# Spectroscopy Methods & Techniques at PETRA III

**Wolfgang Drube**
***DESY***

DESY/European XFEL - Turkey Workshop, Jan. 26, 2016

# Examples of PETRA III spectroscopy techniques

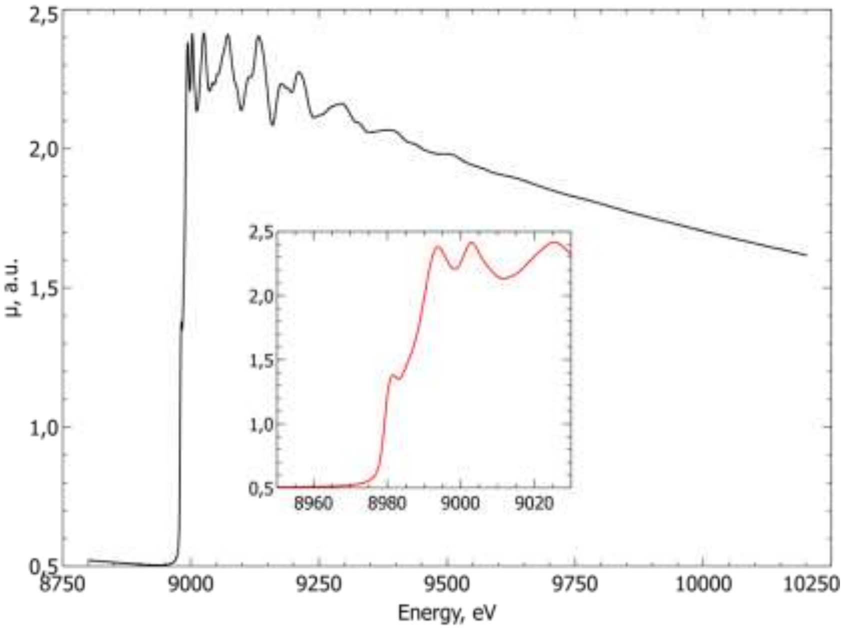
- **X-ray absorption spectroscopy**
  **- transmission**
  **- fast scanning**
  **- fluorescence detection**

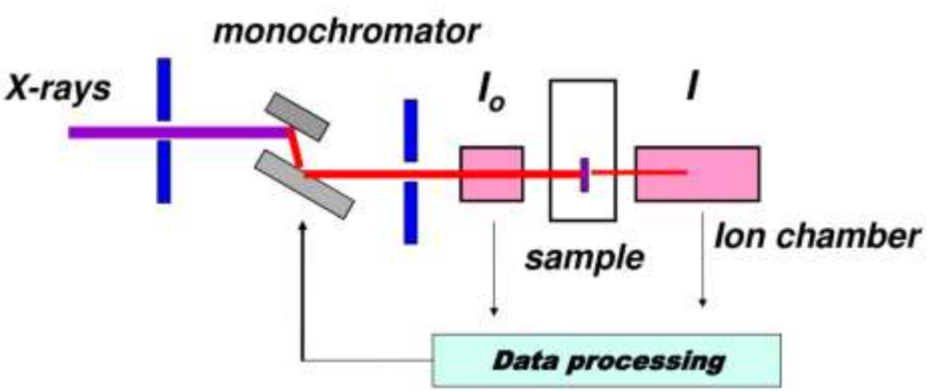
- **Inelastic X-ray scattering**
  **- resonant**
  **- non-resonant**

- **Photoelectron spectroscopy**
  **- soft X-rays**
  **- hard X-rays**

# Examples of PETRA III spectroscopy techniques

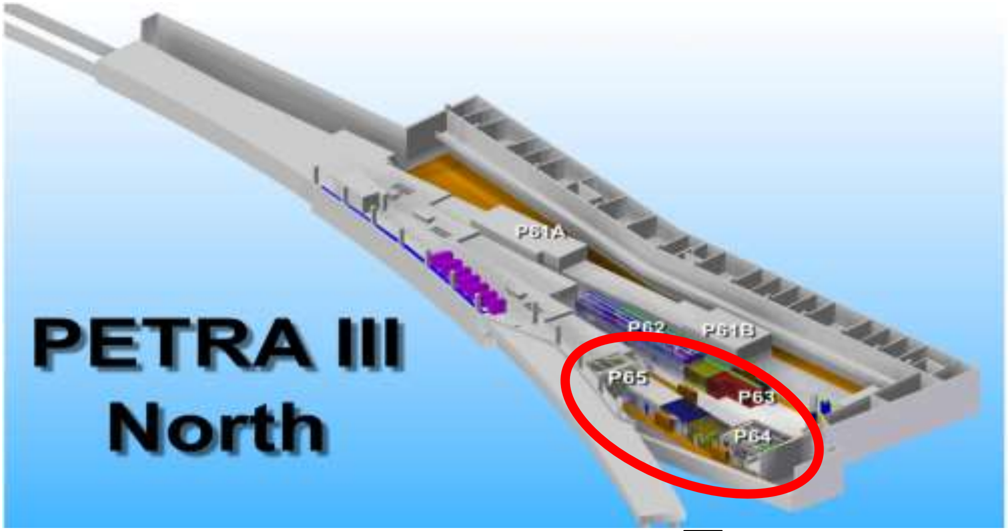
**X-ray absorption spectroscopy**
- **transmission**
- **fast scanning**
- **fluorescence detection**



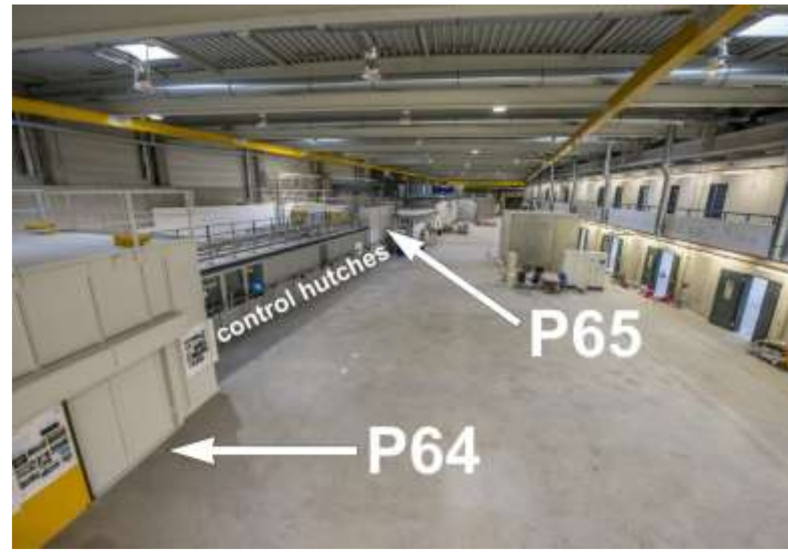




$$\mu t = \ln \frac{I_0}{I}$$

# X-ray absorption spectroscopy




XAFS is a key technique in materials science and chemistry

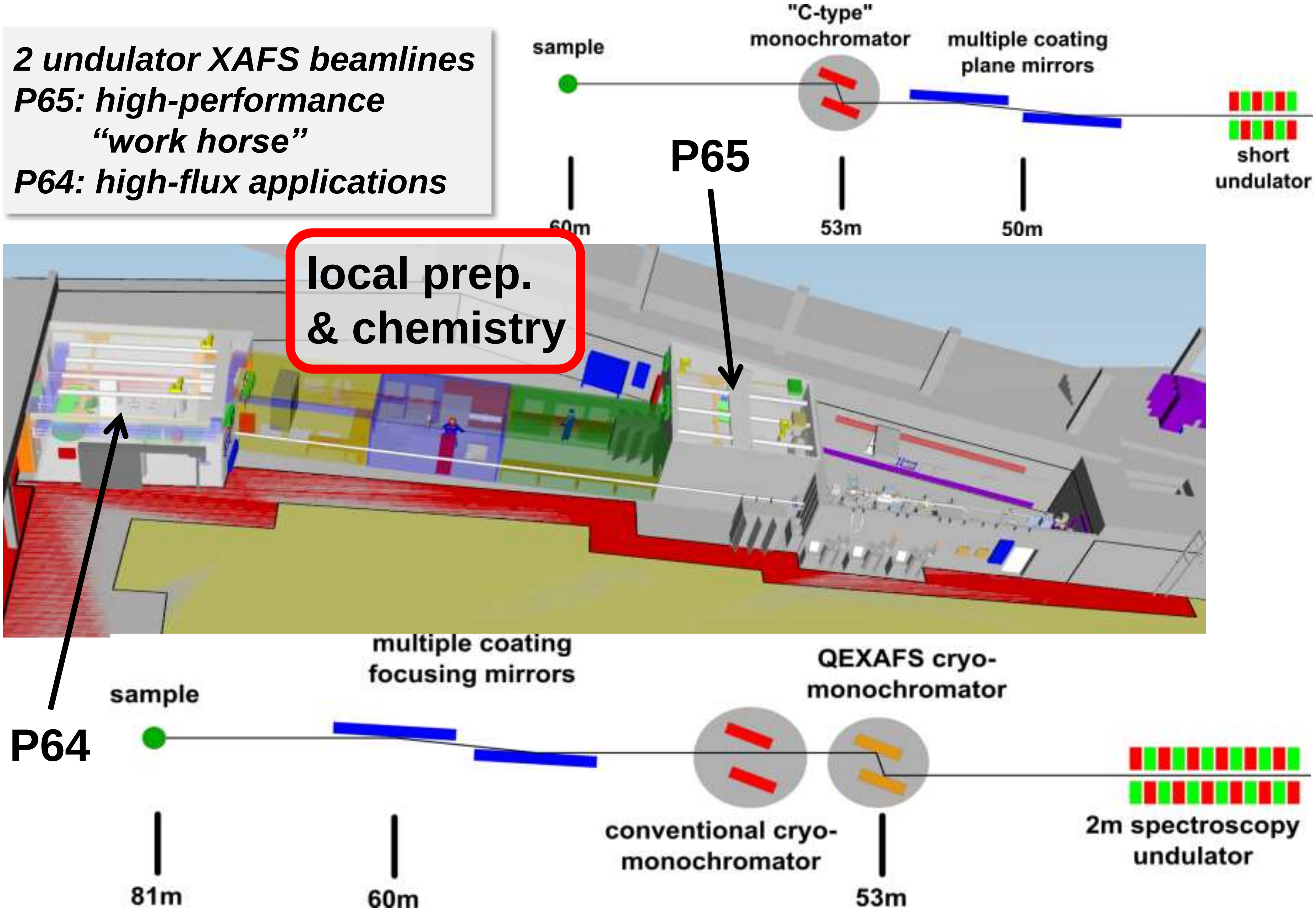



**Two "brand new" XAFS beamlines at the PETRA III extension (north)**

**Currently under commissioning**

# X-ray absorption spectroscopy

*2 undulator XAFS beamlines*
*P65: high-performance*
*“work horse”*
*P64: high-flux applications*



# X-ray absorption beamline P65

*4 – 44 keV / beamsize: 1 x 1 mm²*
*flux : > $10^{11}$ $s^{-1}$ ($10^{-4}$ BW)*
*1– 5 mins per scan (~1200 eV)*

Accessible Elements:
- K-edges: Ca – Nd
- L-edges: Sb - Uuo

Easy operating procedures also for inexperienced users

***Focus on in-situ experiments:***
- ***Catalytical chemistry***
- ***Energy storage / batteries***
- ***Material science***
- ***Environmental and geoscience***

***...***

***In-situ* cell (capillary) with oven and gas supply during first user experiments (Nov. 2015)**

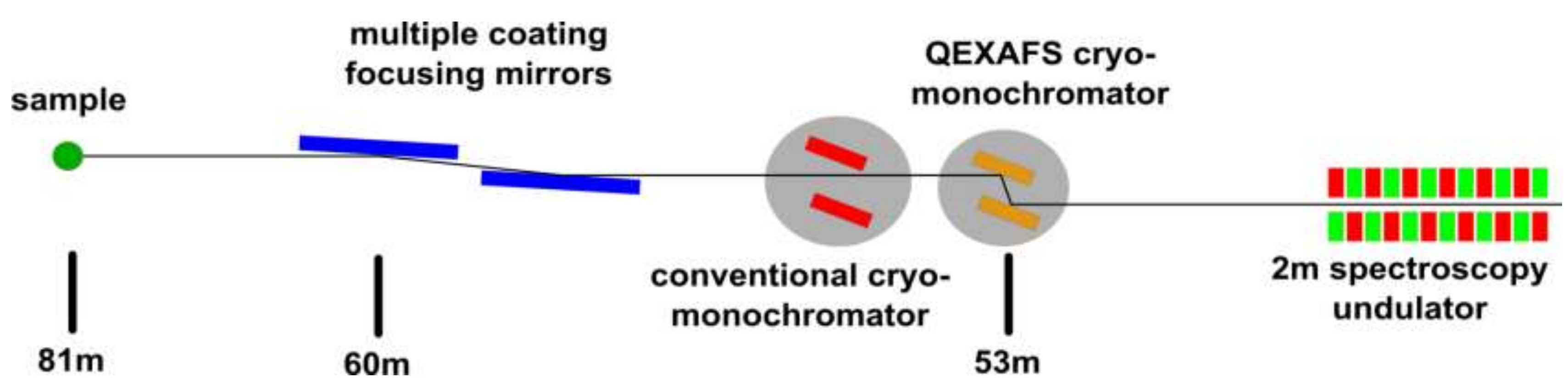
**Contact: Edmund Welter**

# X-ray absorption beamline P64

energies: (2.4)4 – 50 keV
flux: ~$10^{13}$ ph/s (tuned undulator)
~$10^{12}$ ph/s (tapered undulator)
resolution: $1.4 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$
flexible beam size: ~50 µm – 1 mm
scan times: 20ms (QEXAFS) – 300s
100-element Ge-detector (ΔE <260eV)
high-resolution emission spectrometer

**Two cryo monochromators:**
- fast scanning conventional XAFS
- QEXAFS (10-50Hz) undulator tapering

**High flux applications:**
- XAFS of diluted systems
- time resolved XAFS (ms)
- high-resolution (resonant) X-ray emission spectroscopy (RXES, RIXS, HERFD-XAFS)




**Contact: Wolfgang Caliebe**

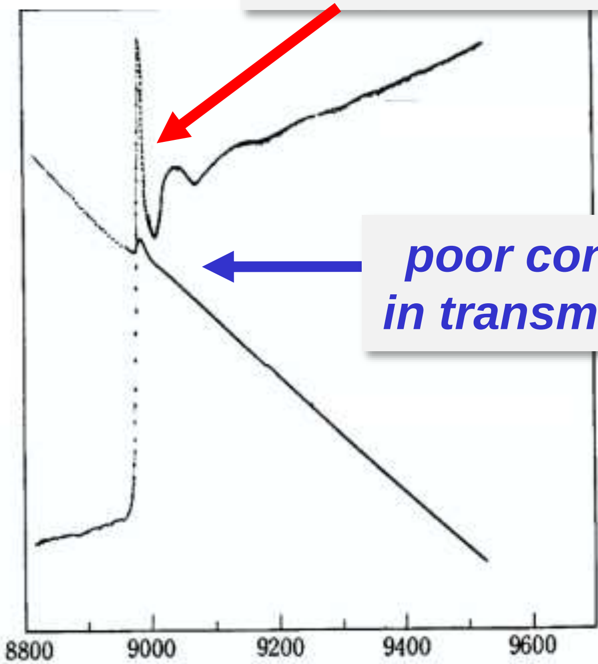
# Diluted systems: fluorescence detection

## *Highly diluted systems*

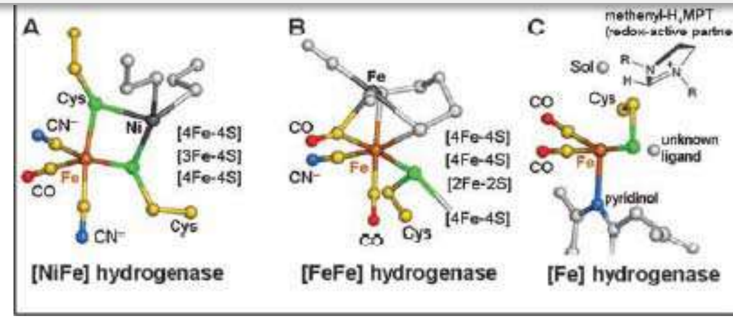
***e.g. Cu K-XAFS of $CuSO_4$ 10mMol aq. solution***

***good contrast using fluorescence***

***poor contrast in transmission***




## *BioXAFS: metal coordination in proteins*

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UNIVERSITÄT PADERBORN
Die Universität der Informationsgesellschaft

***100 pixel HPGe-detector***
***Test at P65 (Nov. 2015)***

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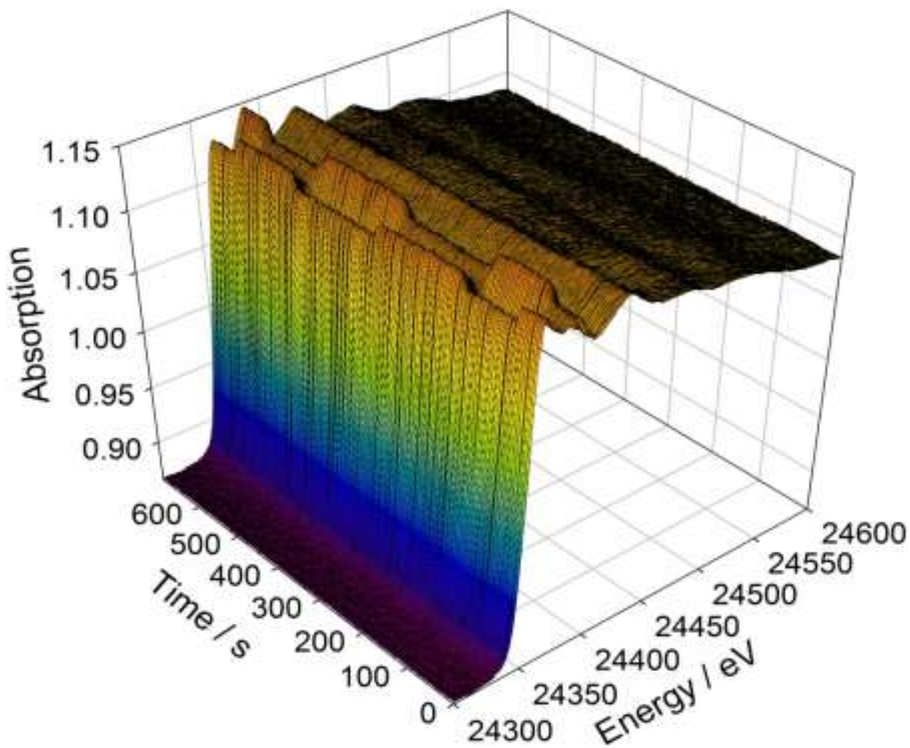
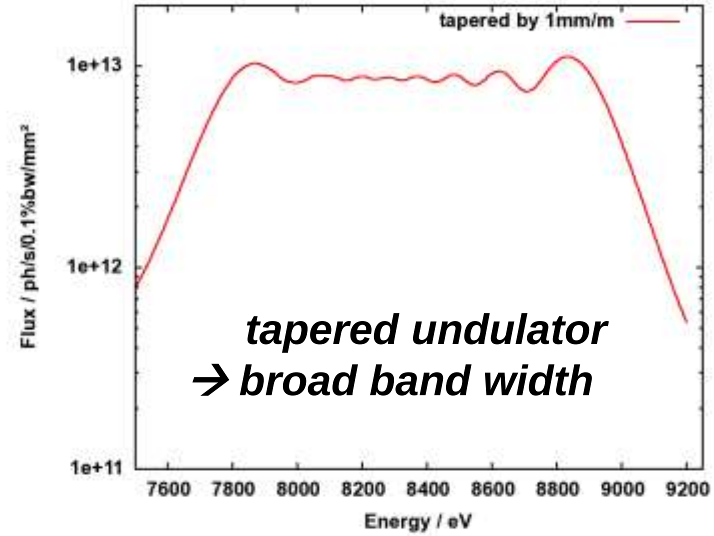
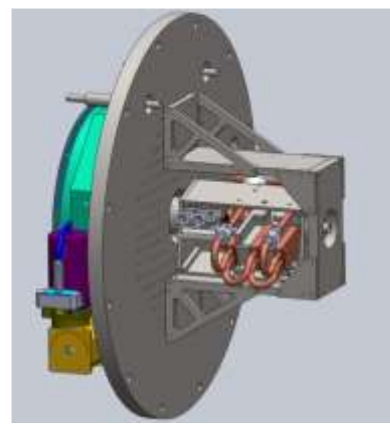
# ms time-resolved studies: QEXAFS

***in-operando*** **heterogeneous catalysis:**
**catalytic partial oxidation of methane**
**$Pd/Al_2O_3$, QEXAFS, 20-50 scans/s**




*J. Stötzel et al, J. Phys. Chem. C 116 , 599 (2012)*



***oscillating cryo-***
***QEXAFS monochr.***
***+ tapered undulator***

***BMBF funded***
***(Frahm, Univ. Wuppertal)***

BERGISCHE UNIVERSITÄT WUPPERTAL

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***Oscillatory behavior, suitable time resolution needed to monitor intermediate states***

**Contact: Wolfgang Caliebe**



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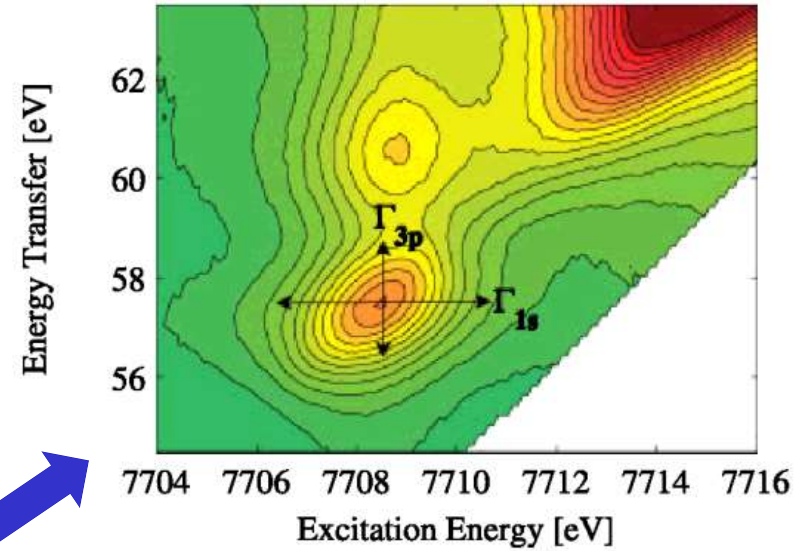
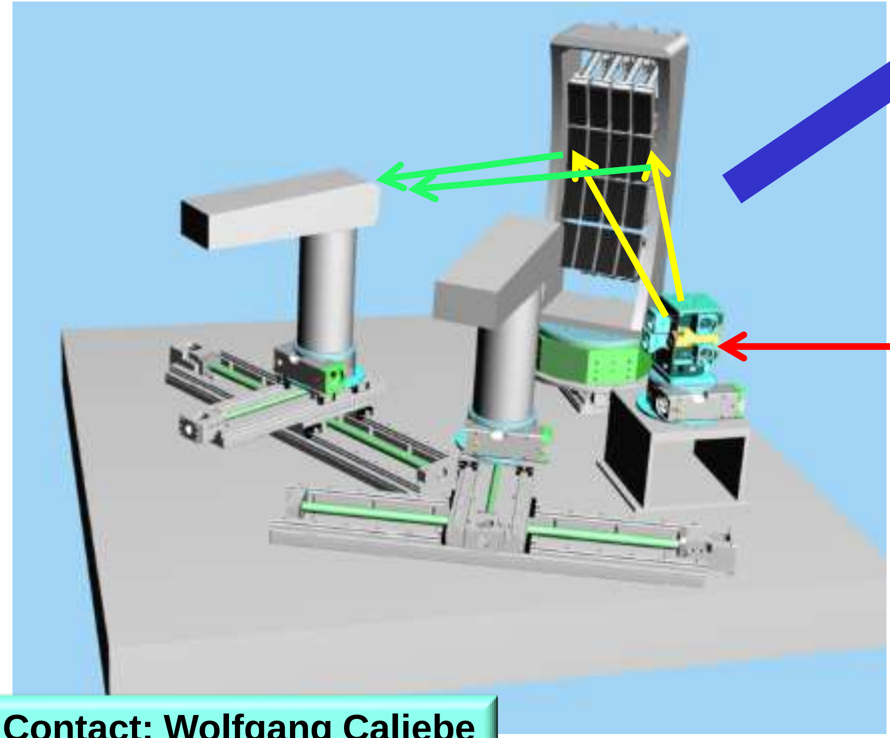
# High-resolution fluorescence detection

*o High-resolution (resonant)*
*X-ray emission spectroscopy*
*o emission line fine structure*
*(HERFD-XAFS)*
*oxidation states, ligands,*
*site-selectivity, …*



Up to 16 analyzer Si-crystals
(111), (311), (400), (220)
cylindrically bent

Two area detectors (Lambda)
emission spectrum $\Delta E$ = 50-150 eV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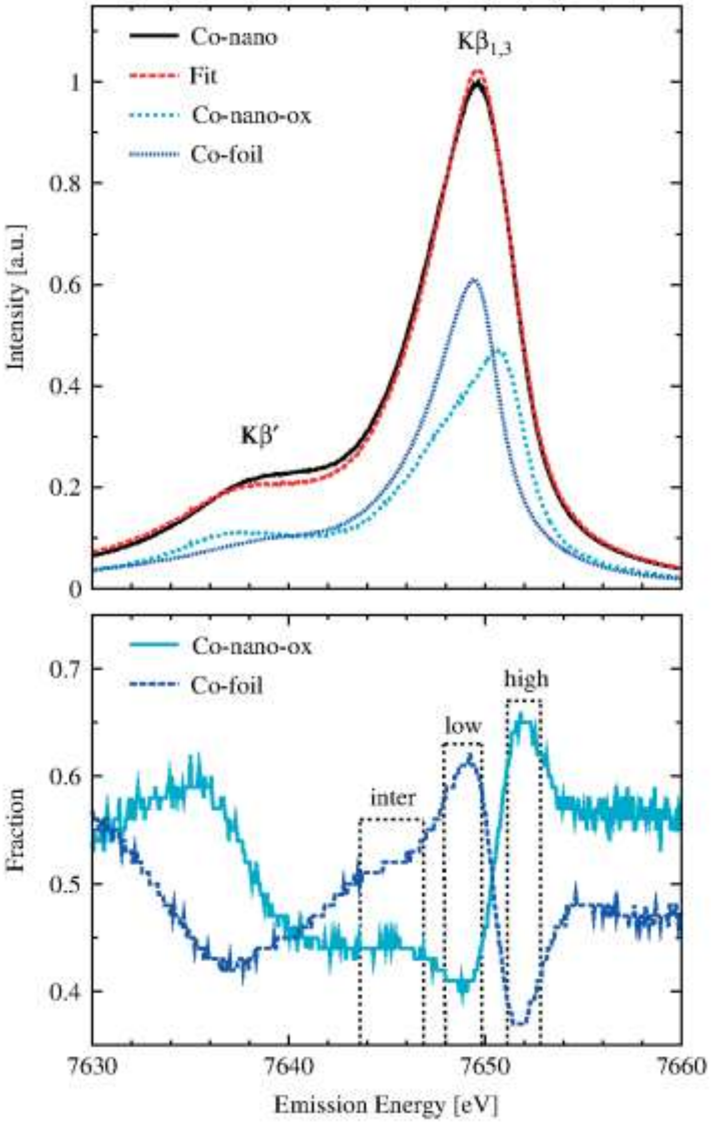
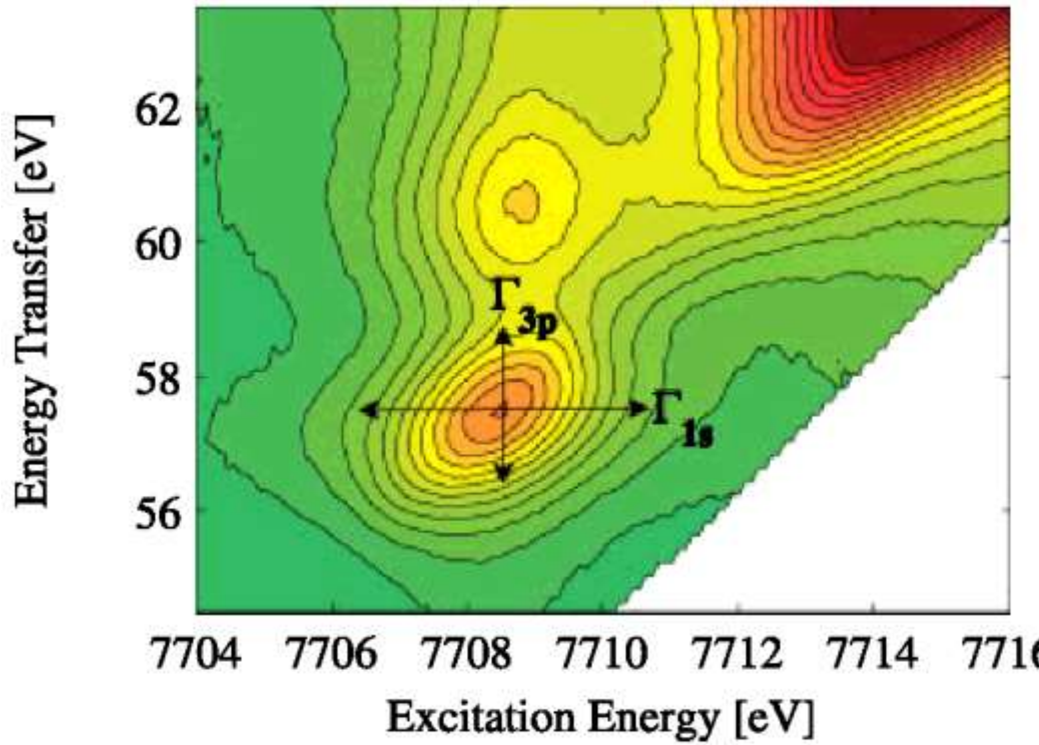
**BMBF funded**
**(M. Bauer, Univ. Paderborn)**


**Contact: Wolfgang Caliebe**

# Example: Co nanoparticles with CoOx-shell




**Kβ fluorescence as a function of excitation energy in the pre-edge region (RIXS-plane), reference sample CoO ("RXES-plane")**

**Kβ fluorescence of Co-foil, completely oxidized Co nanoparticles (Co-nano-ox), and of Co-core CoOx-shell nano-particles, and fractions of Co-foil and Co-nano-ox in Co-core CoOx-shell particles.**

***T.J. Kühn et al,***
***Appl. Organometal. Chem. 25, 577-584 (2011)***

**Contact: Wolfgang Caliebe**

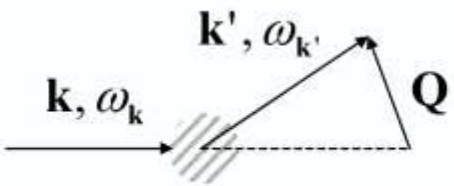
# Examples of PETRA III spectroscopy techniques

**Inelastic X-ray scattering**

- **resonant** → **previous example**
- **non-resonant**

$$H = \frac{e}{mc}\mathbf{p}\cdot\mathbf{A} + \frac{e^2}{2mc^2}\mathbf{A}\cdot\mathbf{A}$$

resonant    non-resonant

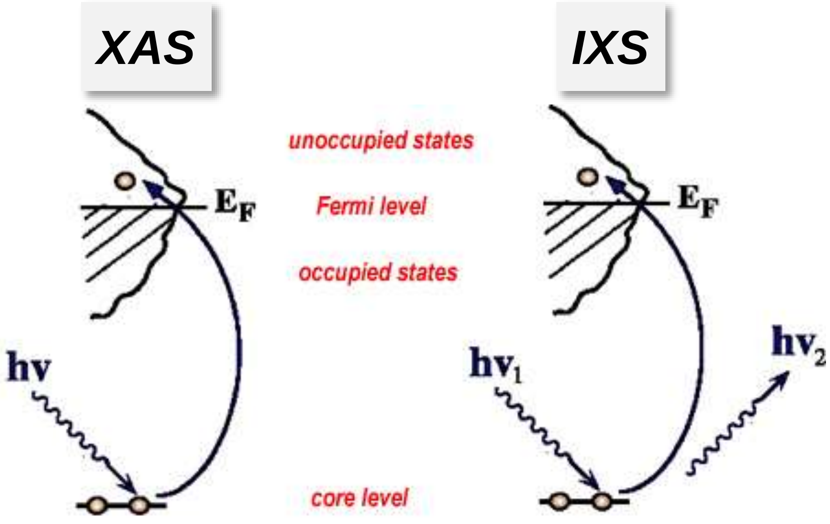


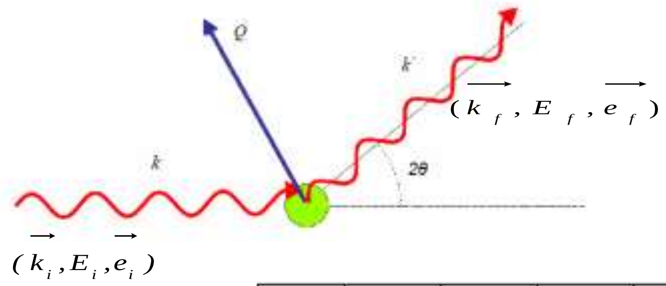

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}'$$

$$\hbar\omega = \hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$$

$$\frac{d^2\sigma}{d\Omega d\omega_{\mathbf{k}'}} = \left(\frac{d\sigma}{d\Omega}\right)_{Th} \left|f(\mathbf{Q})\right|^2 S(\mathbf{Q},\omega)\,, \quad \text{with} \quad S(\mathbf{Q},\omega) \propto \mathrm{Im}\left(\frac{-1}{\varepsilon(\mathbf{Q},\omega)}\right)$$

# Non-resonant inelastic (Raman) X-ray scattering




$$\frac{d^2\sigma}{d\Omega\, d\omega} = \left(\frac{d\sigma}{d\omega}\right)_{Th} S(\vec{q},\omega)$$

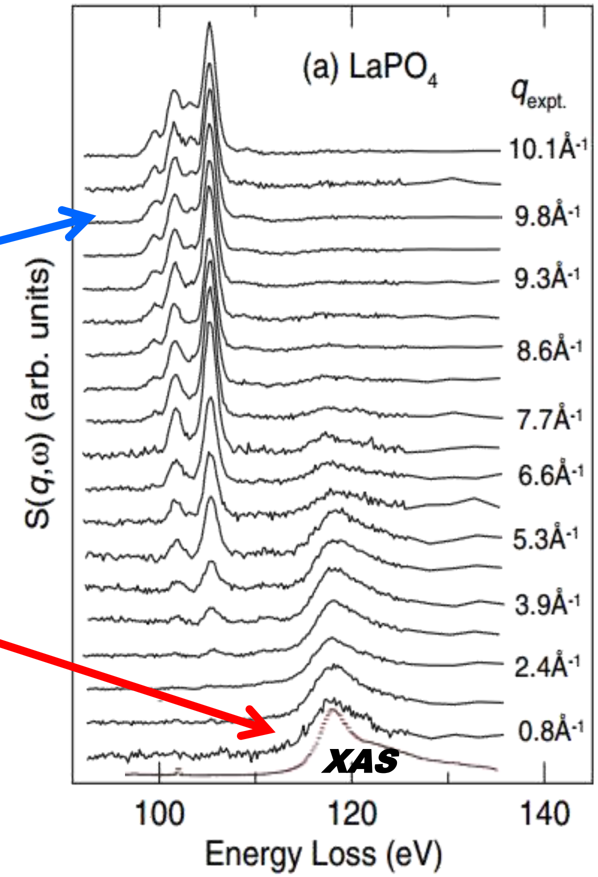
$$= r_0^2 (\hat{\varepsilon}_2 . \hat{\varepsilon}_1)^2 \frac{\omega_2}{\omega_1} \sum_f \left|\left\langle f \left| e^{-i\vec{q}.\vec{r}} \right| i \right\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

large q → multipoles

small q → dipole: XAS

$$S(q,\omega) \propto q^2 \sum_f \left|\langle f | \hat{q}\cdot\vec{r} | i \rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

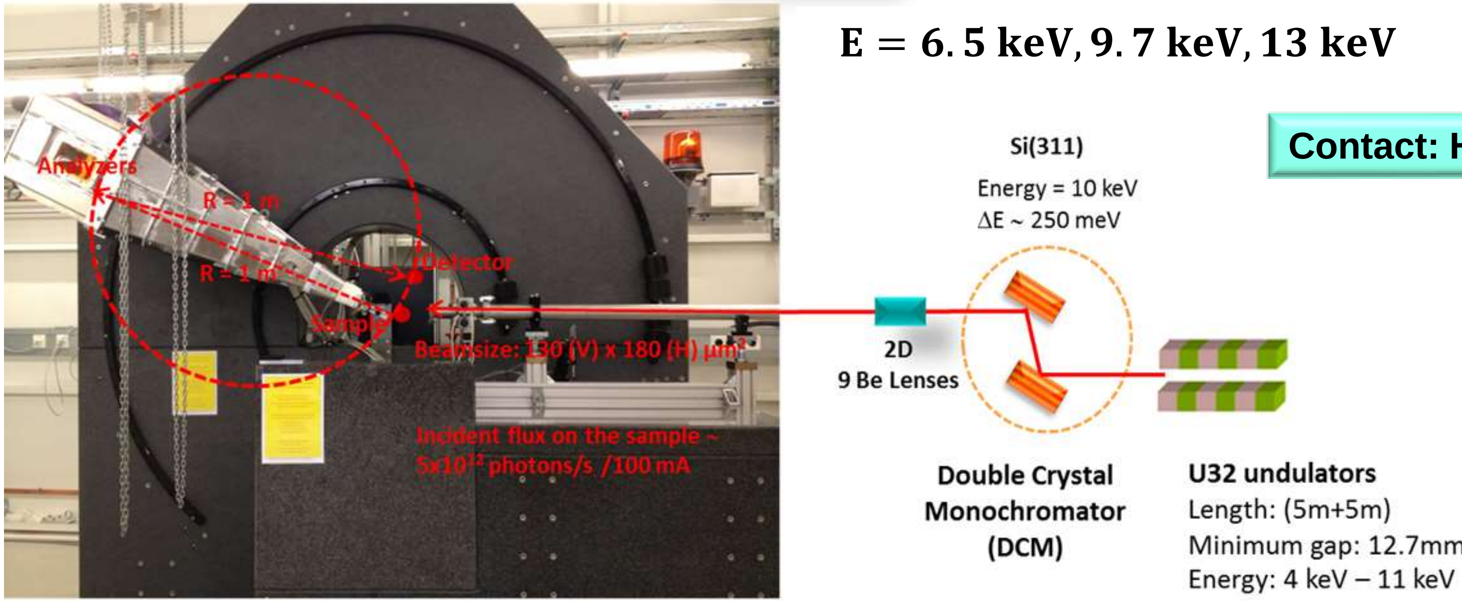
$$\mu(\omega) \propto \sum_f \left|\langle f | \hat{\varepsilon}\cdot\vec{r} | i \rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

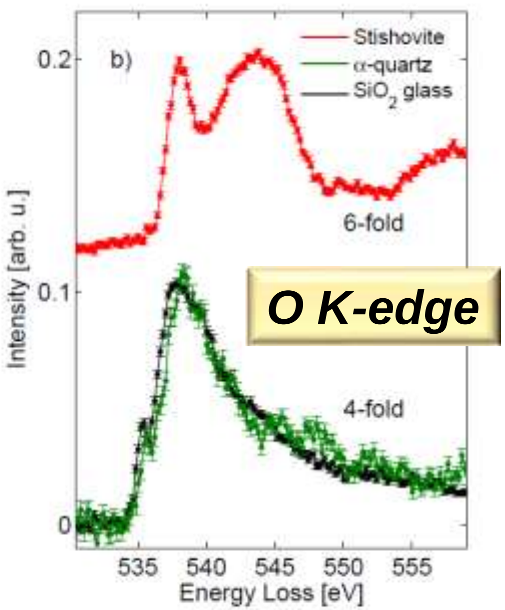


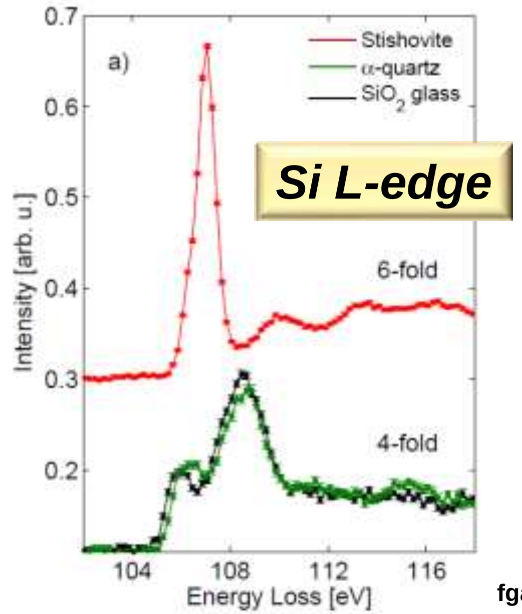
# P01 X-ray Raman scattering instrument

$$\mathbf{E = 6.5\ keV, 9.7\ keV, 13\ keV}$$

**Contact: Hasan Yavas**




**Example: $SiO_2$**

**near edge structure sensitive to local coordination**

# X-ray Raman scattering under extreme conditions

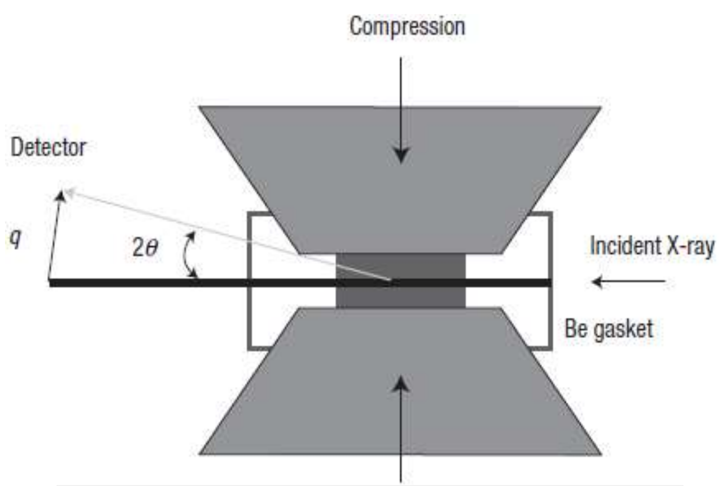
***Example:***
**BN under high pressure**

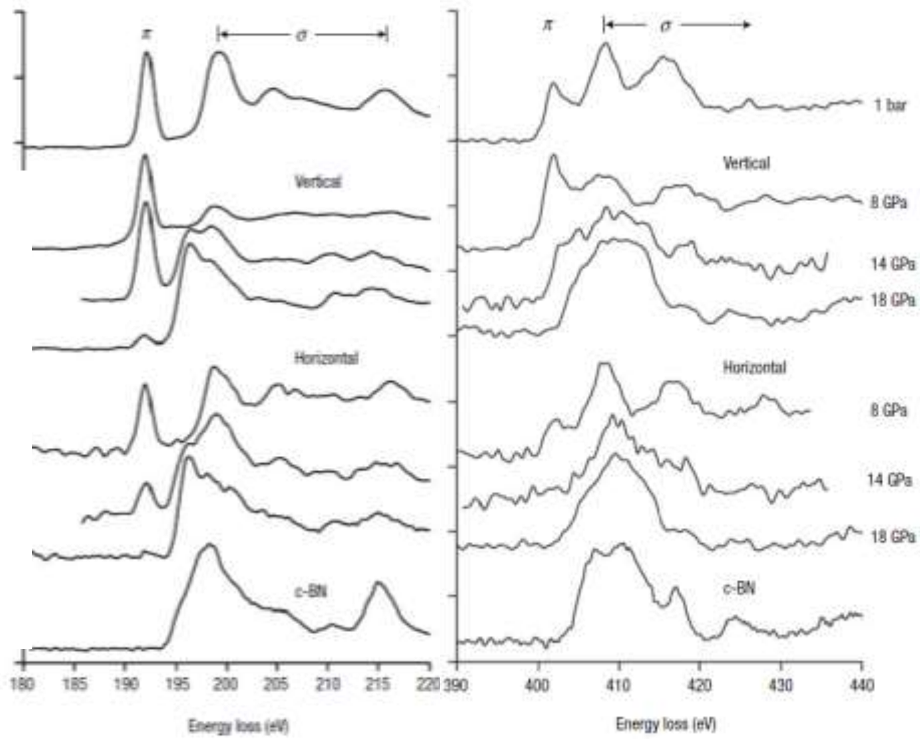
LETTERS

The formation of $sp^3$ bonding in compressed BN

YUE MENG*[1,2], HO-KWANG MAO[2], PETER J. ENG[3], THOMAS P. TRAINOR[3]†, MATTHEW NEWVILLE[3], MICHAEL Y. HU[1,2], CHICHANG KAO[4], JINFU SHU[2], DANIEL HAUSERMANN[1,2] AND RUSSELL J. HEMLEY[2]

***advantage of IXS:***
***keV X-rays can penetrate DAC***



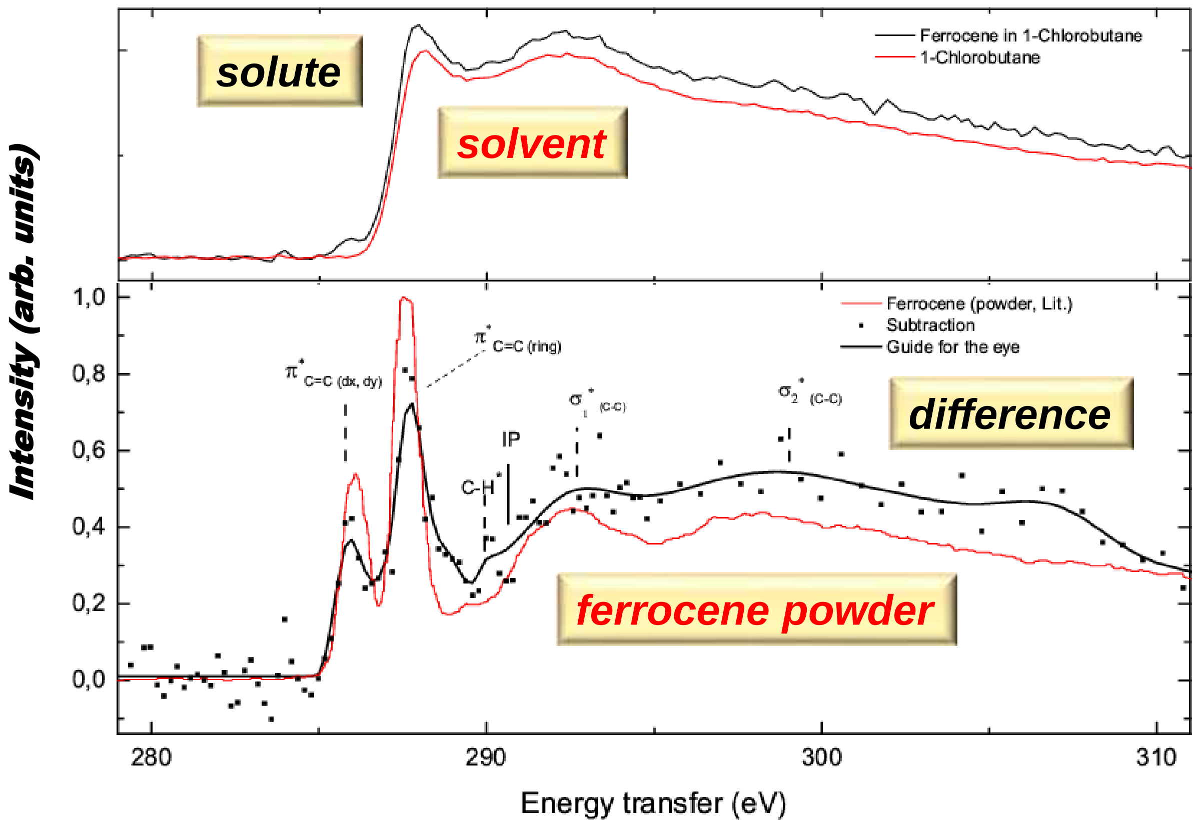



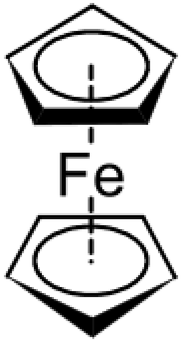

**pressure range 8-18 GPa**
**→ structural transformation & change of bonding**
**→ signature in B K-edge**

Y. Meng et al, Nature Mat. 3, 111 (2004)

# X-ray Raman scattering on liquids

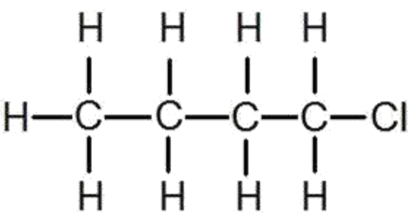
***Example:***
***1M solution of ferrocene in chlorobutan:***
***Bond contrast between solute and solutions***




***Solute:***
***Ferrocene***
***All double bonds***

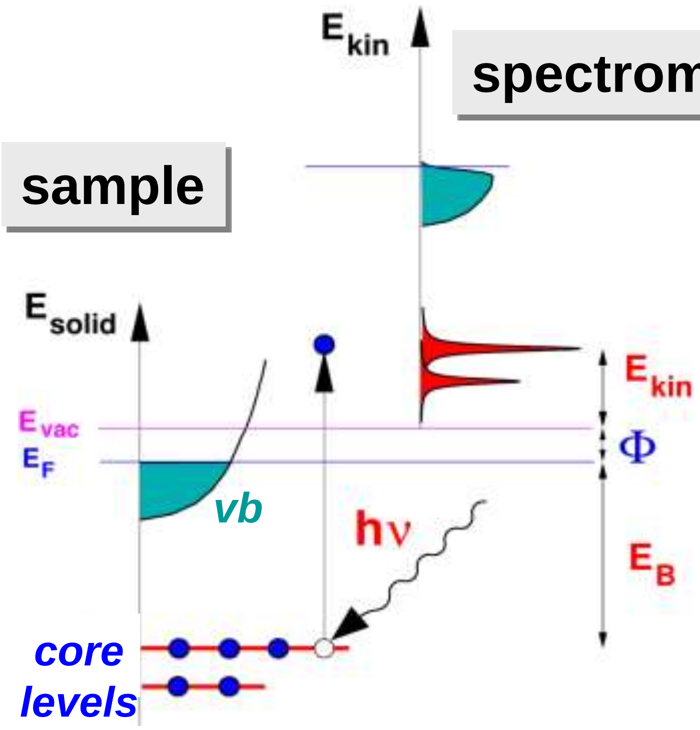
***Solvent:***
***Chlorobutane***
***All single bonds***




**(unpublished yet)** **Contact: Hasan Yavas**

# Examples of PETRA III spectroscopy techniques

**Photoelectron spectroscopy**
**- soft X-rays**
**- hard X-rays**

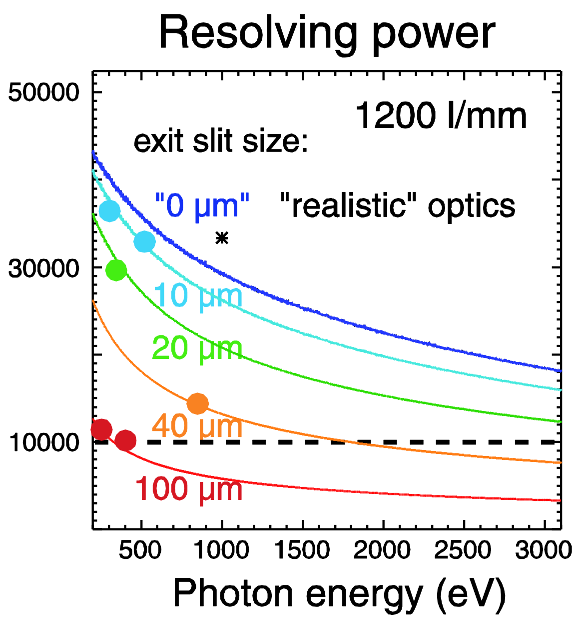


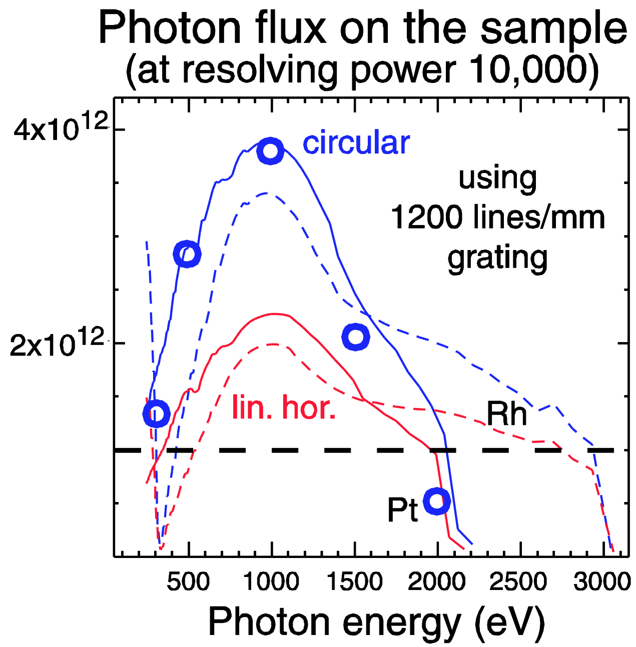

*valence bands*
*core levels*

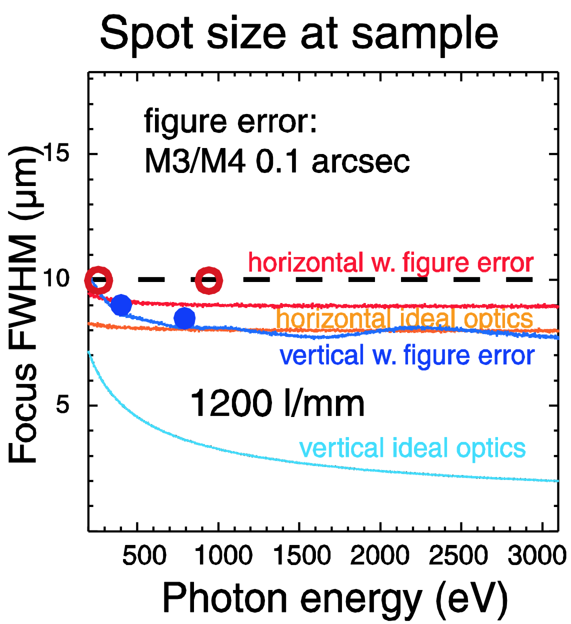
- → *elemental composition*
- → *chemical bonding*
- → *valencies*
- → *electronic density of states $D(E)$*
- → *band structure $E(k)$*
- → *spectral function $A^{<}(k,E)$*

# Variable Polarization XUV Beamline P04

| | |
|---|---|
| **Photon energy range:** | **(<100) 250 - 3000 eV** |
| **Resolving power:** | **> 10,000** |
| **Photon flux:** | **> $10^{12}$ photons/s** |
| **Spot size at sample (h x v):** | **10 µm x 10 µm** |
| **Polarization (switching rate):** | **circular, linear hor./vert (<0.1 Hz)** |



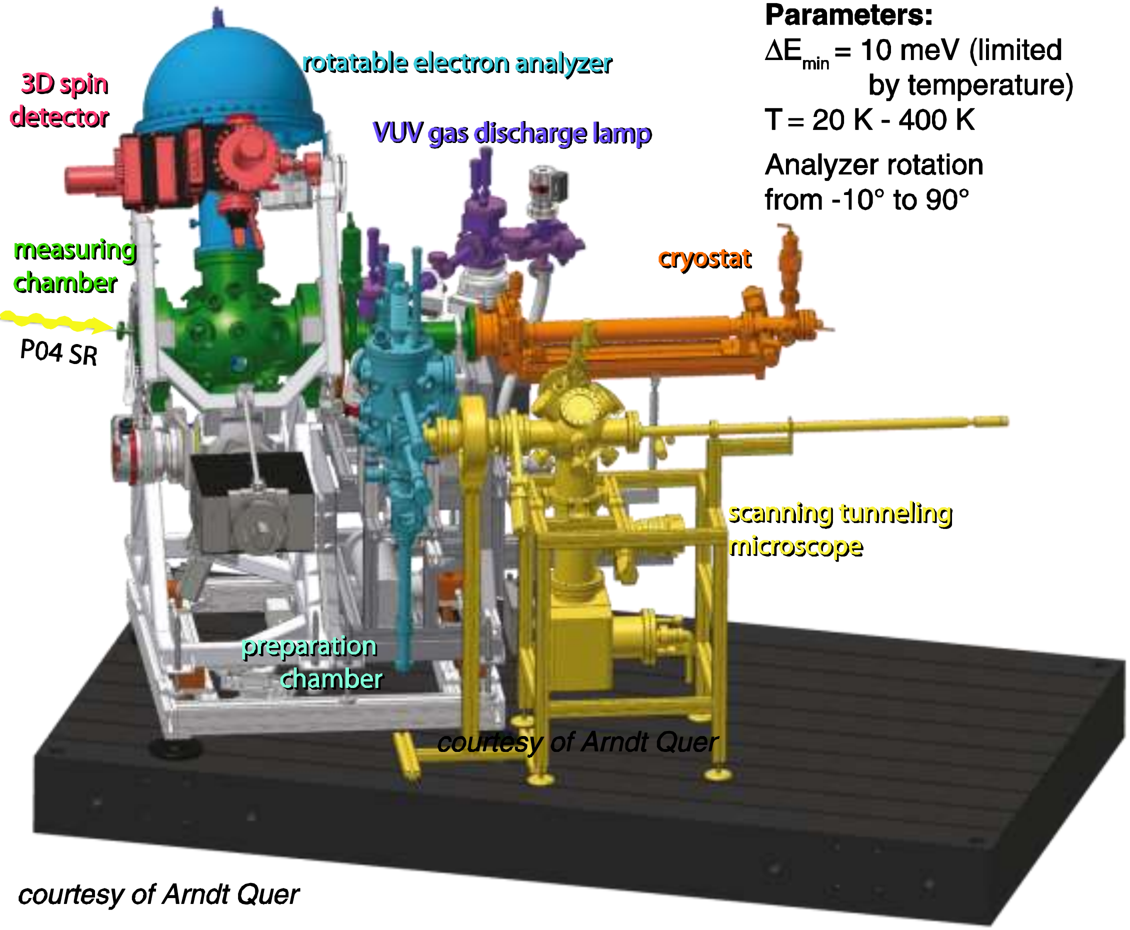




**Contact: Jens Viefhaus**

# P04 User Endstation ASPHERE III for ARPES

**ASPHERE III: Rotatable analyzer**

→ full k-space access without sample rotation

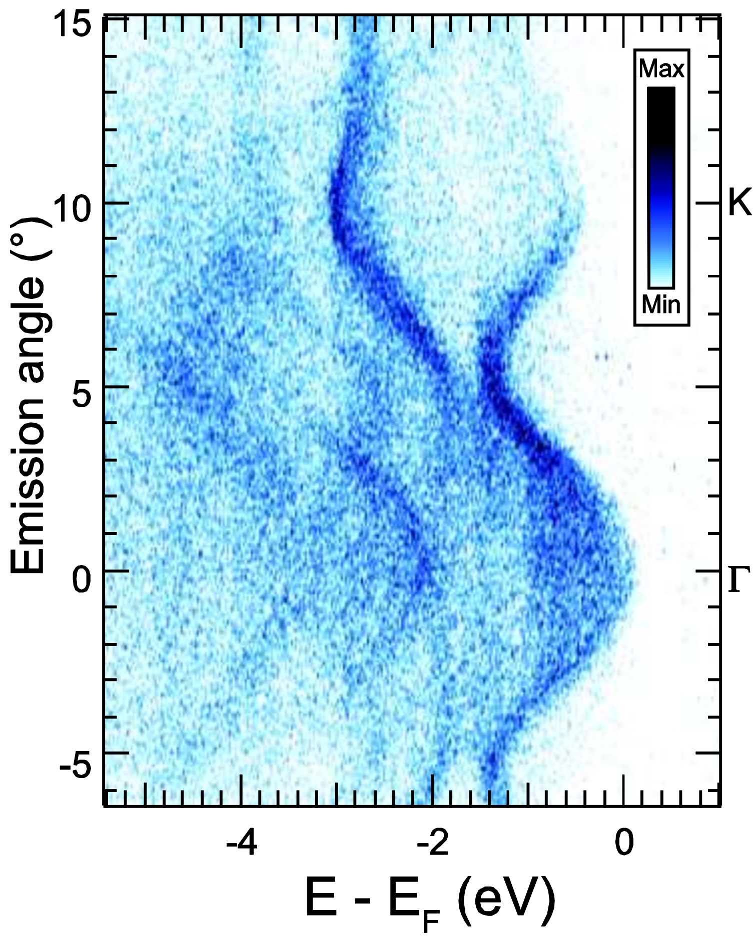



**Parameters:**
$\Delta E_{min}$ = 10 meV (limited by temperature)
T = 20 K - 400 K
Analyzer rotation from -10° to 90°

courtesy of Arndt Quer

**AGs Kipp / Reinert**

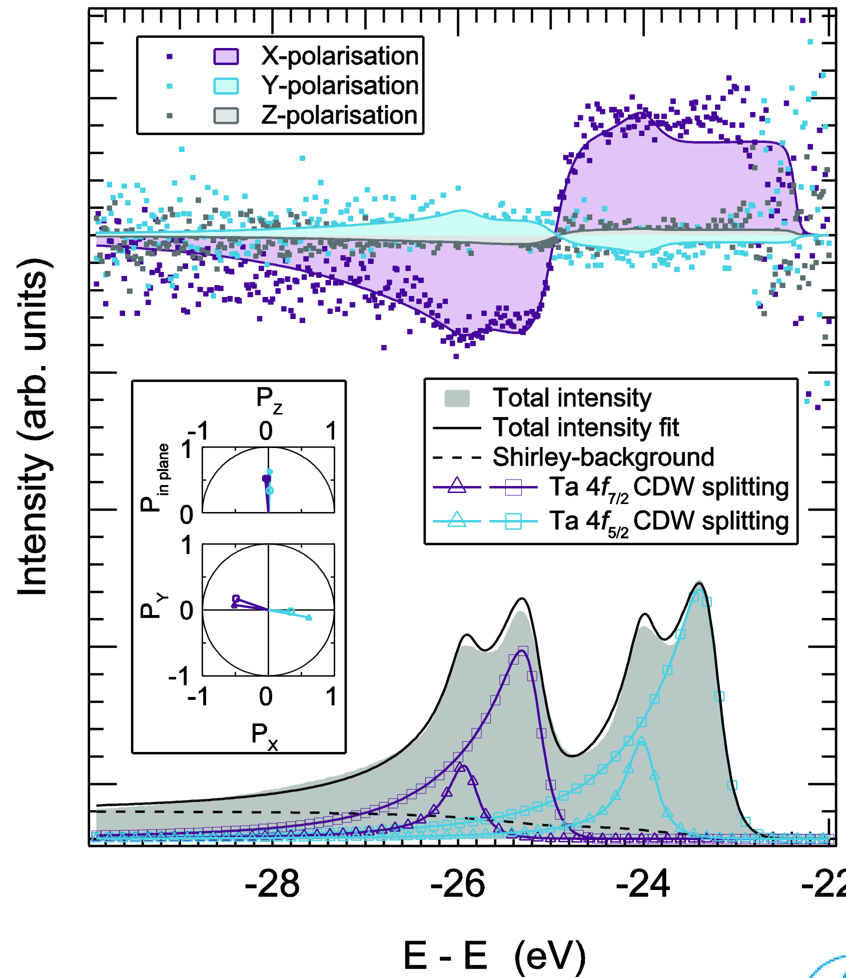
Band structure of 2$H$-$MoS_2$ along Γ-K    hν = 265 eV



# P04 User Endstation Spin-resolved ARPES

## $TaS_2$: CDW induced Ta 4*f* splitting

excited with circularly polarized X-rays

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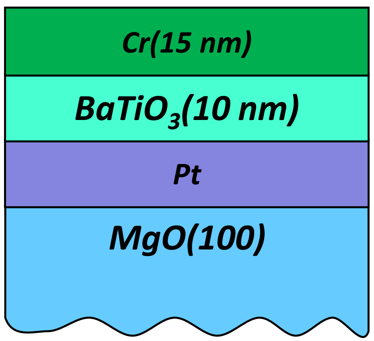
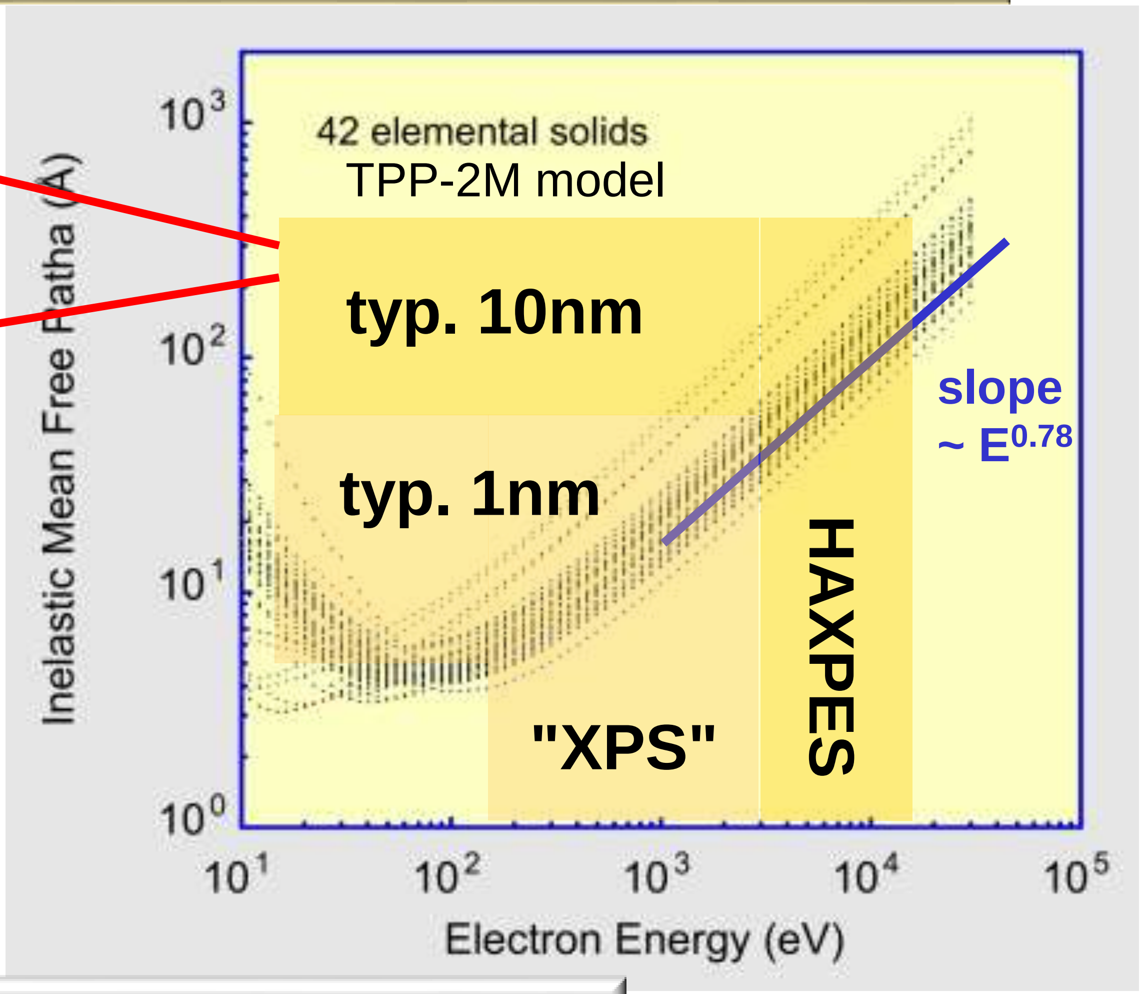
# Using hard X-rays for XPS ( ~3 - 12 keV)

**fast electrons → high volume sensitivity e.g. to study chemical & electronic properties of „device relevant“ interfaces**



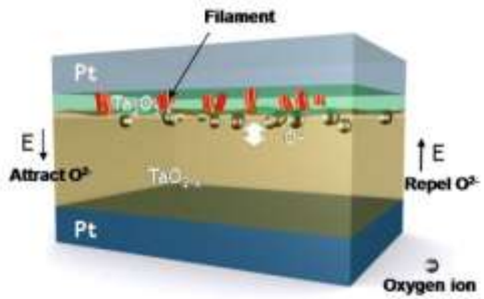



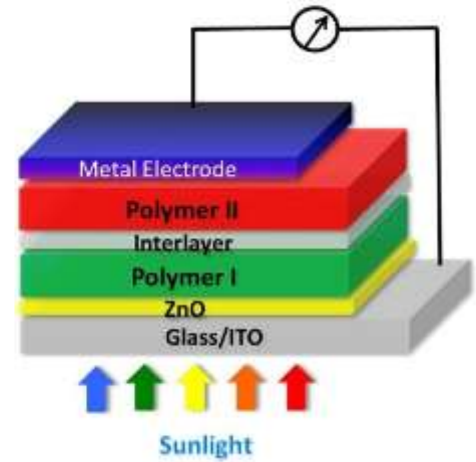

**nm-multilayer stacks**
**→ “functional materials”**

**“… it may be said that the interface is the device”**
**Herbert Kroemer (Nobel Prize lecture, 2000)**

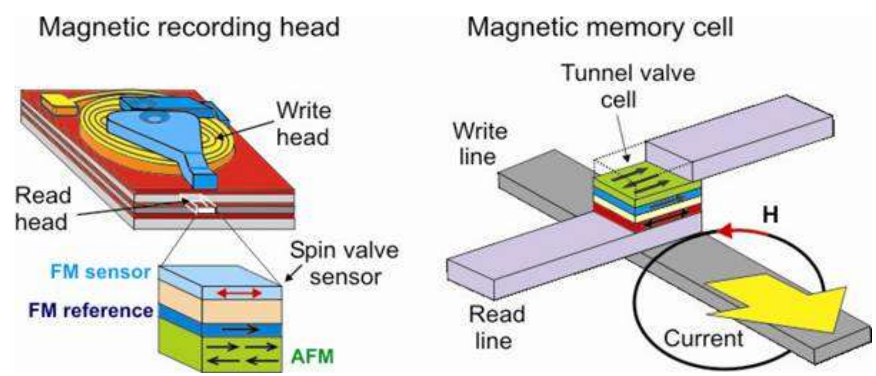
# HAXPES & nano-layered materials

- energy materials (conversion, storage)
- electronic materials (e.g. non-volatile memory)
- spintronics
- sensors
- catalysts
- …

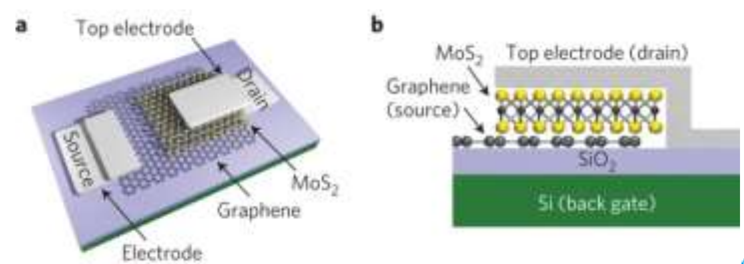


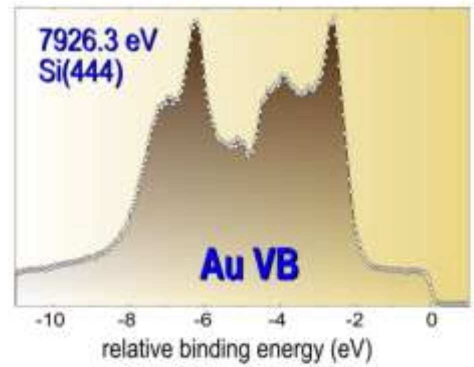

**_devices_**
**multi (nm)-layered structures with functional interfaces**

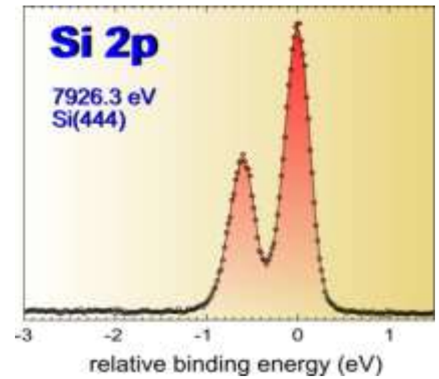



**_HAXPES_**
**“probing depth” nicely matches typical multilayer stack heights**



# P09 (P22) HAXPES instrument




2m spectroscopy X-ray undulator
Photon flux ~ $2\times10^{13}$ $s^{-1}$ into $\Delta E/E = 10^{-4}$
variable photon polarization

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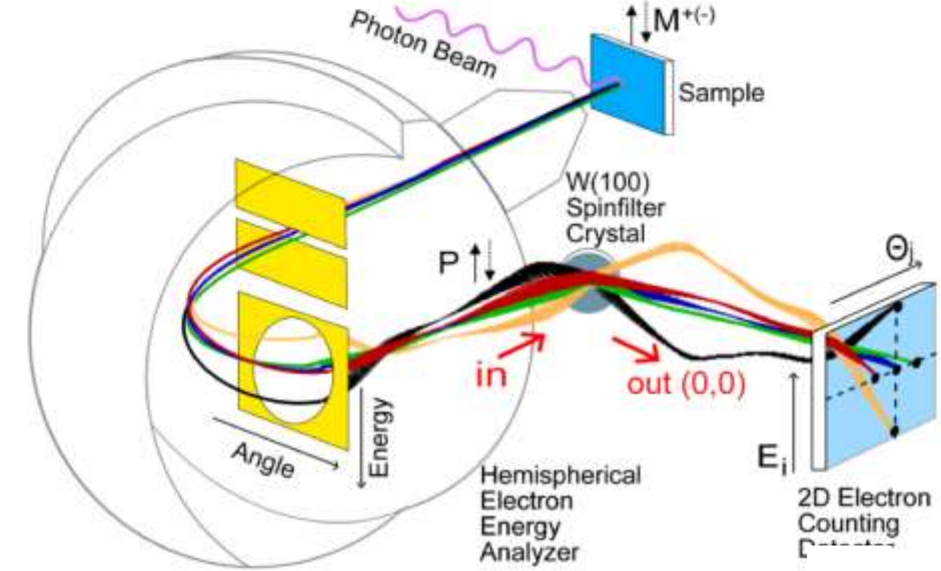
Benchmark spectra at 7926 eV
ΔE ~ 50 meV (photons)
ΔE ~ 110 meV (total)

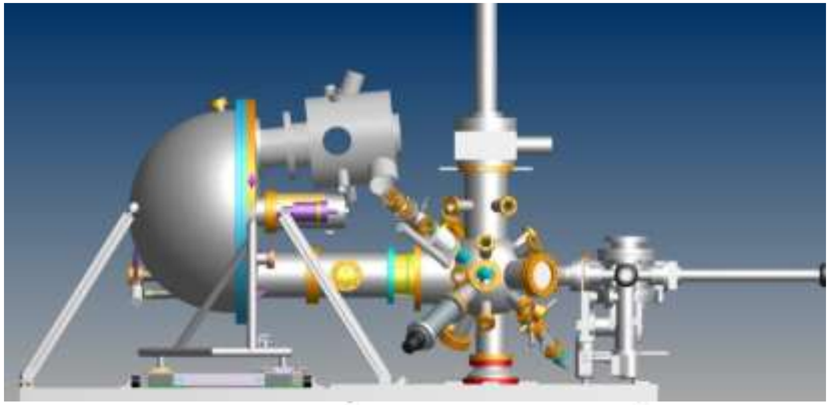
- SPECS Phoibos 225 HV (10.5 kV) with wide angle lens
- Delay-line detector (65 mm MCPs)
- 5-axis manipulator LHe cooling down to < 15 K
- sample mount with 4 electrical contacts
- Mg/Cr X-ray twin anode (1.2/ 5.4 keV) for offline work
- EELS up to 20 keV
- Sputter gun / flood gun

Contact: Wolfgang Drube

# Next: Multichannel spin detection for HAXPES




M. Kolbe et al., PRL 107, 207601 (2011)

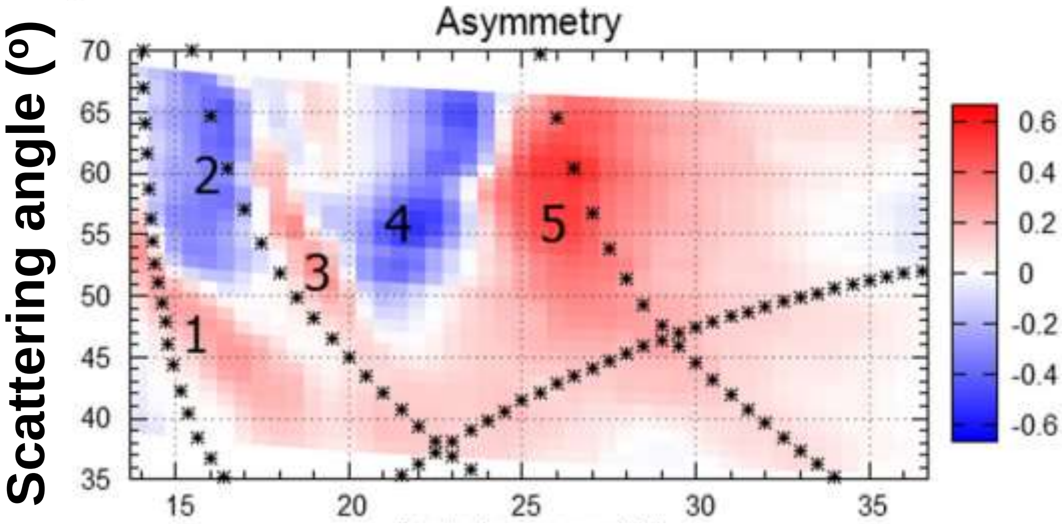


**Test experiments at P09 Oct. 2015**
**BMBF funded (Univ. Mainz)**

**spin-polarized low-energy electron diffraction (SPLEED)**

**→ 2D electron spin-filtering**
**→ substantial improvement of spin detection efficiency**

**exploiting W(100) or Ir(100) spin asymmetry**

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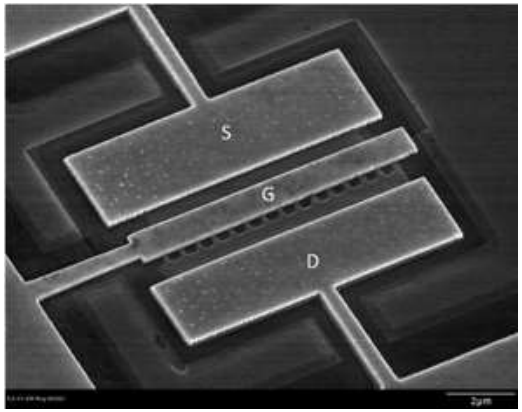
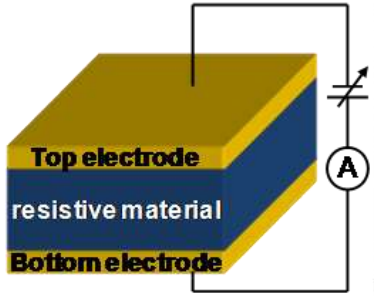
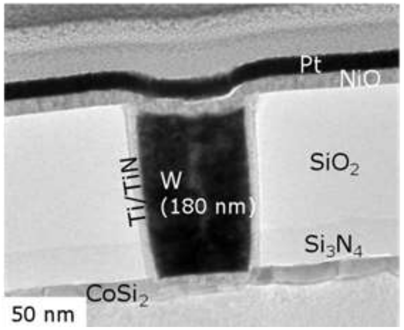
D. Kutnyakhov et al., PRB 91, 014416 (2015)

# Resolving lateral nano structures: HAXPEEM

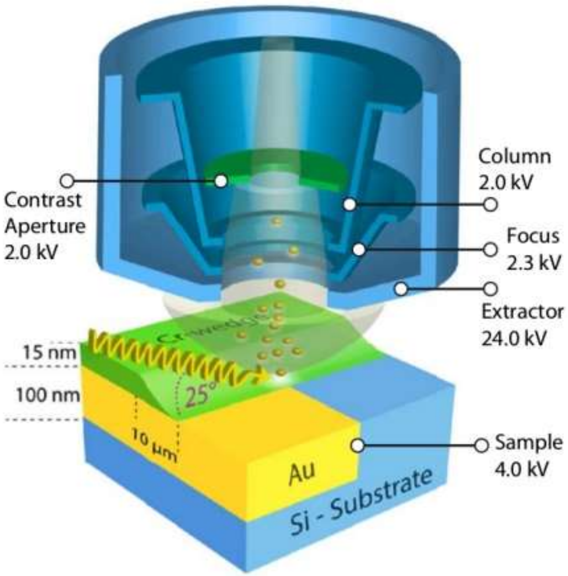


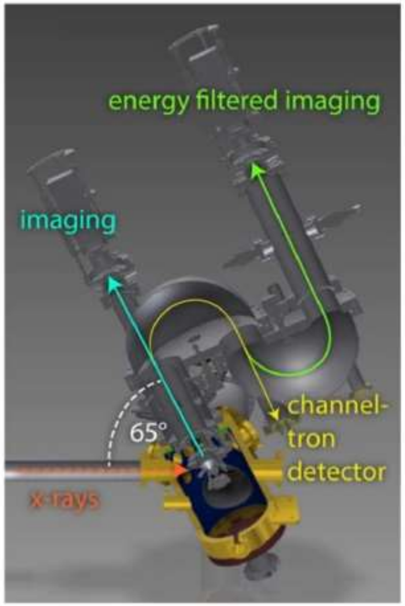




C.M. Schneider *et al*.

**full field electron imaging: energy filtered PEEM**

# Resolving lateral nano structures: HAXPEEM

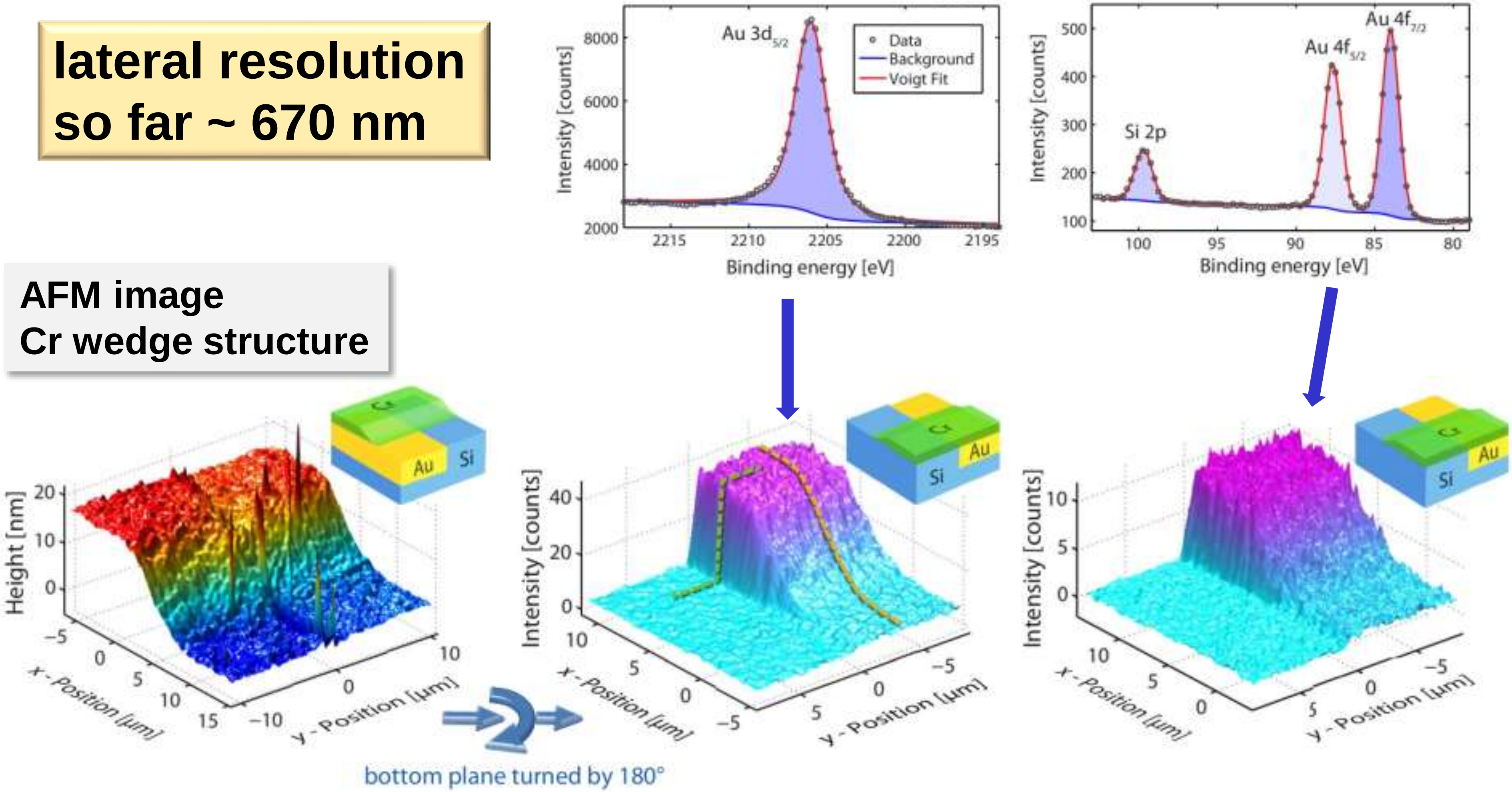
$E_{Ph}$ = 6550 eV

lateral resolution so far ~ 670 nm

AFM image
Cr wedge structure

Au 3d

Au 4f

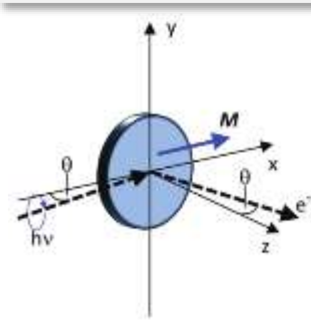


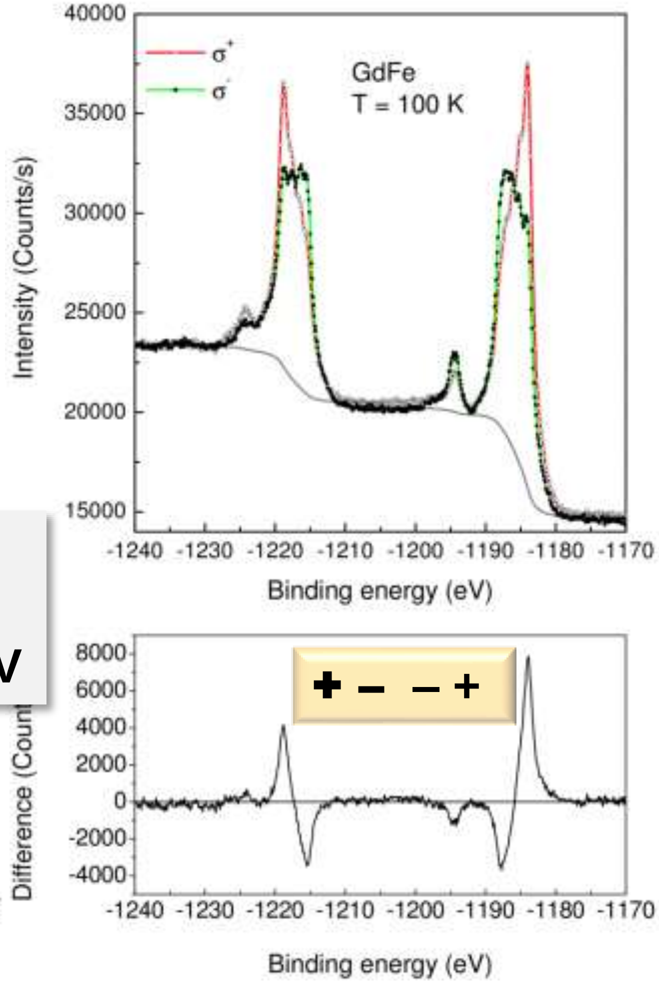

M. Patt et al, Rev. Sci. Instrum. 85, 113704 (2014)

# Electronic & magnetic properties of buried layers

## Magnetic properties of thin buried layers: core level magnetic dichroism


**Gd 3d MCD**
**hv = 5.9 keV**
**ΔE = 150 meV**

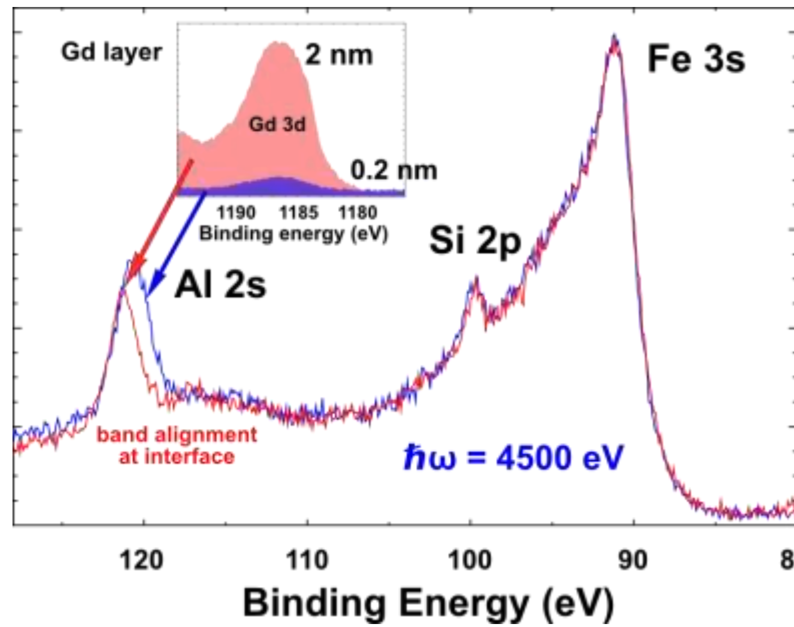



H.J. Elmers et al, PRB 88, 174407 (2013)

## Band alignment at the $Gd/Al_2O_3$ interface in $Fe/Gd/Al_2O_3/Si$ heterostrucures

| | |
|---|---|
| Fe | 6 nm |
| Gd | 0.2 - 2 nm |
| $Al_2O_3$ | 10 nm |
| Si | |




A. Zekevich et al., J. Appl. Phys. 111, 07C506 (2012)

# Summary

**PETRA III is an excellent source for X-ray spectroscopy techniques**