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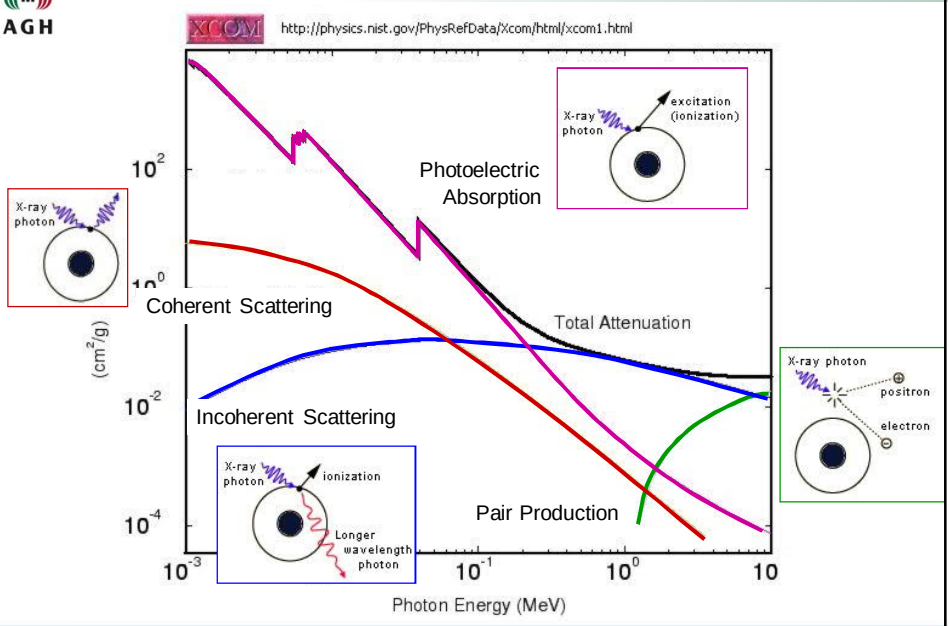
Wysokorozdzielcza spektroskopia rentgenowska

HERFD-XAS: high energy resolution fluorescence detected X-ray absorption spectroscopy

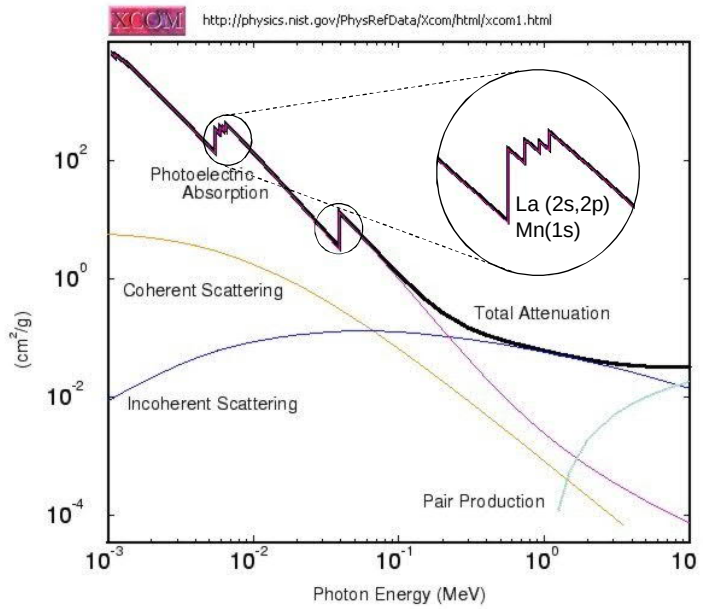
(R)XES: (resonant) X-ray emission spectroscopy

RIXS: resonant inelastic X-ray scattering

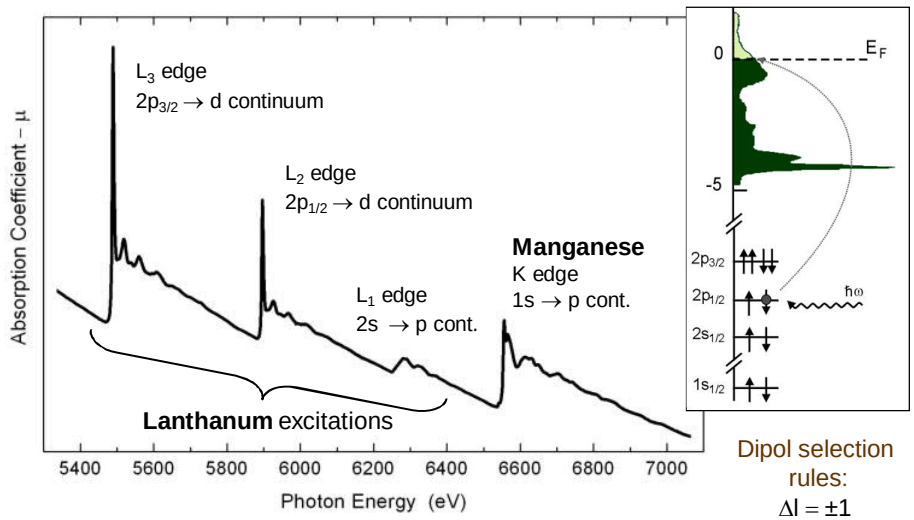
X-ray Interaction with Matter



Resonant X-ray absorption



X-ray absorption spectroscopy (XAS)

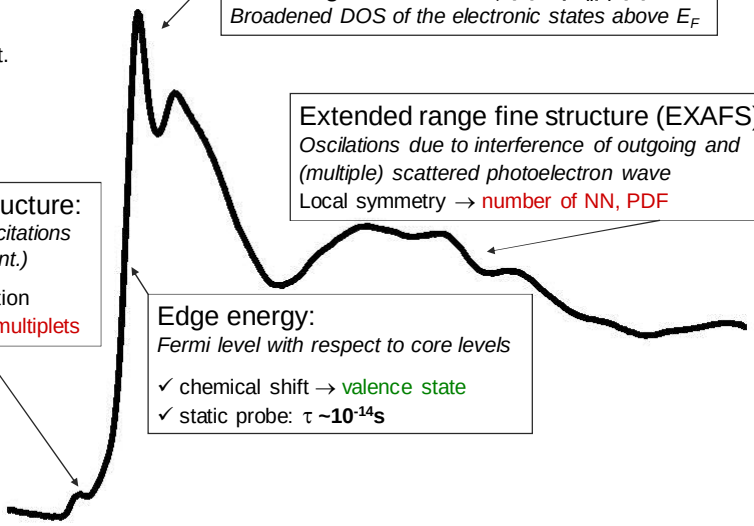


Dipol selection rules:
$\Delta l = \pm 1$
$\Delta j = \pm 1; 0$
$\Delta s = 0$

Element and symmetry sensitive probe of empty electronic states

X-ray absorption spectroscopy (XAS)

TM:K edge
1s → p (d) cont.



Near edge structure: $\mu(E) \sim |M_{if}|^2 \rho(E)$
Broadened DOS of the electronic states above E_F

Extended range fine structure (EXAFS)
Oscilations due to interference of outgoing and (multiple) scattered photoelectron wave
Local symmetry → number of NN, PDF

Pre-edge structure:
quadrupolar excitations (e.g. 1s → d cont.)
✓ p-d hybridisation
→ crystal field multiplets

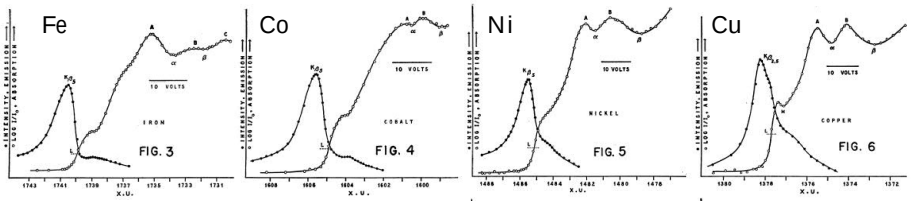
Edge energy:
Fermi level with respect to core levels
✓ chemical shift → valence state
✓ static probe: $\tau \sim 10^{-14}$s

X-ray absorption spectroscopy (XAS)

SEPTEMBER 1, 1939 PHYSICAL REVIEW VOLUME 56

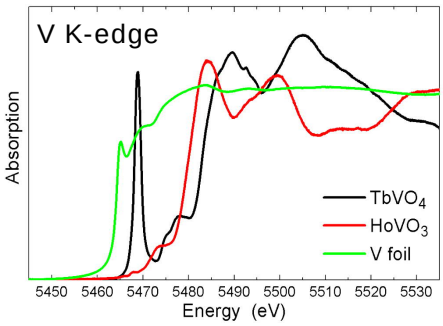
The X-Ray *K* Absorption Edges of the Elements Fe (26) to Ge (32)

W. W. Beeman and H. Friedman
Rowland Physical Laboratory, The Johns Hopkins University, Baltimore, Maryland

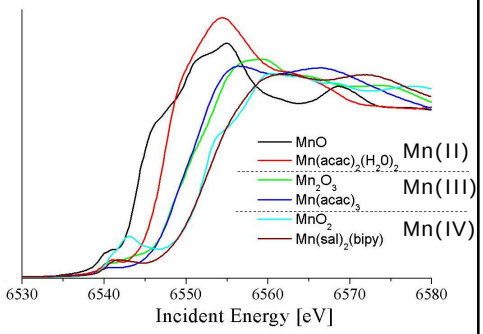


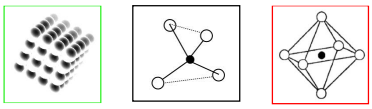
X-ray absorption spectroscopy (XAS)

Metals and oxides



Molecular complexes



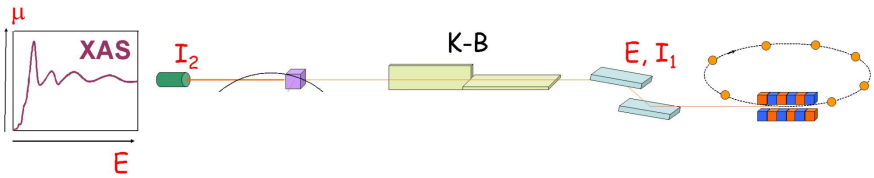


Mn(II) ⟶ Mn(IV)

Courtesy of T.-C. Weng (JACS 2004)

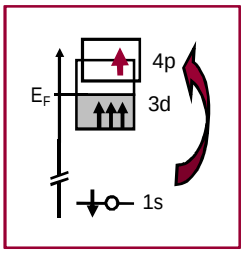
XAS-XES setup

Available @ ESRF (ID26, ID20), NSLS, SLS (SuperXAS), Spring8, APS, SSRL, ...

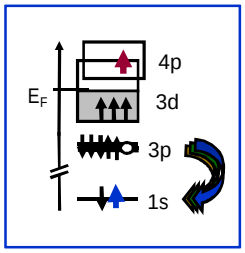


Transmission
$I_2 = I_1 e^{-\mu x}$

Emission (fluorescence) yield: $I' \sim I_1 \mu$



Difficoult for
- single crystals,
- inhomogenous,
- too thin,
- too thick,
- liquid,
- diluted,
- .....



The European Synchrotron

ESRF Members and their share of the budget

- 27.5% France
- 25.5% Germany
- 15% Italy
- 14% United Kingdom
- 4% Spain
- 4% Switzerland
- 6% Benesync (Belgium, The Netherlands)
- 4% Nordsync (Denmark, Finland, Norway, Sweden)

Additional contributions

- 1% Portugal
- 1% Israel
- 1% Austria
- 1% Poland
- 1.05% Centralsync (Czech Republic, Hungary, Slovakia)
- 0.3% South Africa

Take a breath for acknowledgements

Cz. Kapusta, K. Kollbek, J. Stępień, A. Kozłowski
AGH

P. Glatzel, B. Gorges, S. Eeckhout,
K. Kvashnina, J. Swabrick-Grattage
ESRF, Grenoble

O. Safonova, J. Szlachetko, J. Sa
SLS, PSI, Villigen

A. Juhin, Ph. Sainctavit
IMPMC, Universite Pierre et Marie Curie, Paris

K. Knížek, Z. Jirák
Institute of Physics CAS, Prague

M. Balden, C. Adelhelm
MPI für Plasmaphysik, Garching

G. Simon, L. Morellon, R. Ibarra
INA, Universidad de Zaragoza

M. Zając
Solaris, UJ

T.-C. Weng,
R. Alonso Mori
SSRL, Stanford

D. Koziej
ETH, Zurich

G. Vankó
KFKI, Budapest

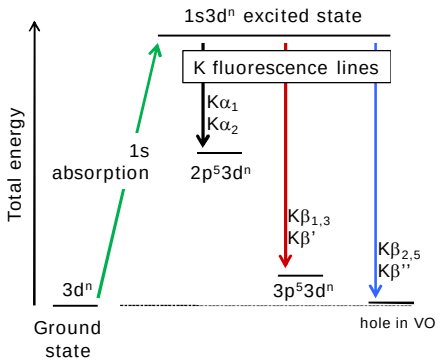
V.Prochazka
Olomouc University

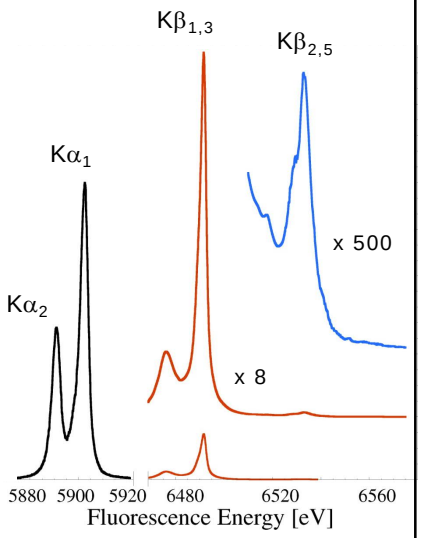
W. Szczerba
BAM, Berlin

M. Kavčič
JSI, Ljubljana

K emission lines

Simillar information as in XPS, but for (diluted, insulating, buried ...) bulky samples





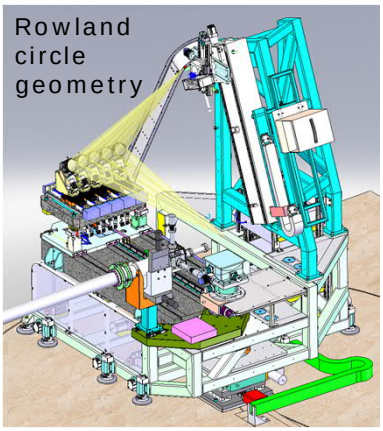
X-ray emission (fluorescence) detection

Energy Bandwidth

Photodiode	n/a
Ge detector	200 eV
Si drift detect	130 eV
Bent Cryst Laue An	50 eV
Bent Crystal Bragg Analyzers	
1-2 eV	< 0.5 m Spectrometer
0.6-1.0 eV	1 m Spectrometer
~ 0.3 eV	2 m Spectrometer

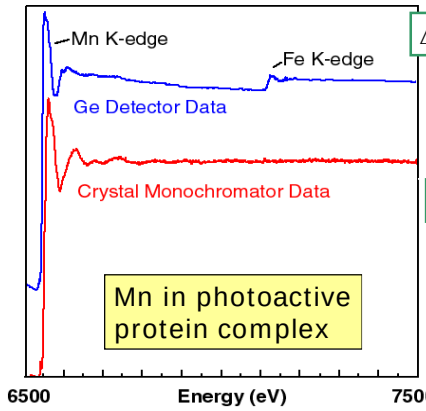
High deadtime at SR sources: ↗ easily saturates ☹

Courtesy of P. Glatzel



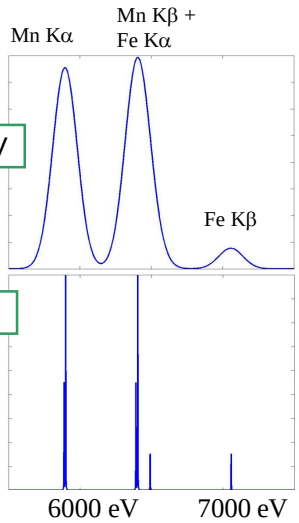
Why do we need high resolution?

instead of
- high solid angle
- large energy range



ΔE = 300 eV

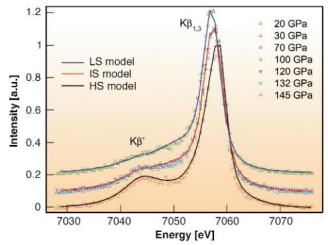
ΔE = 1 eV

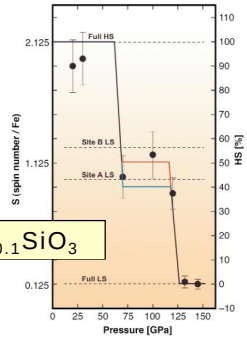


Courtesy of P. Glatzel

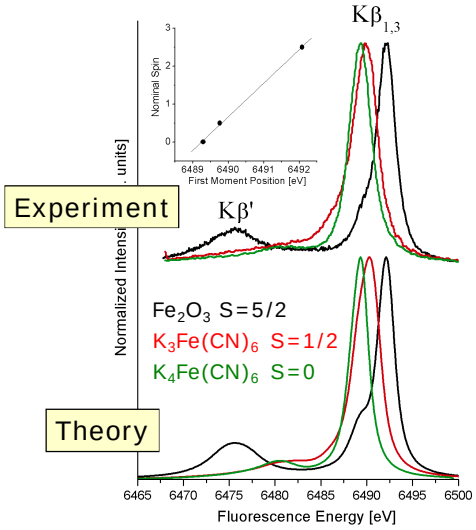
Spin sensitivity of Kβ main line

J. Badro et al., Science (2003 & 2004)





$Mg_{0.9}Fe_{0.1}SiO_3$



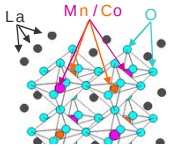
P.Glatzel & U.Bergmann, Coord. Chem. Rev. (2005)

Spin state evolution in $LaMn_{1-x}Co_xO_3$ series

$LaMn_{1-x}Co_xO_3$ magnetoresistive perovskites

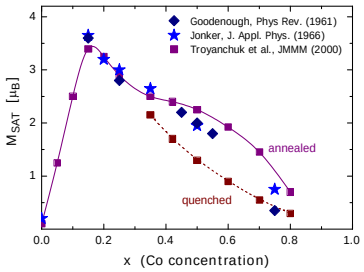
$LaMnO_3$ AFM insulator, orthorhombic, HS Mn^{3+} ($3d^4$, S=2)

$LaCoO_3$ diamagnetic, rhombohedral, LS Co^{3+} ($t_{2g}^6e_g^0$, S=0)
spin excitations at T>90K, $\langle S\rangle_{300K} \approx 0.5-1.2$



Solid solution

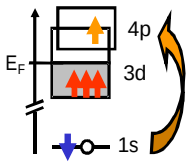
FM conducting, M_{SAT} up to $3.5\mu_B$
structural phase transition at x~0.6
properties depend on synthesis route



Two possible origins of ferromagnetism:

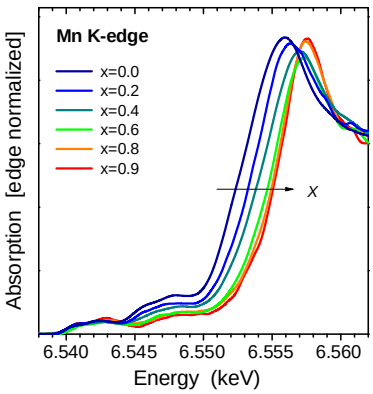
- homovalent substitution (Mn^{3+}/Co^{3+}), Mn^{3+}-O-Mn^{3+} superexchange (SE) only
- $Mn^{4+}+Co^{2+}$ phase with surplus of either Mn^{3+} or Co^{3+} set of SE and double-exchange (DE) intaractions

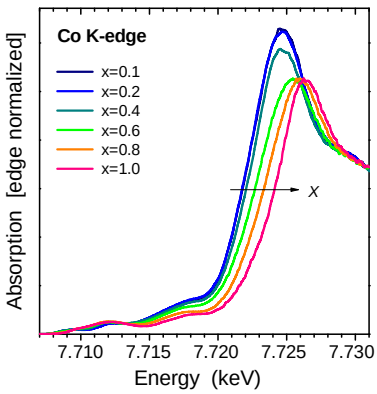
$LaMn_{1-x}Co_xO_3$ series: K-edge XAS



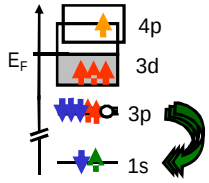
Shift of the edge position
→ decrease of the effective charge and/or
→ change in the 3d/4p hybridization (local structure evolution)

→ both, Co and Mn edges, shift to the same direction
→ charge transfer





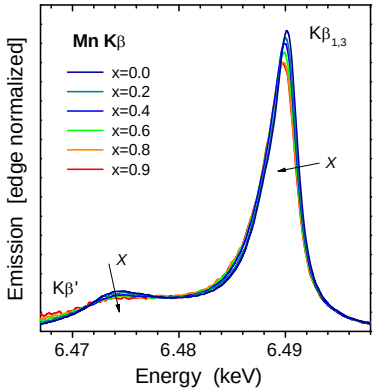
$LaMn_{1-x}Co_xO_3$ series: Kβ XES

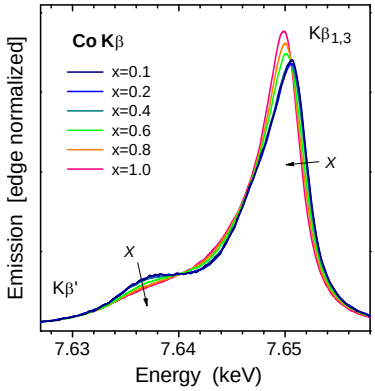


$K\beta_{1,3}$ and Kβ' lineshape

→ spectrum proportional to the 3d spin via 3d-3p exchange interaction

→ Co spectra reveal more pronounced evolution





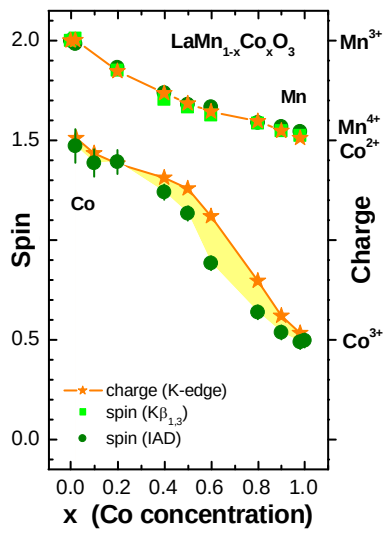
$LaMn_{1-x}Co_xO_3$ series: average Mn and Co spin

Spin derived indirectly using average charge estimation from K-edge XAS:

- HS only model for Mn ($S = n_{3d}/2$)
- mixed Co^{2+}(HS)+Co^{3+}(1/2) model for Co

Spin derived directly from Kβ XES by comparison to the reference samples:

- nice correlation for Mn → HS model confirmed
- significant difference in case of Co → average spin state lower than expected



$LaMn_{1-x}Co_xO_3$ series: average Mn and Co spin

Spin derived from XAS:

- Co^{2+} (S_{HS} =3/2) + Co^{3+} (S_{LS} = 0)

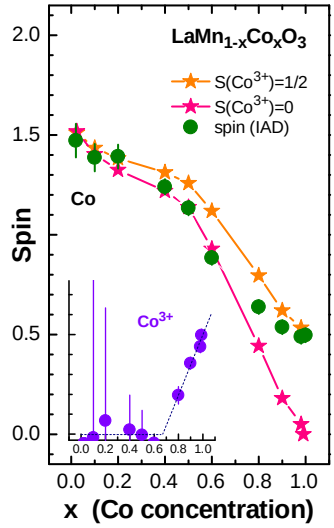
Spin derived directly from Kβ XES

- nice agreement at low and medium doping
- lack of correlation at high x

The explanation:

for x>0.6 the average Co^{3+} spin at 300K rises gradually with x, coincides with structural phase transition at x~0.6

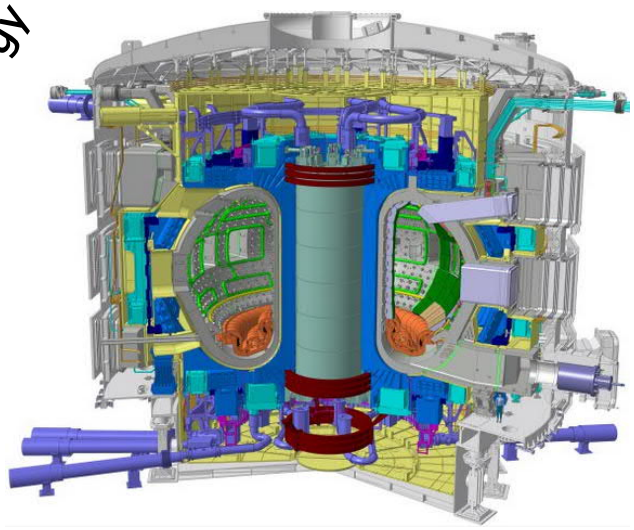
Magnetic properties at high Co content depends on exact oxygen stoichiometry (Co^{3+} phase volume)



M.Sikora et al., J. Appl. Phys. 2008

XAS-XES in „practical" applications

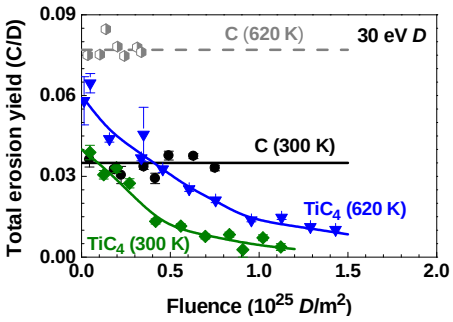
Thermonuclear energy



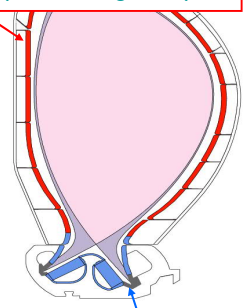
Plasma facing materials for ITER

carbon fiber reinforced carbon (CFC)

- can withstand the highest expected power without major degradation
- good self-sputtering properties
- chemical erosion by hydrogen
- reduced upon doping with transition metals



first wall: modest flux
Be (low Z, O getter)

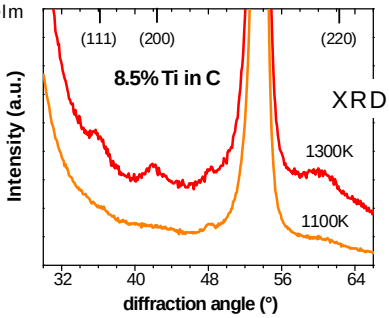


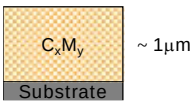
divertor wall: W
high heat flux 10 (20) MW/m^2
target plates: C
transient heat loads (disruptions)

Metal doped carbon films

Courtesy of C. Adelhelm

Search for the best C_xM_y system in terms of resistance, self-sputtering and erosion combined with complete characterization





Best properties upon annealing at T>1100K

RBS : good homogeneity

XRD : traces of crystallization

XPS : Very weak carbide-like spectrum upon annealing, traces of oxide & metallic phase in Ti samples

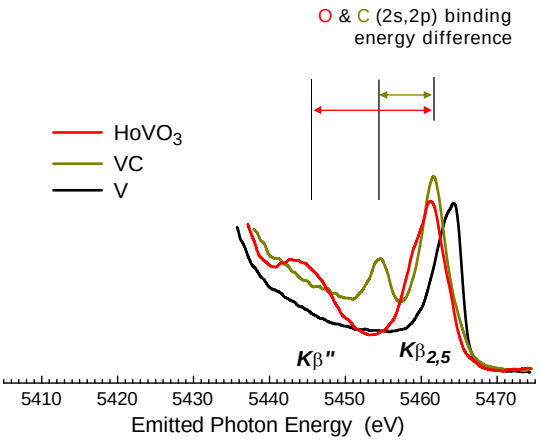
EXAFS : traces of non-carbide phases

Kβ satellite spectra

Oxygen and carbon Kβ'' peaks do not overlap

Kβ'' and $K\beta_{2,5}$ intensity:

- is proportional to the number of ligands
- depends on distance

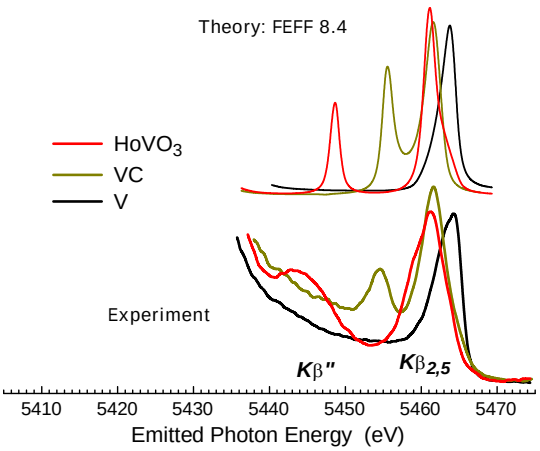


Kβ satellite spectra

Oxygen and carbon Kβ'' peaks do not overlap

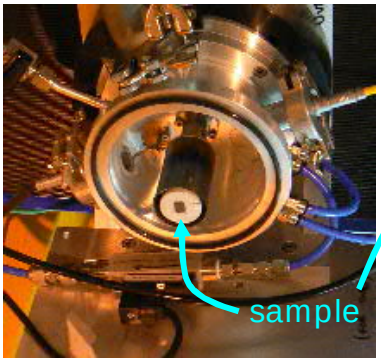
Kβ'' and $K\beta_{2,5}$ splitting

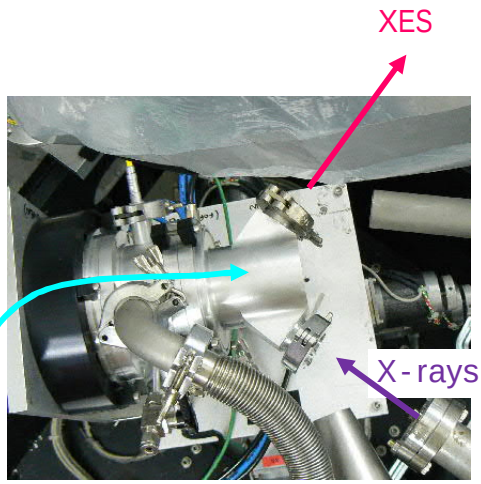
- is nicely reproduced by theoretical calculations



In-situ XES at ID26 (ESRF, Grenoble)

Heating (cooling) speed: 3K/min
Max. temperature: 1300K
Ceramic heaters
Controlled atmosphere





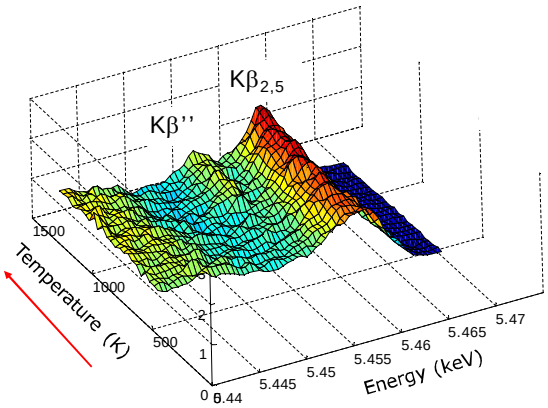
In-situ Kβ satellite spectra

Carbide formation at T~ 900K

Traces of V-O and V-C bonds in as deposited sample

Consistent with ex-situ

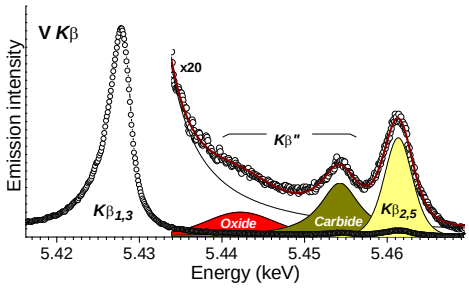
No changes upon cooling

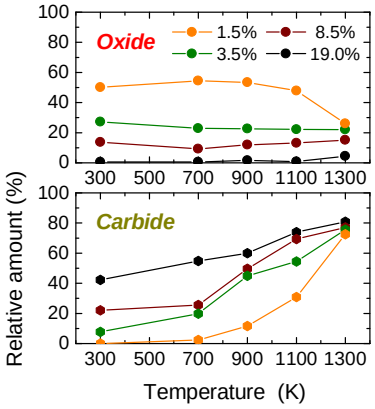


Vanadium neighbourhood

Oxide is formed in 1.5% doped sample and released upon annealing at 1300K

Carbide phase increases with temperature and concentration





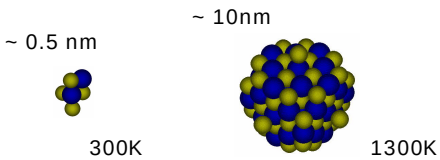
Vanadium neighbourhood

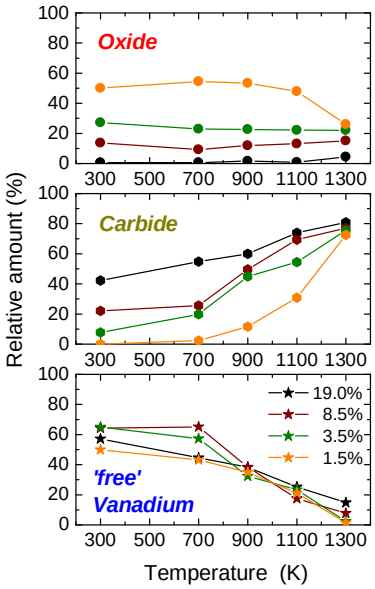
Oxide is formed in 1.5% doped sample and released upon annealing at 1300K

Carbide phase increases with temperature and concentration

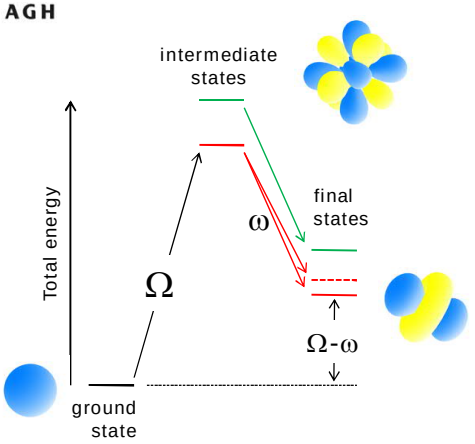
Amount of 'free' V bonds decreases from ~60% to ~10% upon annealing

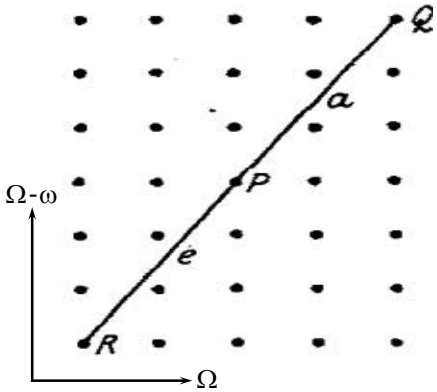
Assuming VC (NaCl-like) structure, $d_{V-C} \approx 2$Å, and taking surface/bulk ratio into account:





Resonant inelastic X-ray scattering (RIXS)





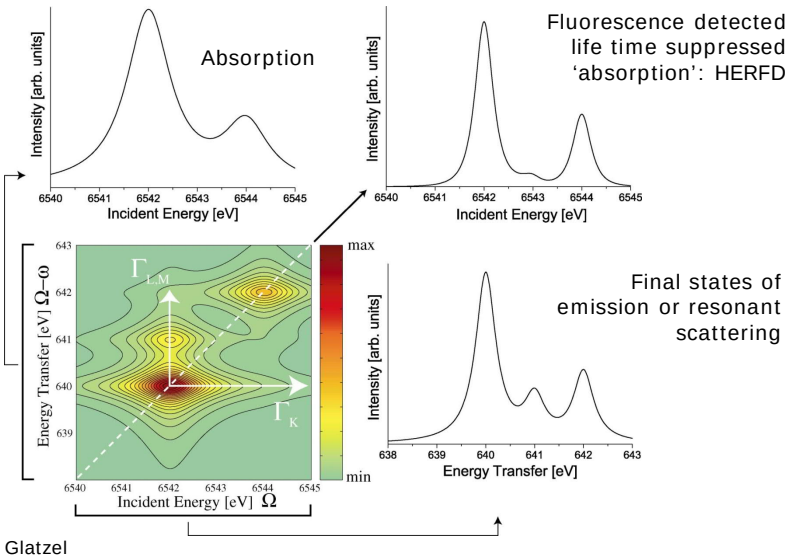
Zeitschrift für Physik. Bd. XXXI.

Über die Streuung von Strahlung durch Atome.

Von **H. A. Kramers** und **W. Heisenberg** in Kopenhagen.

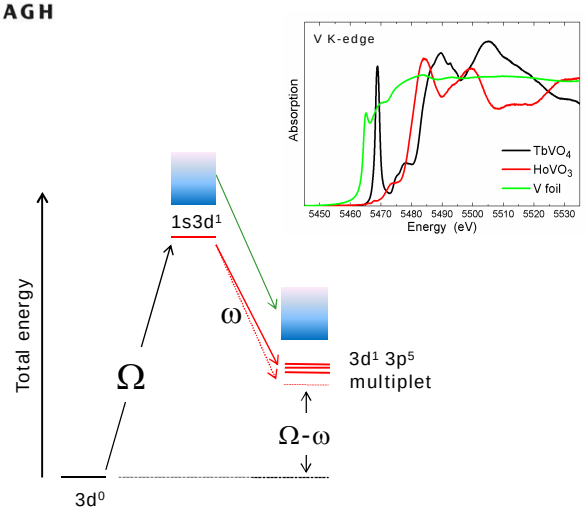
Mit sieben Abbildungen. (Eingegangen am 5. Januar 1924.)

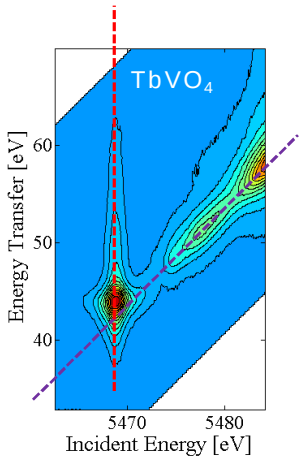
The (Ω,Ω-ω) Plane and Line Plots



Courtesy of P. Glatzel

1s-3p(3d) RIXS of the $3d^0$ system



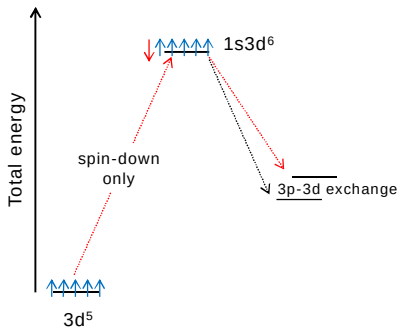


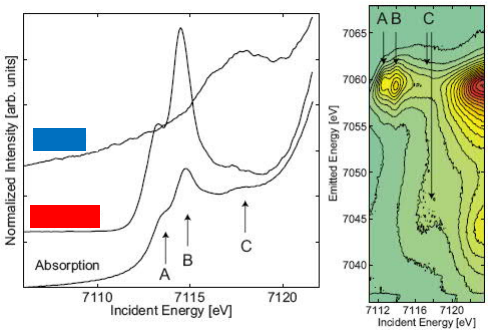
Resonances (fluorescence) along diagonal line

Final state interactions (multiplet, spin-orbit) in vertical direction

Spin resolved absorption in hematite

Origin of the second pre-edge structures

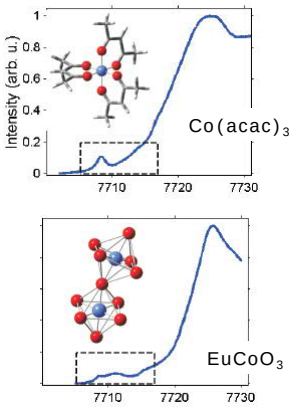


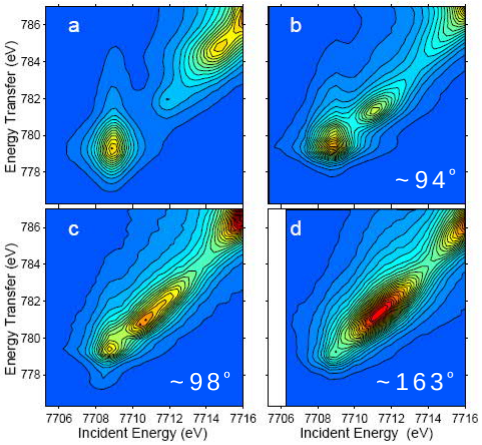


P.Glatzel et al., Phys. Rev. B (2008)

1s-3p(3d) RIXS of the low spin $3d^6$

Origin of the second pre-edge structure

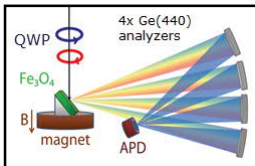


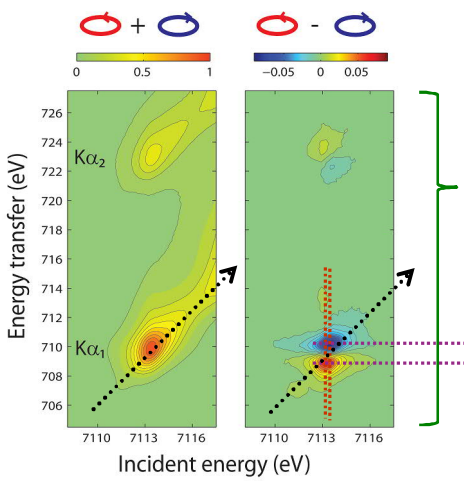


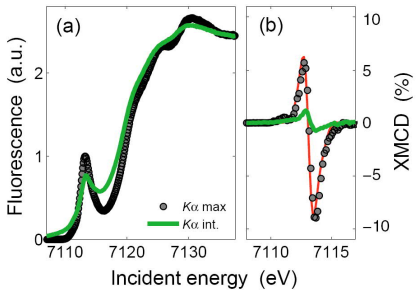
G.Vanko et al., arXiv:cond-mat (2008)

FIG. 4: (color online). $1s2p$ RXES on (a) $Co(acac)_3$, (b) $LiCoO_2$, (c) $AgCoO_2$, (all at T=295K), and (d) $LaCoO_3$ at 20K.

K-edge XMCD enhancement





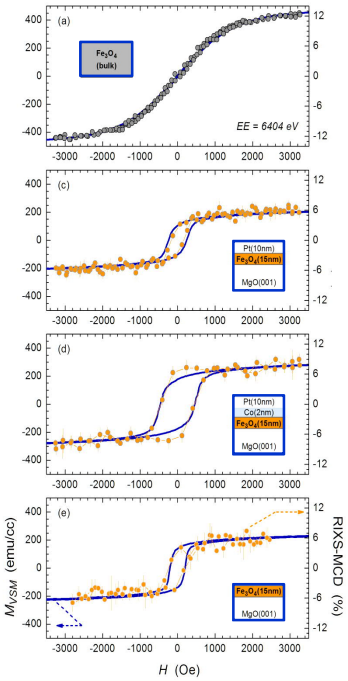


Small shift between positive and negative features in incident energy → IS (or GS) splitting

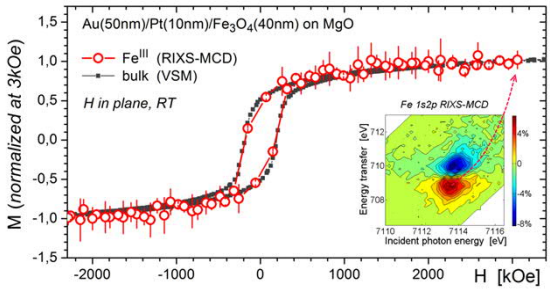
Significant shift in energy transfer → FS (and IS) splitting

M.Sikora, A Juhin, et al., PRL 2010

RIXS-XMCD magnetometry



M.Sikora et al., JAP 2012



RIXS intensity proportional to thickness (volume) of thin layer
→ free from non-resonant background
→ statistical noise mainly

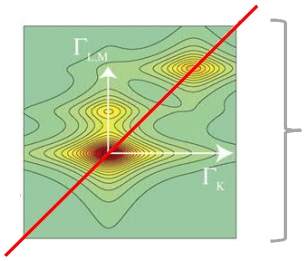
RIXS-MCD scales linearly with bulk M

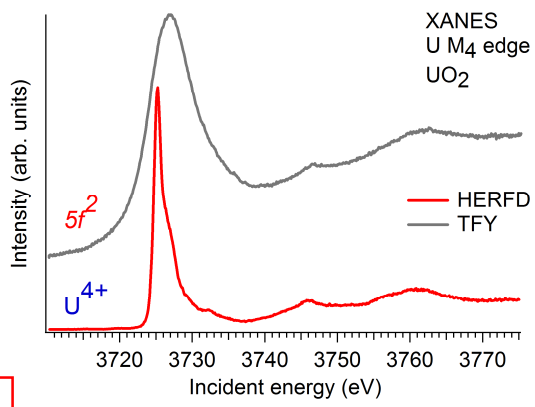
Quantitative probe of net magnetization of buried layers or deep interfaces

HERFD-XAS – spectrum sharpening effect

AGH

High energy resolution fluorescence detection (HERFD)



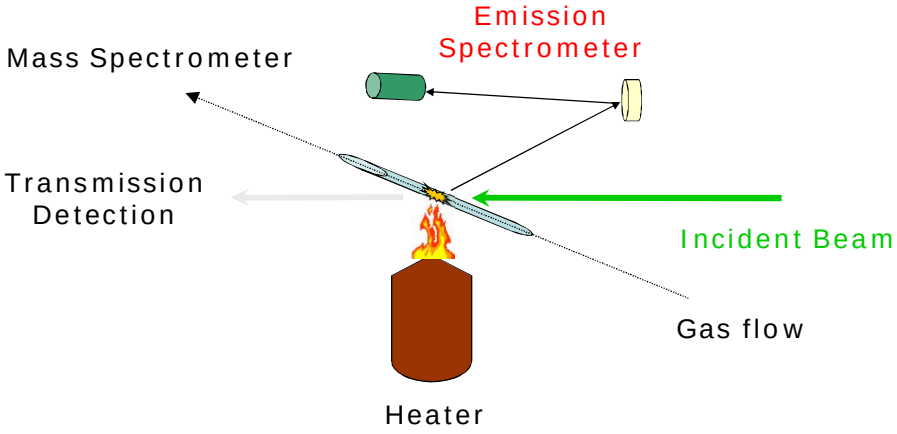


HERFD at the *U* M_4 edge
Dipole: 3d → 5f

K. Kvashnina et al., PRL 2013

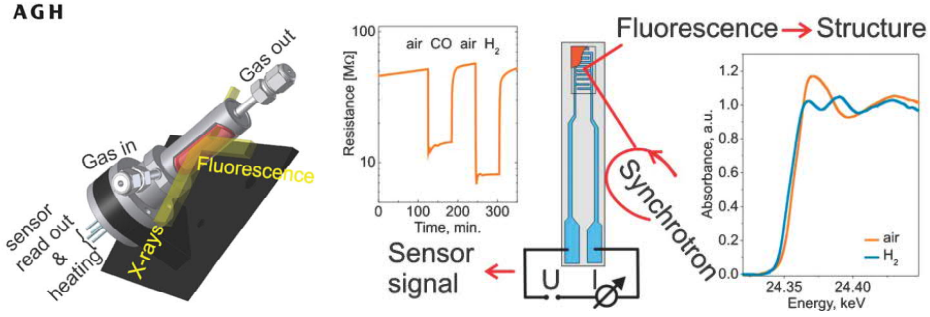
In-situ and operando studies

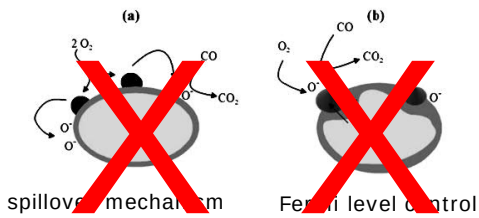
Operando spectroscopy of catalysts at work



Courtesy of P. Glatzel

Operando studies of Pd catalysts at work

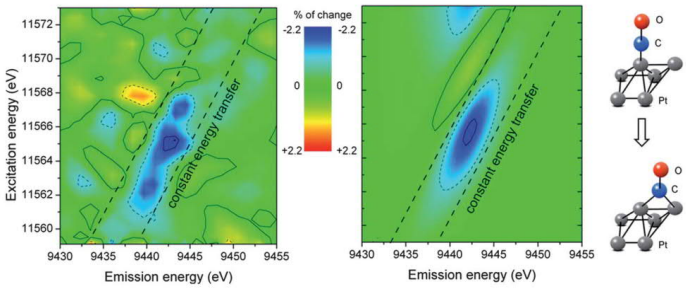


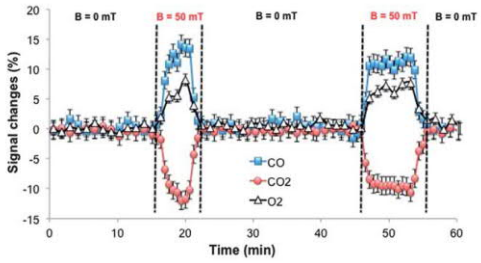


Local structure and coordination of Pd evolves upon exposure to CO & H_2, but NOT the oxidation state

D. Koziej et al., PCCP 2009

Magnetic field controled catalysis





Non-magnetic Pt catalysts, supported on carbon coated magnetic Co nanoparticles

catalytic performance changes in the presence of external magnetic field

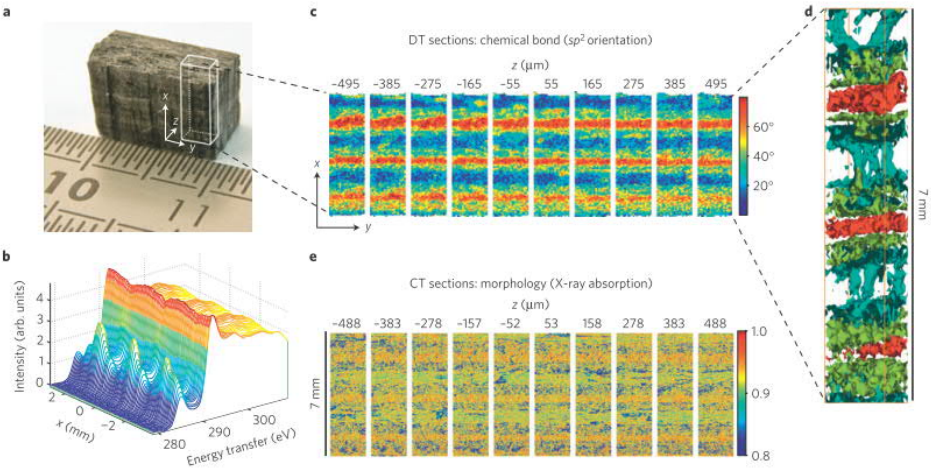
J. Sa et al., Nanoscale 2013

Direct tomography with chemical-bond contrast

Simo Huotari[1,2]*, Tuomas Pylkkänen[1,2], Roberto Verbeni[1], Giulio Monaco[1] and Keijo Hämäläinen[2]

layered C/SiC

Nature Mat. 2011

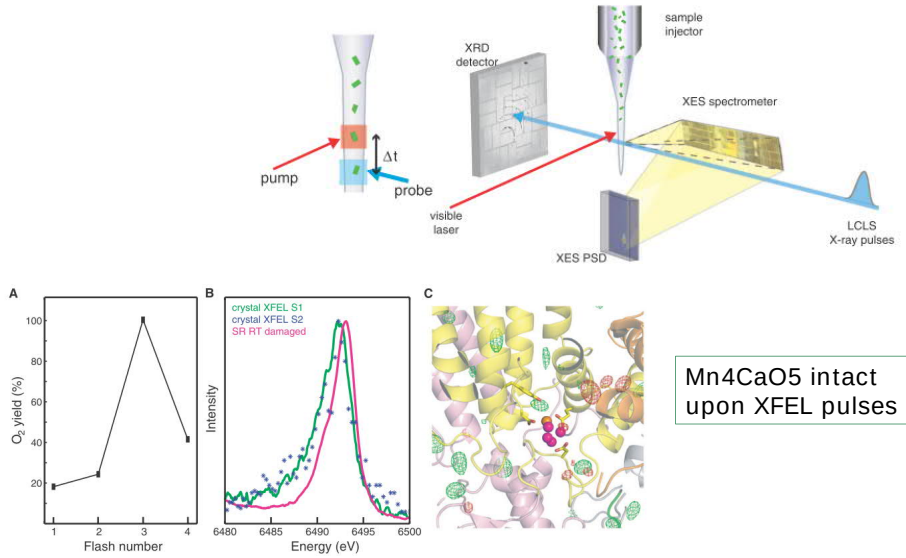


Simultaneous Femtosecond X-ray Spectroscopy and Diffraction of Photosystem II at Room Temperature

Jan Kern *et al.*

Science **340**, 491 (2013);

DOI: 10.1126/science.1234273



Mn4CaO5 intact upon XFEL pulses

Why hard X-ray spectroscopy

Electronic and structural information

Element specific, symmetry sensitive

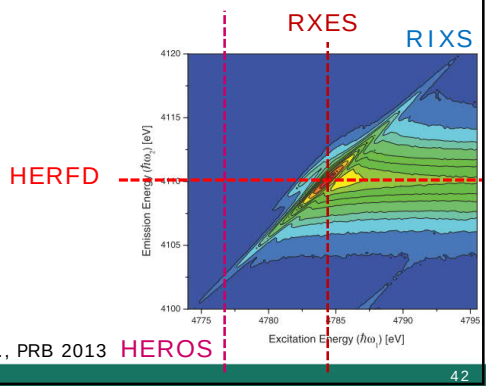
absorption edges, valence band emission

Compatible with extreme conditions

significant penetration depth

Number of complementary techniques

using same set-up:
XAS, XES, ...



M. Kavčič et al., PRB 2013