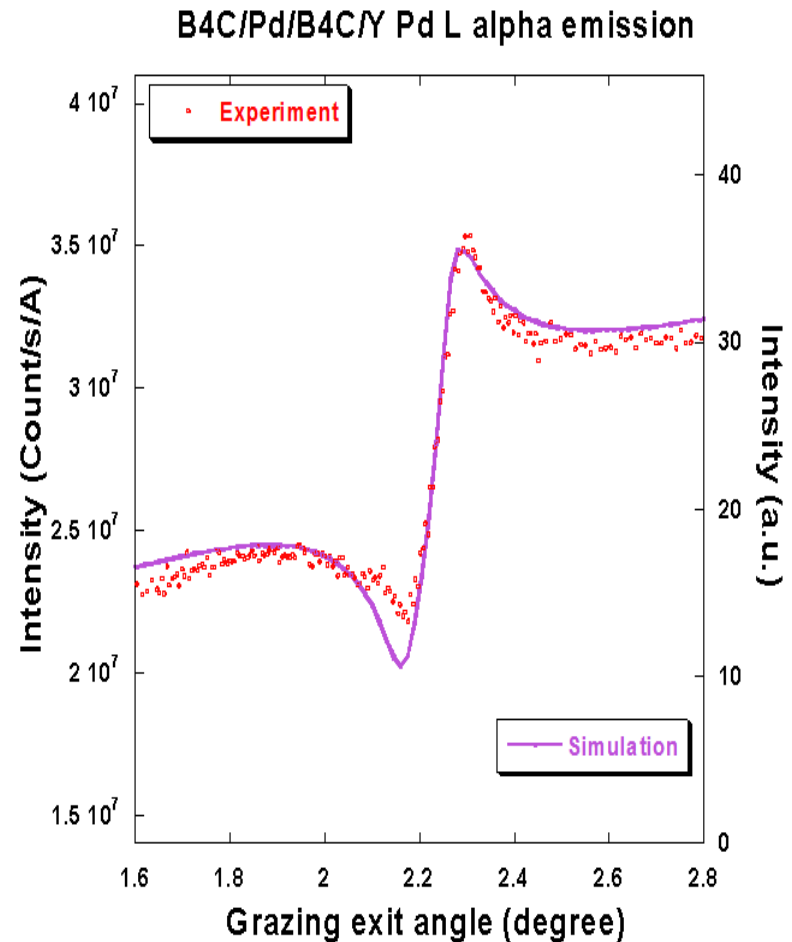


Kossel curves of the series of samples:  
b) With B<sub>4</sub>C barrier layers. The notation gives multilayer structure and layer thickness respectively.



# Simulation

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



# Conclusion

- We have observed the Kossel diffraction of proton induced Pd La emission in Pd/Y based multilayers.
- Nitridation has positive effect in preventing or reducing the interdiffusion between Pd and Y layers.
- The Pd/Y based multilayers with B<sub>4</sub>C barrier layers located at different interfaces can be distinguished by their Kossel curves.
  
- Compared to our previous experiment, the data acquisition is much improved by using an energy dispersive CCD camera.
  
- We have developed a new method to characterize the multilayers: PIXE-Kossel.
  - Simple experimental setup.
  - Element specific diffraction patterns.
  
- Further work is required :
  - Improve handling of data from the CCD camera – background, frame rates etc
  - Improve theoretical simulations, including interface properties