Overview of Advanced Materials and Surface activities at ILL

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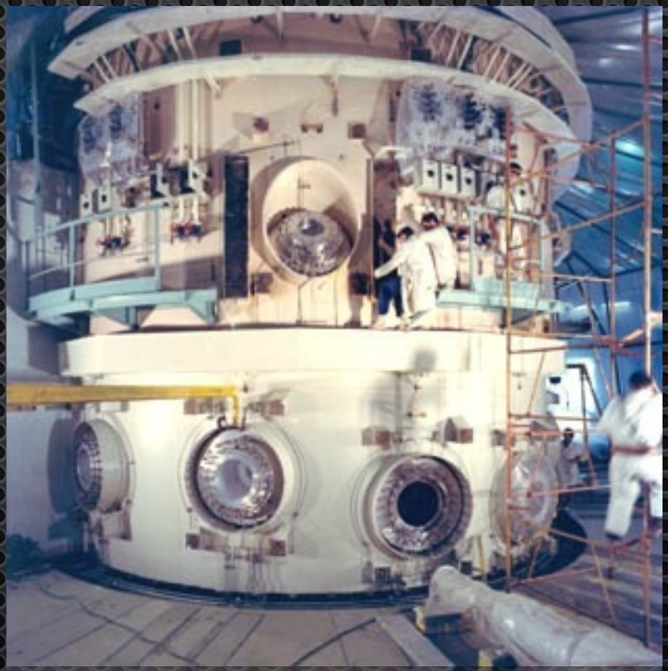
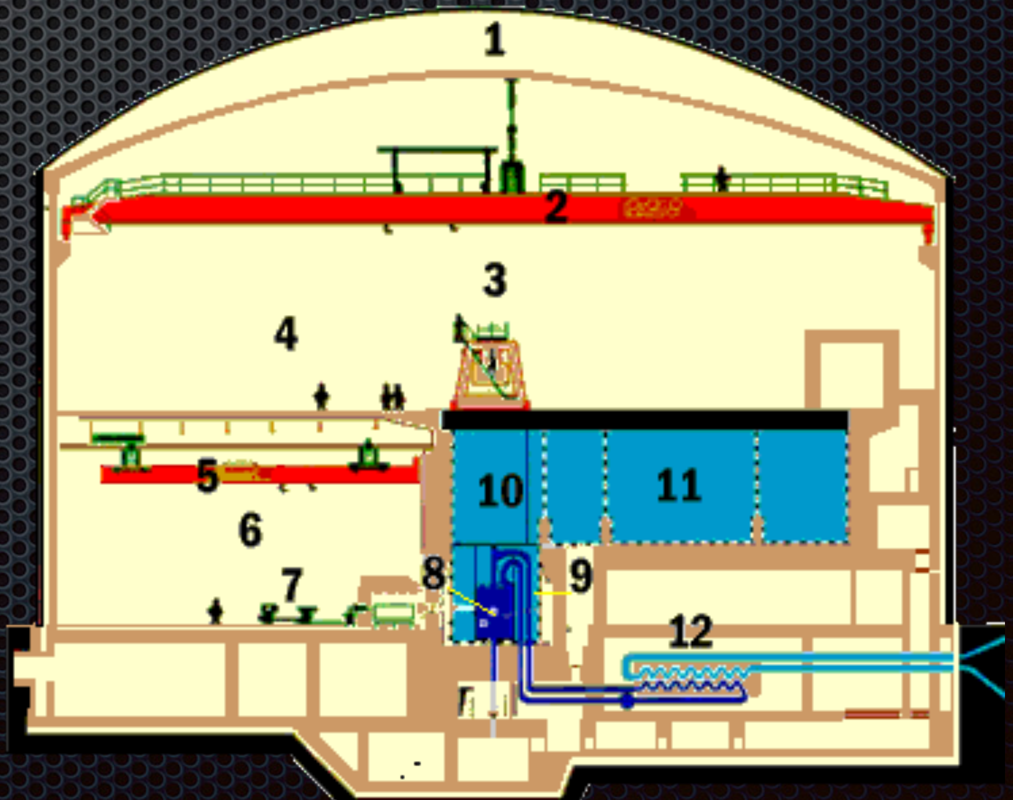
NEUTRONS FOR SCIENCE

EIROforum
Science-Business WAMAS
Workshop on Advanced Materials and Surfaces

The HFR at the ILL

- World leading (continuous) thermal neutron source, still after 40 years
- More powerful reactor source hardly possible
  - Power density just below technological limit
  - Heat evacuation / produced neutron: fission > spallation





We provide …

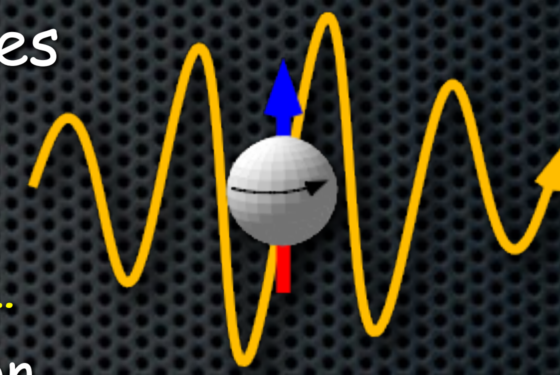
- Neutrons: epithermal, hot, thermal, cold and ultra-cold
  - Neutron scattering instruments → condensed matter research
    - Diffraction & spectroscopy, Nuclear & magnetic structures
- Proposal procedure (free of charge)
  - Selection by external committee 2x /year on scientific merit
  - Results published, possible collaboration with local contact
- Commercial access for industrial users: ***industry@ill.eu***
  - Fast access, intellectual property respected, confidentiality
  - Optional expertise

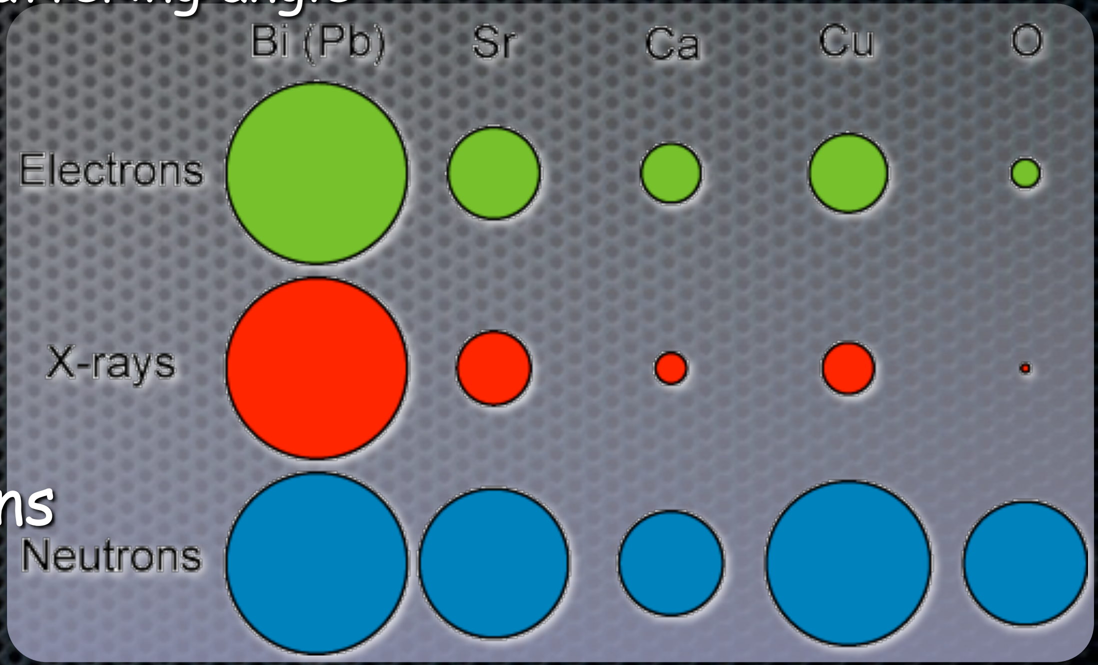
Why neutrons?

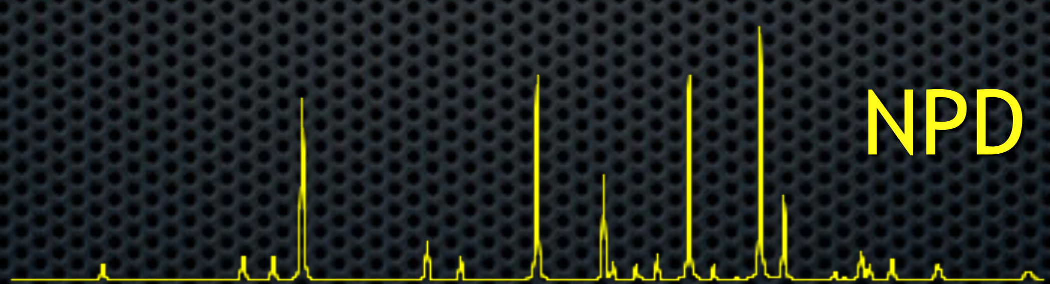
- Neutrons
  - Low intensity
    - ILL is for neutrons what a 6V bicycle lamp is for photons
  - Expensive sources (reactors, spallation sources)
    - One hour of beam time approaches 1000 €!
      - Don't tell this the poor student performing his experiment - making mistakes ...
  - Difficult access (no laboratory facilities)
- X-ray or electron scattering
  - Probe condensed matter
  - Wavelengths fit structure
  - Available at laboratory level
- We need really good reasons
  - ... and the properties of the neutron will give them all ...

Neutron properties: zero charge

- Neutron → highly effective probe of condensed matter
  - only interaction: short-ranged nuclear and magnetic exchanges
    - Interaction probability small
      - **penetrates into bulk of larger samples of condensed matter**
      - **penetrates containers, shielding of furnaces, fridges, pressure cells ...**
    - Weak probe: direct & quantitative link to theory model & simulation
  - Nuclear scattering at nucleus
    - Constant scattering length: Intensity at high scattering angle
    - Arbitrarily changing with Z
      - Light atoms beside heavy ones (H-O, Li-Mn, O-U)
      - Discriminating neighbors (O-N)
    - Arbitrarily changing with A: Isotopic exchange
  - Serious drawbacks:
    - difficult to guide, focus, or detect neutrons

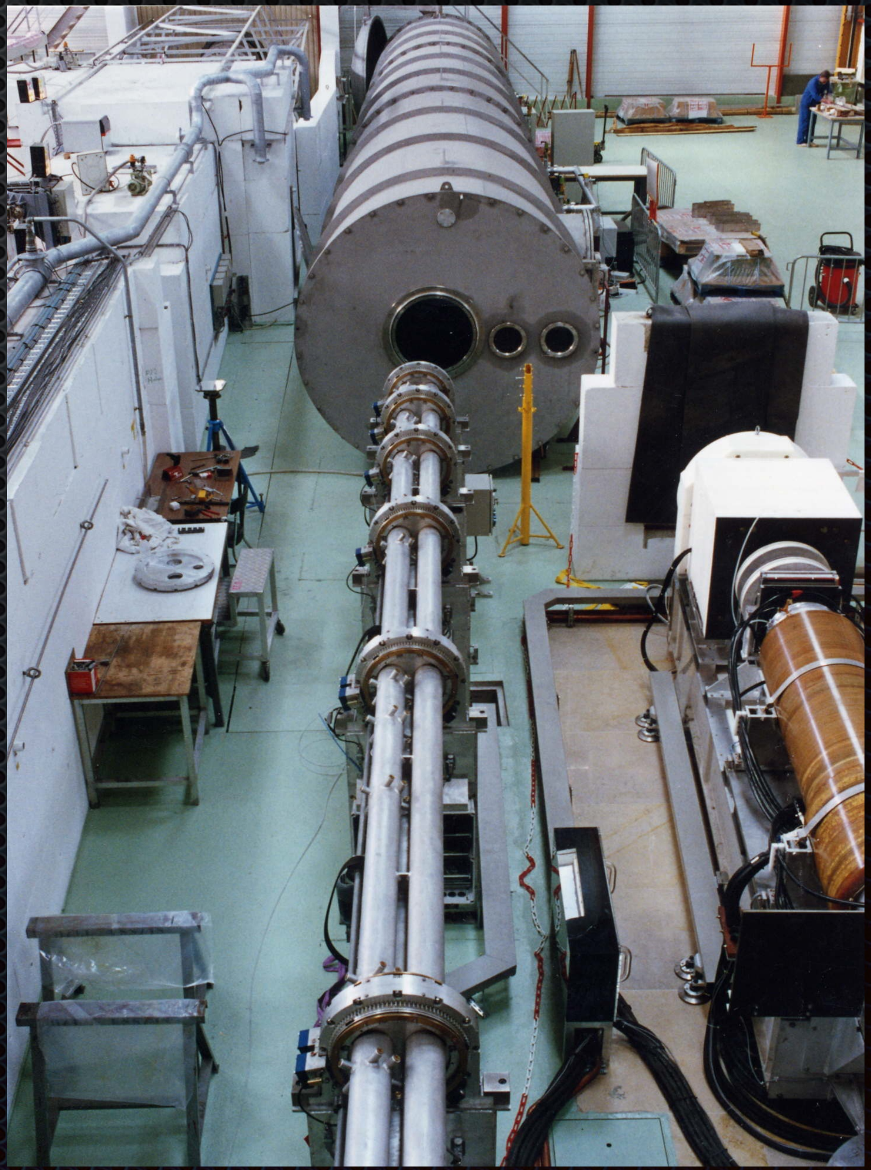






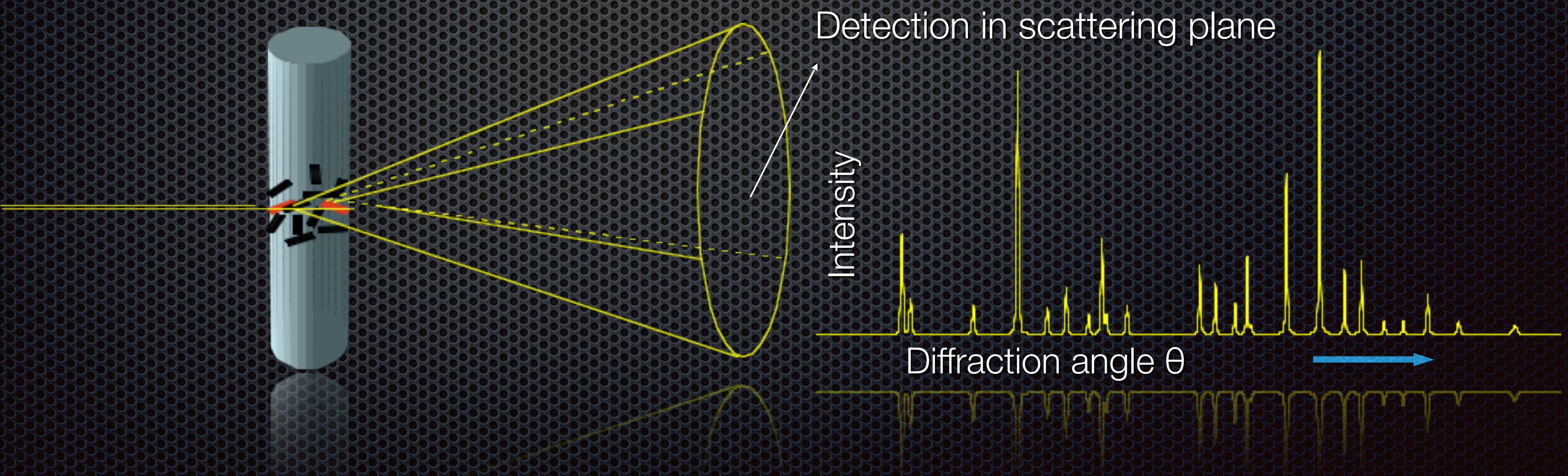
Diffractometers

- Single crystal diffractometers
    - 4-circle diffractometers (D19, D9, D10, D23)
    - Laue diffractometers (Vivaldi, Ladi, OrientExpress, Cyclops)
- Two-axis diffractometers
    - Strain-imager (SALSA at ILL)
    - High resolution powder diffractometers (HRPD: D2b)
    - Liquids and amorphous diffractometers (high-Q: D4)
    - High intensity powder diffractometers (HIPD: D1B, D20)
- Small angle neutron scattering (SANS: D11, D22, D33)
- Reflectometers (Figaro, D17)



Two-axis ("powder") diffractometers

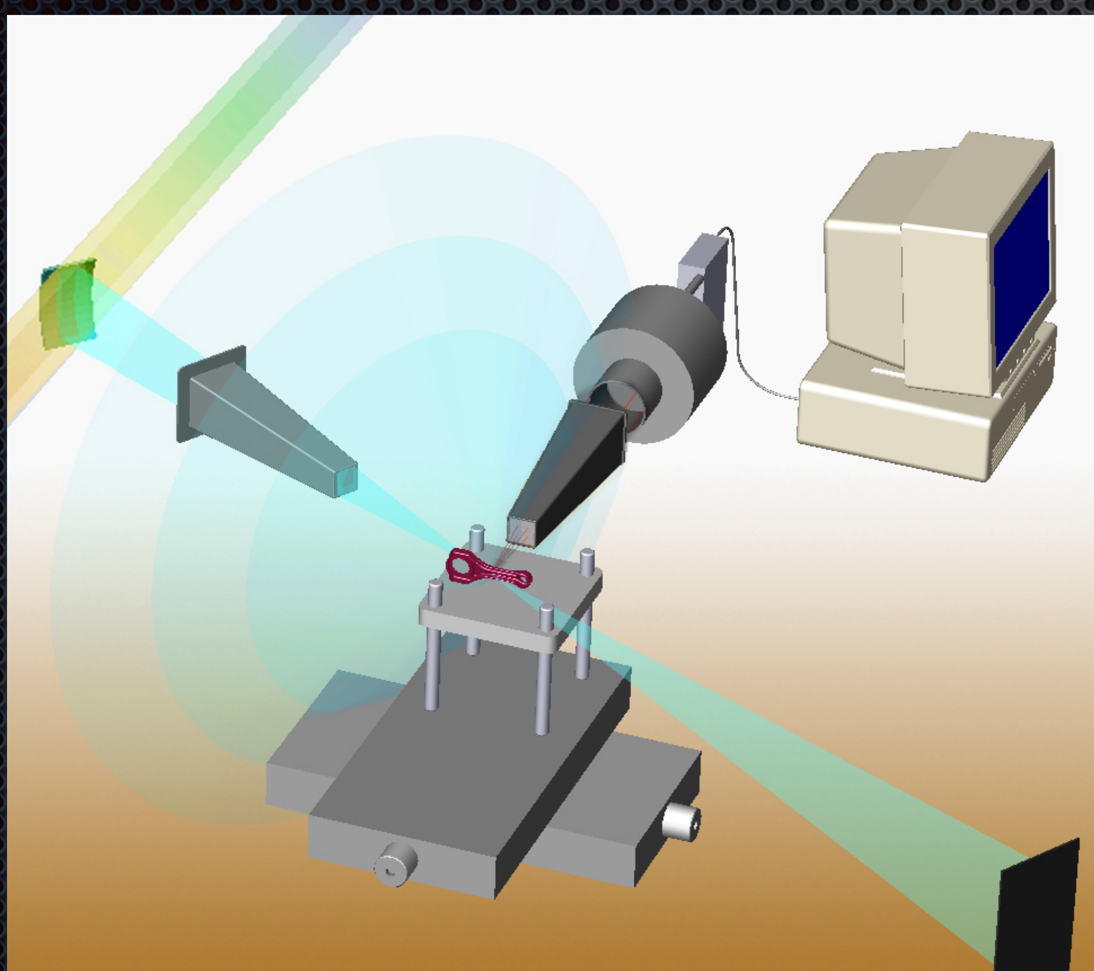
- Intermediate Q range from 1 to 10 Å–1
  - Powder samples for structural refinement
  - Needs adequate resolution:
    - Peaks closely spaced at higher the Q vector and for large unit cells
    - Resolution effectively determines size of refinable unit cell
    - Angular width of Bragg peak ($n\lambda = 2d \sin\theta$):
      - known function of collimations and monochromator mosaic

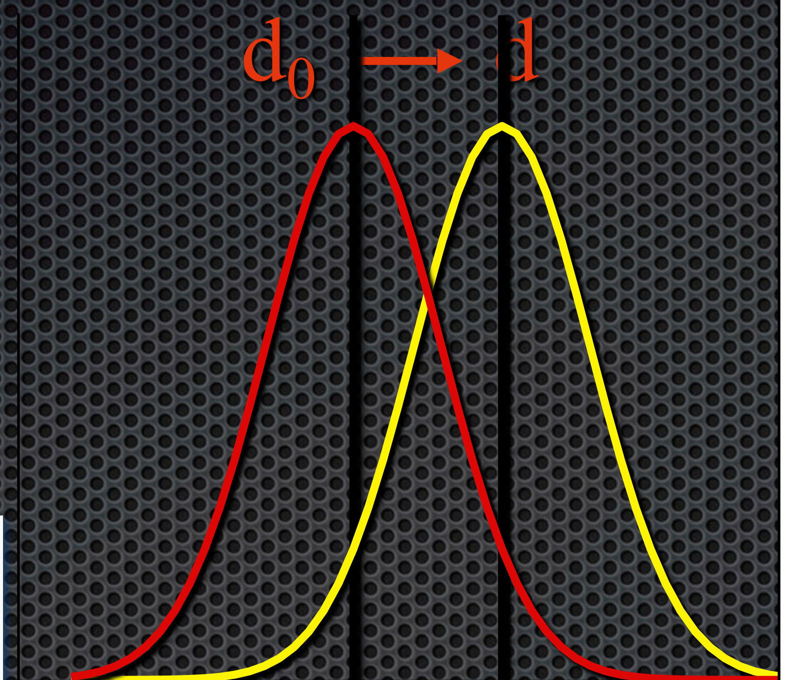


Neutron strain imaging

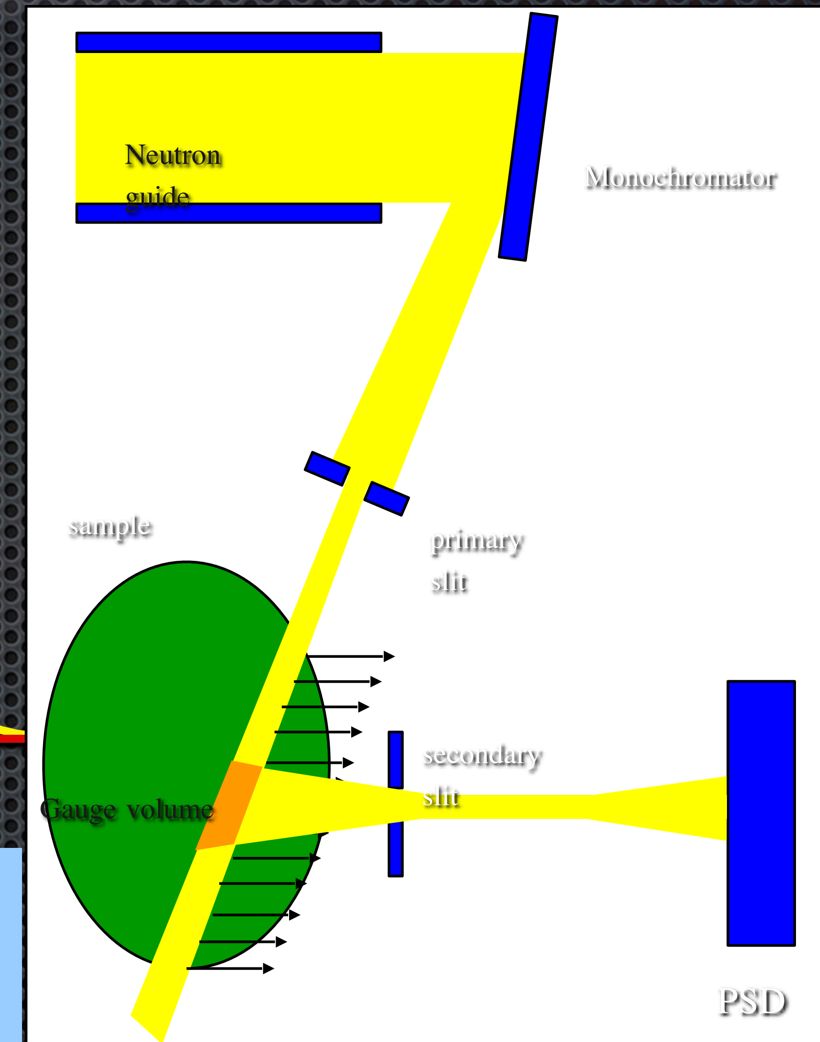
Diffraction from a (small)
- gauge - volume =>

- $n\lambda = 2d \sin\theta$





strain $\varepsilon = \frac{d - d_0}{d_0}$



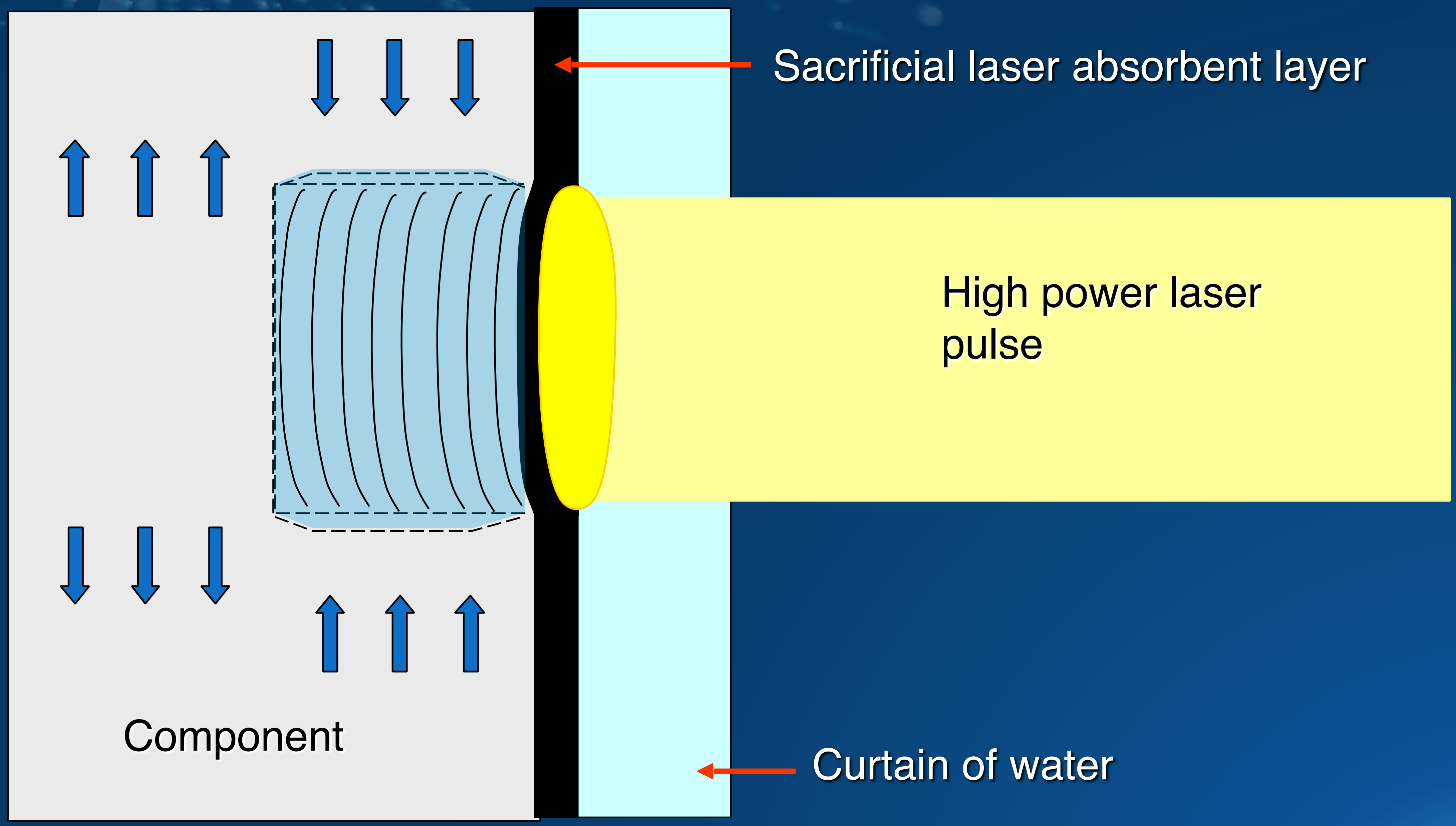
Principal axes known:
3 measurements, Hooke's law

$$\sigma_x = \frac{E(1-\nu)}{(1-2\nu)(1+\nu)}\varepsilon_x + \frac{E\nu}{(1-2\nu)(1+\nu)}(\varepsilon_y + \varepsilon_z)$$

SALSA – Stress Analyzer for Large scaled engineering Applications

Thilo Pirling

Laser Shock Peening(LSP)

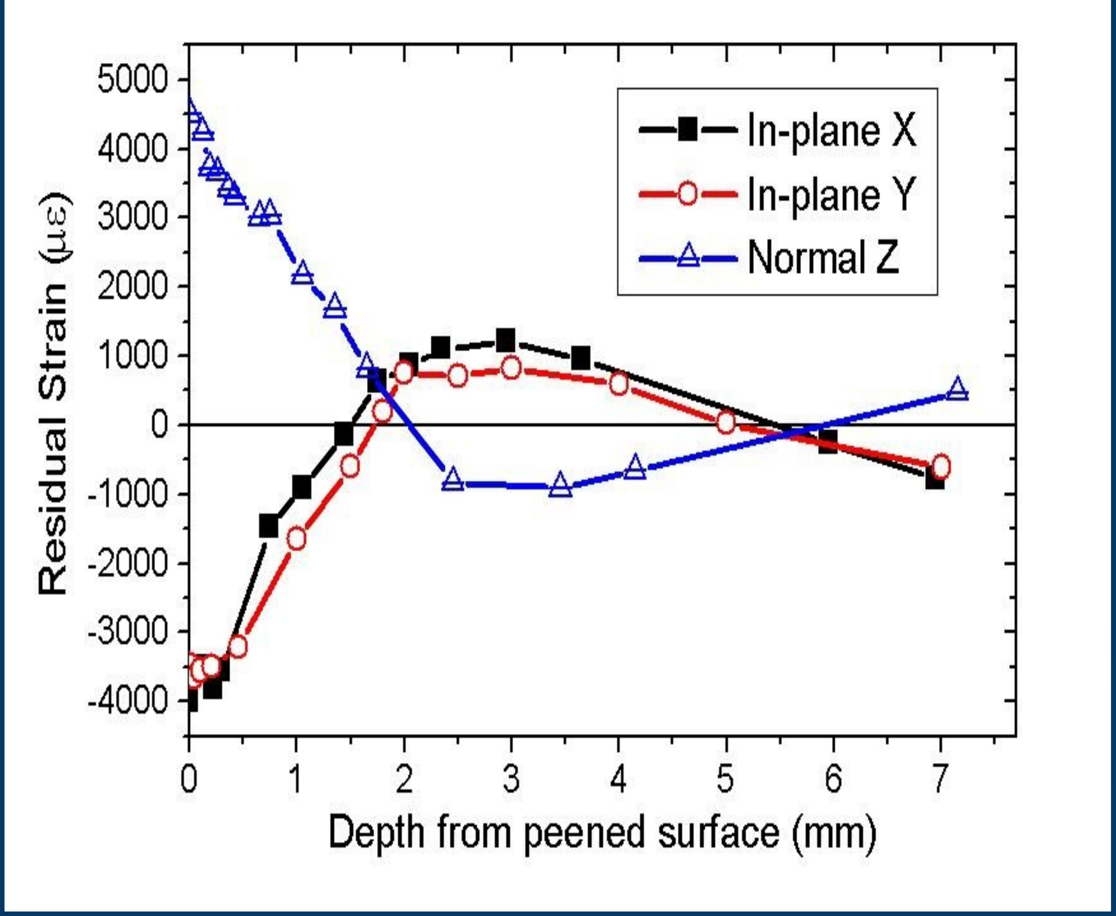


Aerospace materials : Ti-6Al-4V (aero-engine), Al 2024 (aero-structure) and Al/SiC/20p Metal Matrix Composite (next generation)

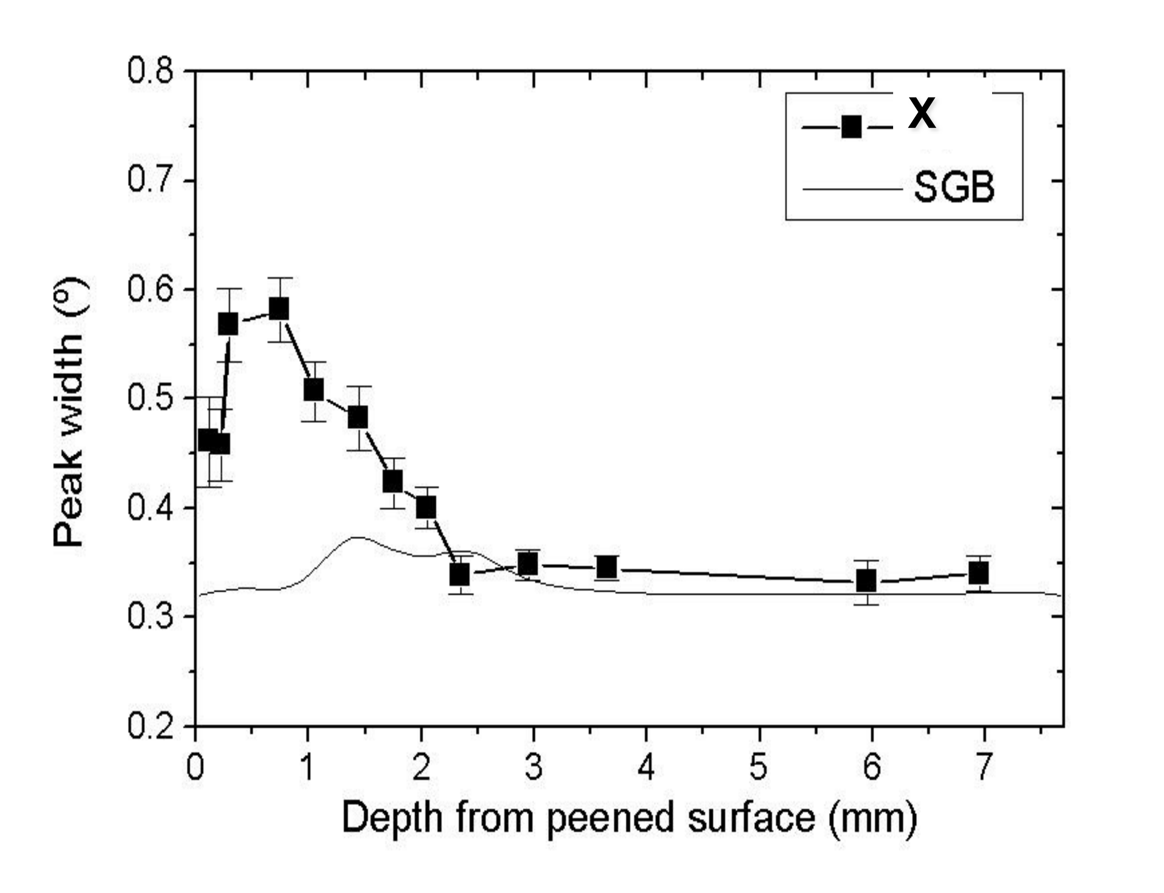
courtesy A. Evans

Laser Shock Peened Ti-6Al-4V

Triaxial strain profiles



Plastic deformation of the surface region leads to broadening of diffraction peak width



Collab. Alexander Evans

Conclusion

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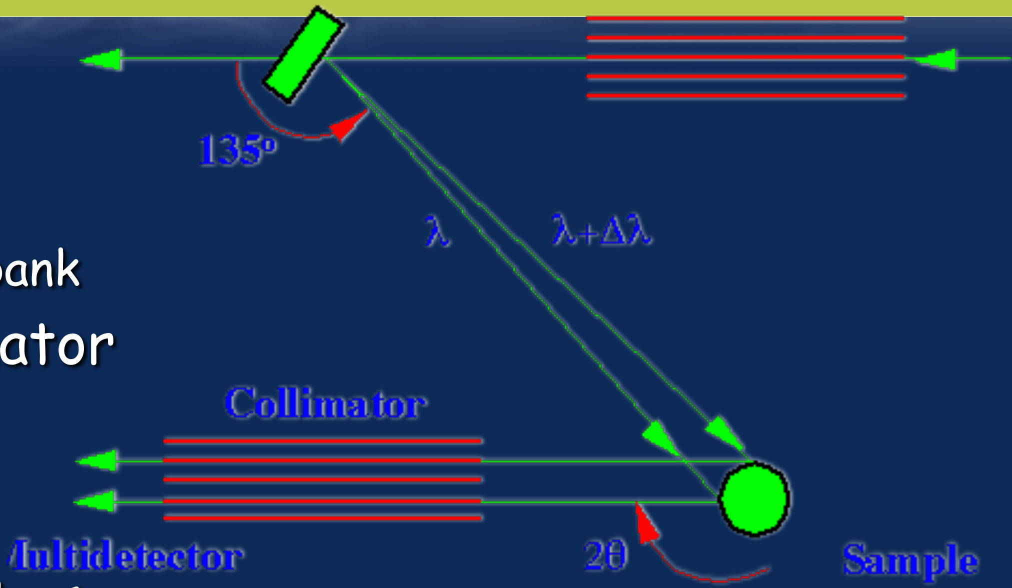
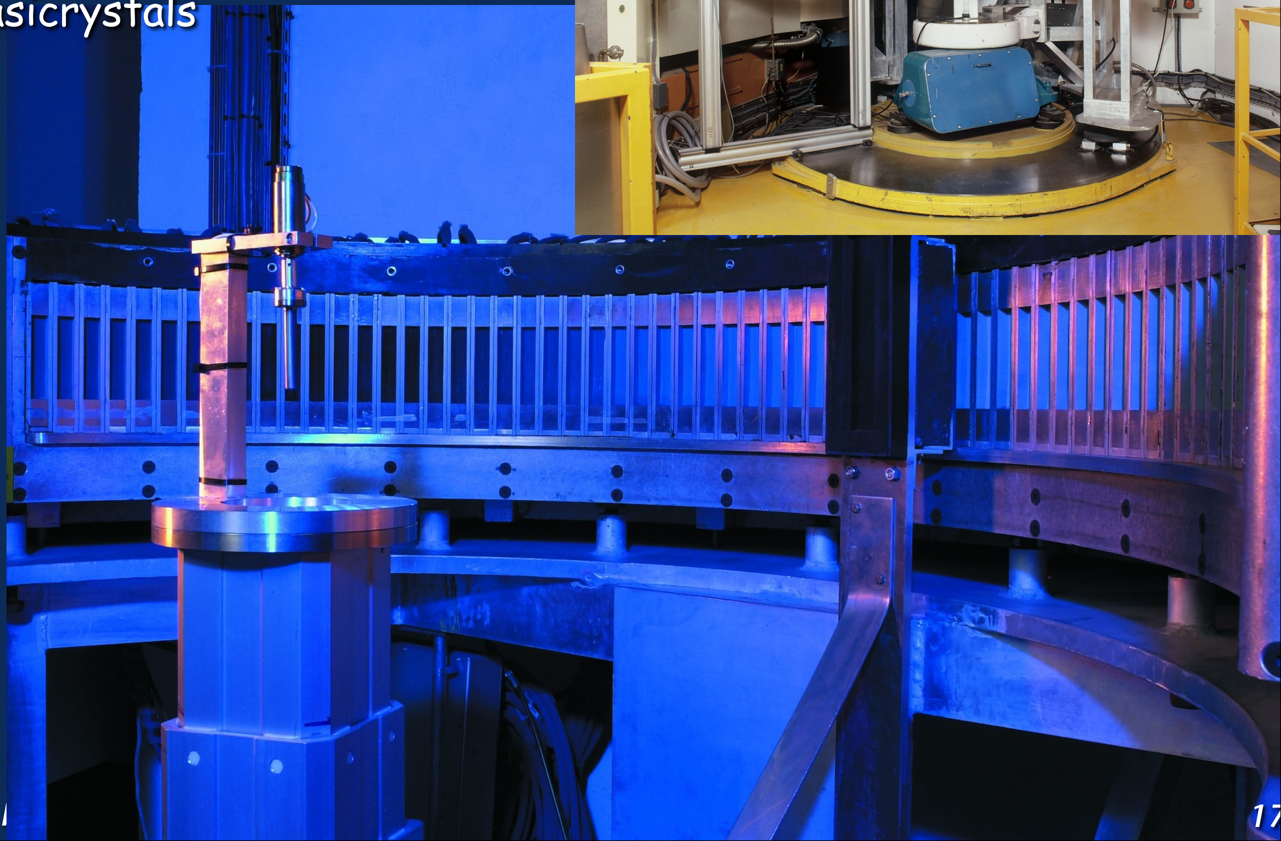
- neutron strain imaging applicable for broad range of samples & applications
  - Neutron strain imaging allows reliable non-destructive stress tensor determination in bulky and complex shaped samples from the surface through the bulk
  - Well defined beam definition and analytical model of experimental set-up enables:
    - near surface and interface stress determination (~30 - 50µm) even at curved surfaces
    - Measurements in coatings (>0.5 mm)
- Instrument SALSA at ILL
  - manipulates samples up to 500 kg weight and between 1 cm and 1.4 m length
  - Most flexible sample movements due to hexapod as sample stage
  - as well very precise positioning (20 - 50 mm)

High resolution 2 axis diffractometers

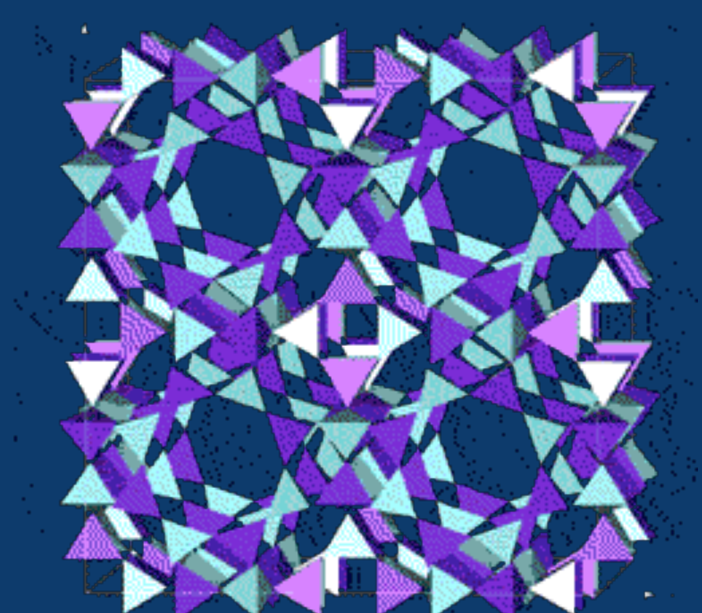
- Common features (D2B at ILL):
  - high take-off angle from the monochromator
  - set of Soller collimators in front of scanning multidetector bank
- D2B: Very high take-off angle (135°) for monochromator
  - Ge monochromator with large mosaic spread of 20′
    - compensate for the corresponding intensity ($\Delta\lambda/\lambda$) loss
  - 300 mm high, focusing vertically onto about 50 mm
  - 200, now 600 mm high multidetector bank and Soller collimators
    - match this large incident vertical divergence
    - diffraction pattern : 50, now 25 steps of 0.05° in 2θ
    - 64, now 128 detectors spaced at 2.5° , now 1.25°
    - Scans take typically 30 minutes and repeated to improve statistics
  - Rietveld structure refinement of polycrystalline powder patterns
    - zeolites with absorbed molecules, superconductors, quasicrystals
  - Magnetism: high resolution at large d-spacings
    - higher wavelengths of 2.4 Å and 6 Å

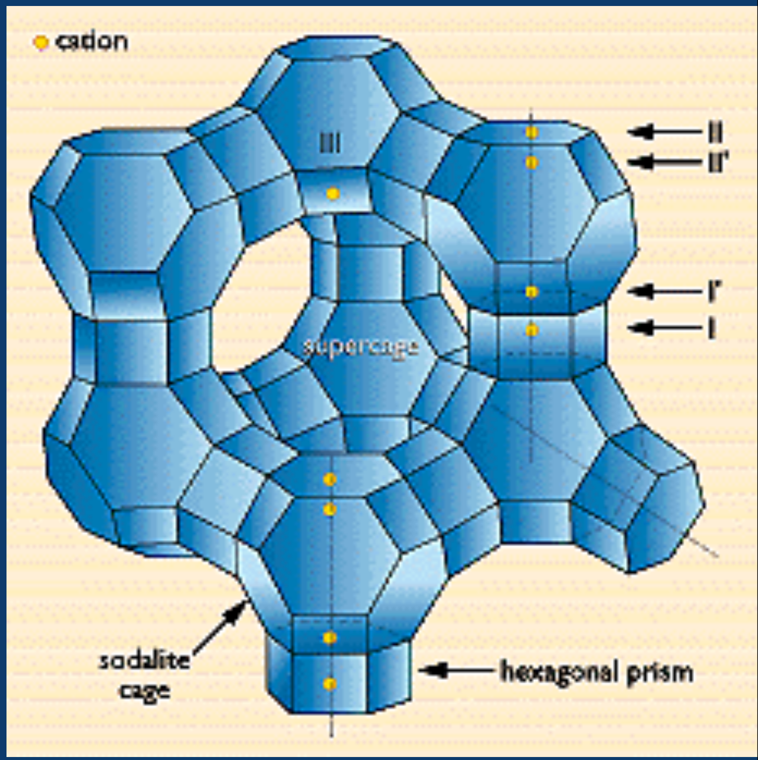




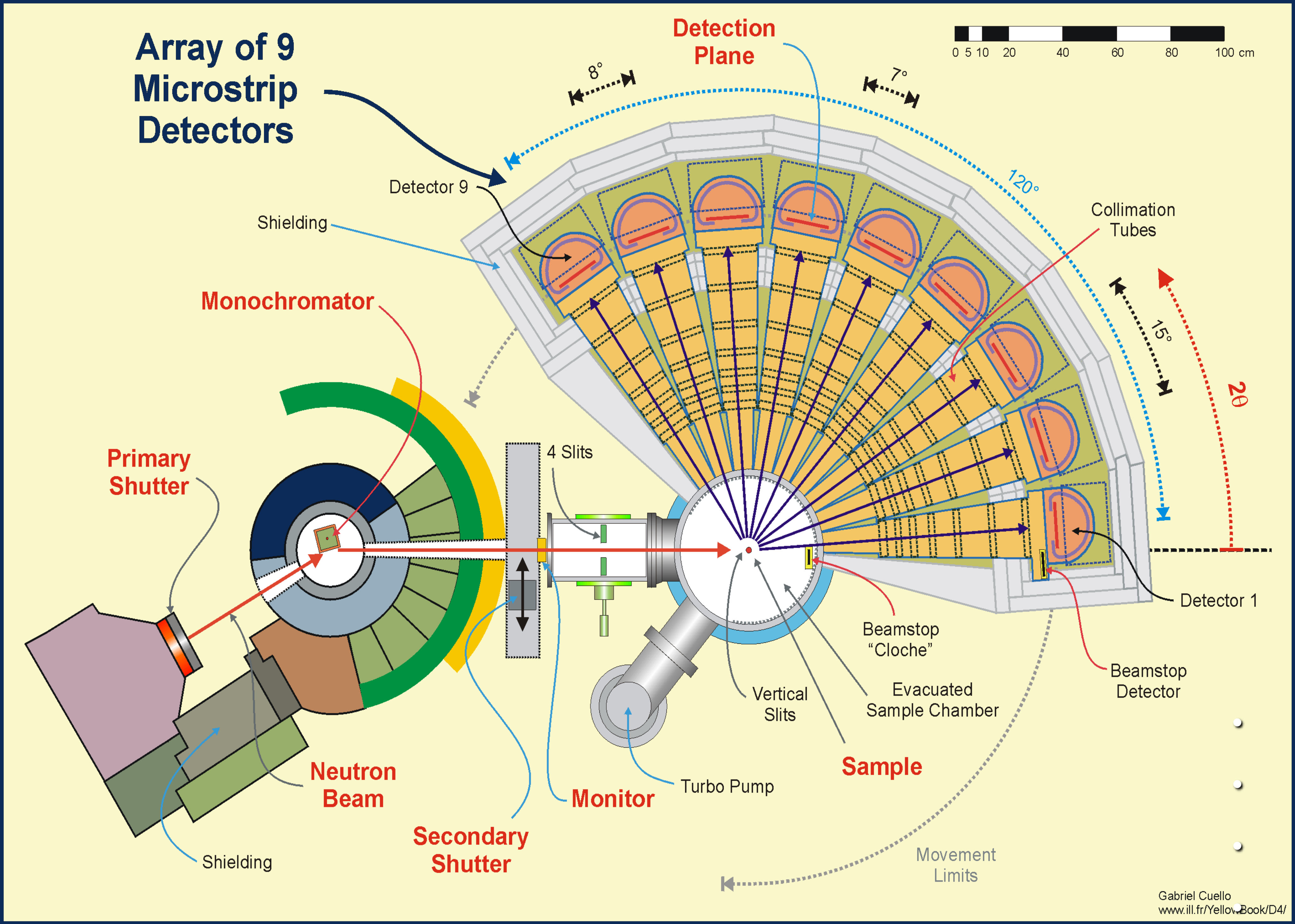
Zeolites

- Aluminosilicates or related materials
  - complex cage and channel structure
  - absorb different ions and molecules selectively
  - important role in industry as catalysts or complex builder
  - many skeleton structures determined by X-ray diffraction (XRD)
  - but oxygen and hydrogen positions by neutron powder diffraction
    - especially inside the cavities
  - requiring high resolution due to large unit cells





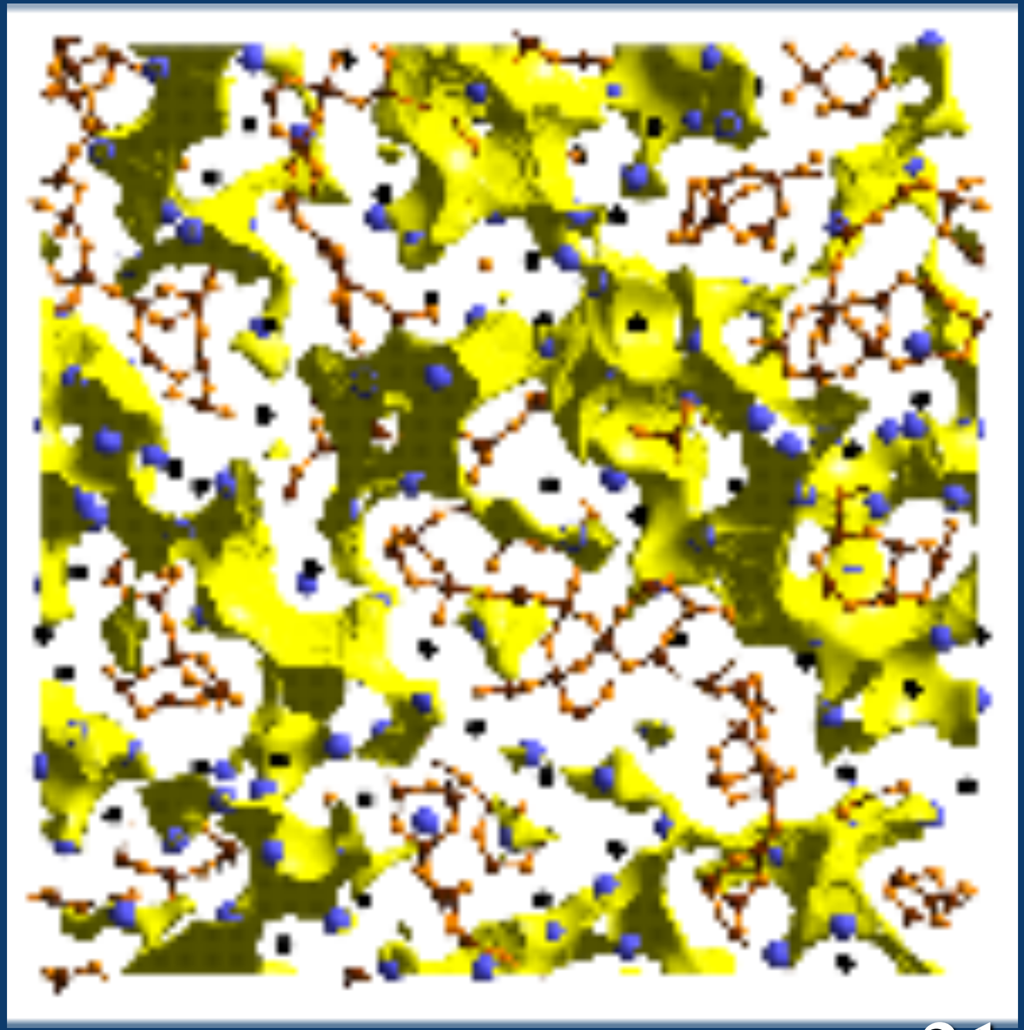
Liquids diffractometer D4C



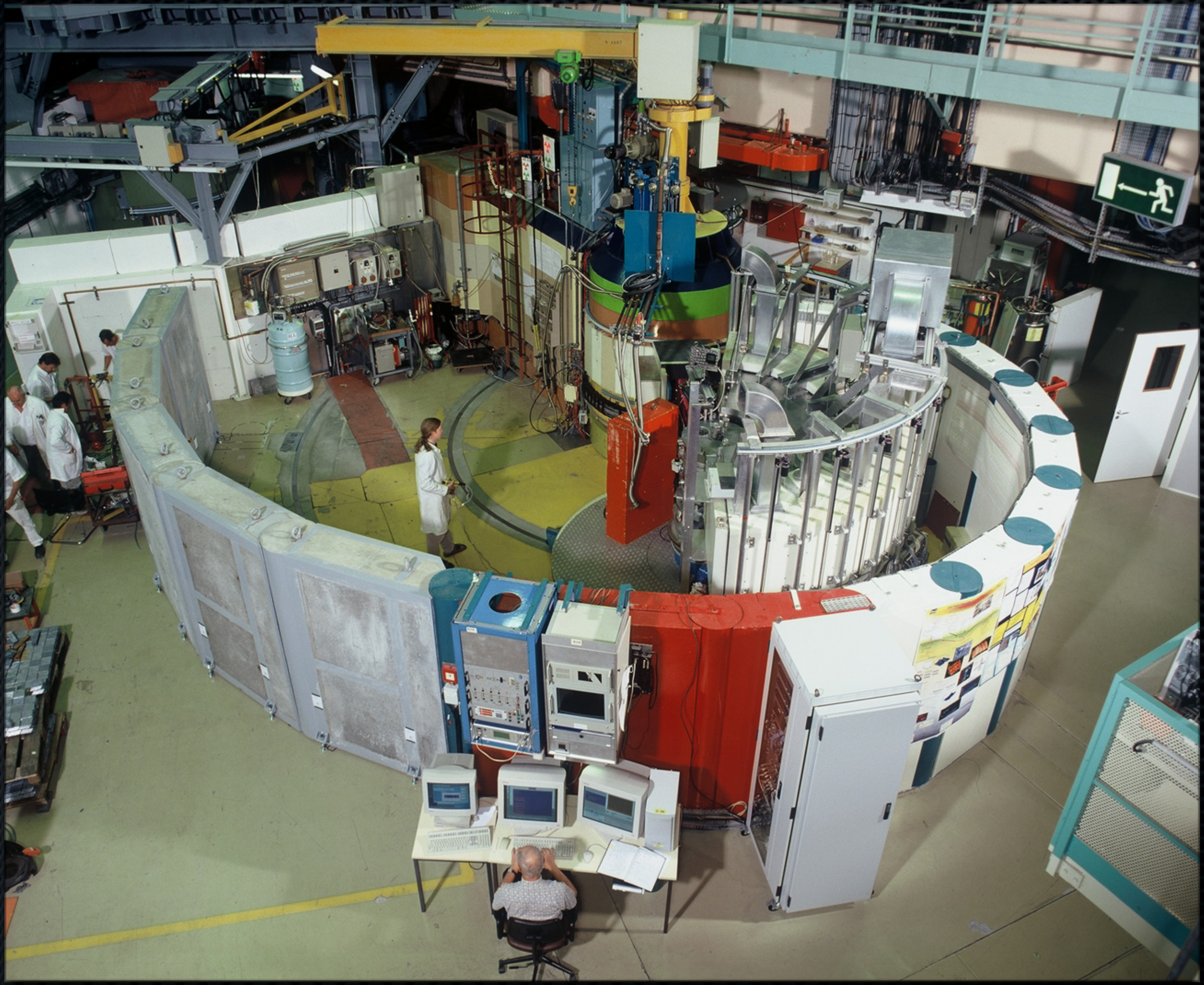
- Large Q-range
- High stability
- High flux
- Very low background
- Simple corrections

Glasses

- Neutrons: high absolute accuracy for determination of glass structure factors
  - e.g., for the ion conducting glass $(AgI)_x(AgPO3)_{1-x}$,
    - having potential applications in microbatteries.
    - silver ion pathways in the glass matrix modelled from neutron data.

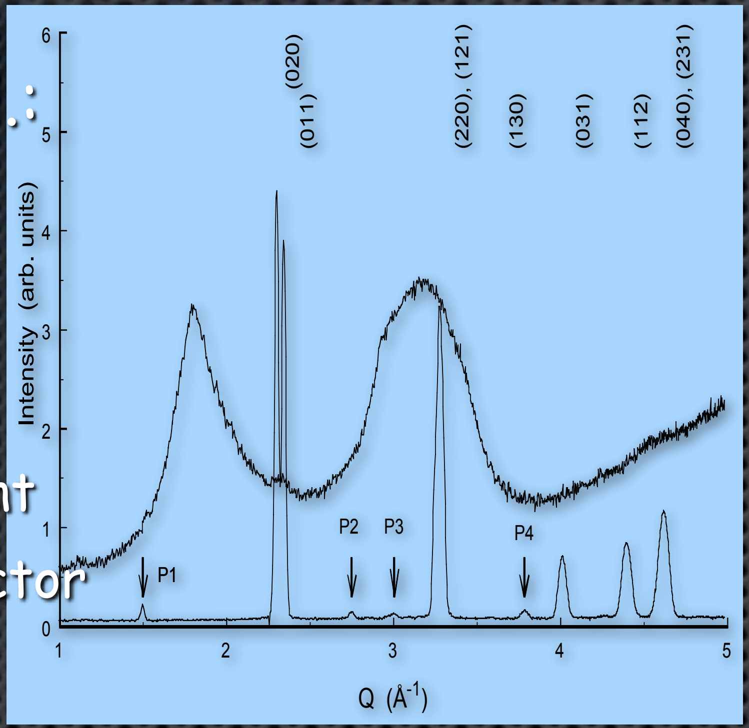


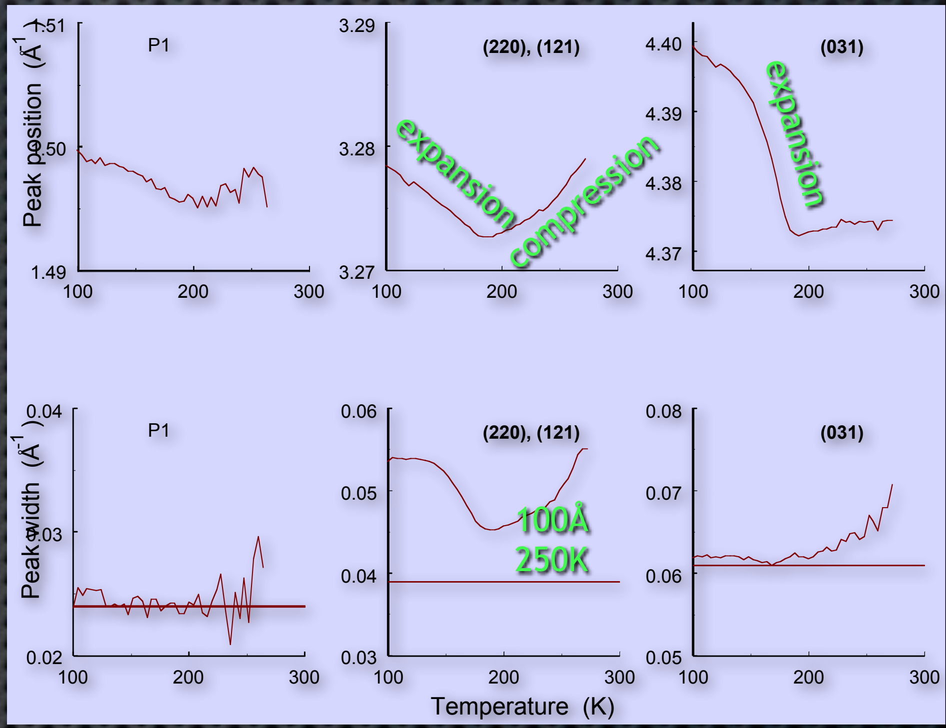
High intensity powder diffractometer D20

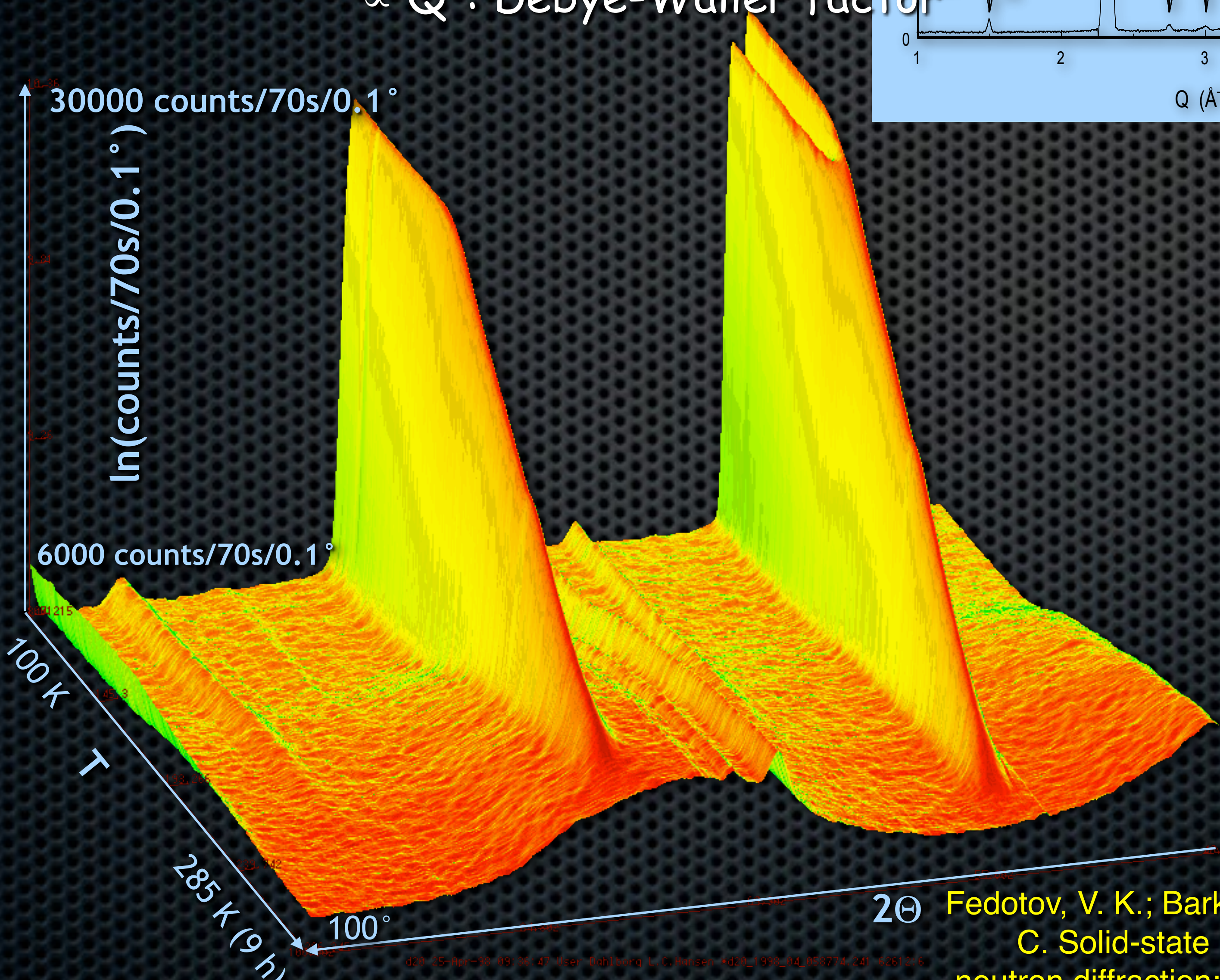


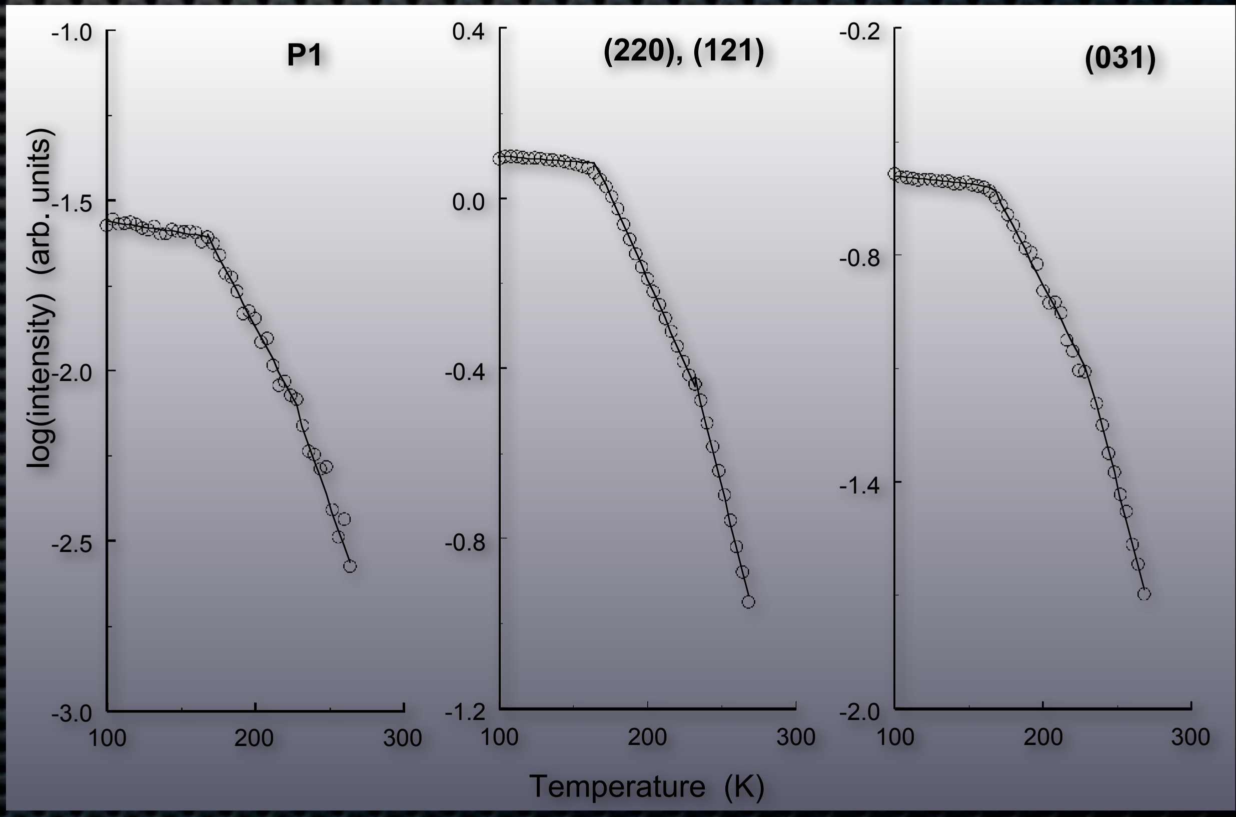
Amorphisation of GaSb

- Dahlborg, Fedotov et al.:
  - 2 crystalline phases
  - 3 decay stages
  - Fit to e^{-CT} with C …
    - Constant: decay constant
    - $\propto Q^2$: Debye-Waller factor





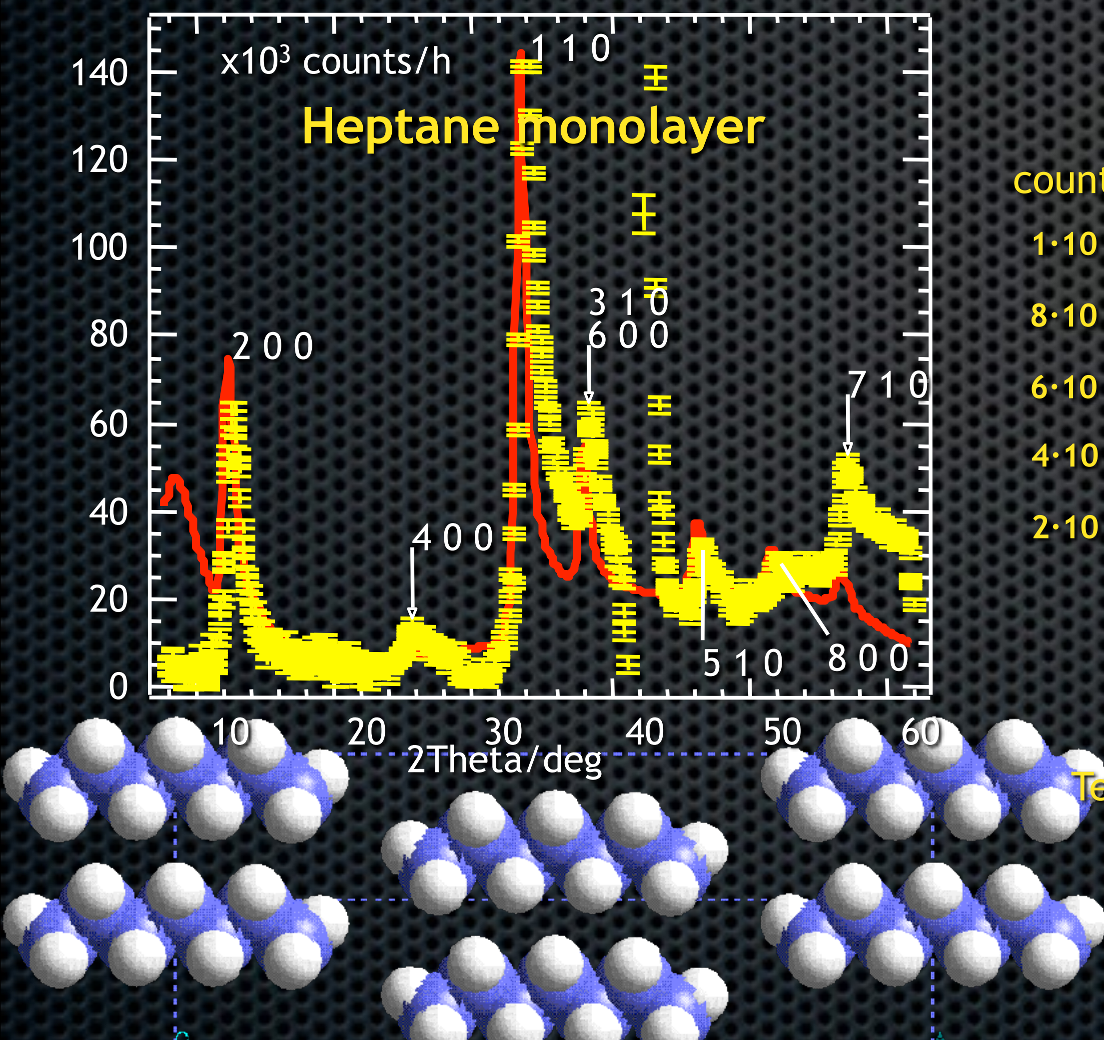


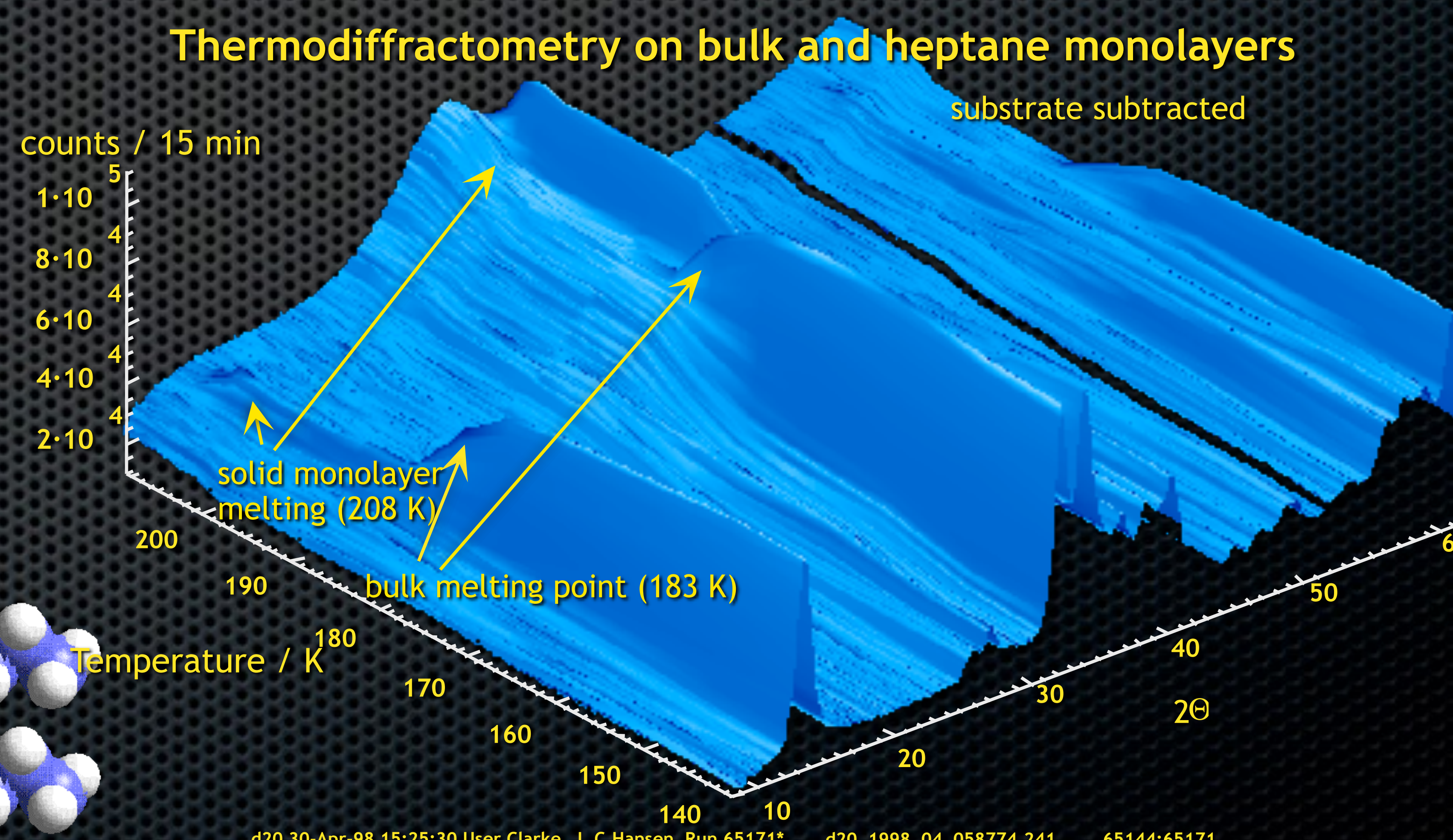


Fedotov, V. K.; Barkalov, O. I.; Ponyatovsky, E. G.; Calvo-Dahlborg, M.; Dahlborg, U.; Hansen, T. C. Solid-state amorphization of a quenched high-pressure GaSb phase studied by real-time neutron diffraction: evolution of the crystalline phase. *J Phys Condens Matter* **2009**, *21*, 045402.

Physisorption: alkanes

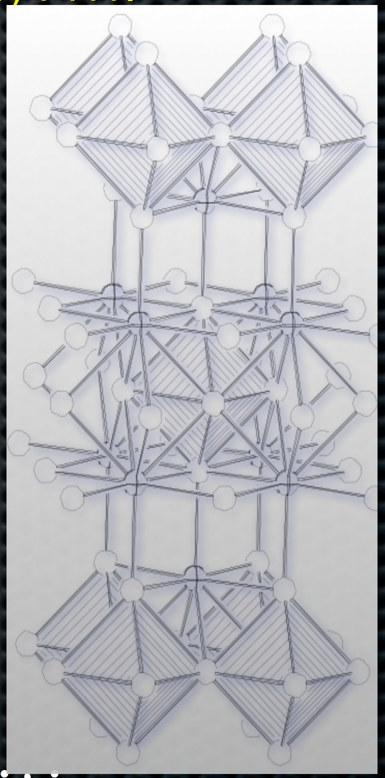
- Clarke et al.: Solid alkane mono-layers on graphite
  - 2D structure & phase transition bulk to mono-layers
  - Huge graphite background contribution to be subtracted (differential method)
  - High detector stability (10^{-4}) and intensity needed (D20)



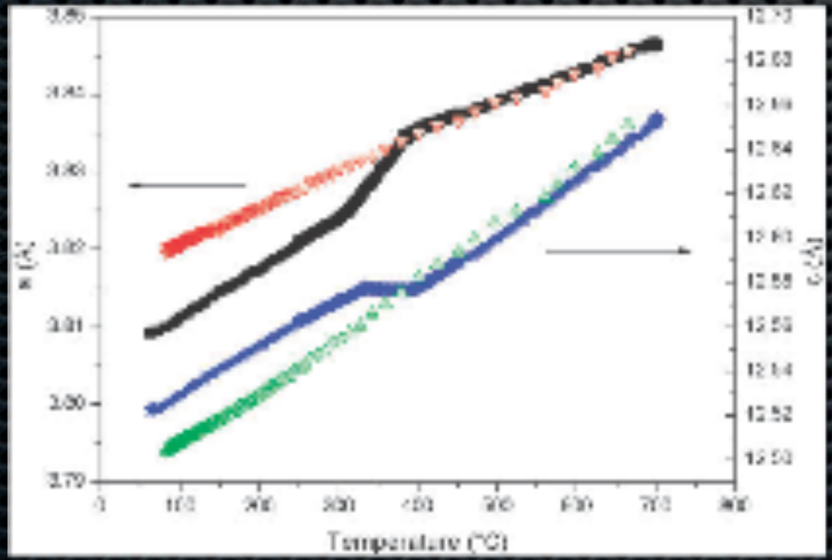


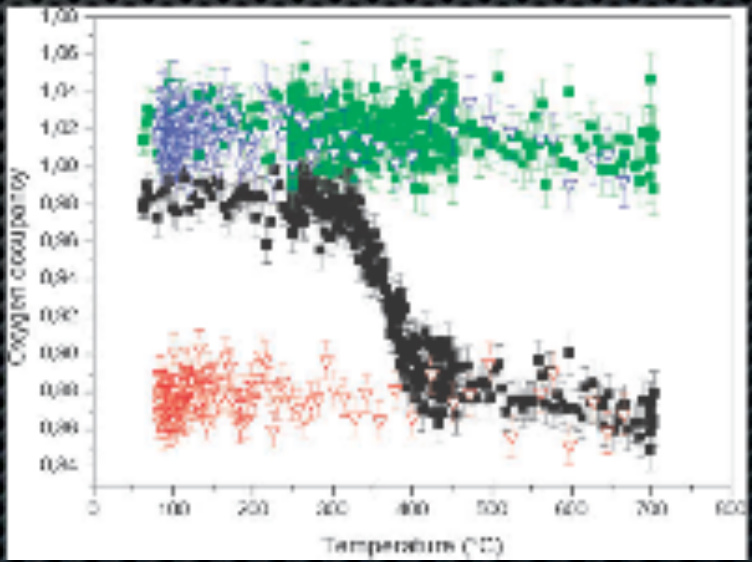
High-T solid-H_2 and -O_2 reactions

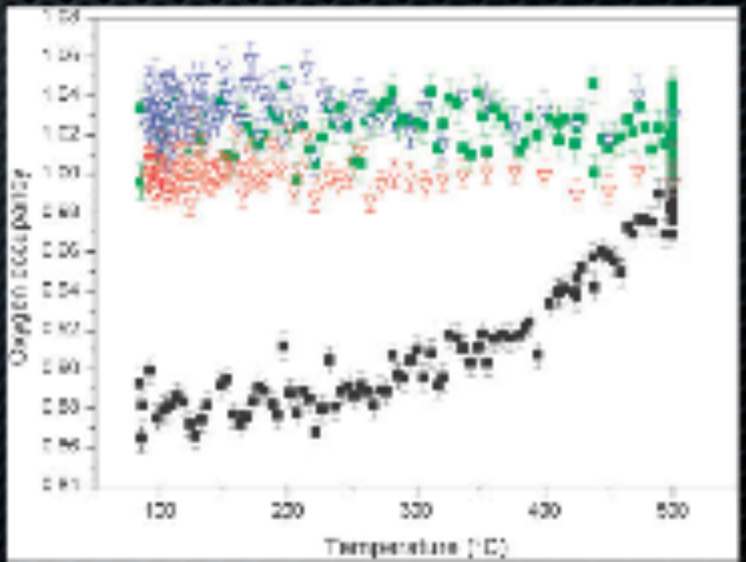
- F. Tonus, M. Bahout, P.F. Henry, S.E. Dutton, T. Roisnel, P.D. Battle, *Chem Commun* (2009) 2556.
- F. Tonus, M. Bahout, P.D. Battle, T. Hansen, P.F. Henry, T. Roisnel, *J Mater Chem* **20** (2010) 4103.
- F. Tonus, C. Greaves, H. El Shinawi, T. Hansen, O. Hernandez, P.D. Battle, M. Bahout, *J Mater Chem* **21** (2011) 7111.



- Ruddlesen-Popper oxides $A_{1+n}BO_{3+n\pm\delta}$
  - high temperature oxide ion conducting devices
    - oxygen separating membranes
    - sensors
    - solid-oxide fuel cells SOFCs
  - accommodation of excess oxygen and oxygen vacancies
- n = 1: $Pr_2Sr_2CrNiO_8$
  - axial (Pr/SrO_2 layers) & equatorial (Cr/NiO_2 layers) oxygen positions
  - thermal evolution in reducing (H_2 flow) and oxidizing conditions (O_2)

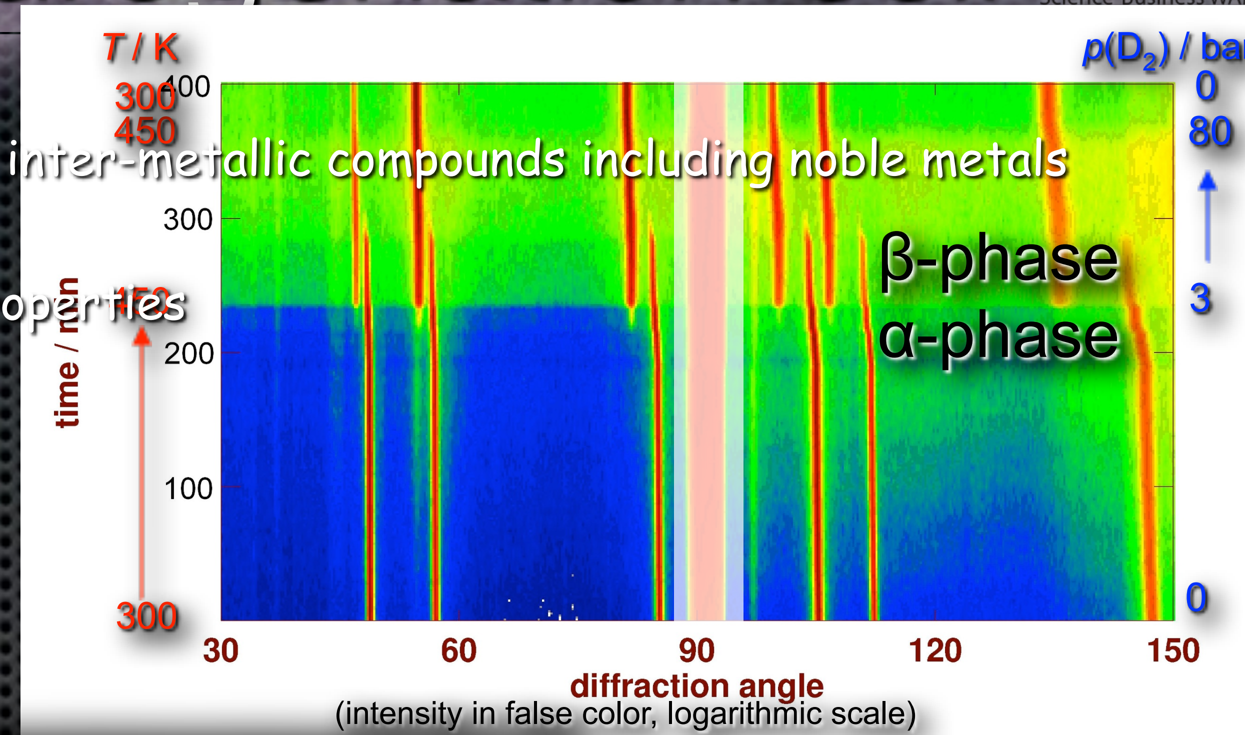


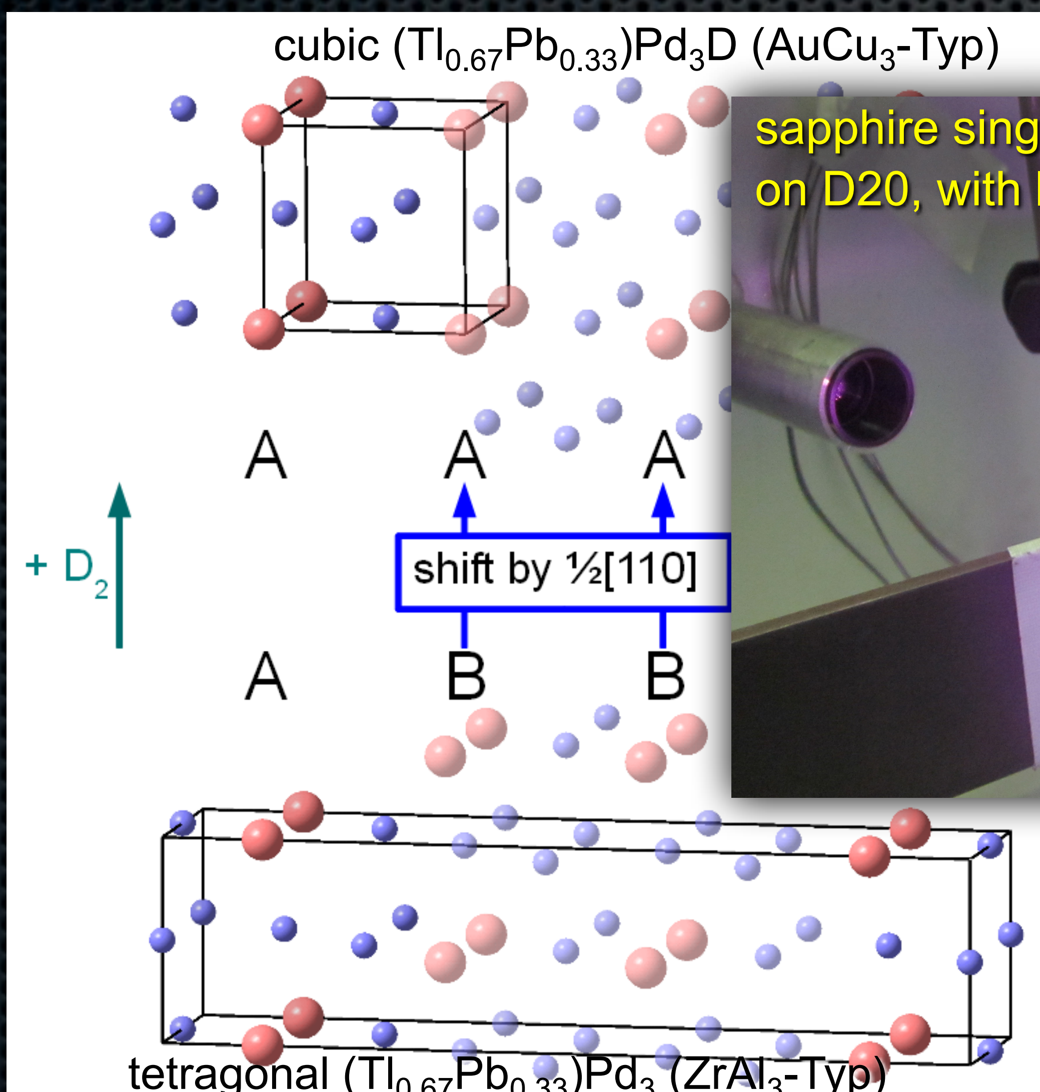


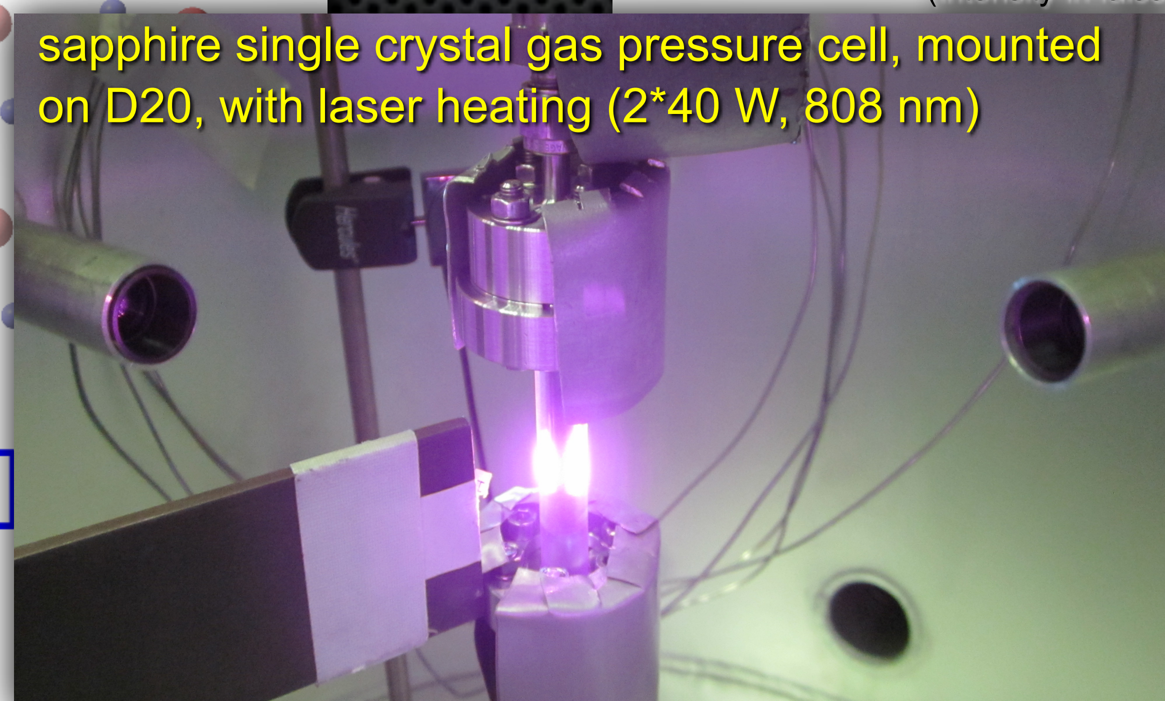


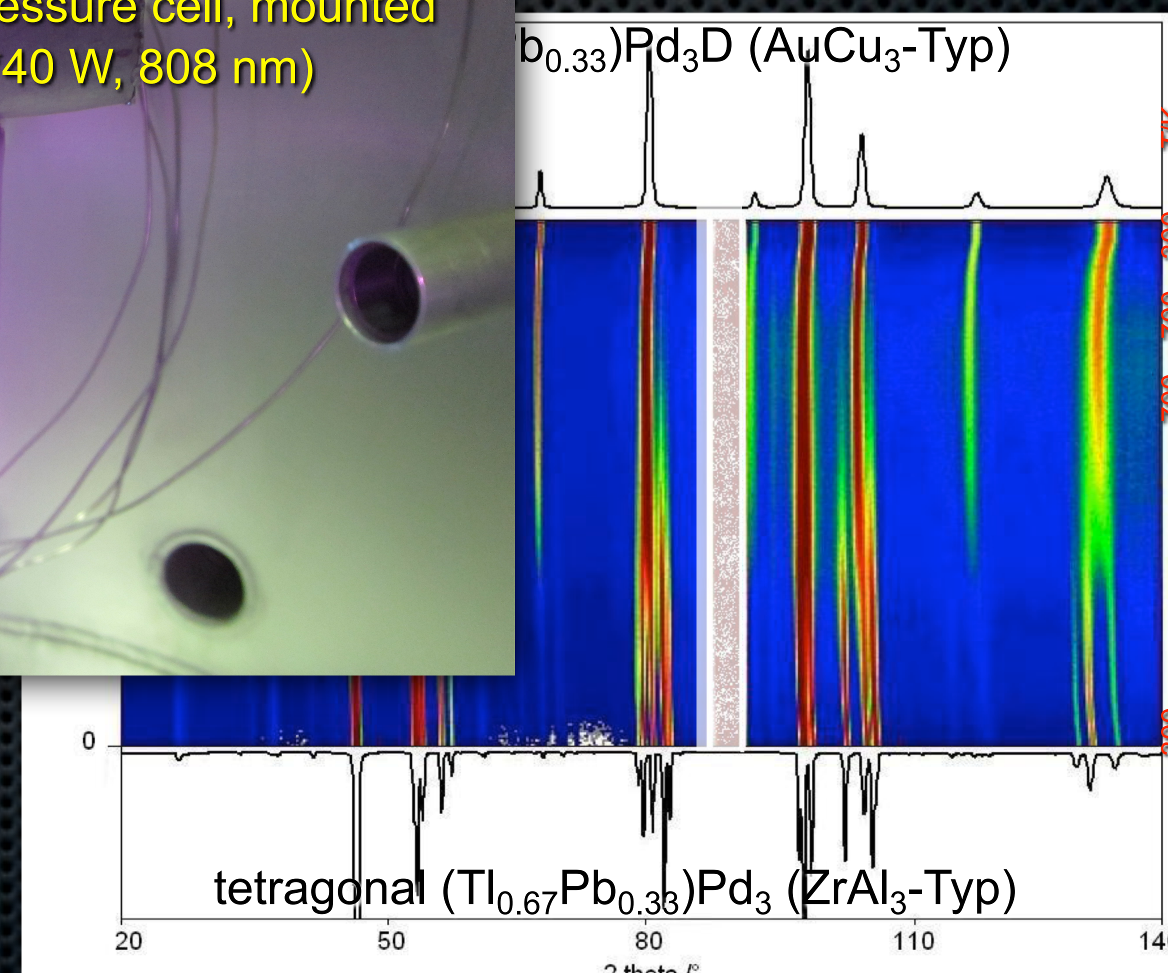
Saphire in situ hydrogenation cell

- Hydrogen absorption & desorption characteristic of inter-metallic compounds including noble metals such as palladium:
  - hydrogen embrittlement, electronic & magnetic properties
- in situ deuteration of palladium:
  - $(Tl_{2/3}Pb_{1/3})Pd_3 + \frac{1}{2}D_2$ (20bars)





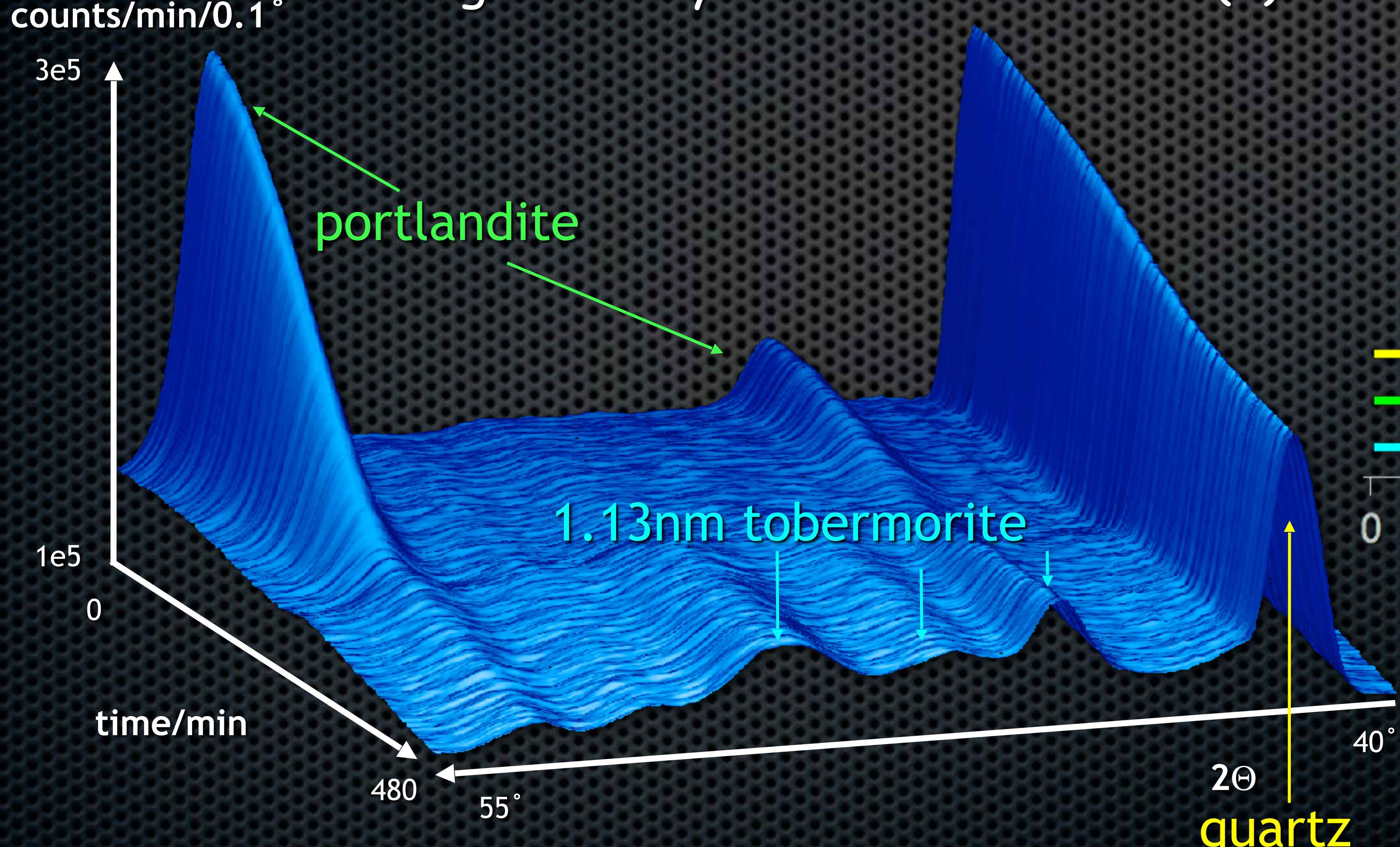


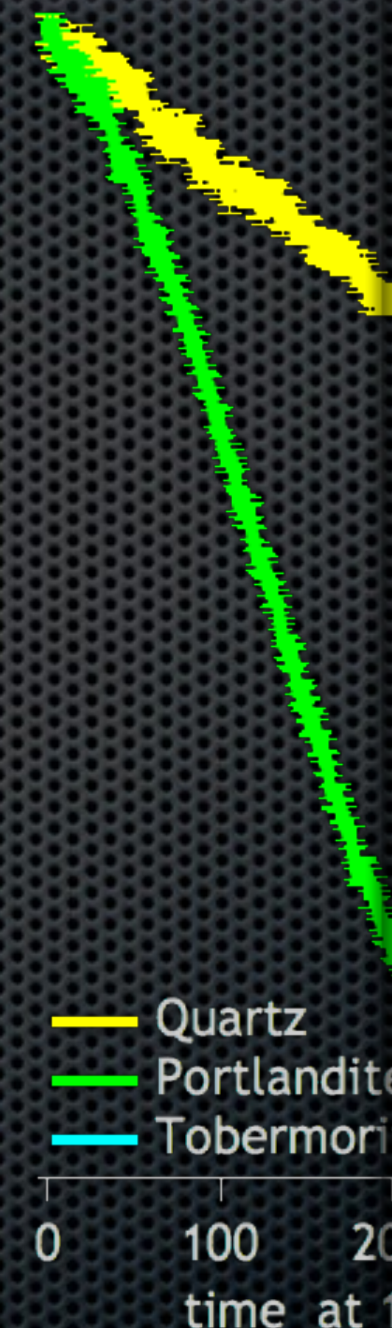


N. Kurtzemann, H. Kohlmann, *Z Anorg Allg Chem* 636 (2010) 1032.

Mechanism and kinetics of steam-curing

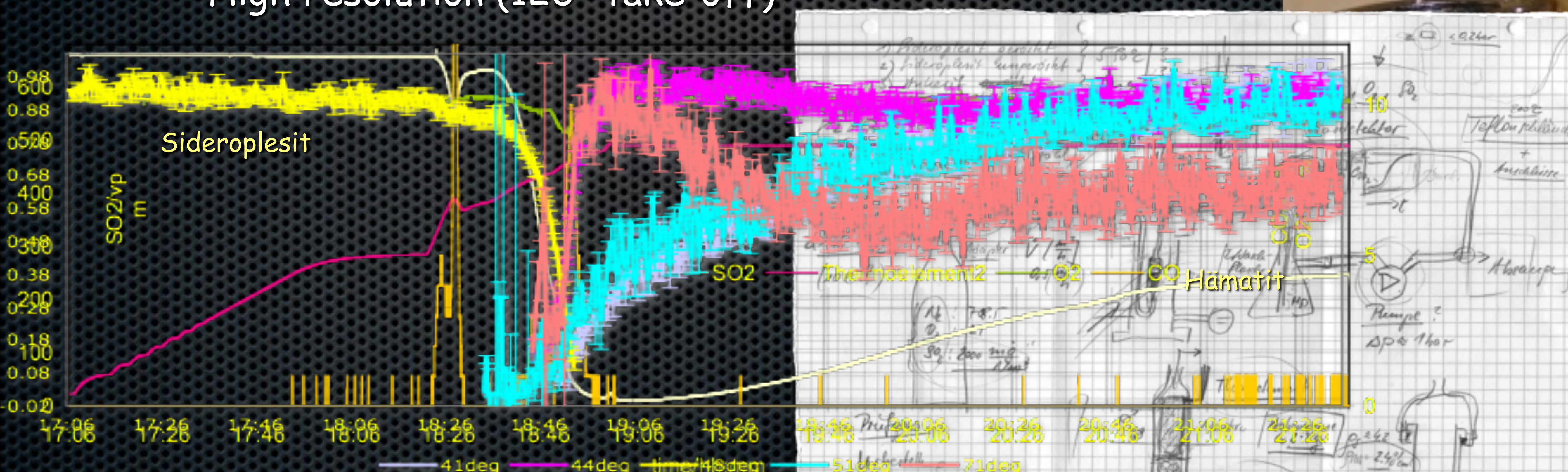
- Autoclaved aerated concrete AAC
  - Portlandite solved in 3h
  - Tobermorite forms after 5h
  - Quartz decays continuously
    - forming semi-crystalline Ca-rich CSH(I)





flue gas desulphurisation & magnetic roasting

- carbonaceous sideroplesite (42% Fe)+SO_2→FeO_y (ferromagnetic)
  - gangue mineral ankerite (among others) remains paramagnetic
- in situ diffraction experiment:
  - pure sideroplestite and artificial flue gas
  - quartz, later steel, gas flow reactor
    - "crystallographical" thermometer
  - High resolution (120° take-off)



A. Kogelbauer, Voest Alpine Erzberg GmbH, Austria
A. Böhm, Institute of mineral processing, University Leoben

Self-propagating High-T Synthesis (SHS)

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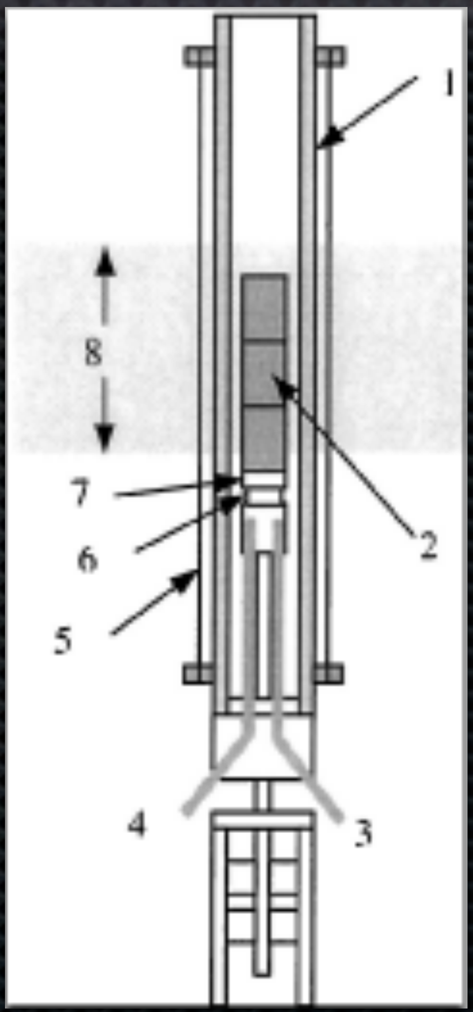
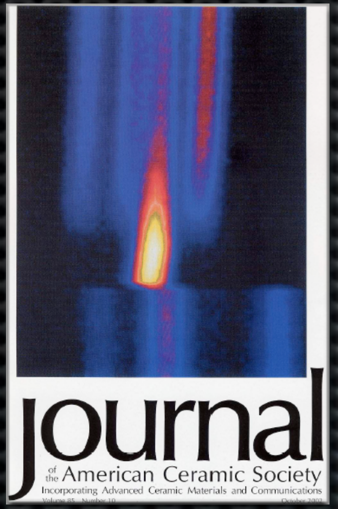
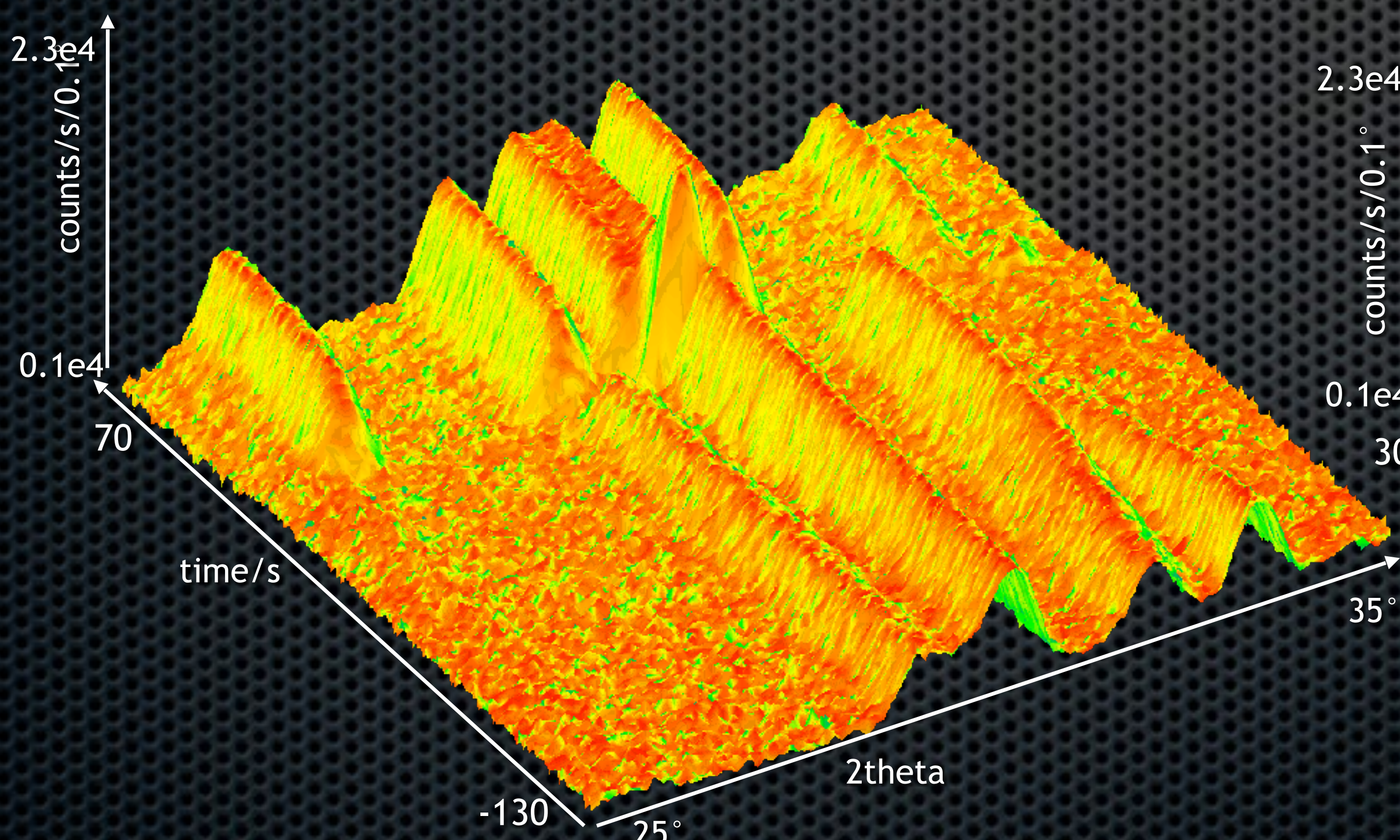
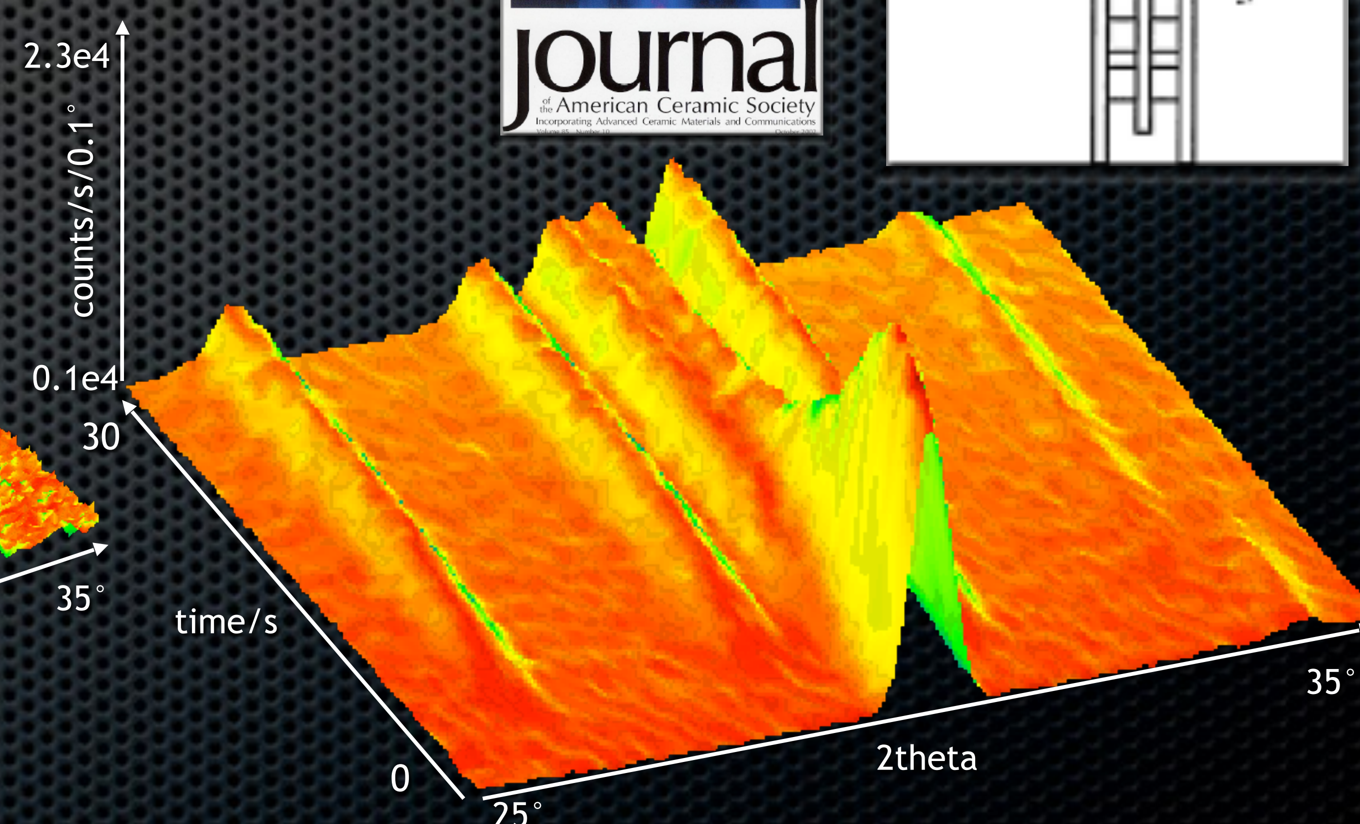
EIROforum Science-Business WAMAS

- Titanium silicon carbide Ti_3SiC_2
- Self-propagating High-temperature Synthesis (SHS)
  - Riley, Kisi et al.: 3 Ti : 1 Si : 2 C, 20 g pellet in furnace
  - Heating from 850 C to 1050 C at 100 K/min
  - Acquisition time 500 ms (300 ms)
- Hot isostatic pressing expensive





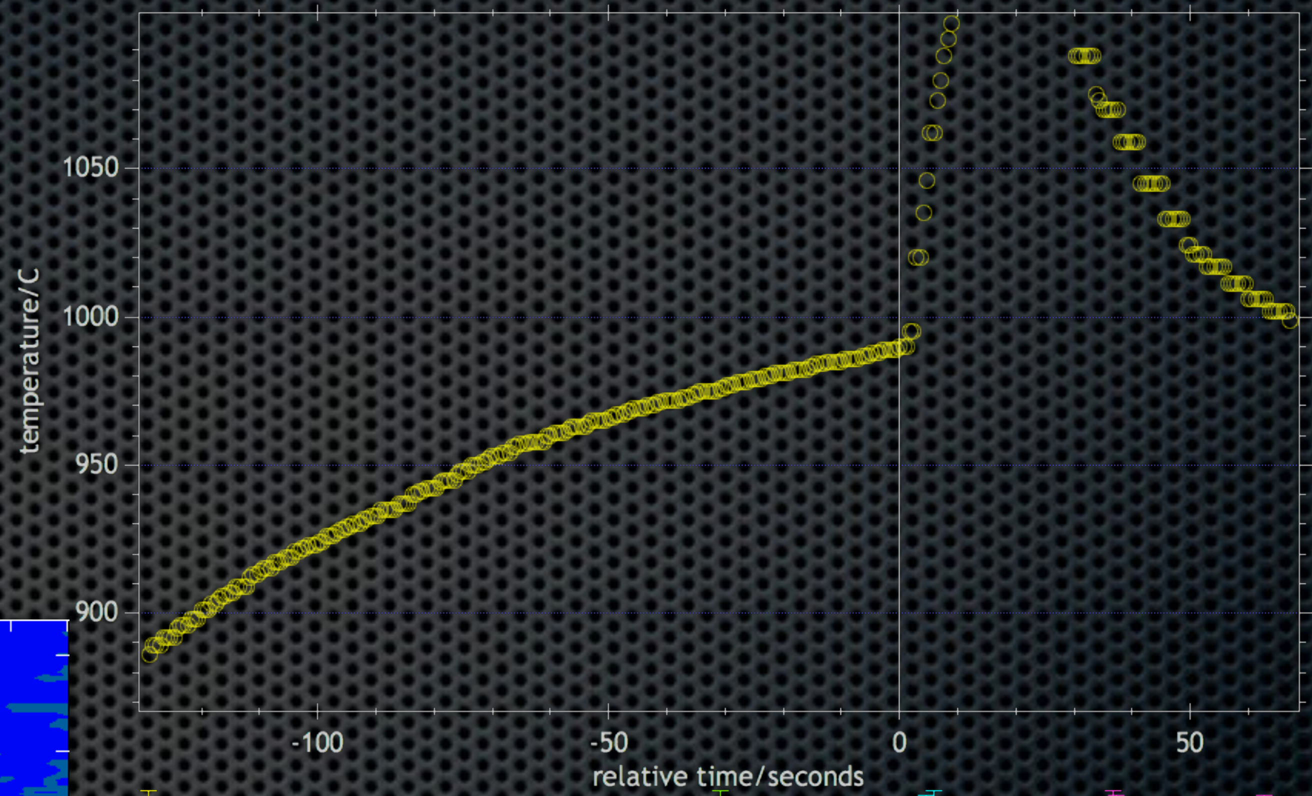


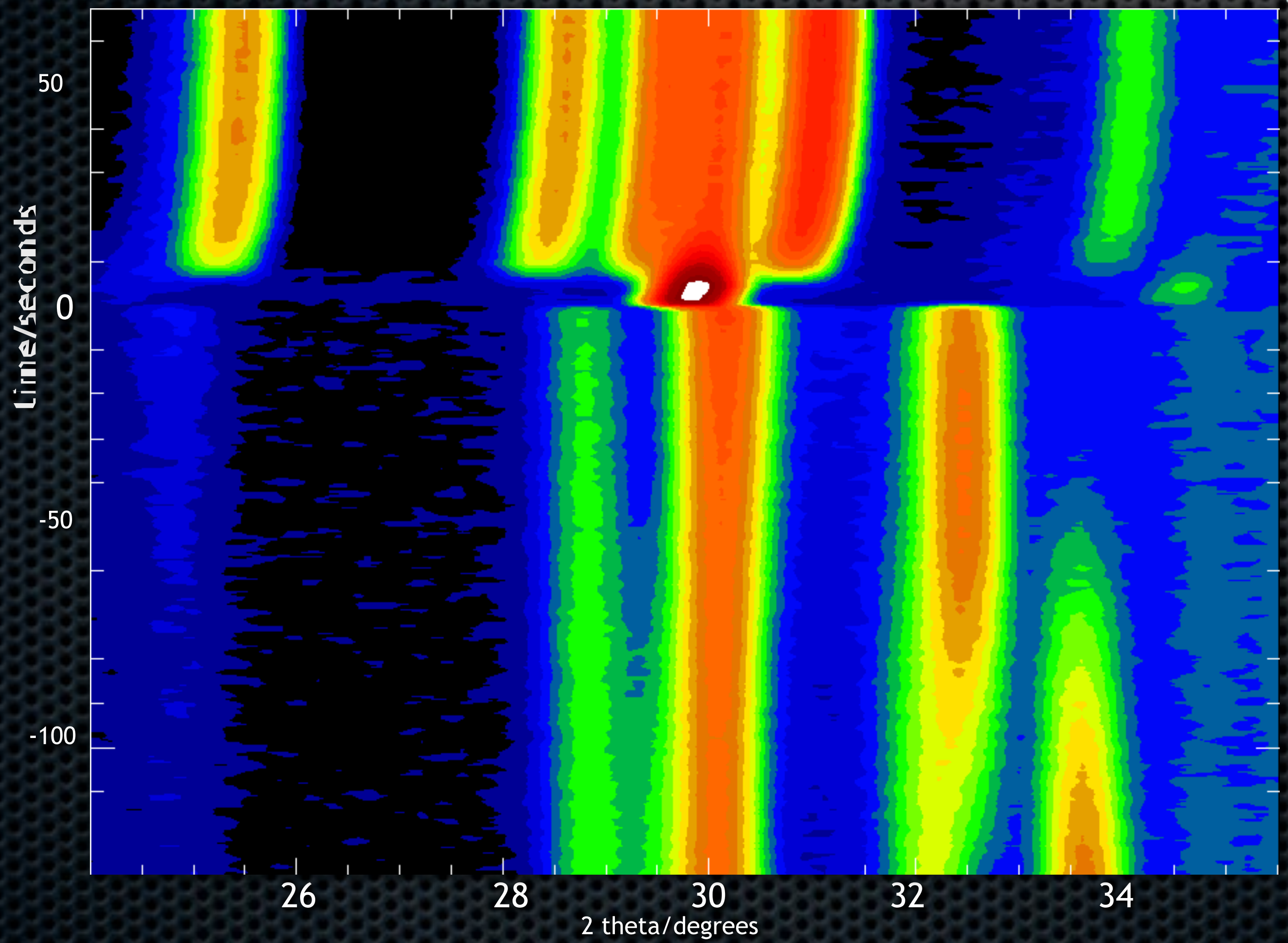


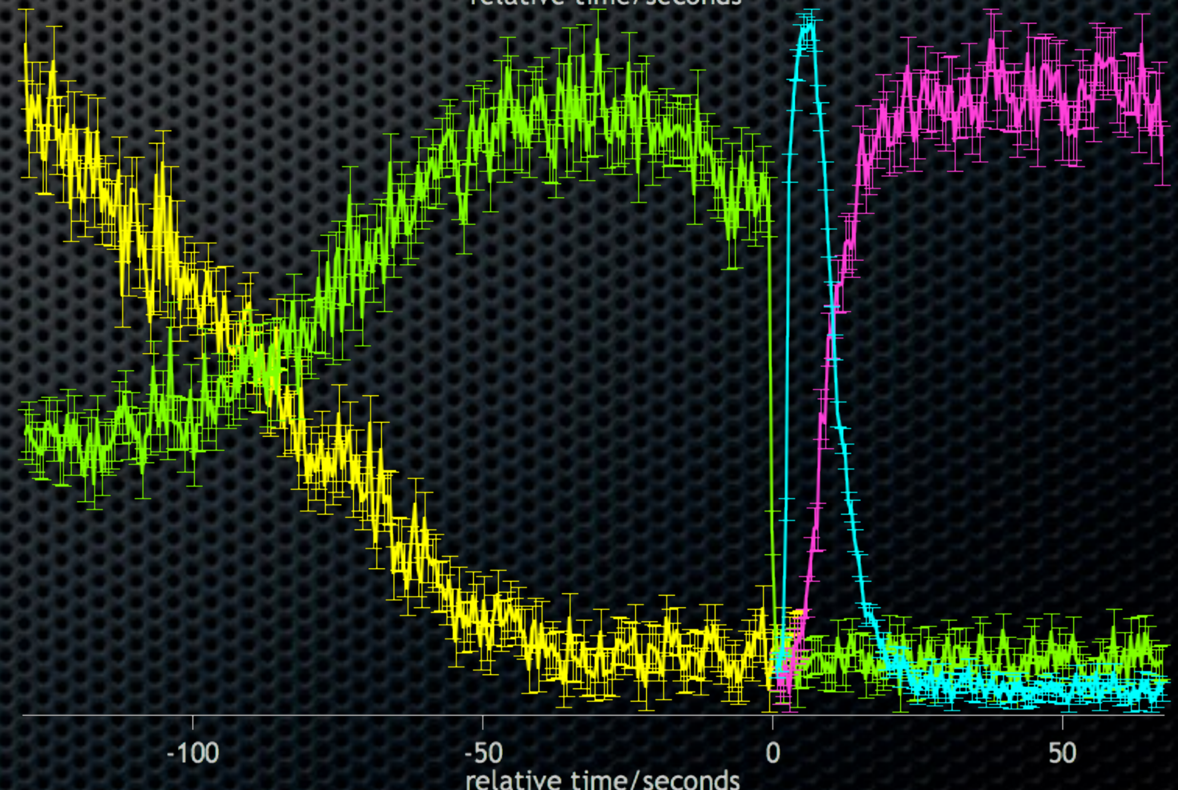
D.P. Riley, E.H. Kisi, T.C. Hansen, A. Hewat, *J. Am. Ceramic Soc.* **85** (2002) 2417-2424.

Self-propagating High-T Synthesis (SHS)

- Ti α-β transition: starting at 870 C
- Pre-ignition: TiC_x growth during 1 min
- Melting (?) in 0.5 s: Intermediate phase
  - TiC, Si substituted
  - formed in 0.5 s, 2s delay
  - Heating up to 2500 K
- Product Ti_3SiC_2: starts after 5 s incubation
  - time constant about 5 s



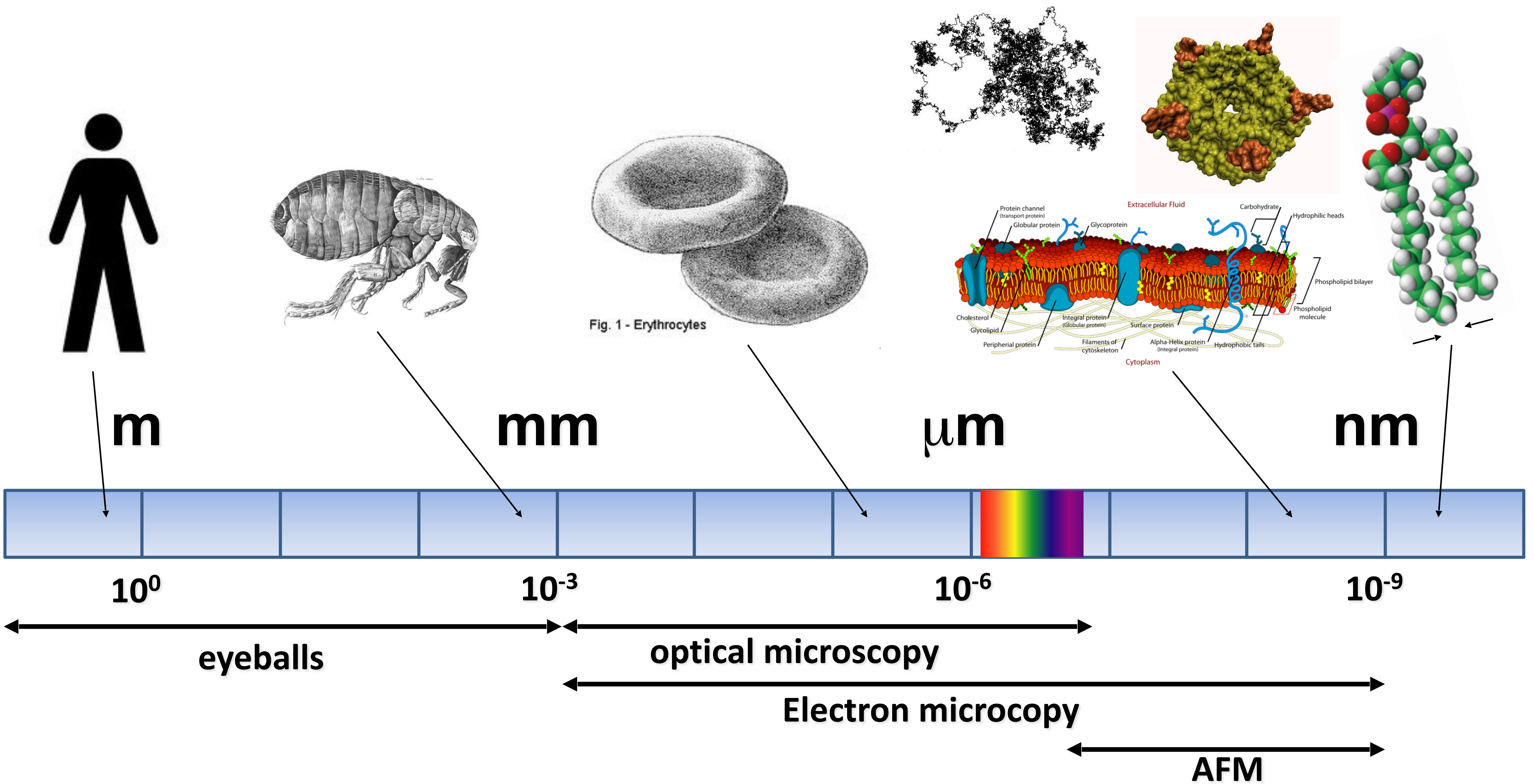




Last not least: surfaces

by Richard CAMPBELL

Interfacial length scales



SAXS/SANS

XRR/**NR**

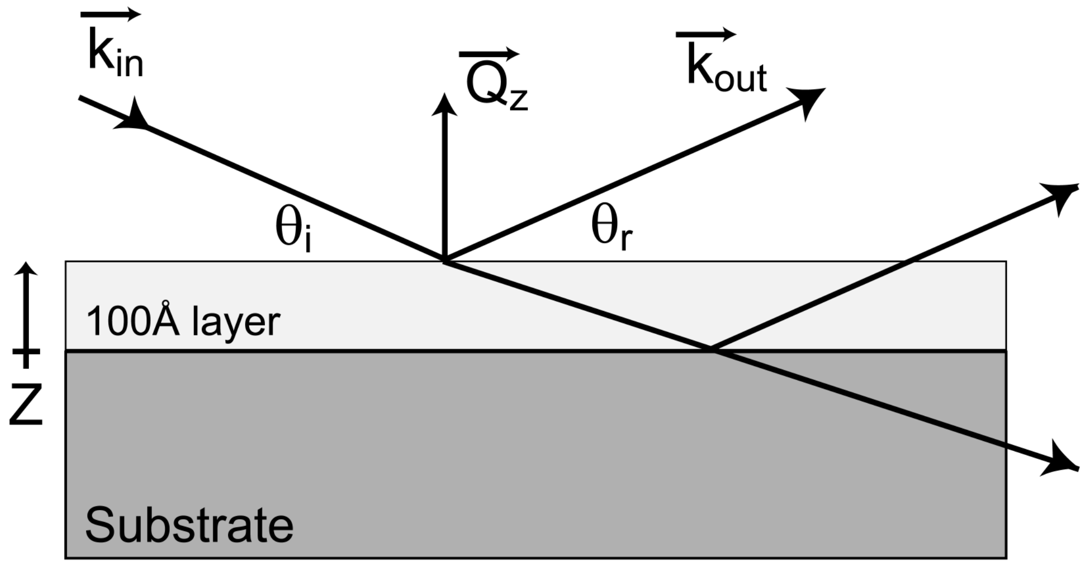
diffraction

Cold neutrons: λ = 0.2-3 nm

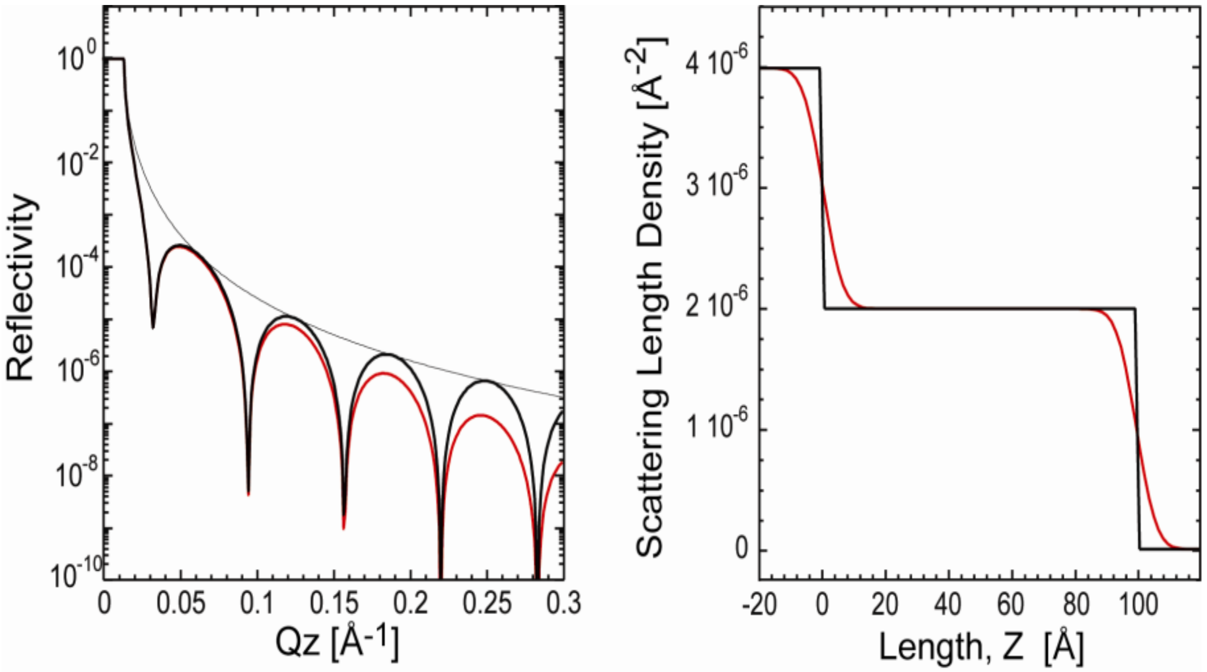
- ideal to probe nano scale interfacial structures

Neutron reflectivity (NR)…

…a technique to study interfaces and thin films



$$|\vec{Q_z}| = \frac{4\pi \sin(\theta)}{\lambda}$$



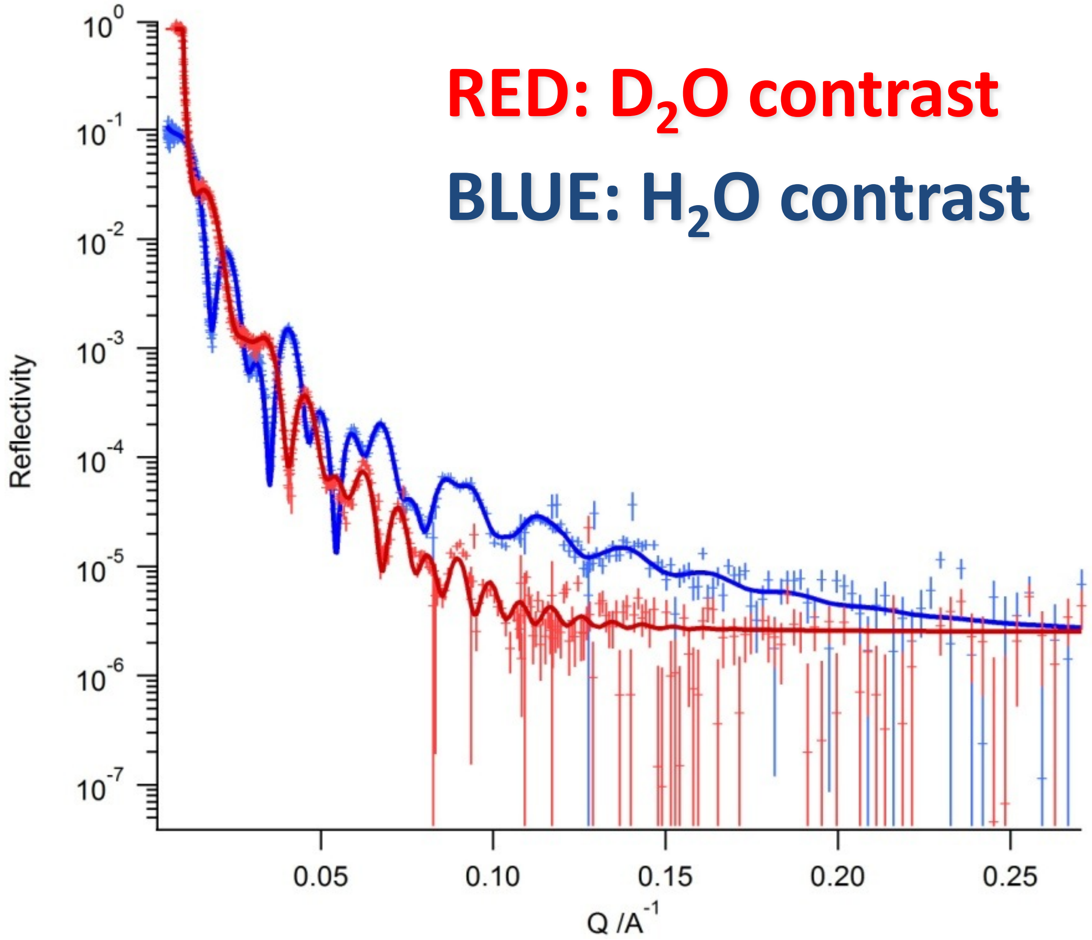
Neutrons strike a flat sample at small glancing angles

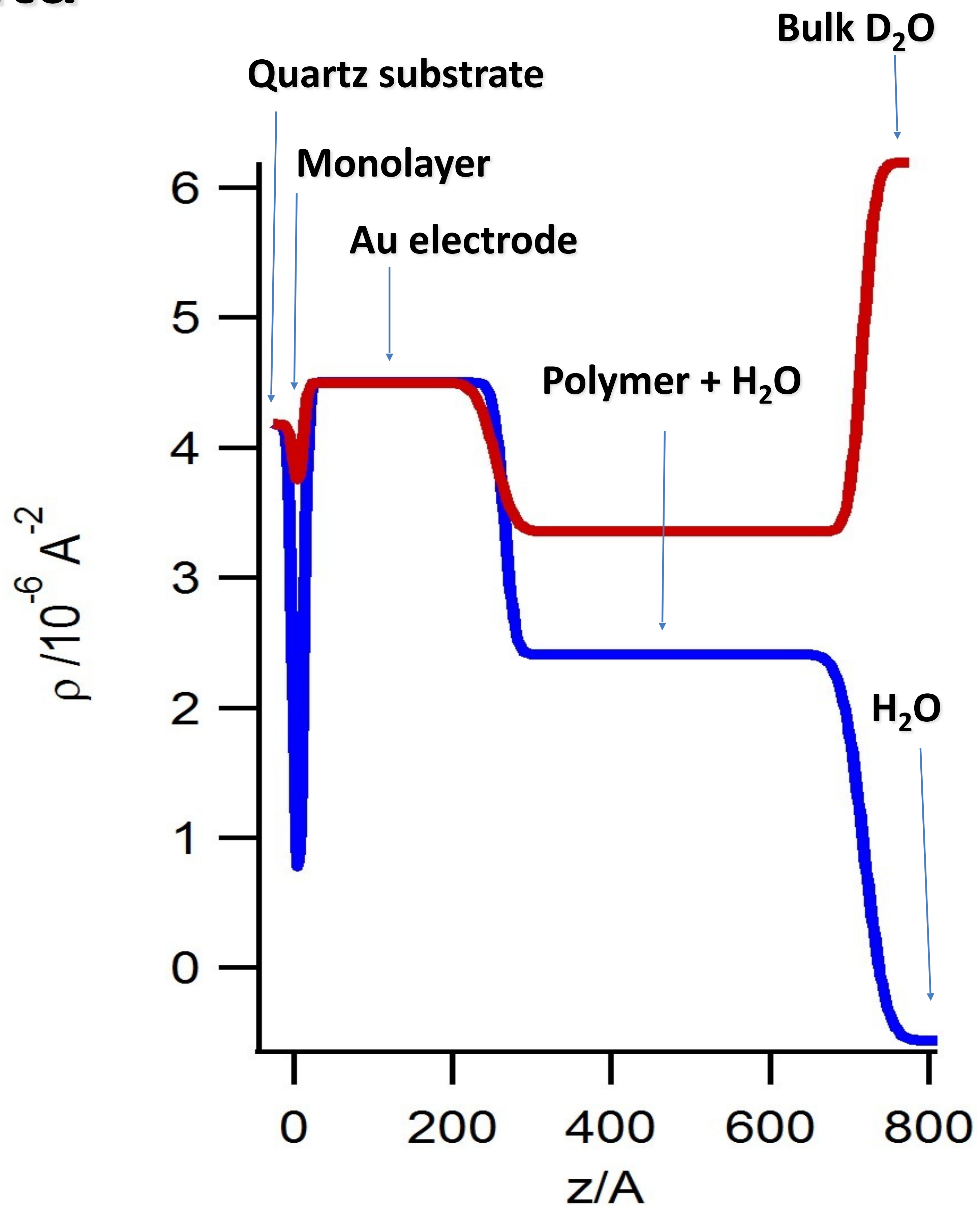
- Reflection and refraction from interfaces
- Interference between the various reflections

Provides out-of-plane structure

- Average density normal to the interface
- Layer thickness, density and roughness
- Ideal nano scale probe for structure & composition

An example of NR data





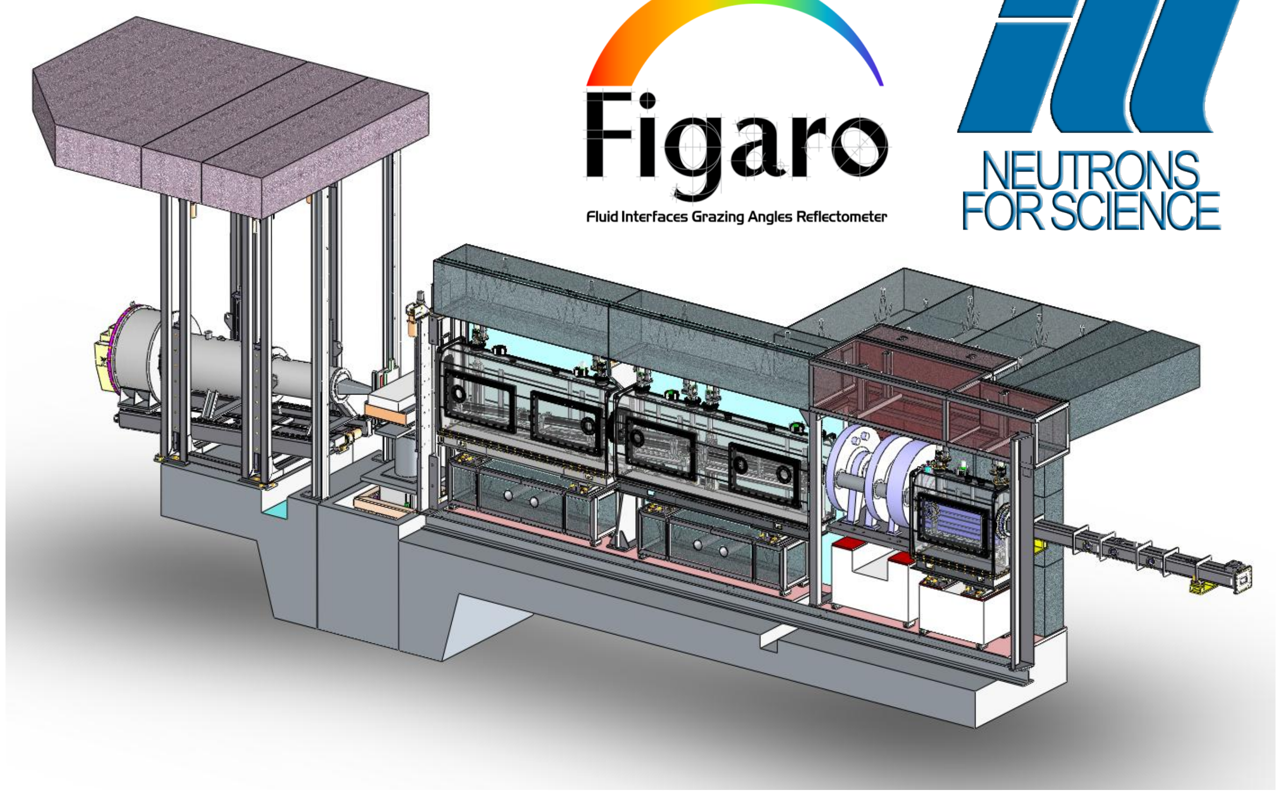
Electroactive polymer deposition on Au electrode

Multiple contrasts improve confidence in the model and quantify water content in the polymer film

Fluid Interfaces Grazing Angles ReflectOmeter

FIGARO stats:

- world-leading instrument from 2009
- white beam flux of 1.4×10^{8} n mm^{-2} s^{-1}
- flux at sample: 4×10^{2} n mm^{-2} s^{-1}
- Large beam size: 0.5-5 mm x 40 mm
- Resolution: 1-10% $\Delta Q/Q$
- Dynamic range of 6-7 orders in R



Figaro
Fluid Interfaces Grazing Angles Reflectometer

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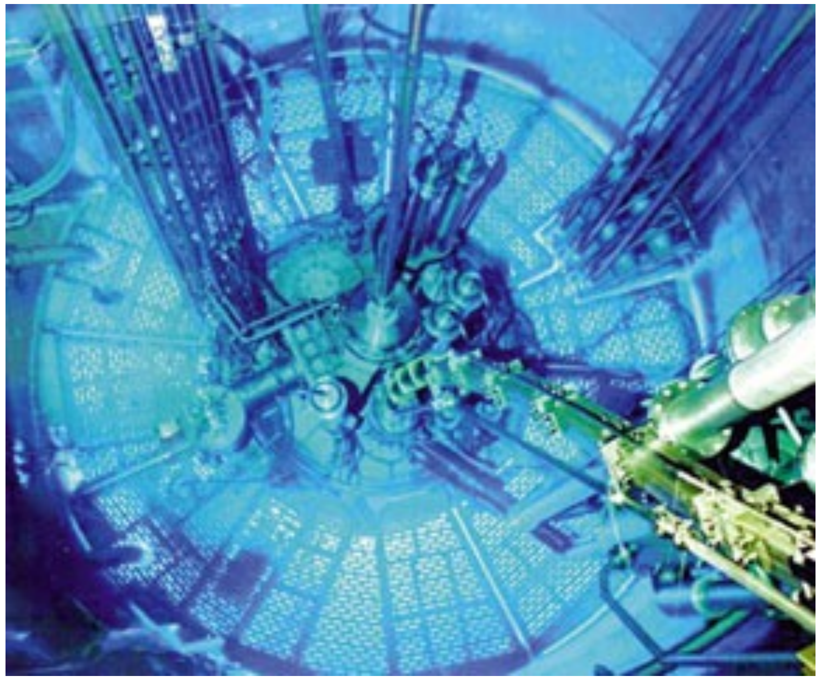

ILL reactor

FIGARO examples:

- polymer film structure
- nanoparticle interactions
- DNA & protein studies
- solvent drying in glues & paints
- rheology of polymer blends
- virus interactions with model membranes
- detergent & formulation optimization