Inelastic x-ray scattering

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Outline - I

1) Introduction

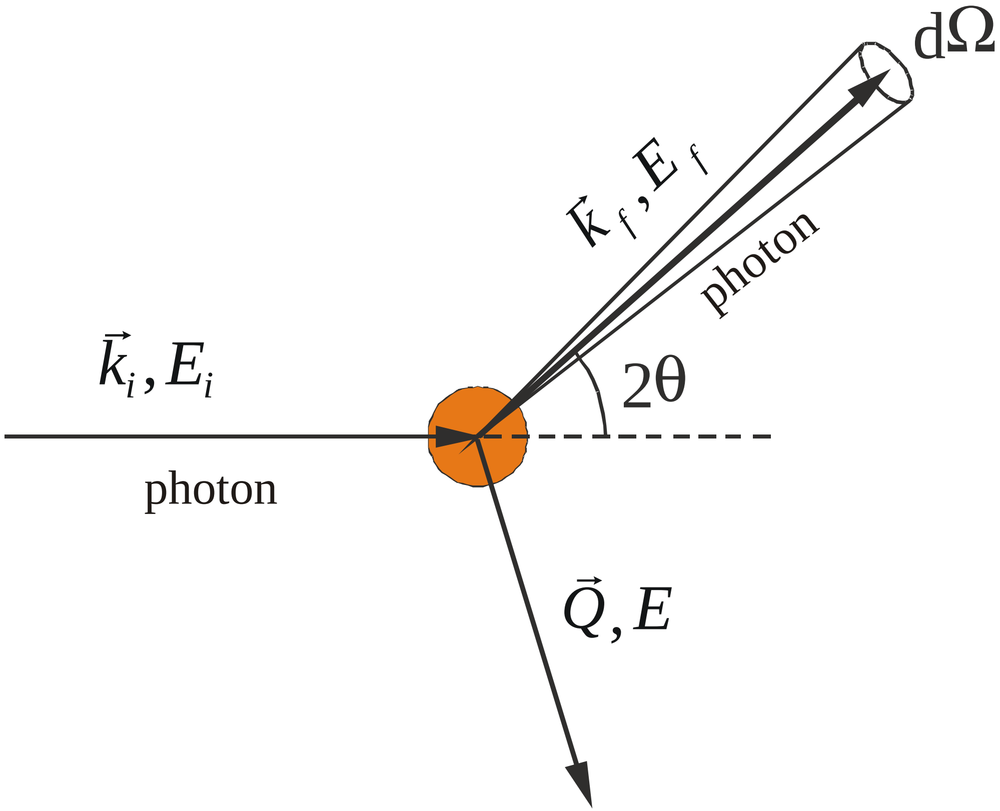
scattering kinematics
generic excitation spectrum & information content
some instrumental aspects

2) Resonant IXS
"XAS beyond the core hole lifetime broadening"

3) X-ray Raman scattering
"Soft x-ray XAS in the hard x-ray range"

4) IXS – phonons

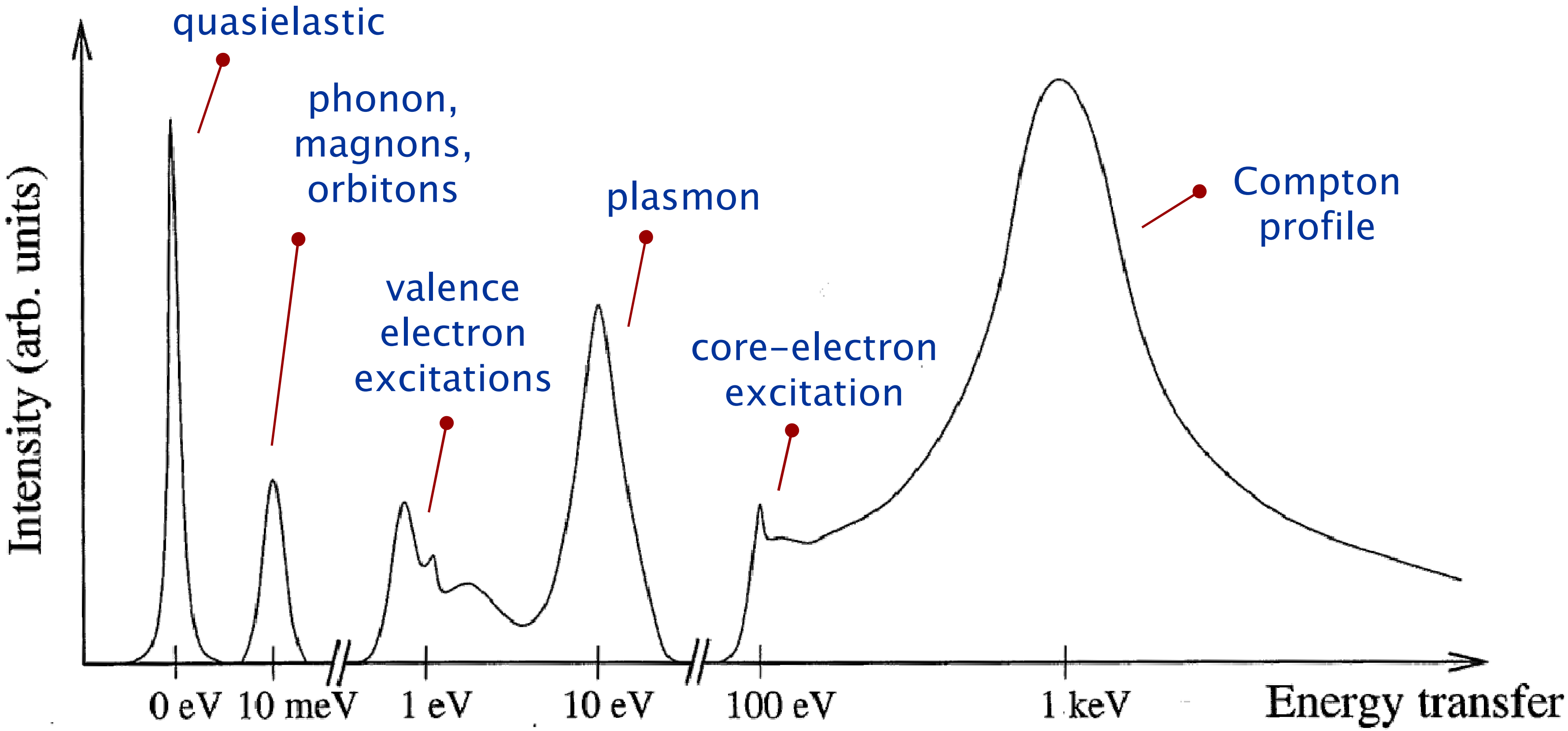
Introduction I – scattering kinematics



- Energy transfer: E_f - E_i = ΔE = **1 meV – several keV**

- Momentum transfer: $\vec{k}_f - \vec{k}_i = \vec{Q}$ **= 1 – 180 nm^{-1}**

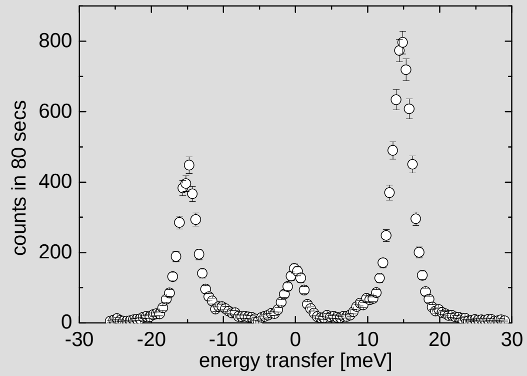
Introduction II - schematic IXS spectrum



S. Galombosi, PhD thesis, Helsinki 2007

Introduction III – overview 1

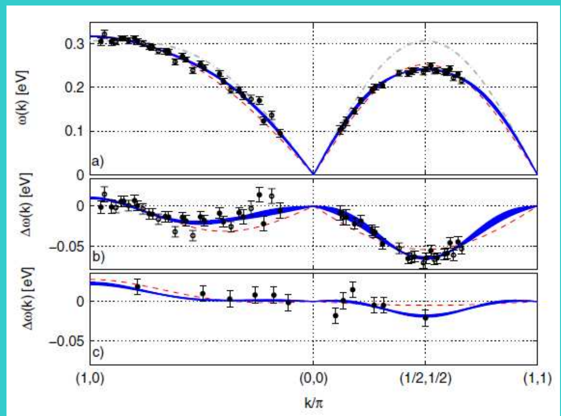
Phonons



Lattice dynamics

- elasticity
- thermodynamics
- phase stability
- e^--ph coupling

Magnons

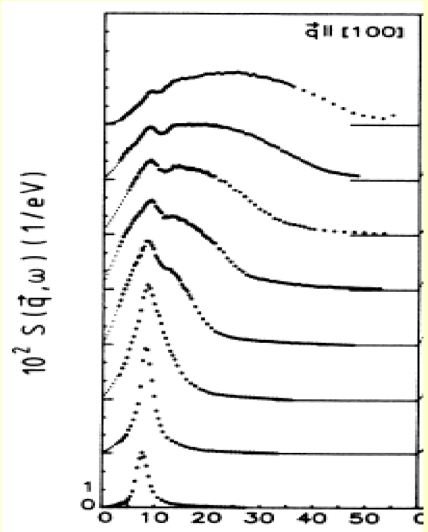


Spin dynamics

- magnon dispersions
- exchange interactions

Introduction IV – overview 2

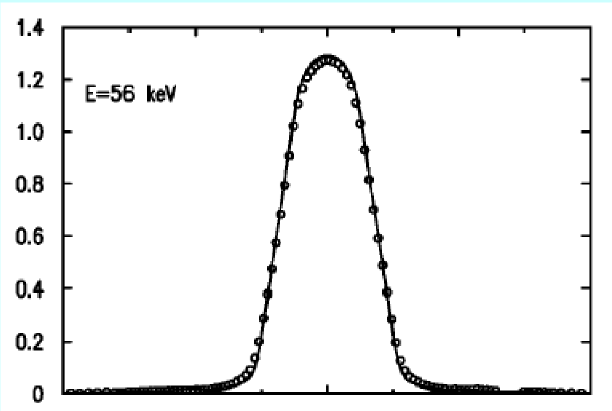
S(Q,ω)



Electron dynamics ε(q,ω)

- plasmons
- excitons
- orbitons

Compton scattering

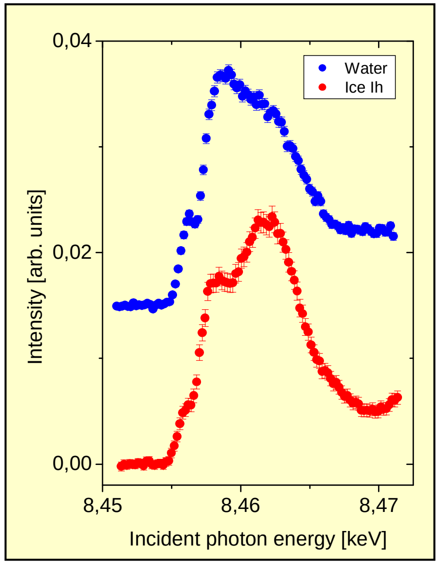


Impulse distribution of electrons

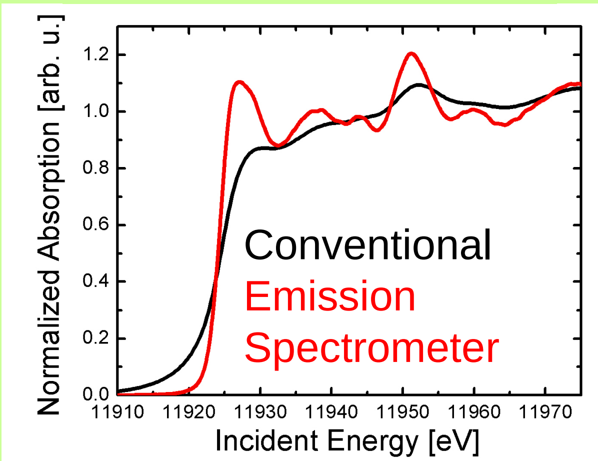
- chemical bonding
- local structures

Introduction V – overview 3

X-ray Raman scattering



RRS, HERFD XAS, ..



IXS from core electrons

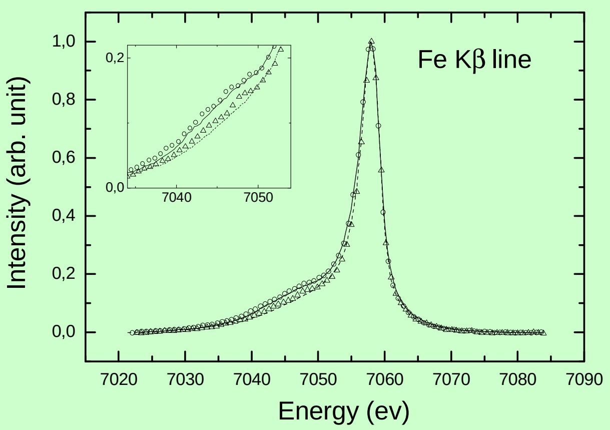
- electronic structure
- bulk sensitivity for low Z materials
- access to final states beyond the dipole limit

Resonant IXS from core electrons

- electronic structure
- reduced life time broadening

Introduction VI – overview 4

X-ray emission



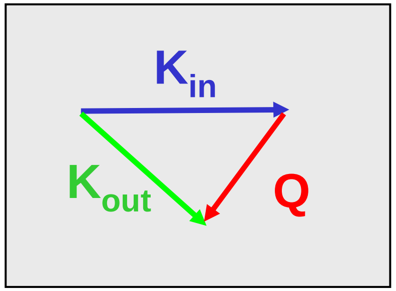
X-ray emission/fluoresence

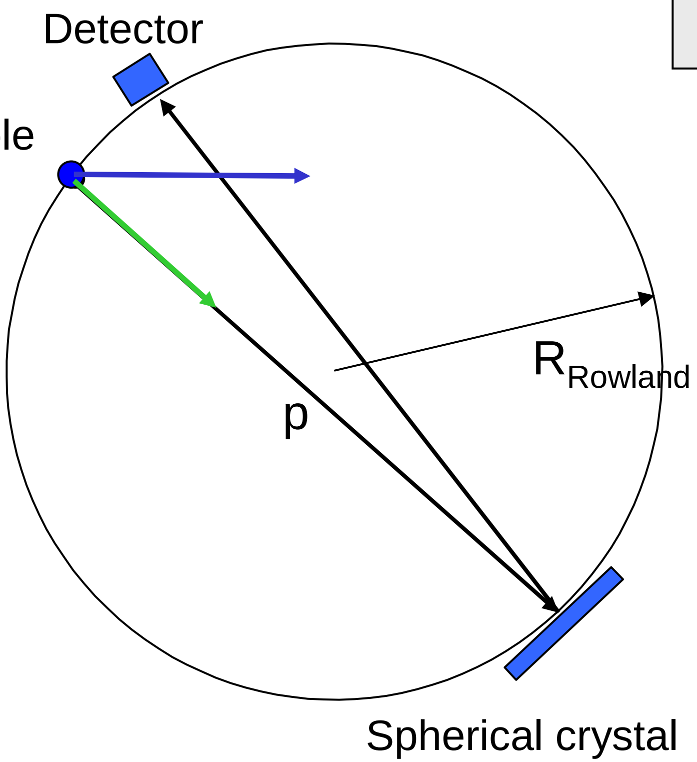
- element selective
- valence selective
- spin selective
- ligand selective

Introduction VII – IXS instrumentation

Energy analysis of scattered X-rays

- $\Delta E/E = 10^{-4} - 10^{-8}$
- some solid angle

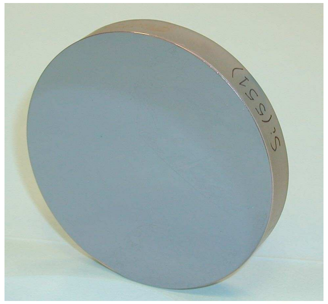




Rowland circle crystal spectrometer

$$p = R_{crystal} \cdot \sin\theta_B$$

$$R_{crys} = 2 \cdot R_{Rowl}$$



Introduction VIII – IXS at the ESRF

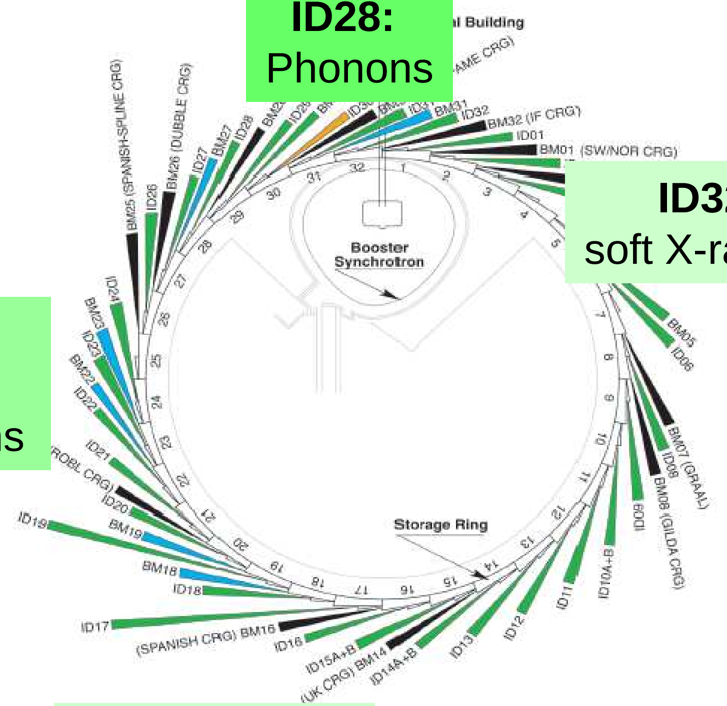
ID26:
XAS and emission spectroscopy

ID28:
Phonons

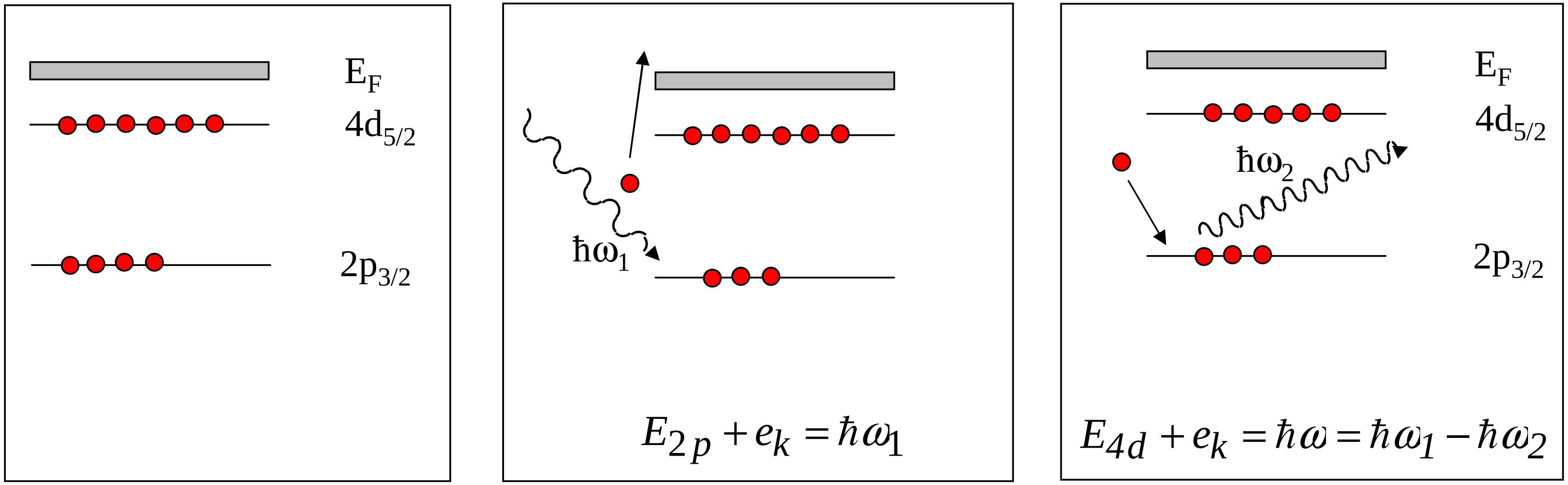
ID32:
soft X-ray IXS

ID20:
Electronic and
magnetic excitations

ID15B:
Compton: 30%



Resonant IXS from core electrons - I



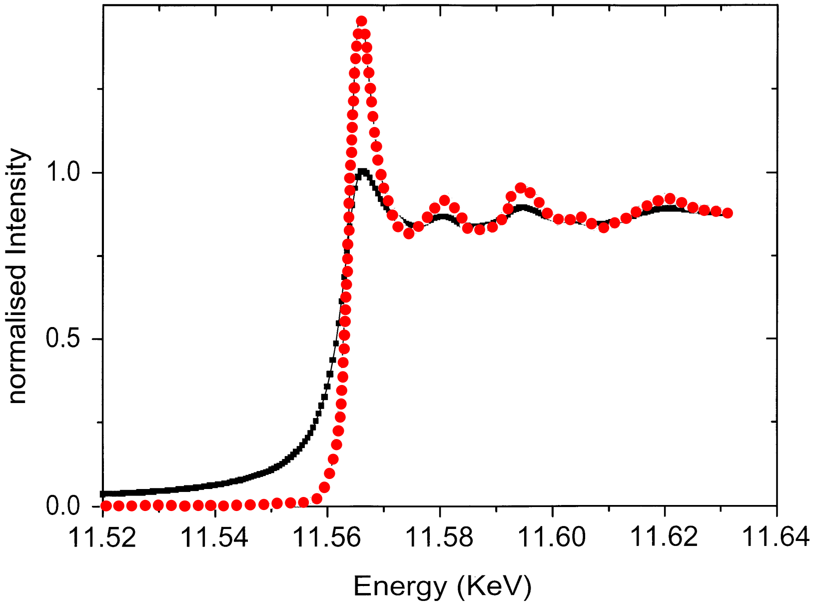
- Incident photon energy is tuned through the $2p_{3/2}$ edge.

- The radiative decay channel, following the filling of the $2p_{3/2}$ core hole, is monitored.

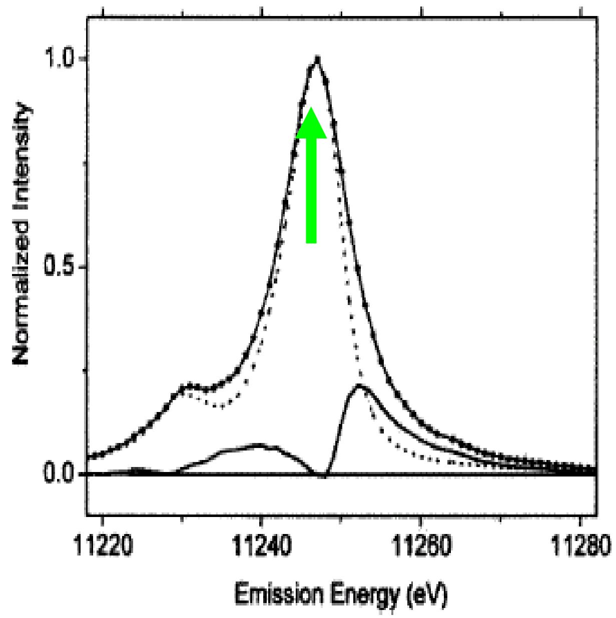
Resonant IXS from core electrons - II

“XAS beyond the core hole lifetime broadening”

XAS and **PFY/HERFD XAS**
Pt metal L_3 edge



Pt $L\beta_2$ emission line
$4d \rightarrow 2p_{3/2}$



- E_{scatt} fixed, E_{inc} tuned through absorption edge.
- Spectral sharpening by energy selection of emission channel.

F.M.F. De Groot. M. Krisch and J. Vogel; Phys. Rev. B 66, 196112 (2002)

Resonant IXS from core electrons - II

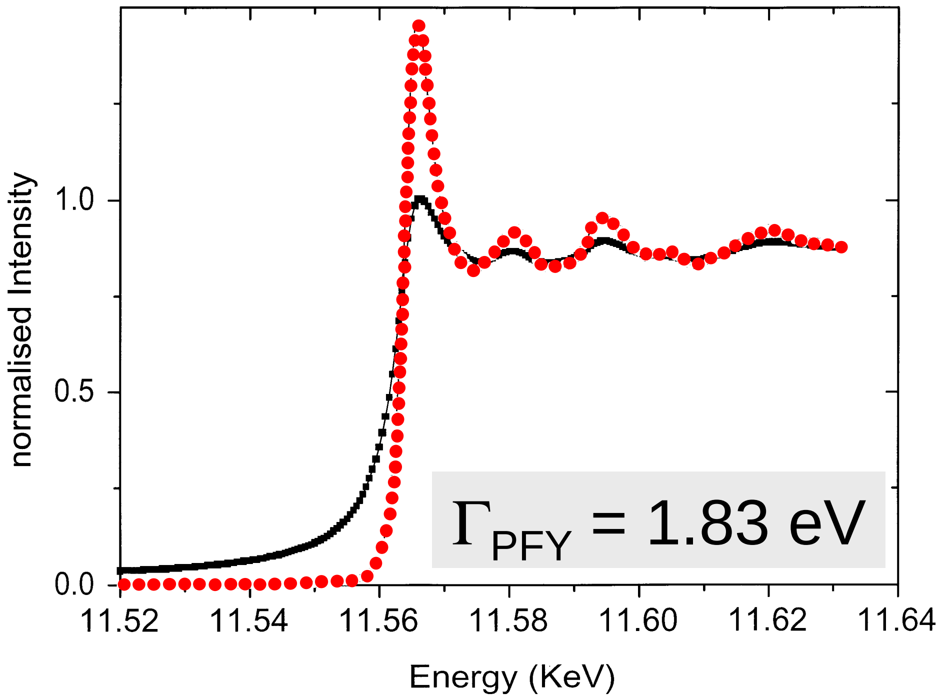
Partial Fluorescence Yield X-ray Absorption Spectroscopy
or
High Energy Resolution Fluorescence Detected XAS

$$1/\Gamma_{PFY} = \sqrt{1/\Gamma_{2p}^2 + 1/\Gamma_{4d}^2}$$

Pt L_3-edge

Γ_{L3} = 7 eV

$\Gamma_{M4,5}$ = 1.9 eV

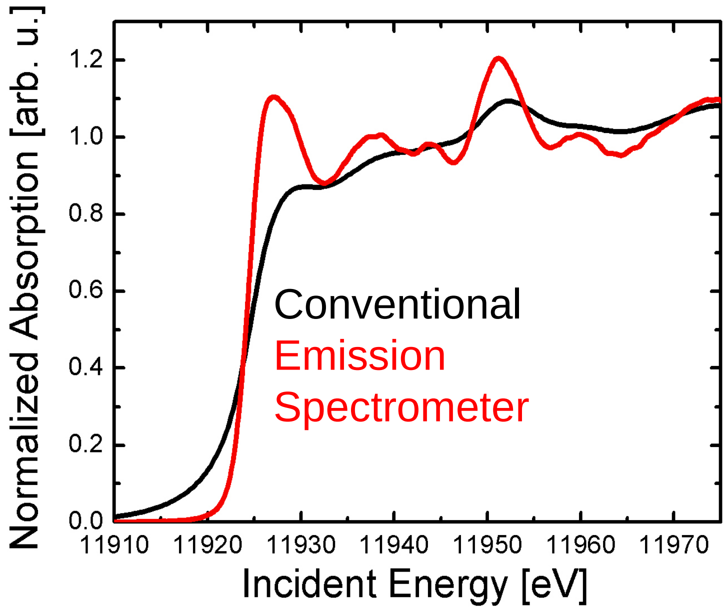


Significant spectral sharpening !!!

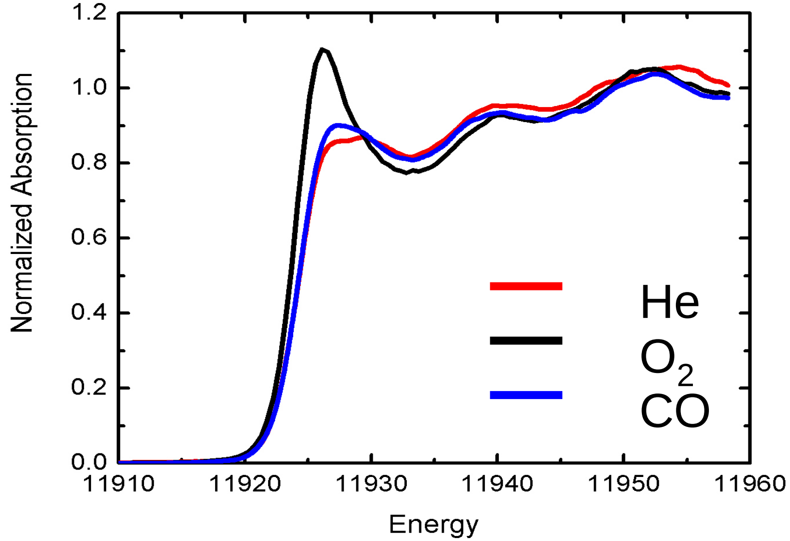
F.M.F. De Groot. M. Krisch and J. Vogel; Phys. Rev. B 66, 196112 (2002)

RIXS from core electrons– Applications 1

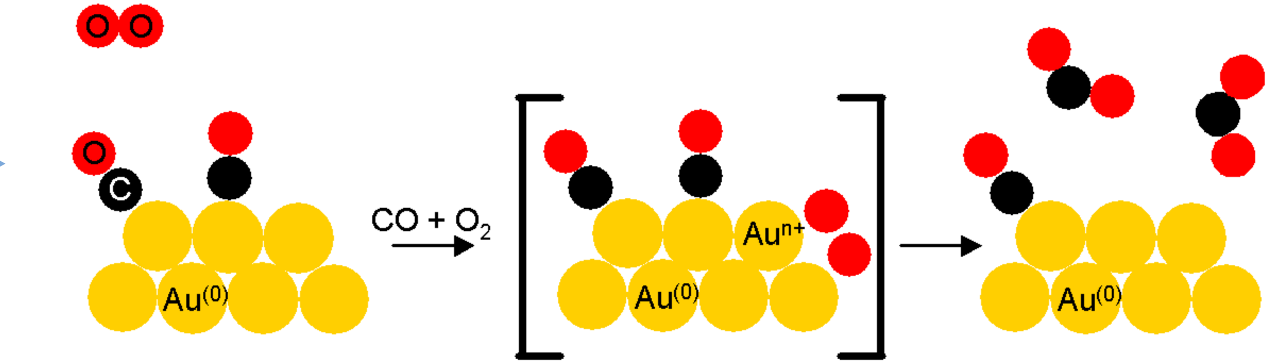
CO oxidation over gold nano-particles by high energy resolution XANES



In-situ study



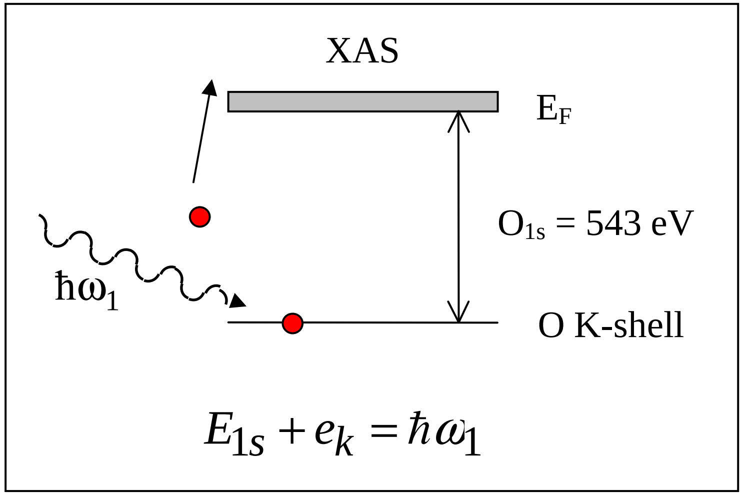
Reaction mechanism

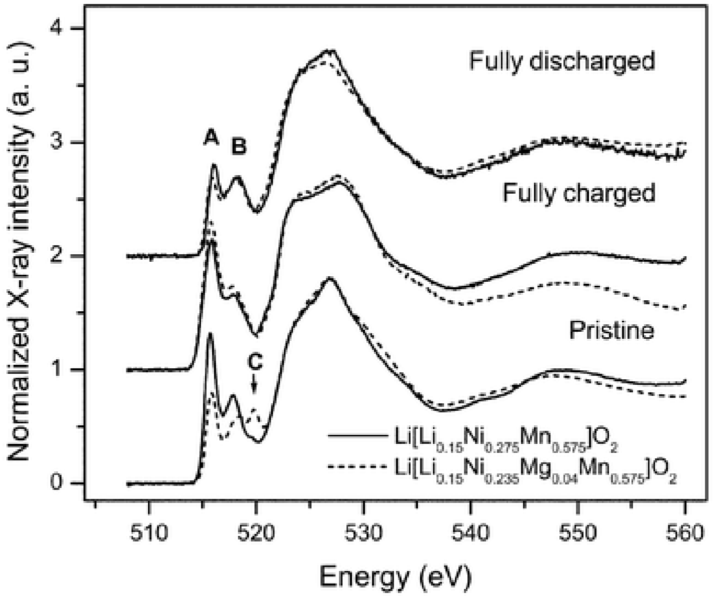


J. Van Bokhoven et al., Ang. Chem. 45 4651 (2006)

X-ray Raman scattering - I

X-ray absorption spectroscopy





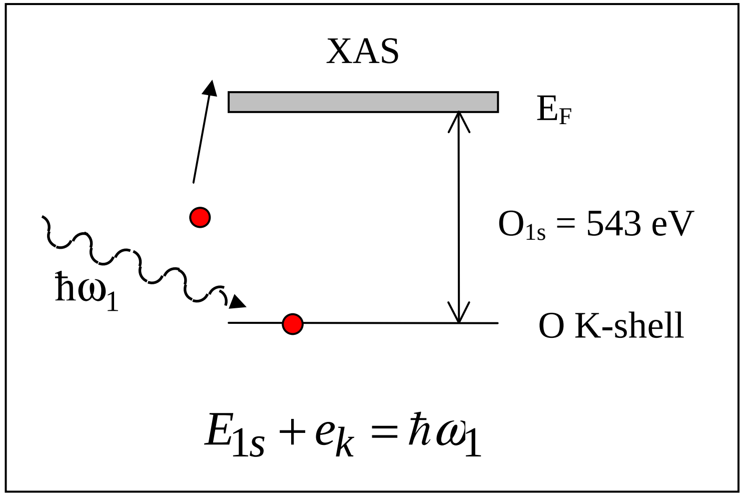
Incident photon energy is tuned through the oxygen K-edge

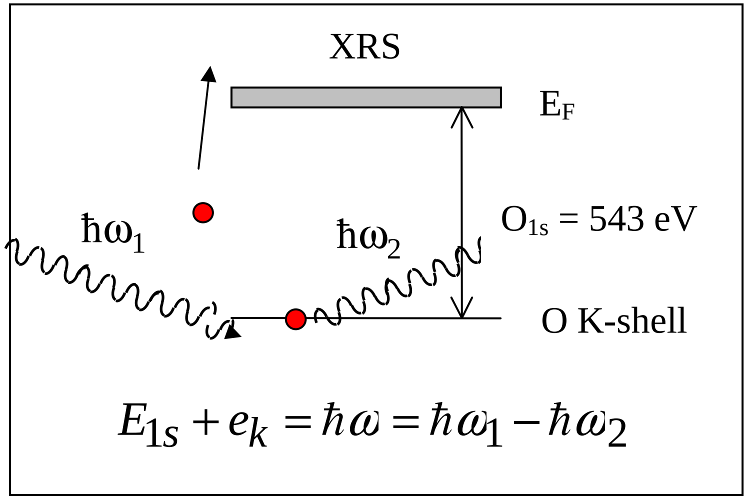
Soft X-rays => (U)HV environment, surface sensitivity (?), experimental constraints

Soft-XAS: Y.-K. Sun et al.; J. Mater. Chem. 13, 319-322 (2003)

The European Synchrotron | ESRF

X-ray Raman scattering - II





Role of incident photon energy in XAS is played by the energy transfer in XRS

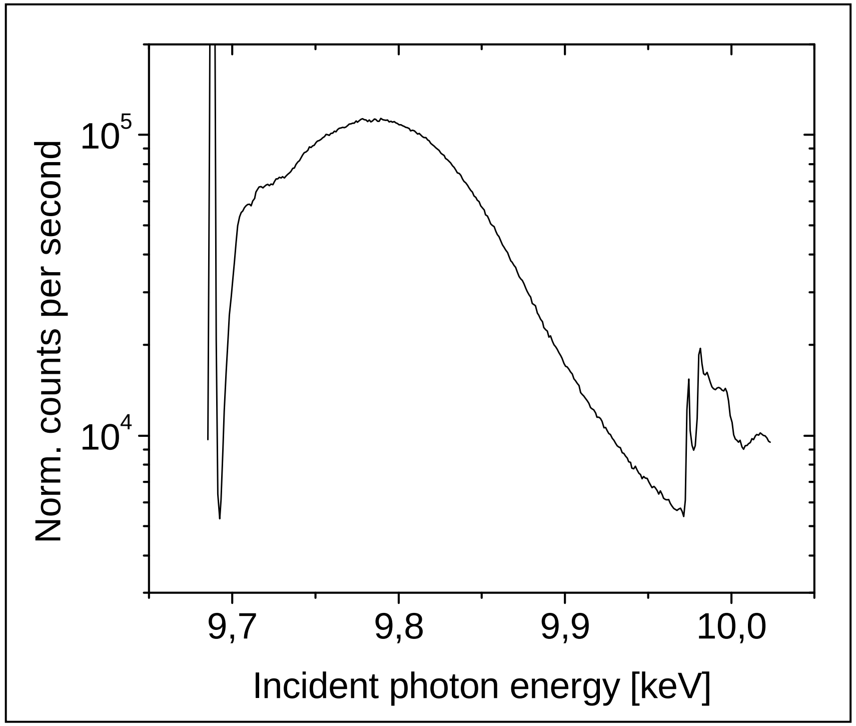
=>

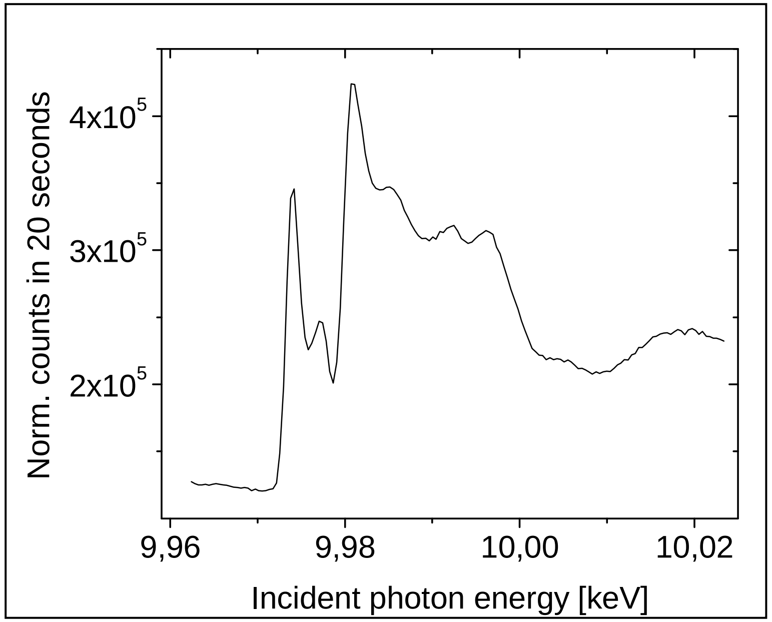
certain freedom in the choice of the incident photon energy

Hard X-rays => Bulk sensitivity; Access to buried layers
High pressure and/or temperature

X-ray Raman scattering - III

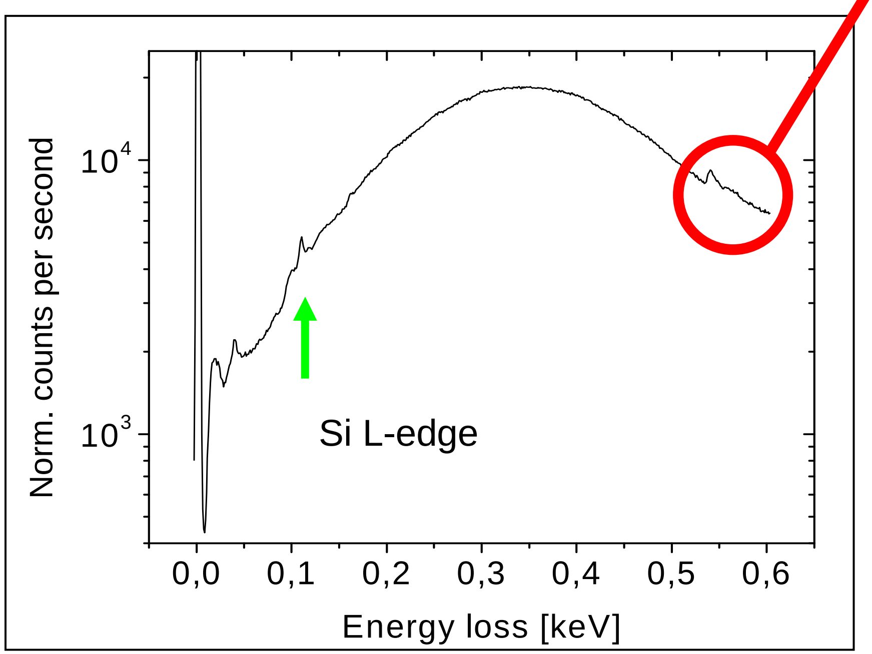
pyrolytic graphite (1 mm)
carbon K-edge: 284 eV
Q = 50 nm^{-1}

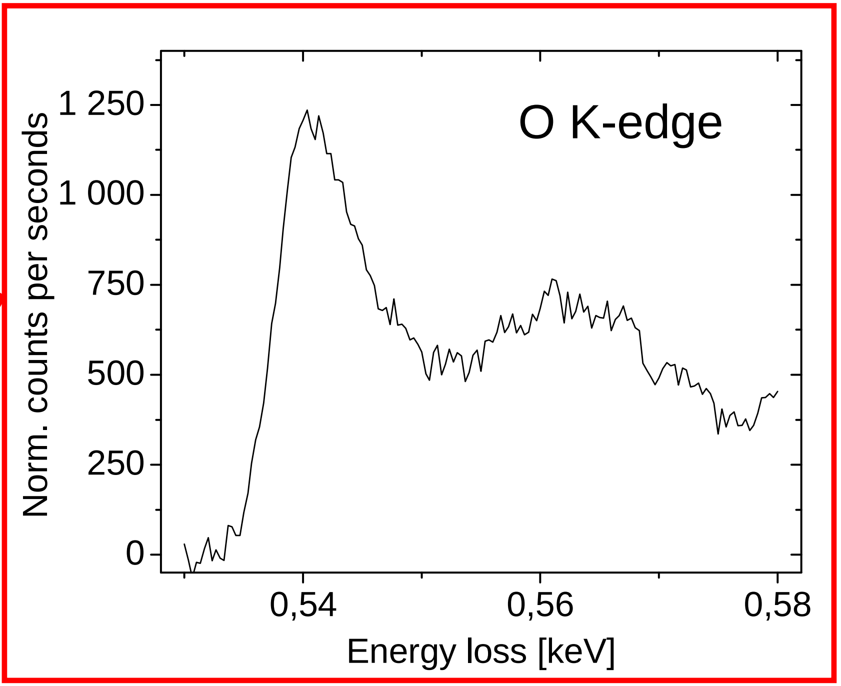




X-ray Raman scattering - IV

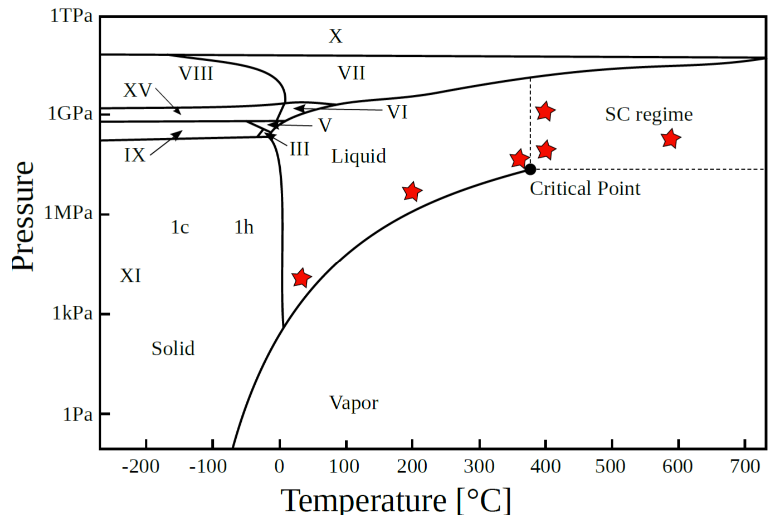
borosilicate glass (130 μm)
oxygen K-edge: 540 eV
Q = 97 nm^{-1}

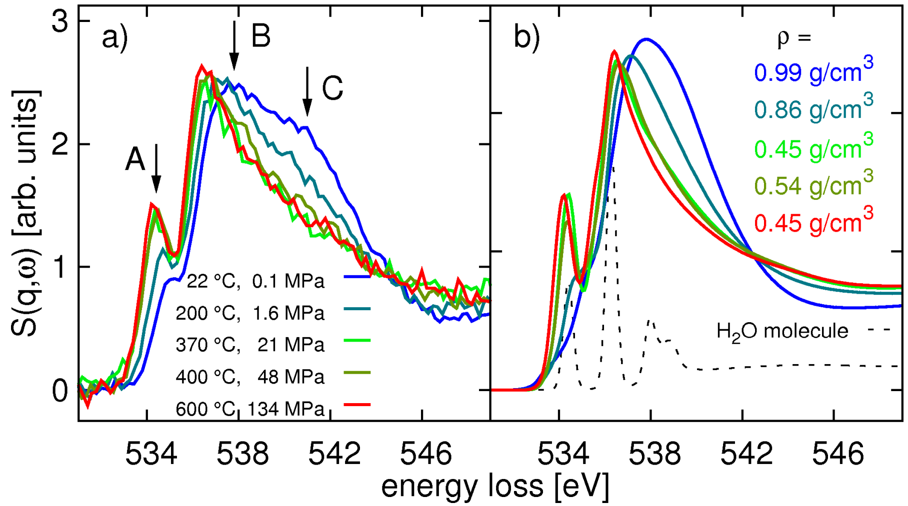


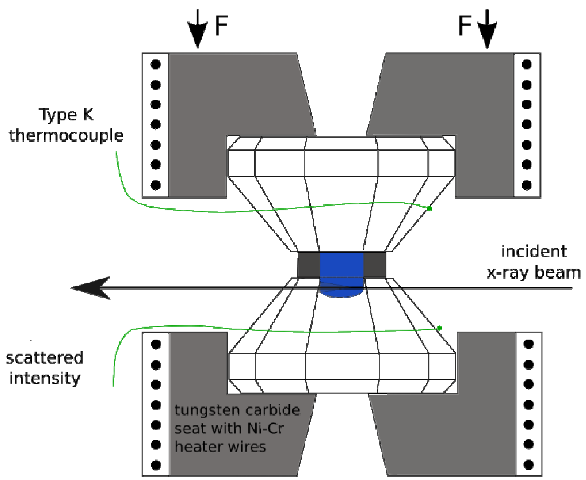


X-ray Raman scattering – Example 1

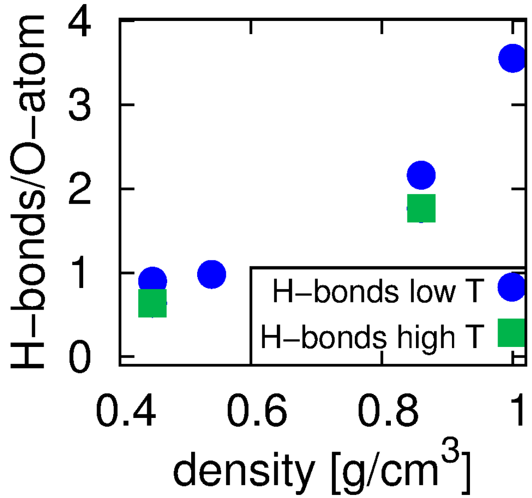
Microscopic structure of water at elevated P and T







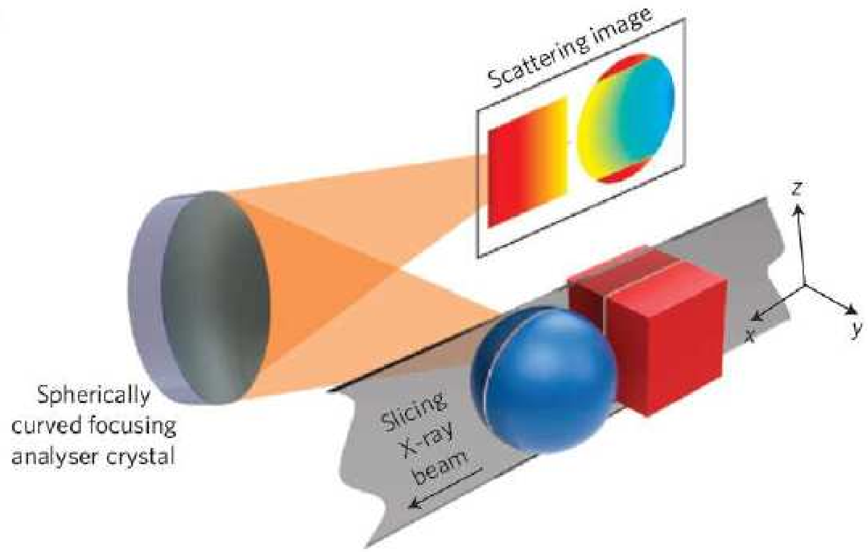
Resistively heated diamond anvil cell

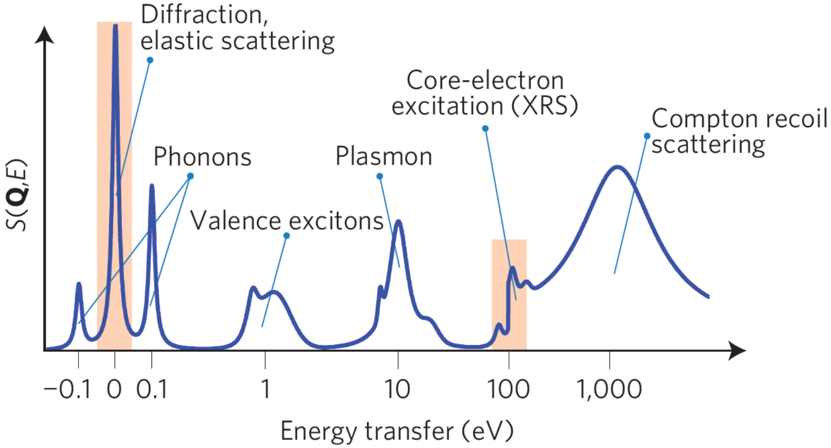


Ch. Sahle et al.; Proc. Nat. Acad. Science (2013)

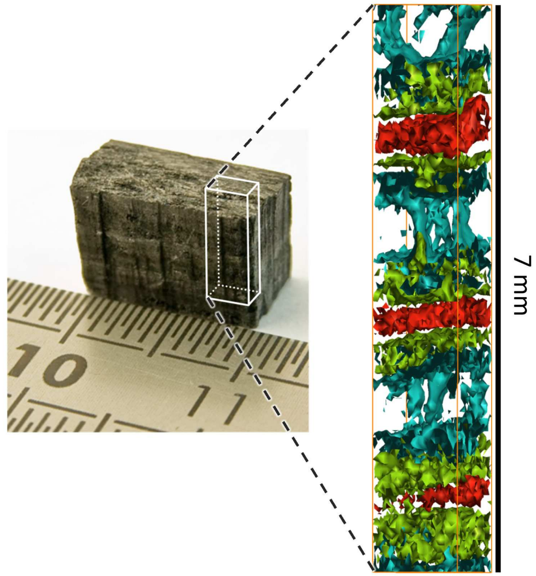
X-ray Raman scattering – Example 2

Direct tomography with chemical-bond contrast





Sample of carbon fibre-reinforced silicon carbide



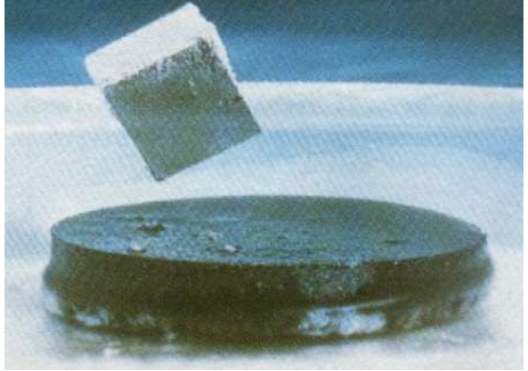
3D map of the *sp*² chemical bonds (different colors represent different carbon bond orientations).

S. Huotari et al.; Nature Materials 10, 489 (2011)

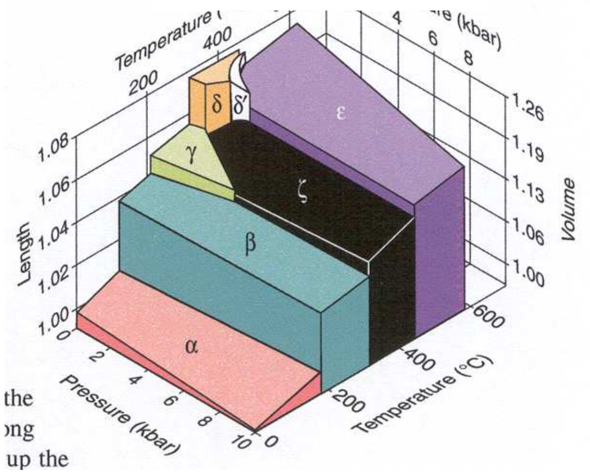
IXS from phonons - I

Relevance of phonons

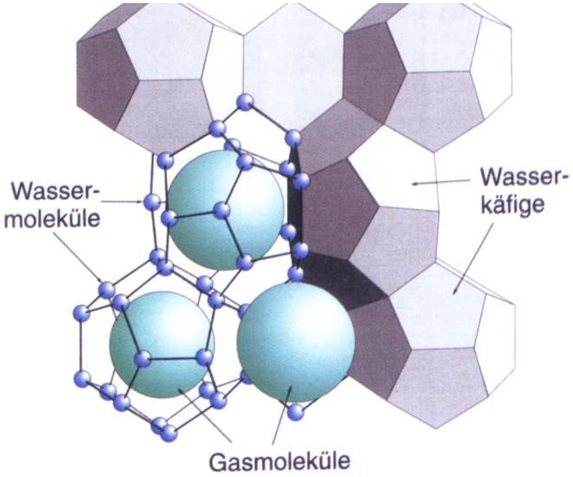
Superconductivity



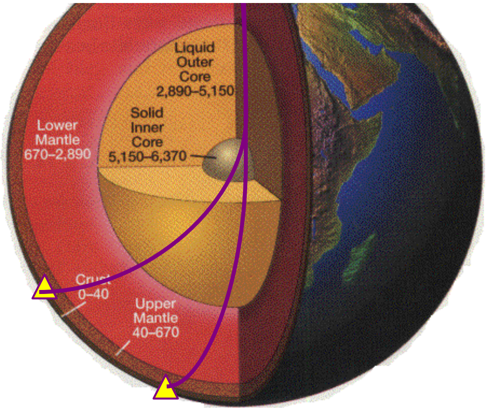
Phase stability



Thermal Conductivity



Sound velocities and elasticity



IXS from phonons - II

Vibrational spectroscopy: a short history

Infrared absorption - 1881

W. Abney and E. Festing, R. Phil. Trans. Roy. Soc. 172, 887 (1881)

Brillouin light scattering - 1922

L. Brillouin, Ann. Phys. (Paris) 17, 88 (1922)

Raman scattering – 1928

C. V. Raman and K. S. Krishnan, Nature 121, 501 (1928)

TDS: Phonon dispersion in Al – 1948

P. Olmer, Acta Cryst. 1 (1948) 57

INS: Phonon dispersion in Al – 1955

B.N. Brockhouse and A.T. Stewart, Phys. Rev. 100, 756 (1955)

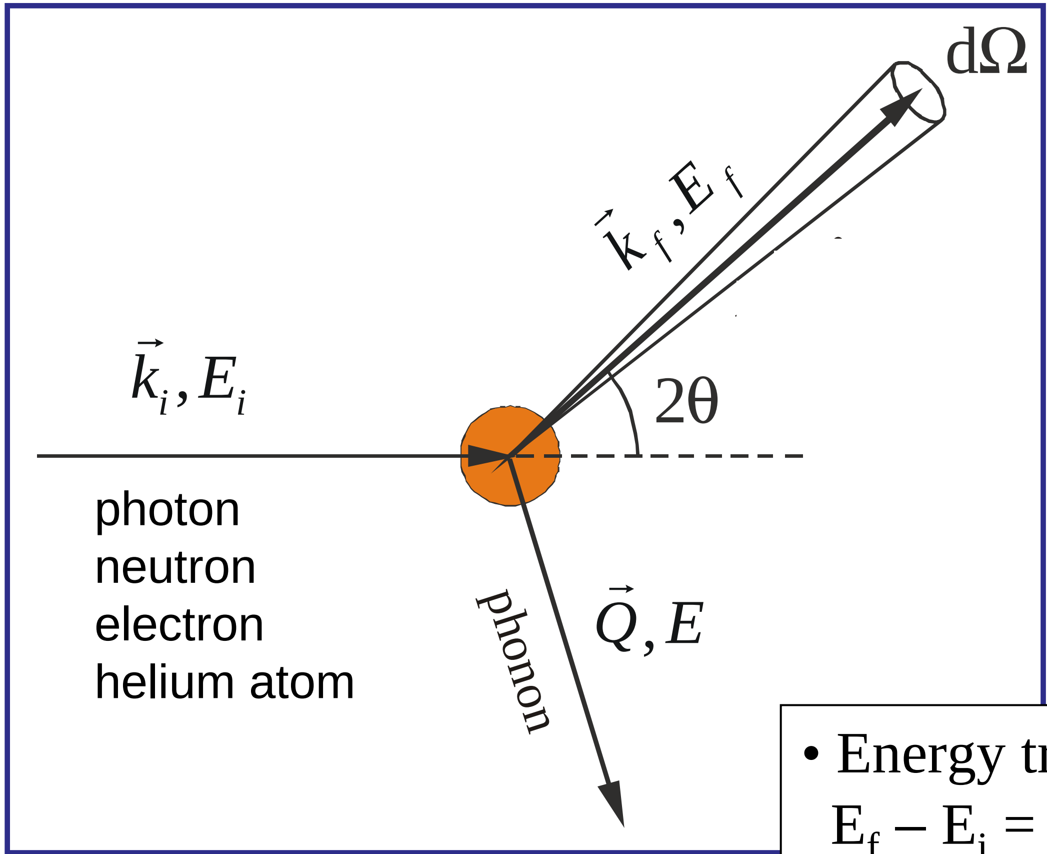
IXS: Phonon dispersion in Be – 1987

B. Dorner, E. Burkel, Th. Illini and J. Peisl, Z. Phys. B – Cond. Matt. 69, 179 (1987)

NIS: Phonon DOS in Fe – 1995

M. Seto, Y. Yoda, S. Kikuta, X.W. Zhang and M. Ando, Phys. Rev. Lett. 74, 3828 (1995)

IXS from phonons - III

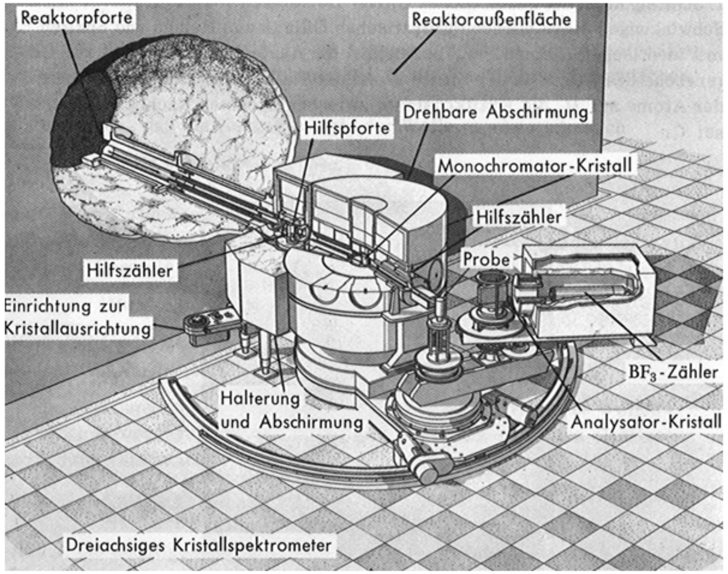


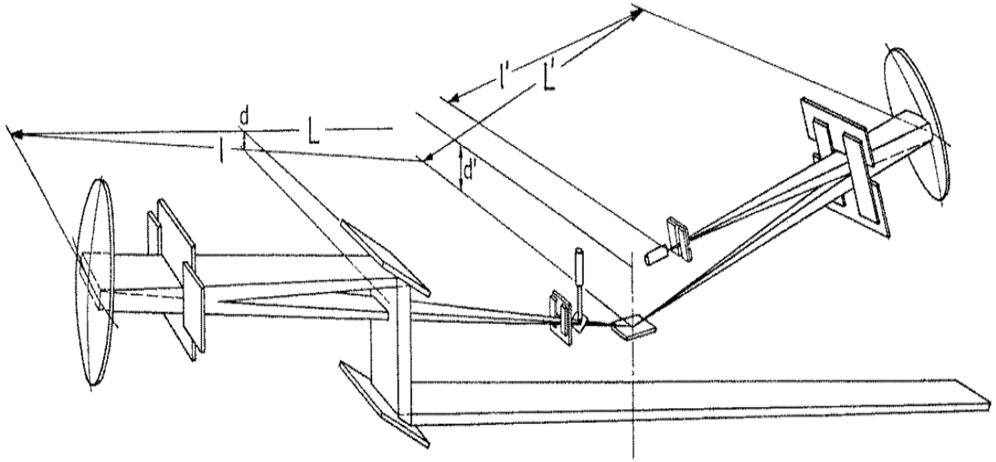
- Energy transfer:

  $E_f - E_i = E$ (0.001 – 1 eV)
- Momentum transfer:

  $\vec{k}_f - \vec{k}_i = \vec{Q}$ (0.0001 – 100 nm^{-1})

IXS from phonons - IV





The instrument INELAX at the HARWI wiggler line of HASYLAB.

Brockhouse (1955)

Thermal neutrons:

E_i = 25 meV

k_i = 38.5 nm^{-1}

$\Delta E/E$ = 0.01 – 0.1

Burkel, Dorner and Peisl (1987)

Hard X-rays:

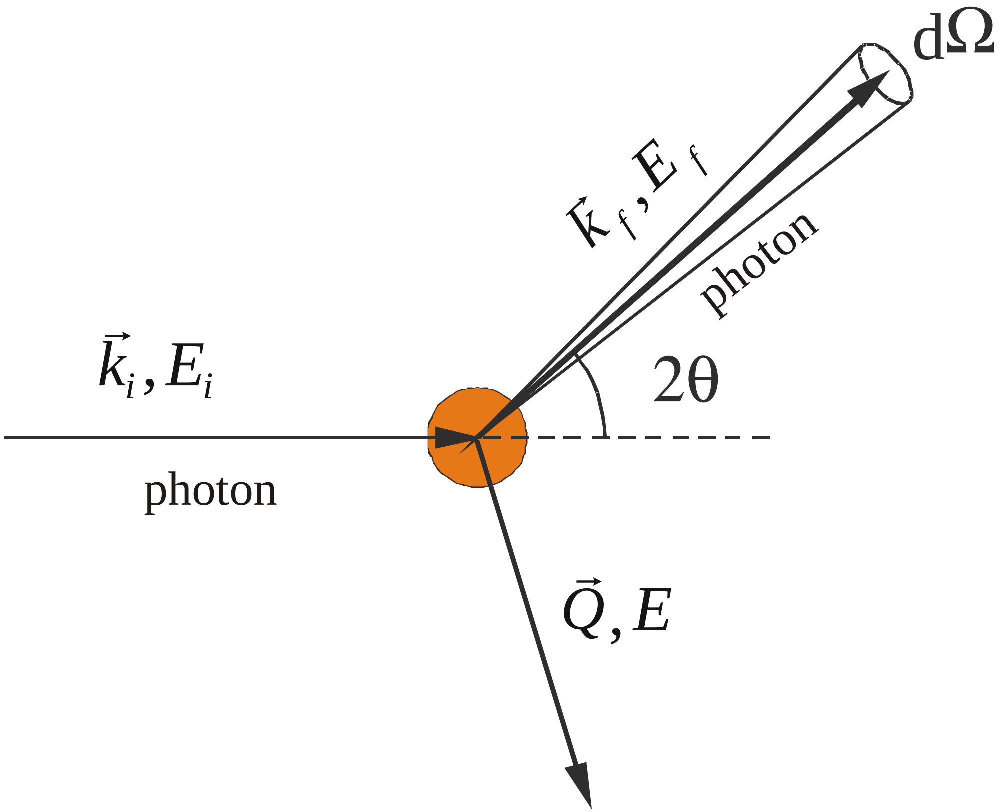
E_i = 18 keV

k_i = 91.2 nm^{-1}

$\Delta E/E \leq 1 \times 10^{-7}$

IXS from phonons - V

IXS: Scattering kinematics

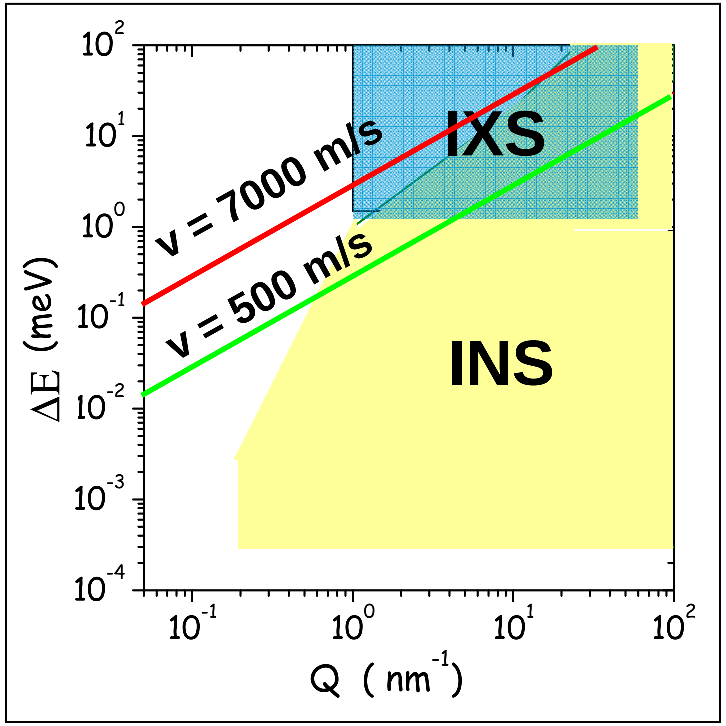


$$\begin{cases} E = E_i - E_f \\ \left|\vec{Q}\right| = 2\left|\vec{k}_i\right|\sin(\theta) \end{cases}$$

momentum transfer is defined only by scattering angle

IXS from phonons - VI

No kinematic limitations: ΔE independent of Q



$Q = 4\pi/\lambda \cdot \sin(\theta)$

$\Delta E = E_i - E_f$

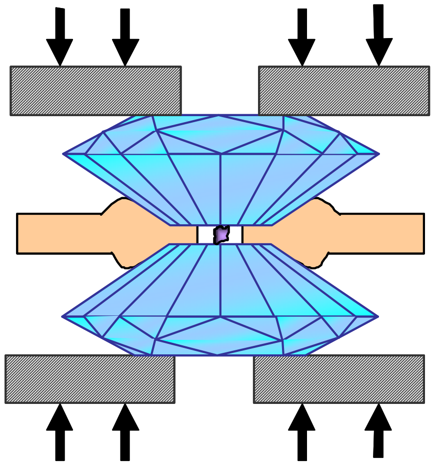
Disordered systems:

Explore new Q-ΔE range

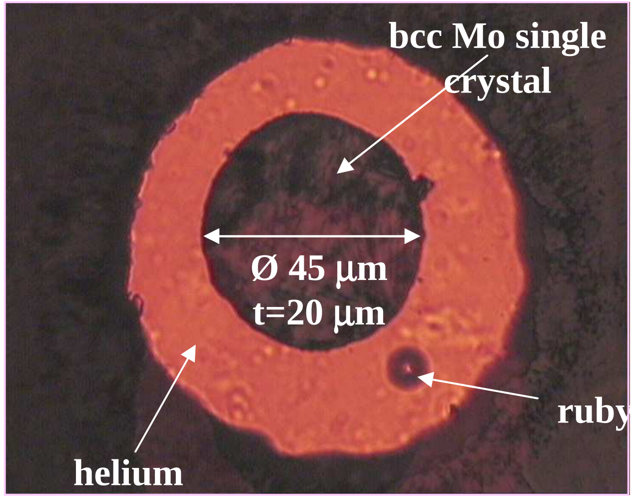
- Interplay between structure and dynamics on ≈ nm length scale
- Relaxations on the picosecond time scale
- Excess of the VDOS (Boson peak)
- Nature of sound propagation and attenuation

IXS from phonons - VII

Small sample volumes: $10^{-4} – 10^{-5}$ mm^3



Diamond anvil cell



- (New) materials in very small quantities
- Very high pressures > 1Mbar
- Study of surface phenomena

IXS from phonons - VIII

IXS

$$\frac{\partial^2\sigma}{\partial E\partial\Omega} = r_0^2 \frac{k_1}{k_2} (\vec{\varepsilon}_1 \cdot \vec{\varepsilon}_2) f(Q)^2 \, S(\vec{Q},E)$$

- no correlation between momentum- and energy transfer
- ΔE/E = 10^{-7} to 10^{-8}
- Cross section ~ Z^2 (for small Q)
- Cross section is dominated by photoelectric absorption (~ $\lambda^3 Z^4$)
- no incoherent scattering
- small beams: 100 μm or smaller

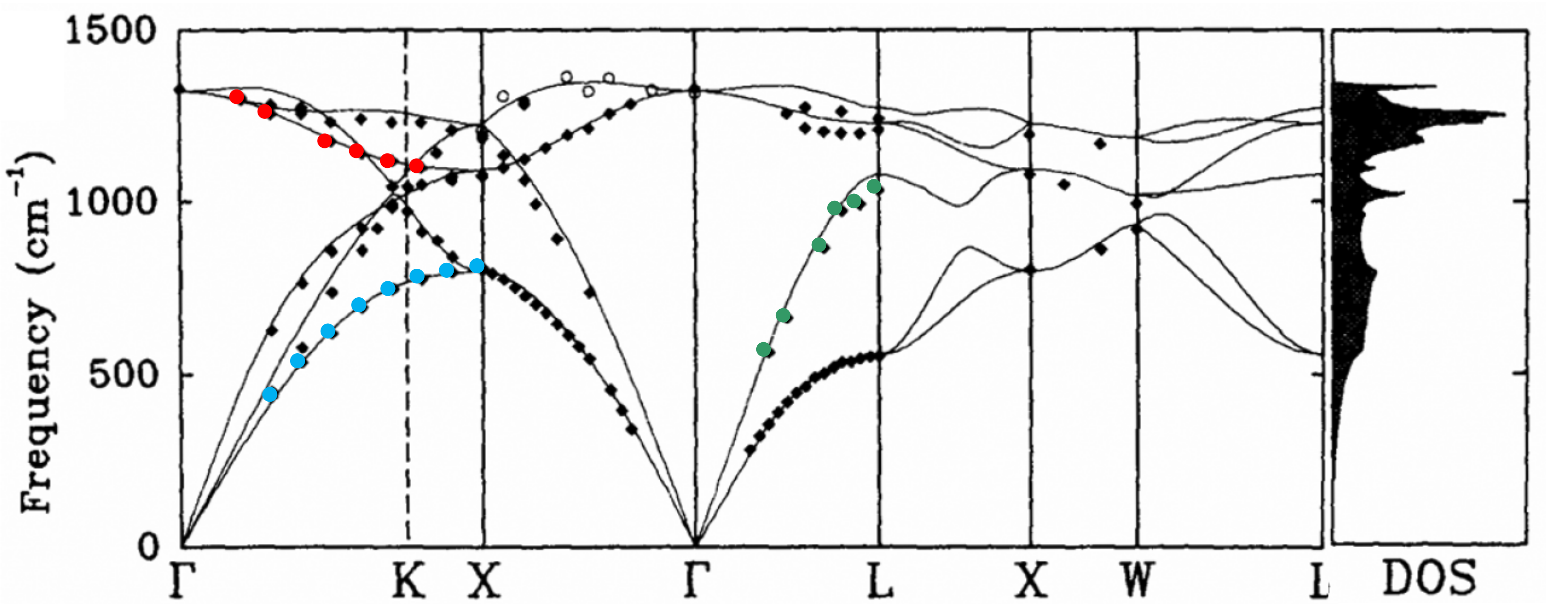
INS

$$\frac{\partial^2\sigma}{\partial E\partial\Omega} = b^2 \frac{k_1}{k_2} S(\vec{Q},E)$$

- strong correlation between momentum- and energy transfer
- ΔE/E = 10^{-1} to 10^{-2}
- Cross section ~ b^2
- Weak absorption => multiple scattering
- incoherent scattering contributions
- large beams: several cm

IXS from phonons - XI

Phonon dispersion and phonon density of states

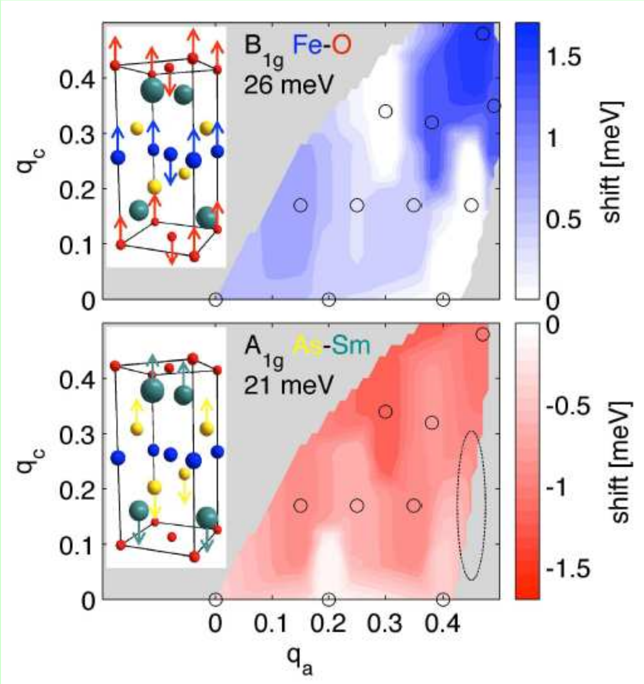


- <u>single crystals</u>
  - triple axis: (very) time consuming
  - time of flight: not available for X-rays

- <u>polycrystalline materials</u>
  - reasonably time efficient
  - limited information content

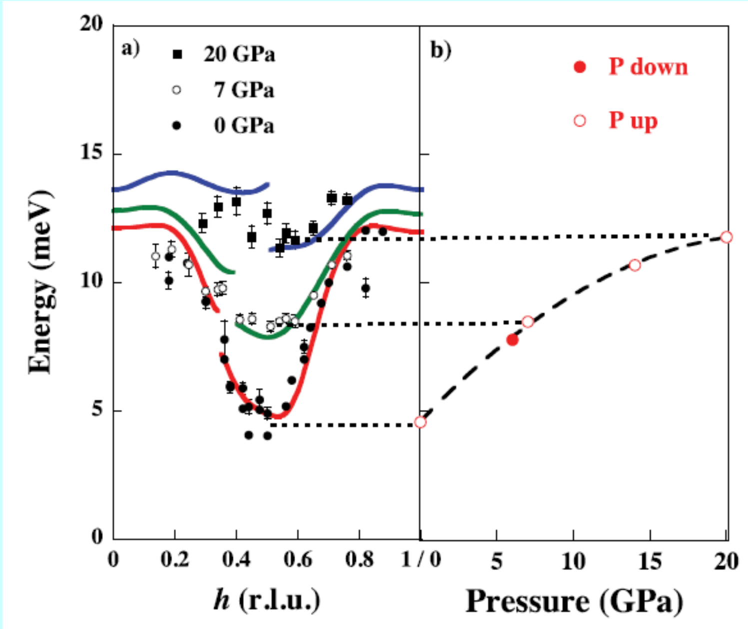
IXS from phonons – correlated electron systems

Doping dependence in $SmFeAsO_{1-x}F_y$



M. Le Tacon et al.; Phys. Rev. B 80, 220504

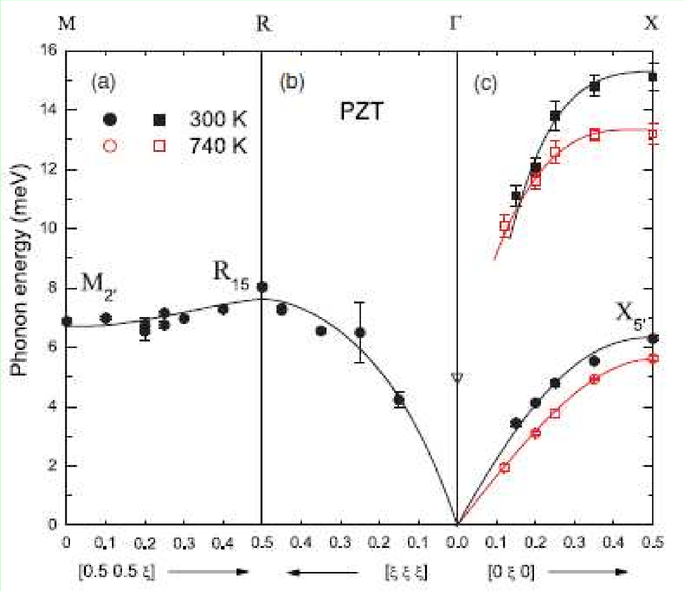
e-ph coupling in α-U



S. Raymond et al.; PRL 107, 136401

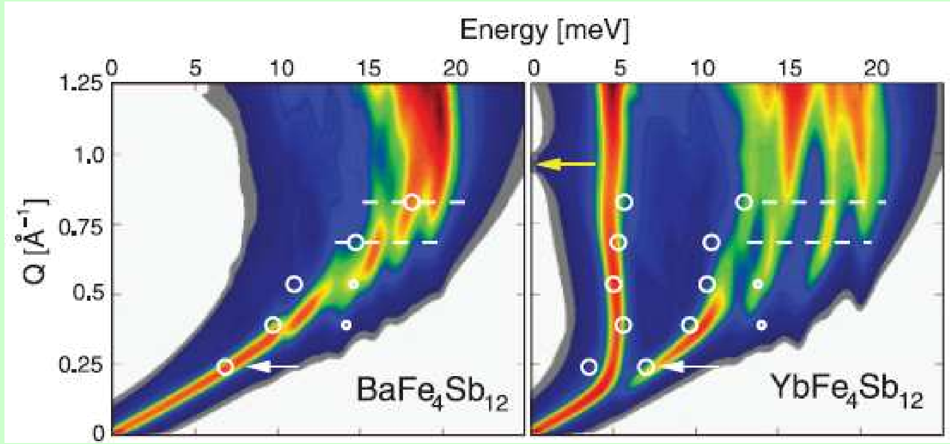
IXS from phonons – functional materials

Piezoelectrics $PbZr_{1-x}Ti_xO_3$



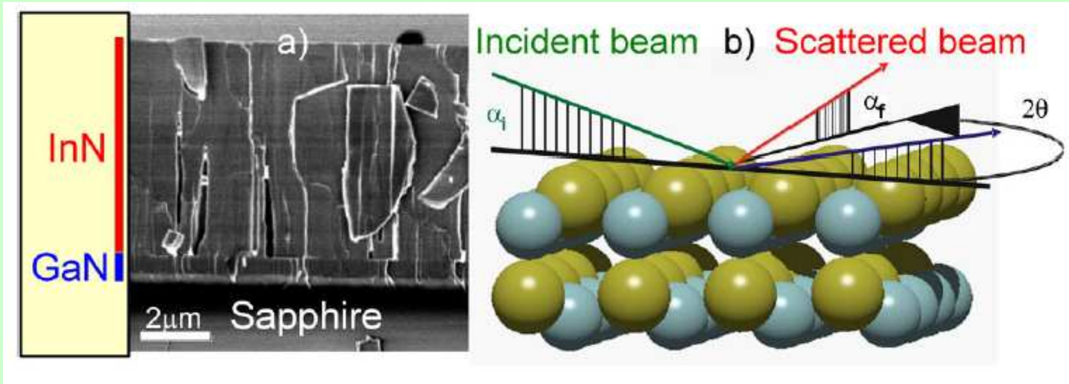
J. Hlinka et al.; PRB 83, 040101(R)

Skutterudites



M.M. Koza et al.; PRB 84, 014306

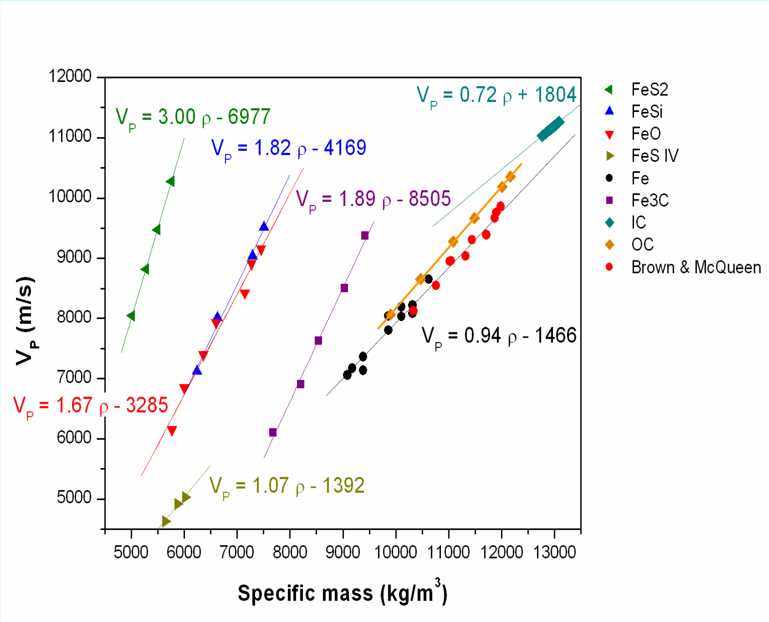
InN thin film lattice dynamics



J. Serrano et al.; PRL 106, 205501

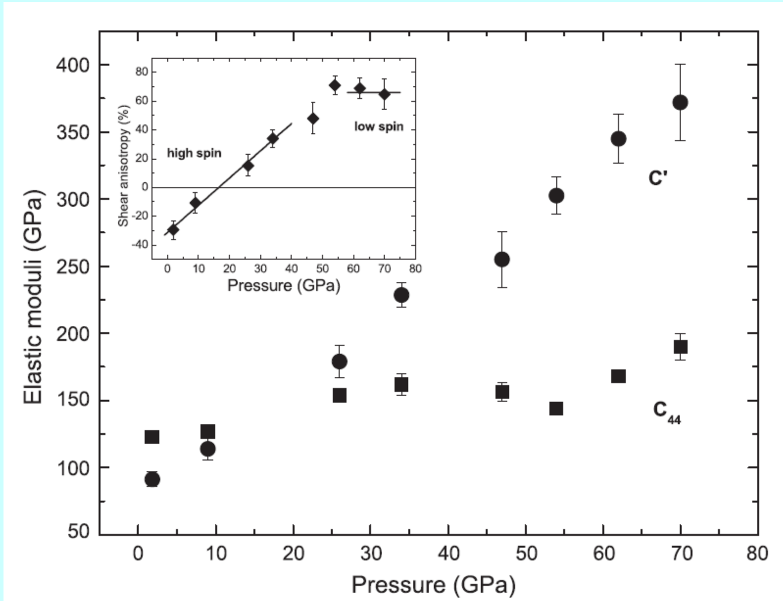
IXS from phonons – Earth and planetary science

Sound velocities in Earth's core



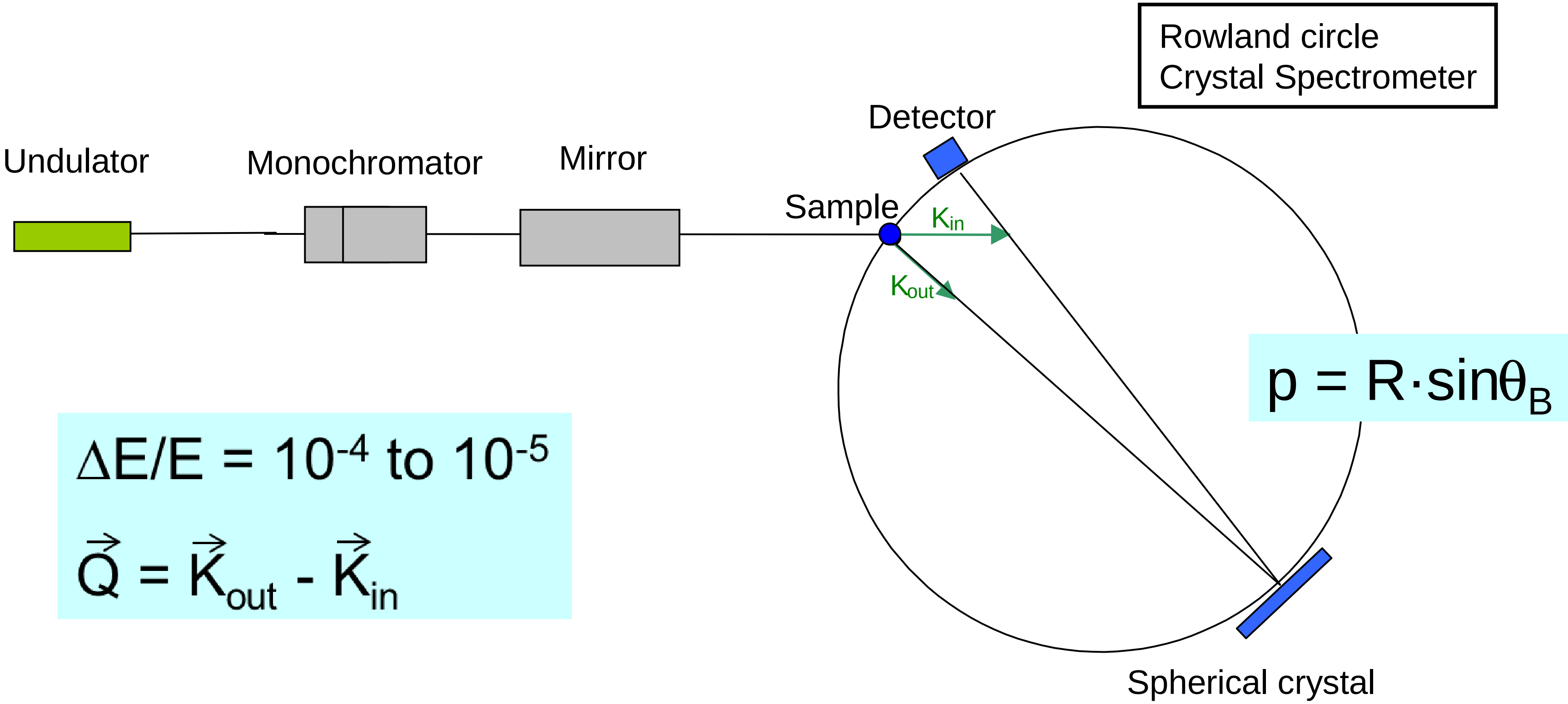
J. Badro et al.; Earth Plan. Science Lett. 98, 085501

Elastic anisotropy in $Mg_{83}Fe_{0.17}O$



D. Antonangeli et al.; Science 331, 64

Instrumentation for IXS - I



$p = R \cdot \sin\theta_B$

$\Delta E/E = 10^{-4}$ to 10^{-5}

$\vec{Q} = \vec{K}_{out} - \vec{K}_{in}$

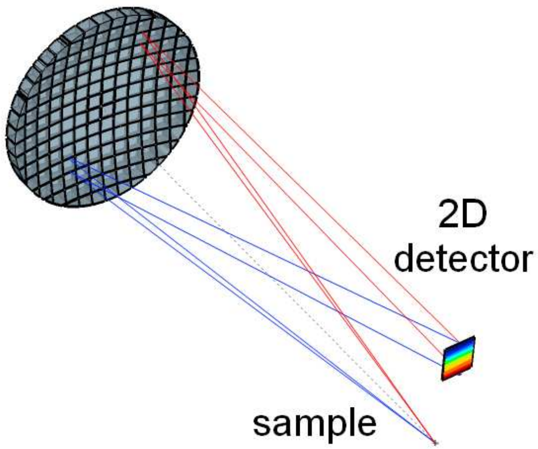
R = 1 or 2 m
Si (Ge) (333, 440, 551, …) crystals
Bragg angles θ_B: 65º - 90º.
$\Delta E = 0.15 – 2$ eV

Instrumentation for IXS - II

Crystal analysers

Anodic Bonded Elastically Bent Analyzers

medium energy resolution
Very thin wafers (Si)
Curvature radius 1 and 2 m
Energy compensation algorithm



Diced Analyzers

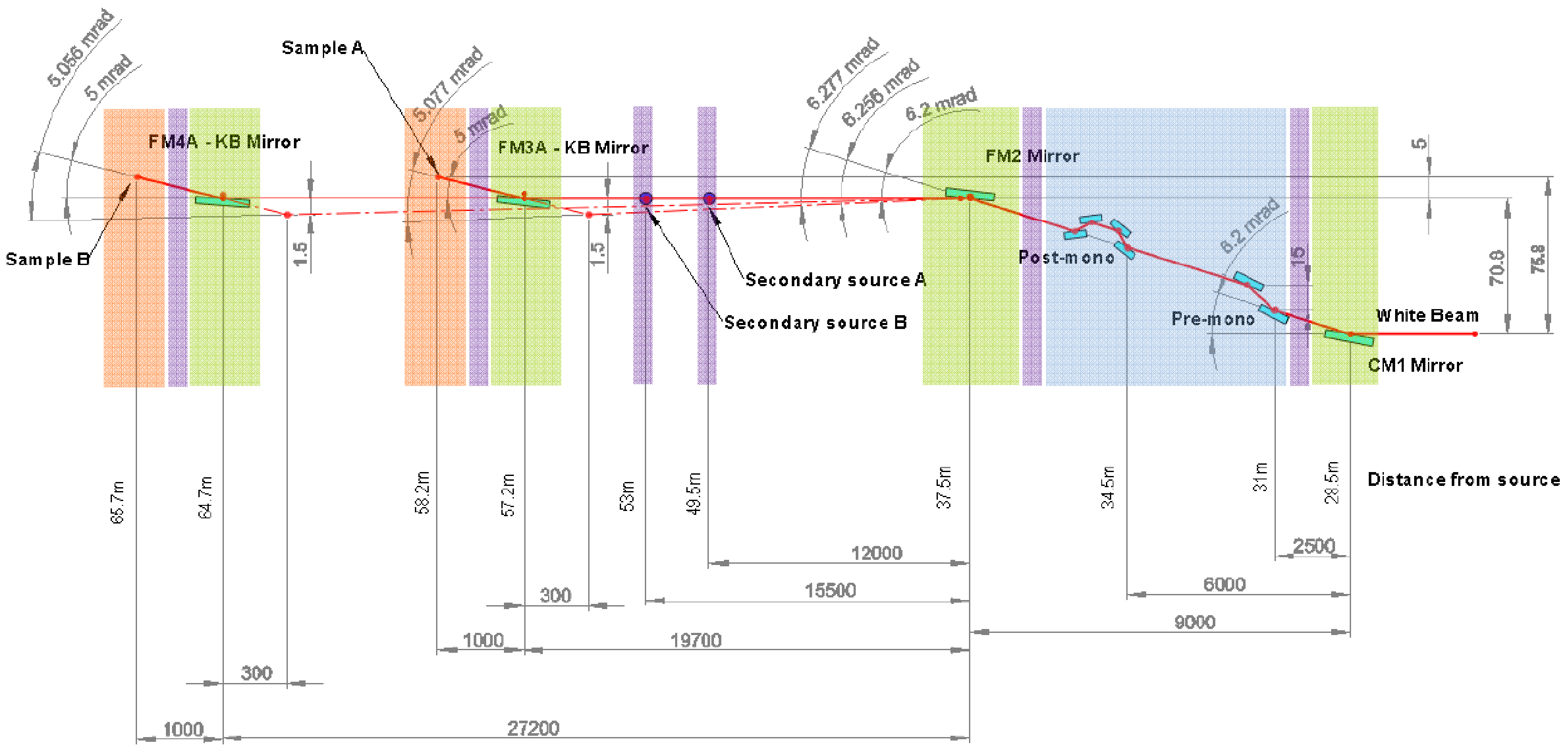
very high energy resolution
cube size 0.8 mm x 0.8 mm x 3 mm
Curvature radius 1, 2, 6.5 m
Energy compensation algorithm

In-house R&D: Roberto Verbeni et al; J. Synchrotron Rad. 16, 469 (2009)

Instrumentation for IXS - III

ID20 @ ESRF

spectrometers monitoring monochromators focusing



lateral view

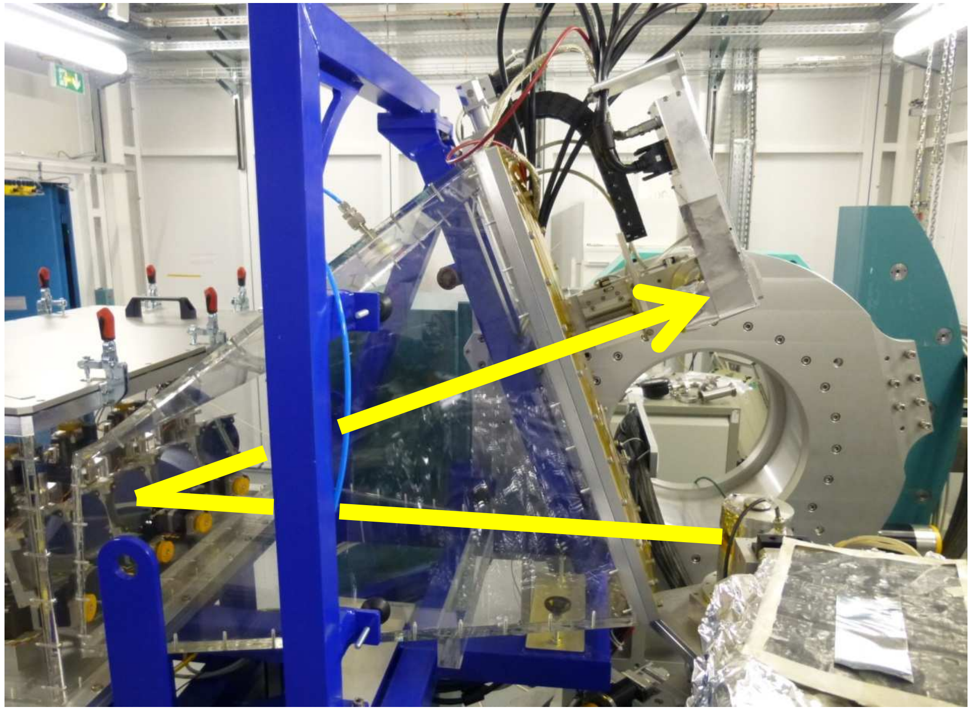
Instrumentation for IXS - IV

RIXS Spectrometer (ID20 - EH2)

Scan of both incident and scattered energy

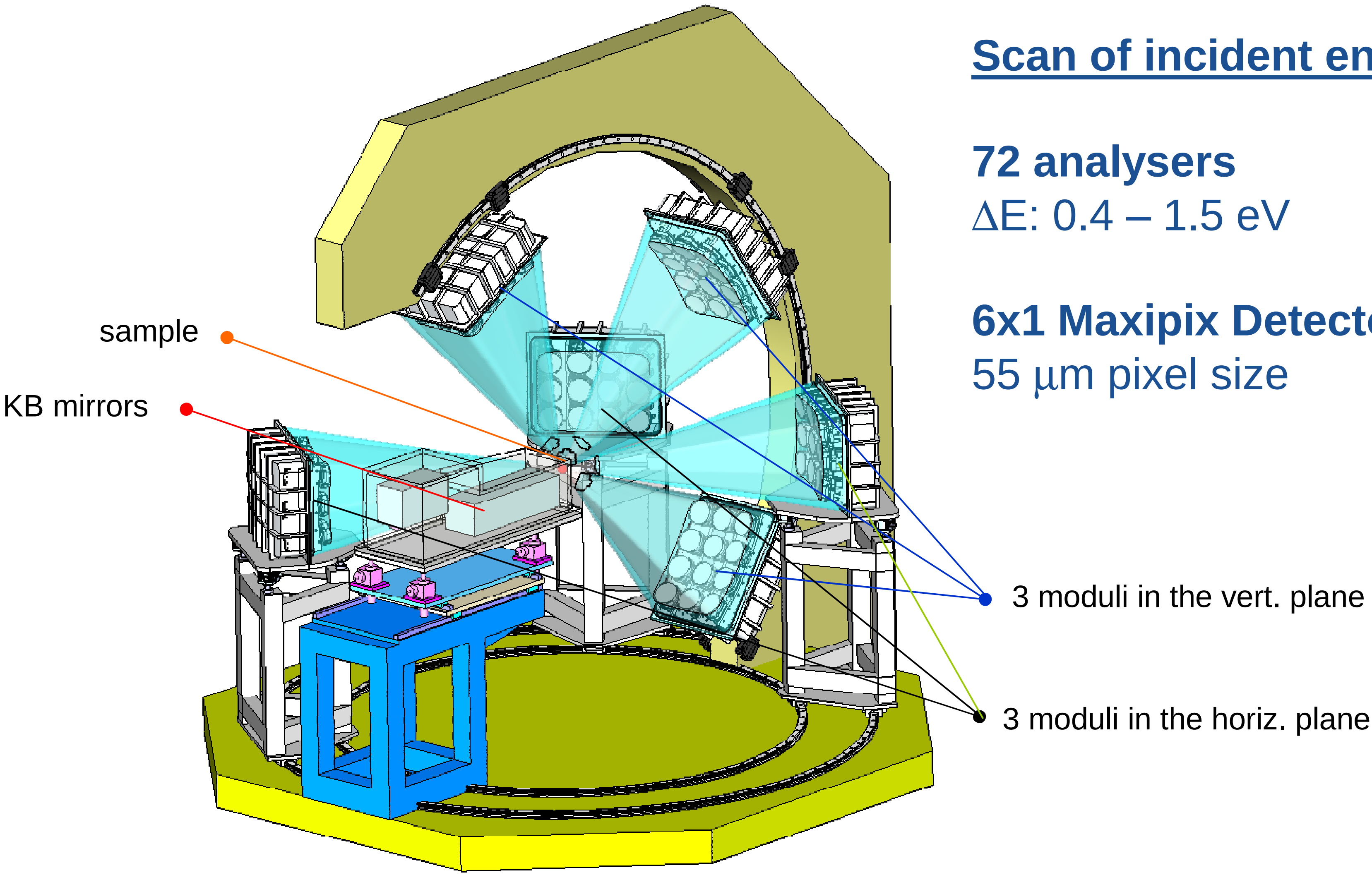
5 bent or diced analysers
ΔE down to 25 meV
High flux and/or several **q**'s

1x5 Maxipix Detectors
55 μm pixel size
Energy compensation algorithm
Background removal



Instrumentation for IXS - V

X-ray Raman Spectrometer ID20 - EH3



Scan of incident energy

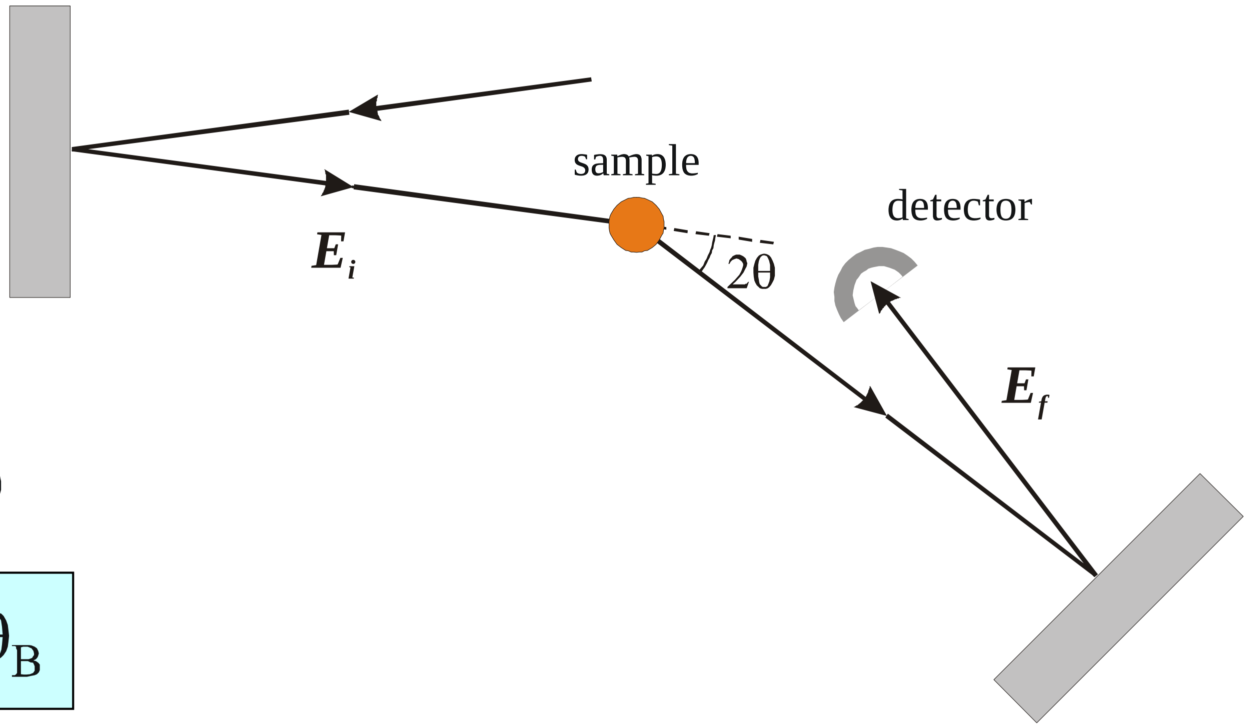
72 analysers
ΔE: 0.4 – 1.5 eV

6x1 Maxipix Detectors
55 μm pixel size

Instrumentation for IXS - VI

IXS set-up on ID28 at ESRF

Monochromator:
Si(n,n,n), $\theta_B = 89.98^o$
n=7-13
λ_1 **tunable**



$$Q = 4\pi/\lambda \cdot \sin(\theta)$$

$$\lambda = 2 \cdot d(T)\ \sin\theta_B$$

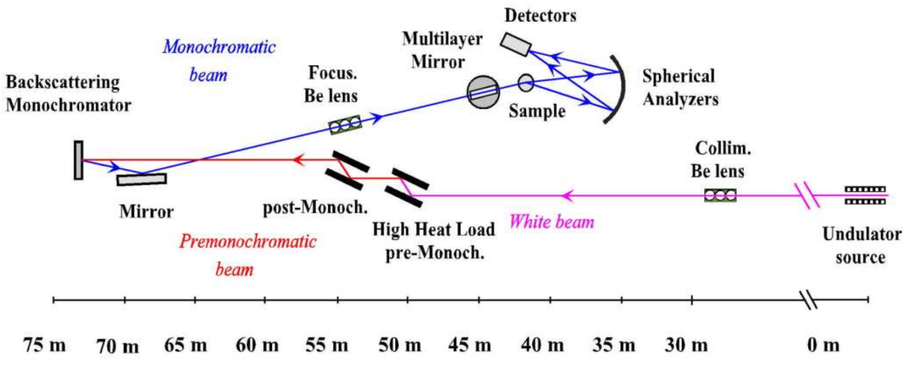
$$\Delta d/d = \Delta E\ /E = -\alpha(T) \cdot \Delta T$$

$\alpha = 2.58 \cdot 10^{-6}$ 1/K at room temperature

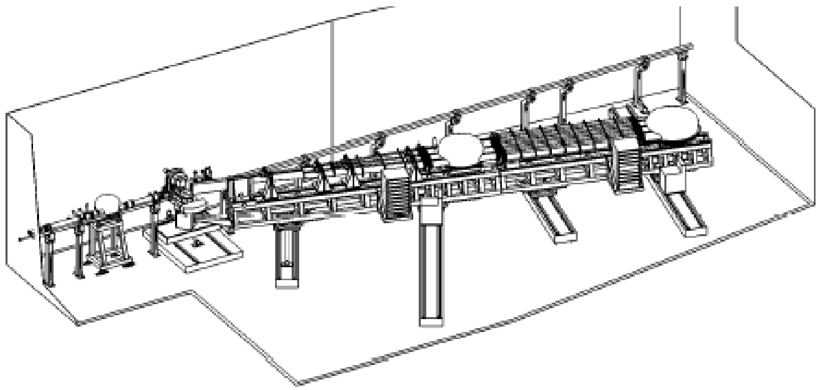
Analyser:
Si(n,n,n), $\theta_B = 89.98^o$
n=7-13
λ_2 **constant**

Instrumentation for IXS - VII

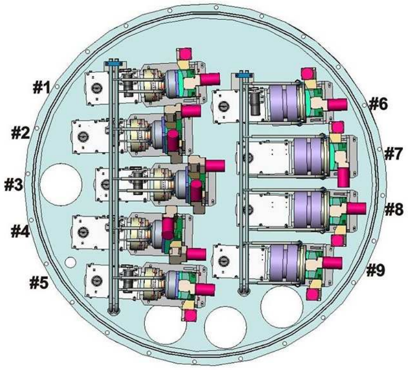
ID28 @ ESRF



9- analyser crystal spectrometer



Reflection	E_{inc} [keV]	ΔE [meV]	Q range [nm^{-1}]
(8 8 8)	15.816	6	2 - 73
(9 9 9)	17.794	3.0	1.5 - 82
(12 12 12)	23.725	1.3	0.7 - 100



Spot size on sample: 270 x 60 μm^2 -> 14 x 8 μm^2 (H x V, FWHM)

Further reading

- W. Schülke; *Electron dynamics by inelastic x-ray scattering*, Oxford University Press (2007)

- J.P. Rueff and A. Shukla; Rev. Mod. Physics 82, 847 (2010) *Inelastic x-ray scattering by electronic excitations under high pressure*

- L.J.P. Ament et al.; Rev. Mod. Physics 83, 705 (2011) *Resonant inelastic x-ray scattering studies of elementary excitations*

- M. Krisch and F. Sette; *Inelastic x-ray scattering from Phonons*, in Light Scattering in Solids, Novel Materials and Techniques, Topics in Applied Physics 108, Springer-Verlag (2007).

- A. Bosak, I. Fischer, and M. Krisch, in *Thermodynamic Properties of Solids. Experiment and Modeling,* Eds. S.L. Chaplot, R. Mittal, N. Choudhury. Wiley-VCH Weinheim, Germany (2010) 342 p. ISBN: 978-3-527-40812-2