EUROPEAN
SPALLATION
SOURCE

The changing face of neutron powder diffraction

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Simulator Meeting, Lund, 20th April

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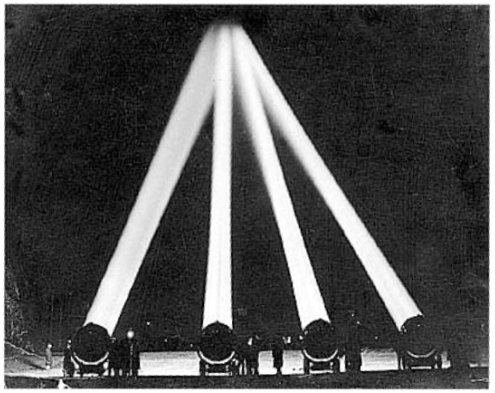
Summary

- Introduction
- Historical PND experiment
- Step change in instrumentation (1990s)
- Example experiments
- Current state of the art instruments (2011)
- Where next?
- My Interests
- Conclusions

X-rays v neutrons as a probe

X-ray or electron scattering

- Effective probe for condensed matter
- Wavelengths ideal for structural analysis
- Available at laboratory level
- High intensity synchrotron sources

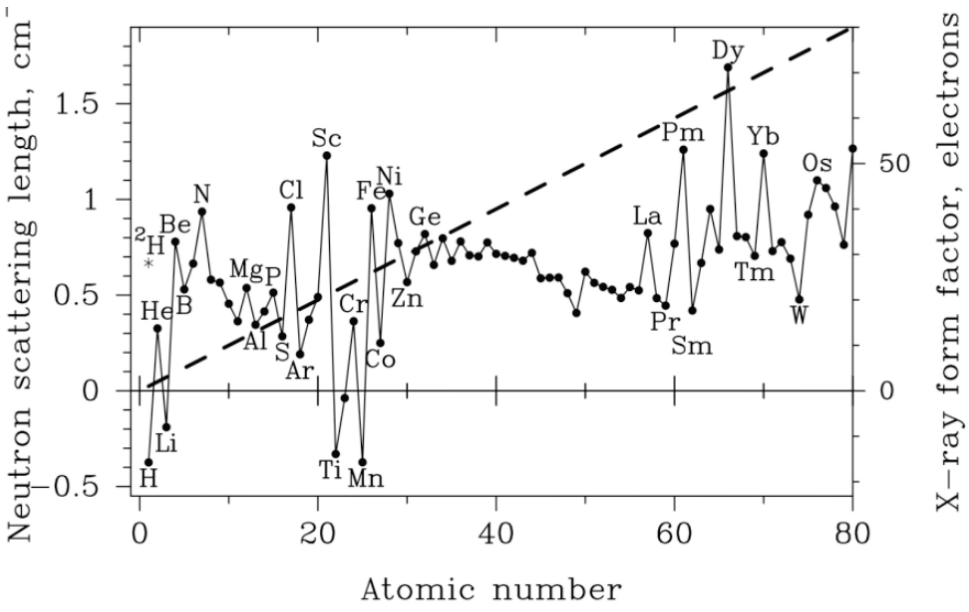


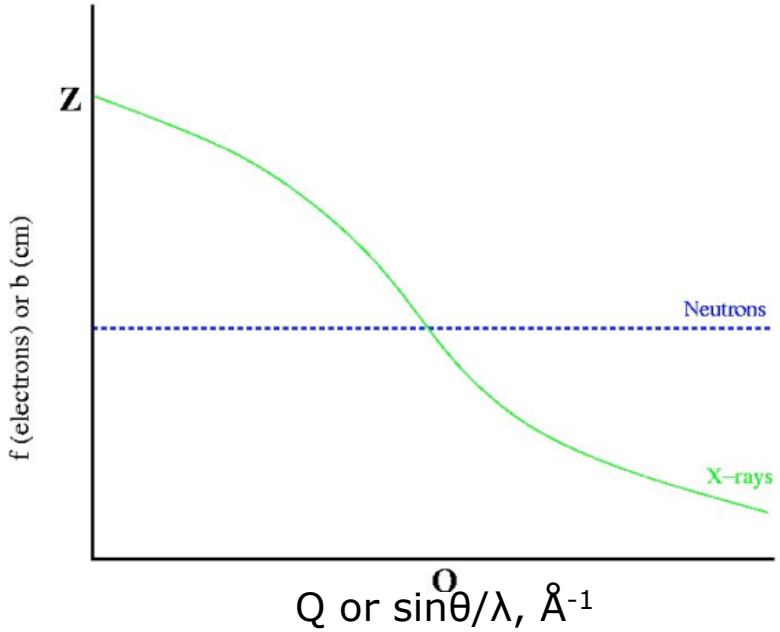
Neutrons

- Effective probe for condensed matter
- Wavelengths ideal for structural analysis
- Low intensity
- Expensive sources
- Difficult access

How can neutrons compete?

X-ray v neutron scattering





Neutrons are

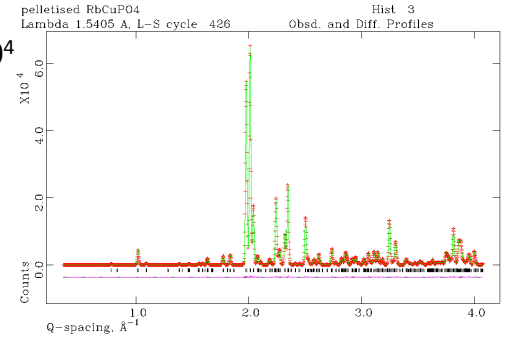
- Not heavy atom dominated
- Significant differences in adjacent elements
- Isotopes have different scattering length
- Scattering almost invariant in Q

Neutrons are also

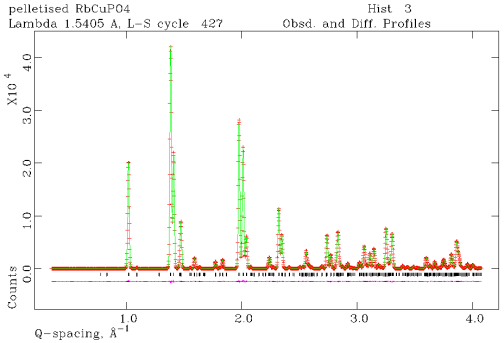
– low energy and so non-damaging
– penetrating
– magnetic moment
– spin

Heavy atom domination in X-ray

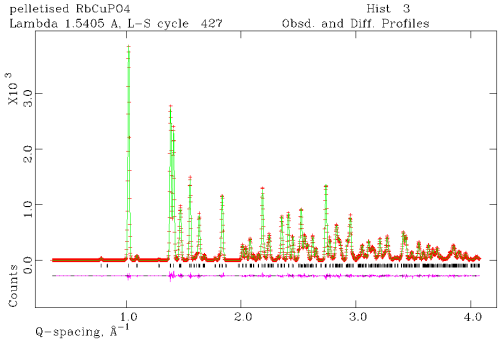
6x10^4



4x10^4



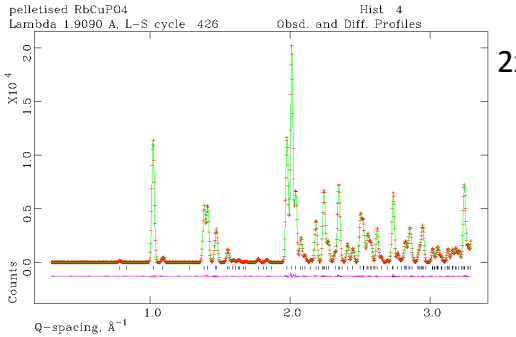
4x10^3



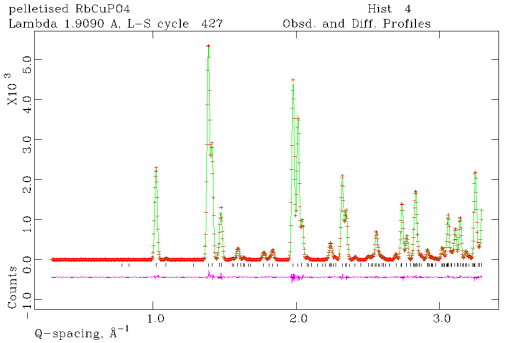
X-ray (left) and neutron (right) scattering of $RbCuPO_4$

Rb scattering 10 times that from O in X-ray data but similar from neutron data

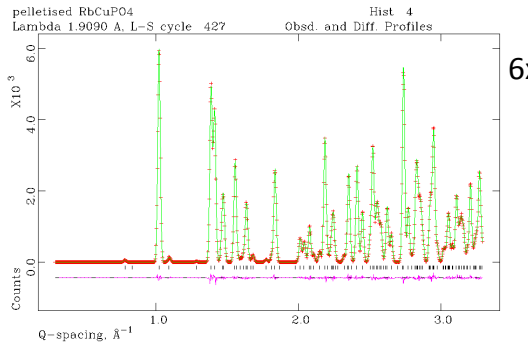
Notice also that patterns are not just summations of the contributing elements - evidence of the phase problem



2x10^4



6x10^3



6x10^3

Scattering contrast X-ray v neutron

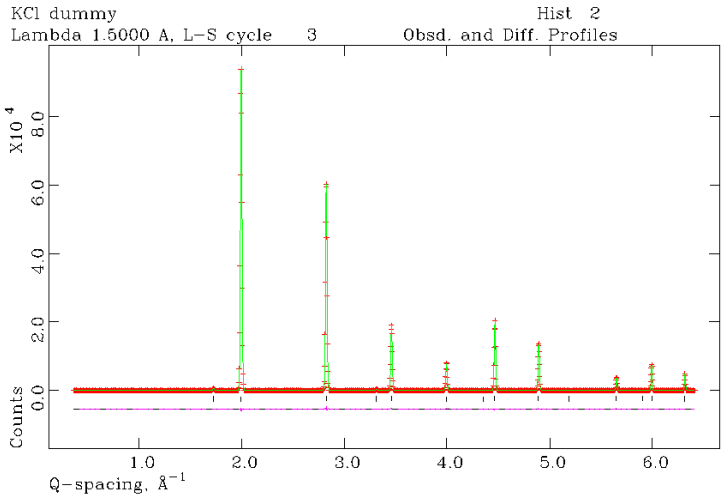
KCl

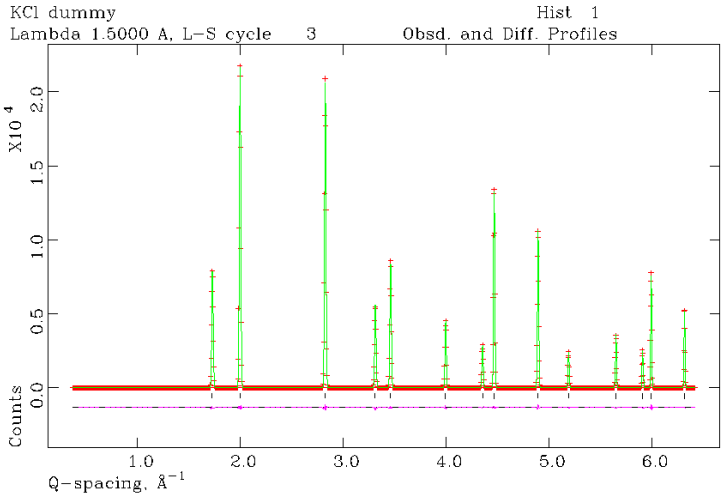
Fm-3m *a* = 6.29 Å

K z = 19

Cl z = 17

But $K^+ = Cl^- = 18\ e^-$

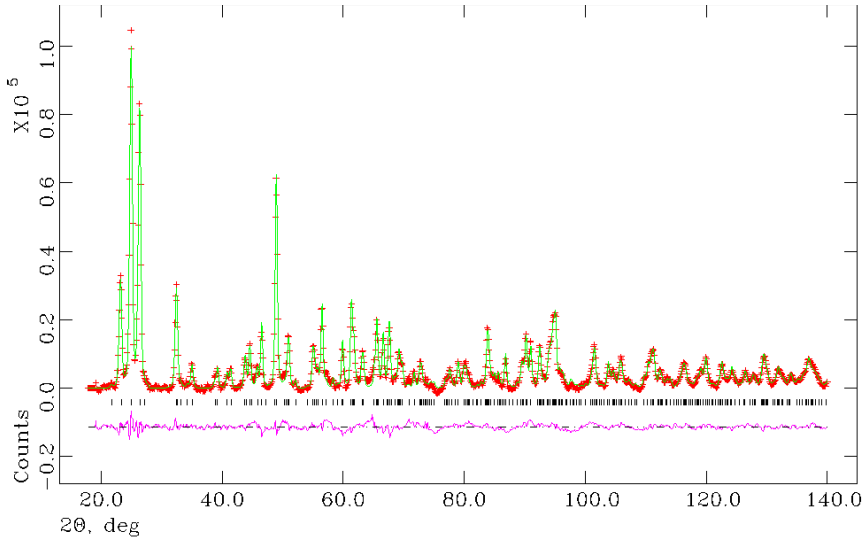


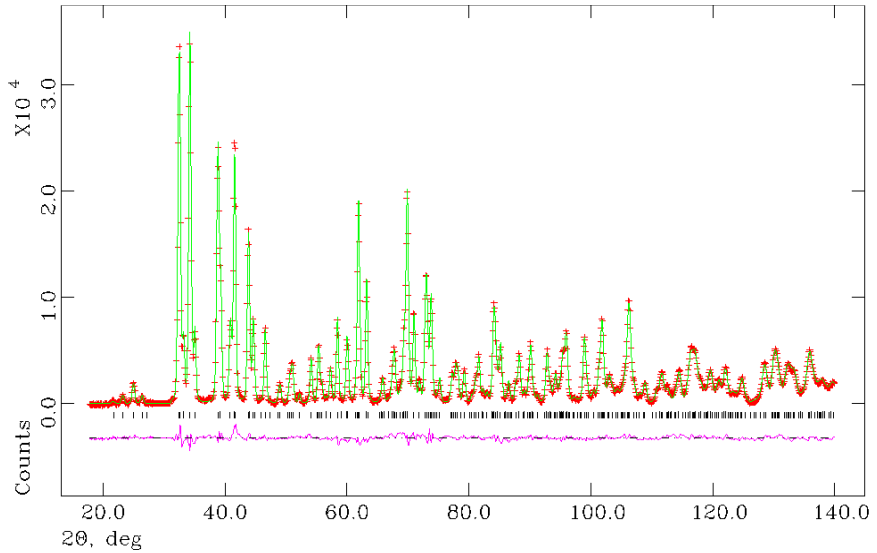


Without care KCl indexes from X-ray data on a cell that is ½ that from neutron data

Scattering contrast between neighbouring elements is crucial

Isotope scattering lengths





SrH_2 (top) v SrD_2 (bottom)

Scattering lengths

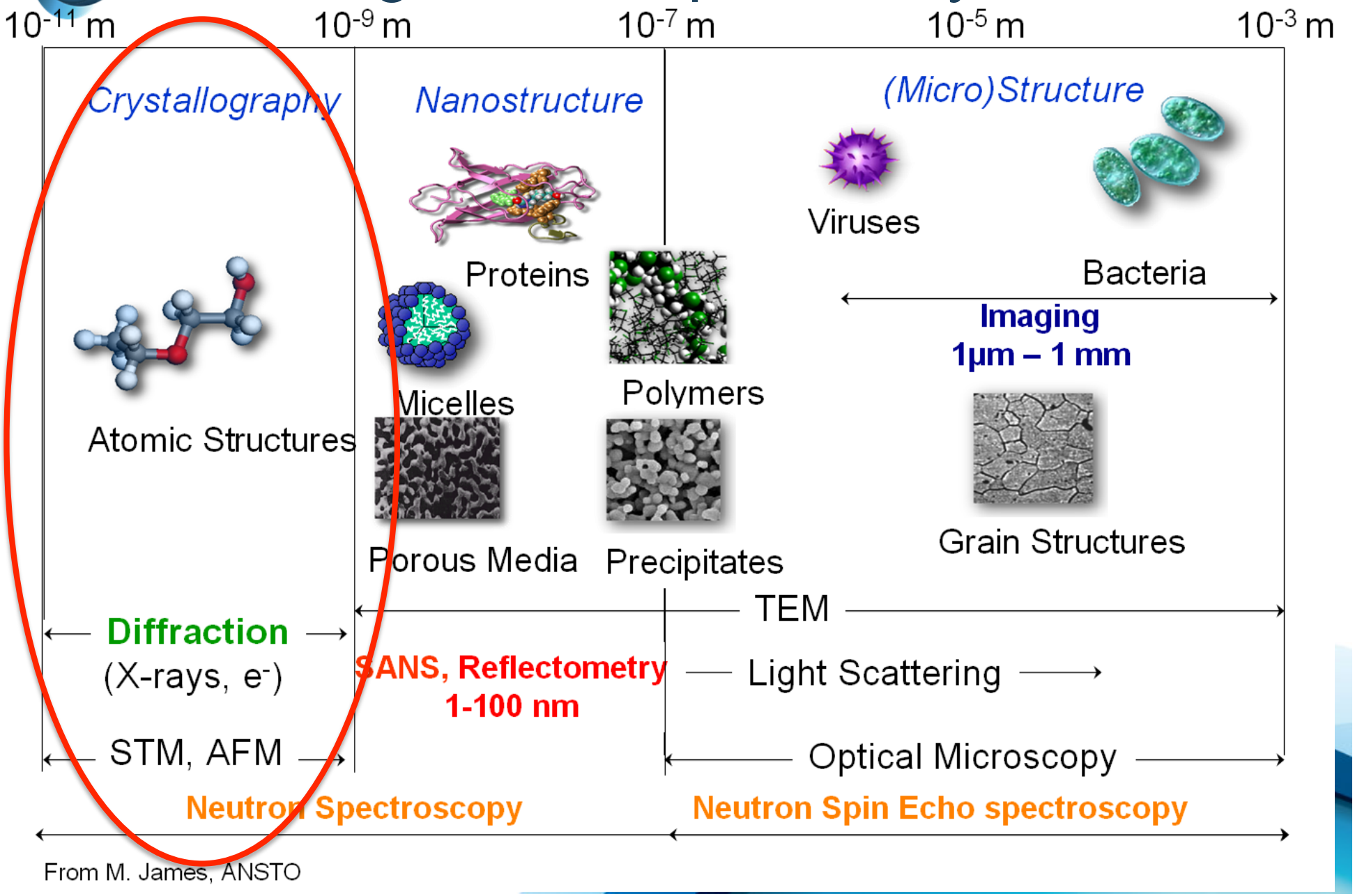
H -3.739 fm

D 6.67 fm

Allows features to be seen that are missed by X-ray diffraction where H and D are equivalent.

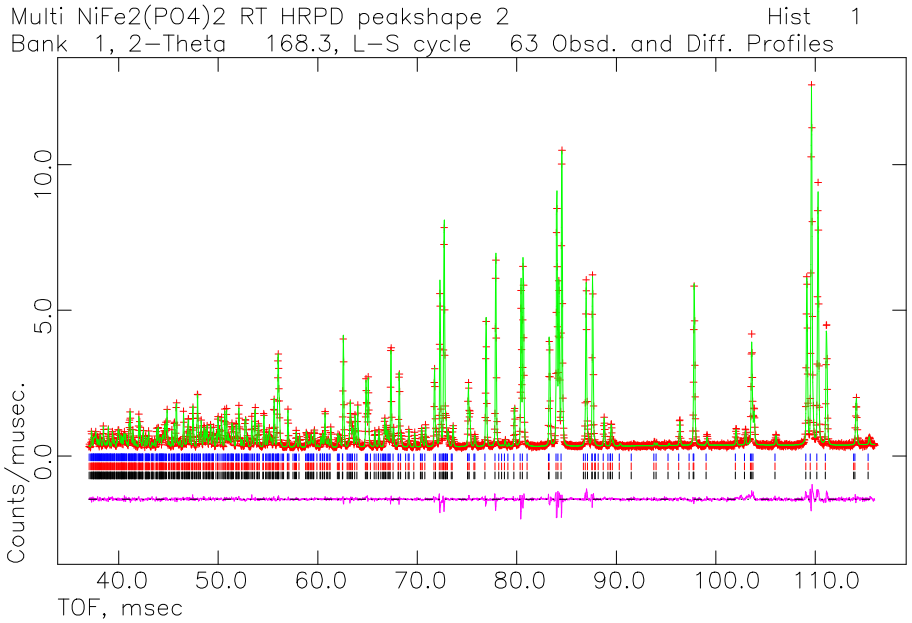
Also H / D contrast studies

Length scales probed by neutrons



From M. James, ANSTO

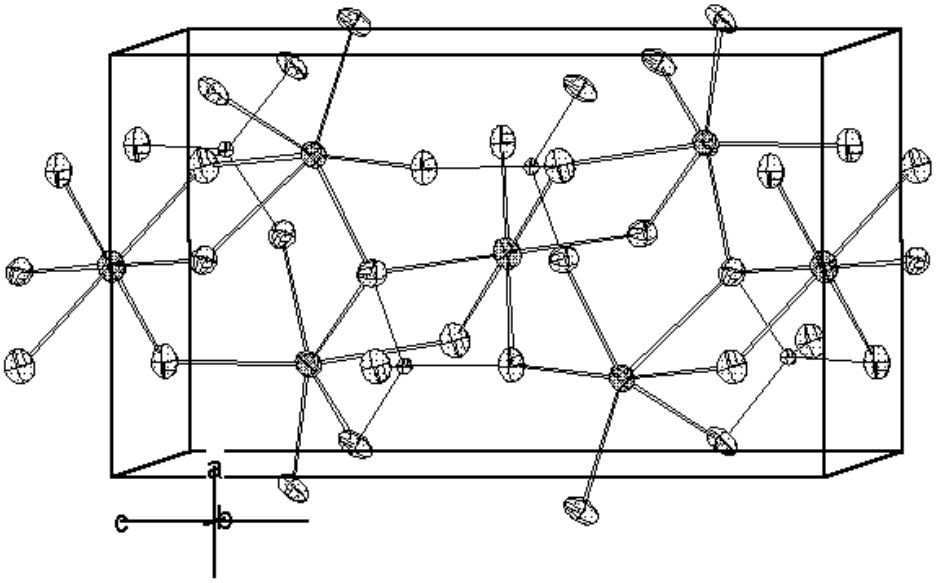
Historical PND



Single pattern
Long data collections (12h +)
Fixed conditions of T, P, Mag. Field

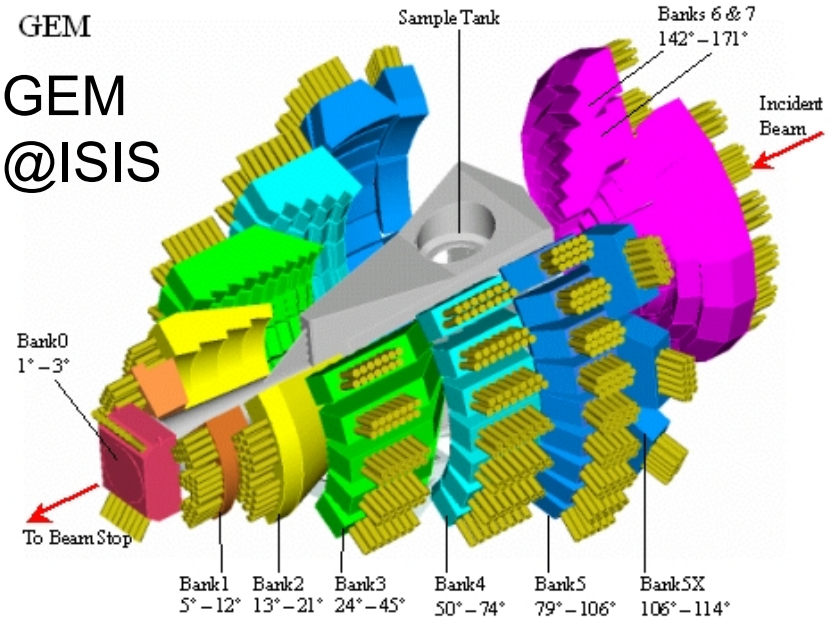
Spallation
oldHRPD, oldPOLARIS

Reactor
D1A, oldD2B, D1B

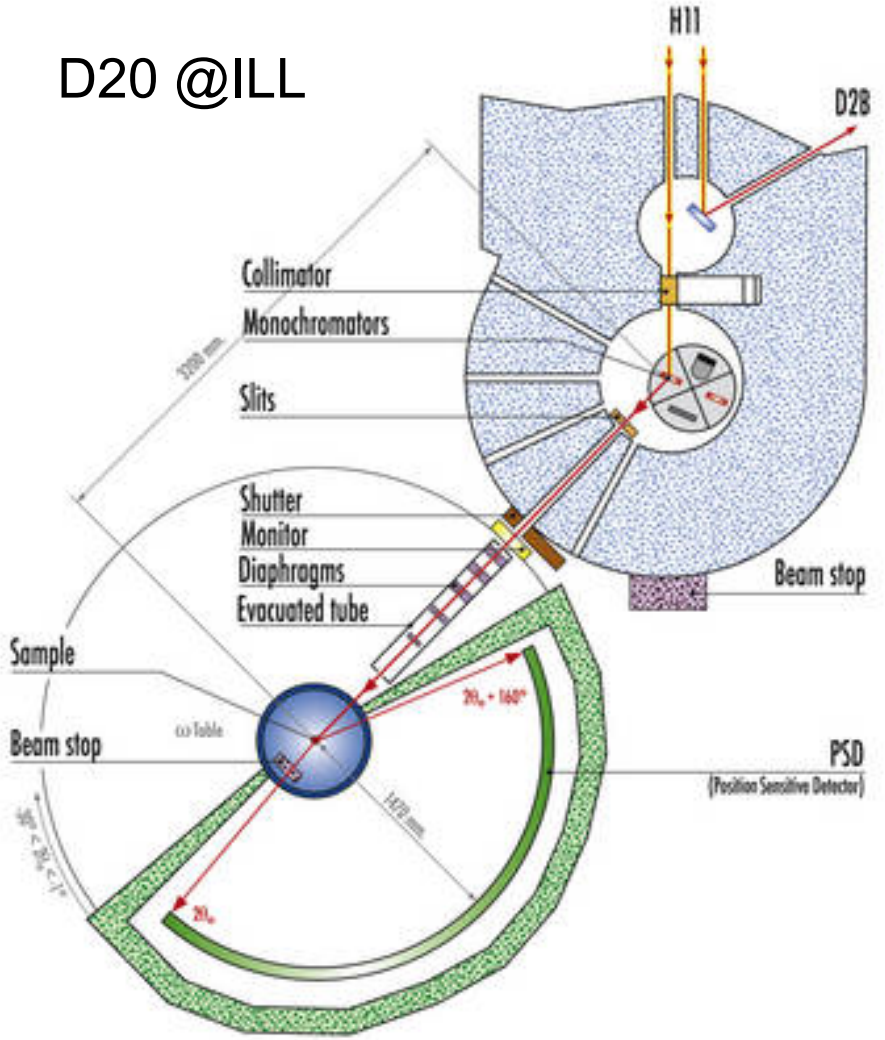


Step change in instrumentation

GEM
@ISIS



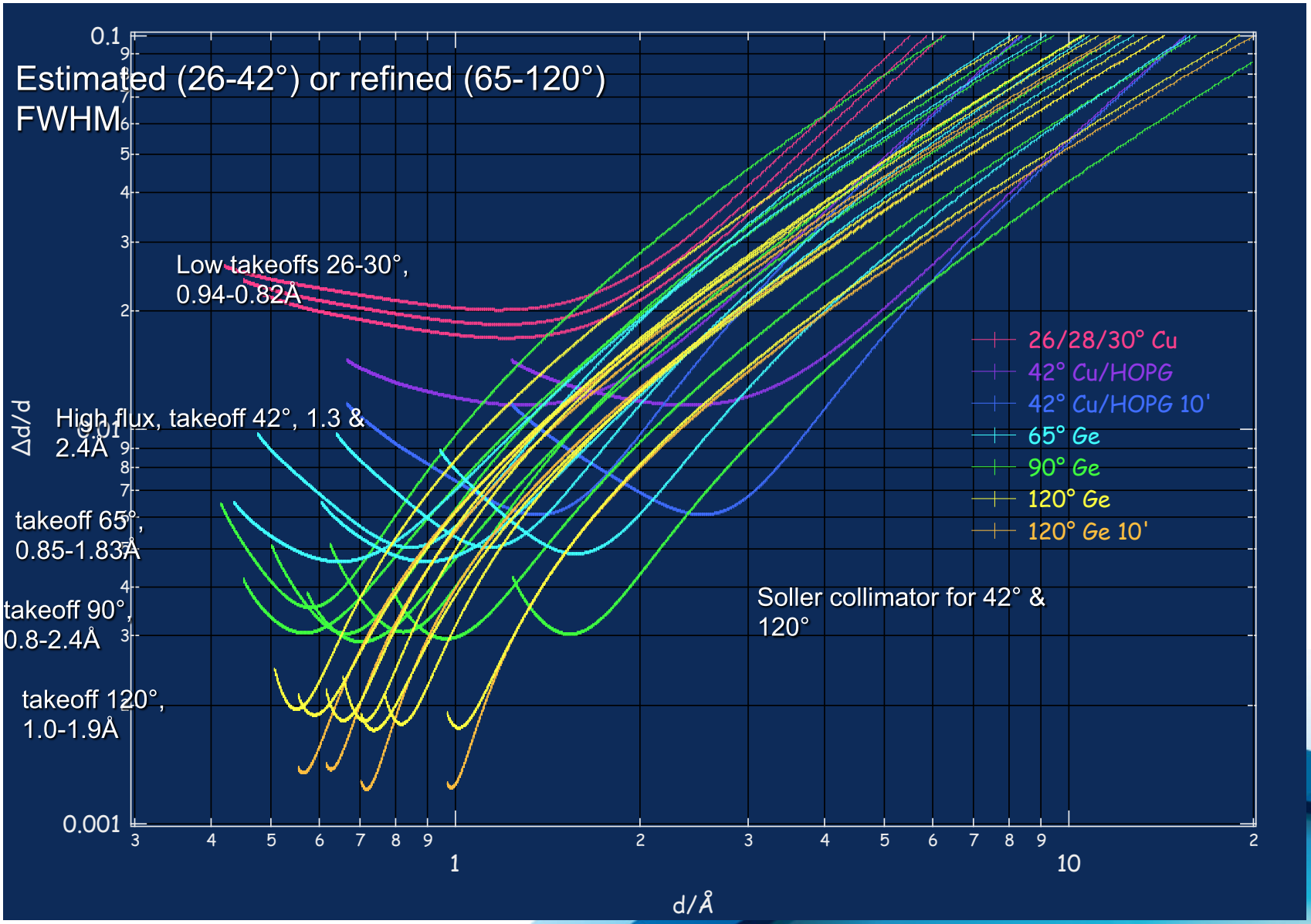
D20 @ILL



High count rate / efficiency
Large detector arrays
Optimised beam transport
Flexible

New experiment types (in situ)
New science

Flexibility of D20



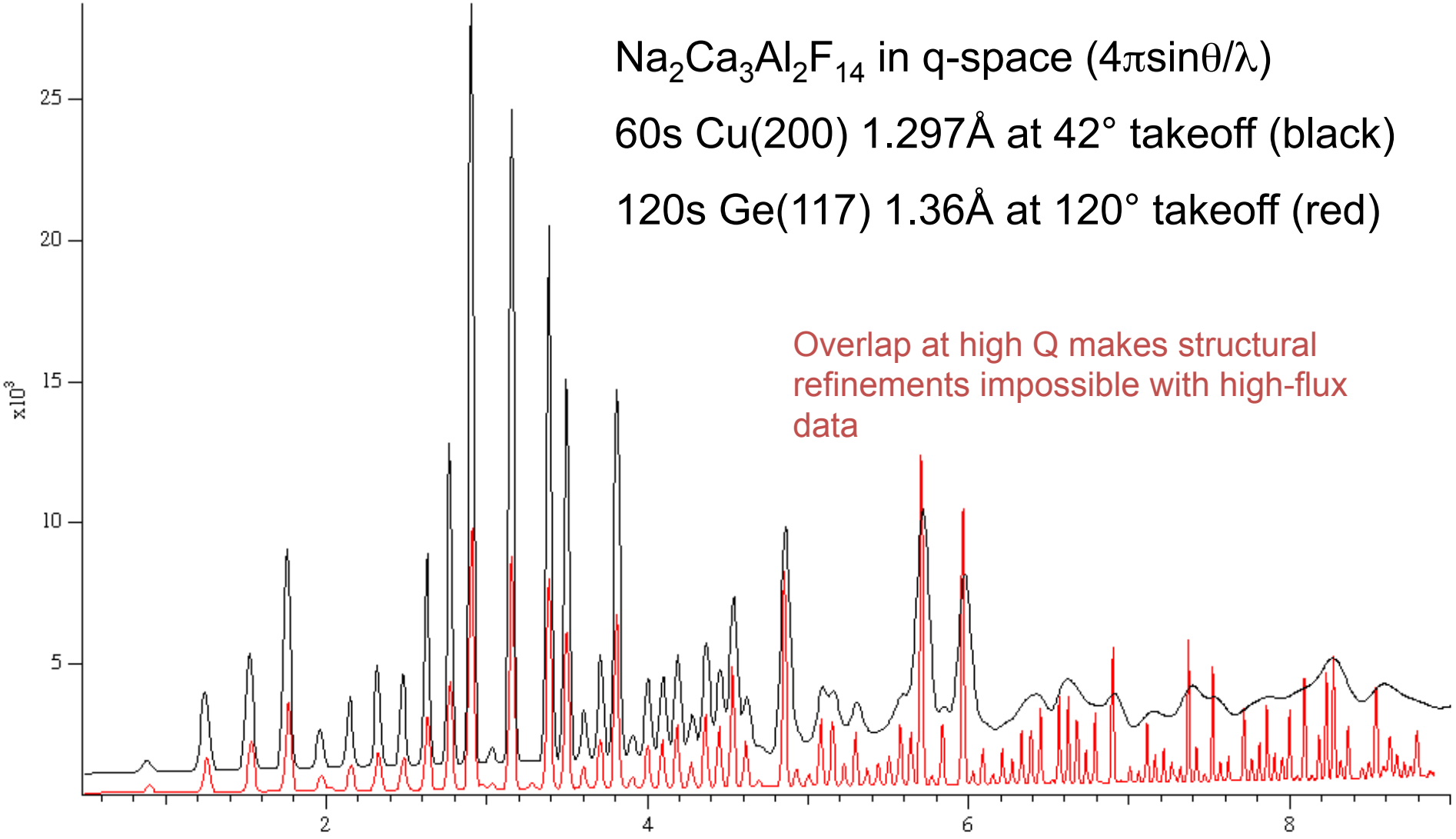
Flexibility of D20

$Na_2Ca_3Al_2F_{14}$ in q-space ($4\pi\sin\theta/\lambda$)

60s Cu(200) 1.297Å at 42° takeoff (black)

120s Ge(117) 1.36Å at 120° takeoff (red)

Overlap at high Q makes structural refinements impossible with high-flux data



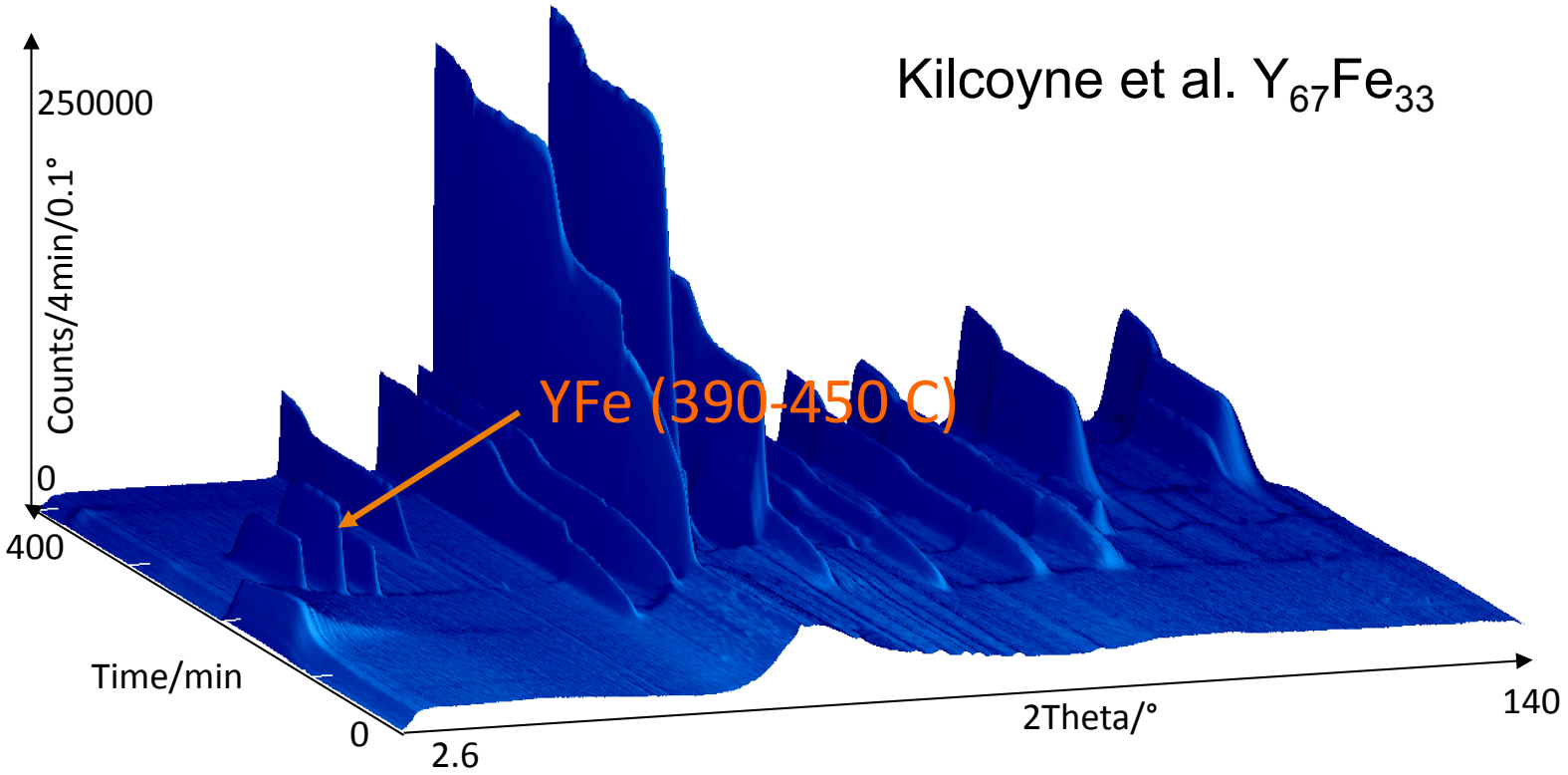
New Science – parametric studies

- What do we mean by parametric studies?

Data collection as a function of a changing variable

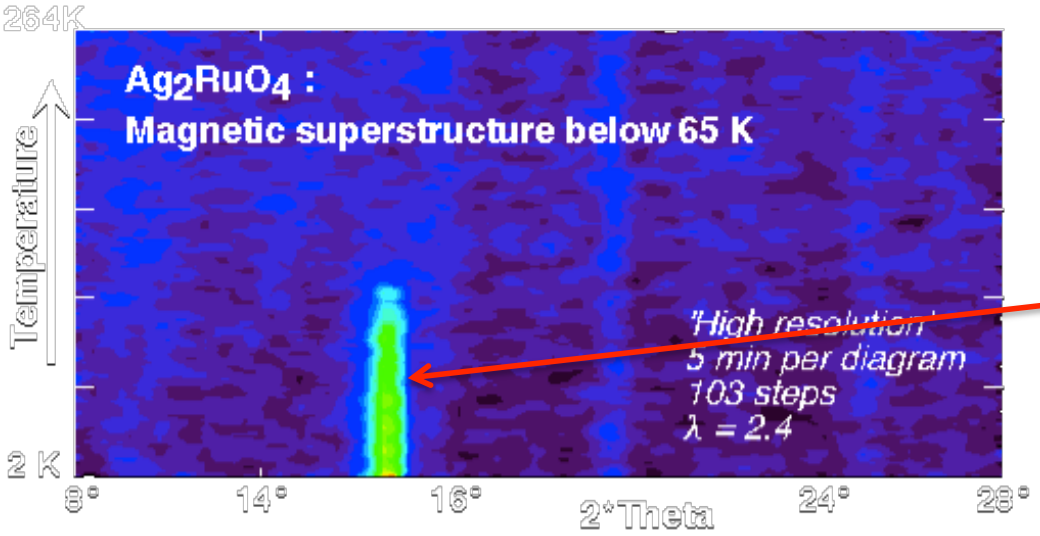
- Temperature: *thermodiffractometry: I*(2θ,*T)*
- Time *I(2*θ*,t)*
- Combination of temperature/time: *I*(2θ,T,*t)*
- Pressure: *I*(2θ,*p)*
- Magnetic field: *I*(2θ,*H)*
- Texture: many sample orientations: *I*(2θ,χ,φ*)*
- Strain: many sample positions: *I*(2θ*,* x, y, z*)*
- Stoichiometry: *I*(2θ,*x)* (many samples)
- Gas loading / Gas type: *I*(2θ,*partial pressure, gas)*
- Humidity: *I*(2θ, *RH)*
- Others can be envisaged…

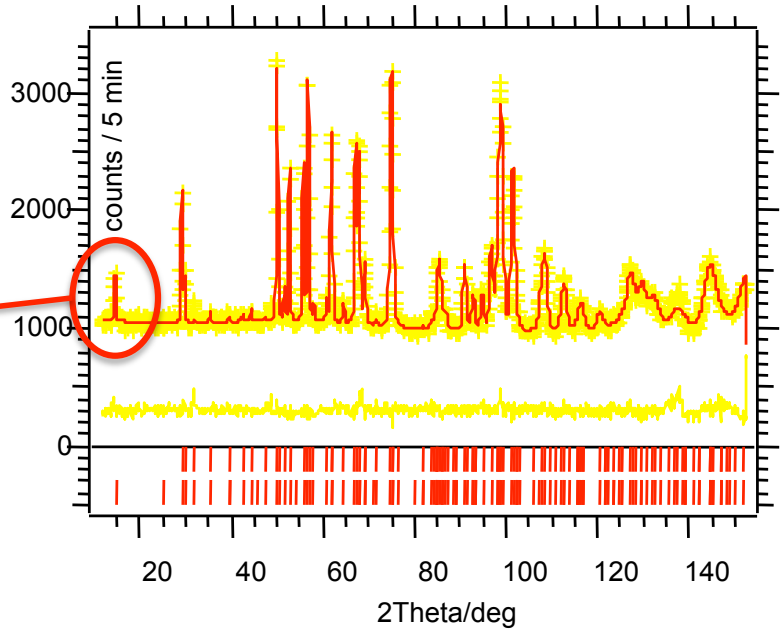
Crystallisation

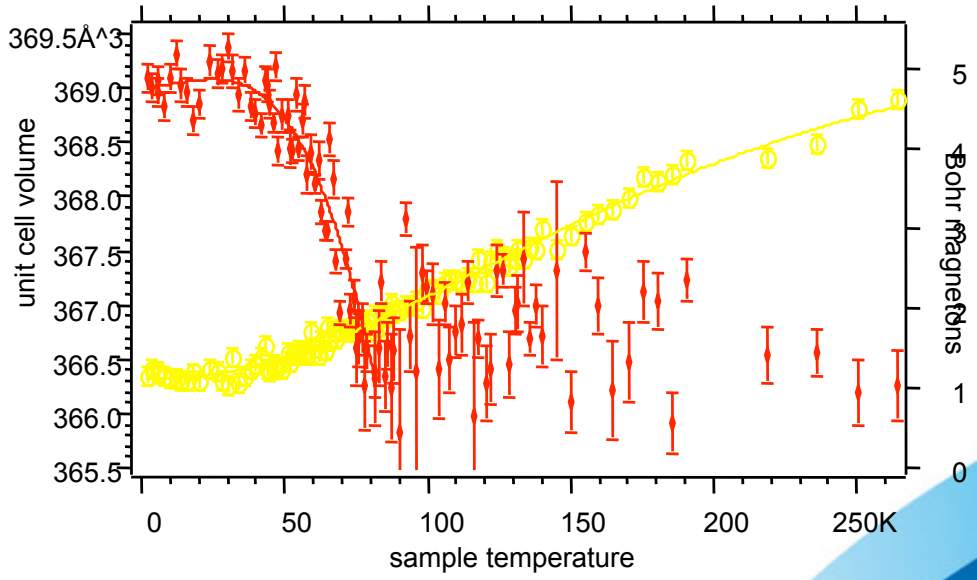


- *in situ* exploration of the phase diagram of Y-Fe RT to 600 °C
- observation of hitherto unknown, metastable phase YFe
- kinetics of phase transitions
- Final product Laves-phase YFe_2

Magnetic phase transitions

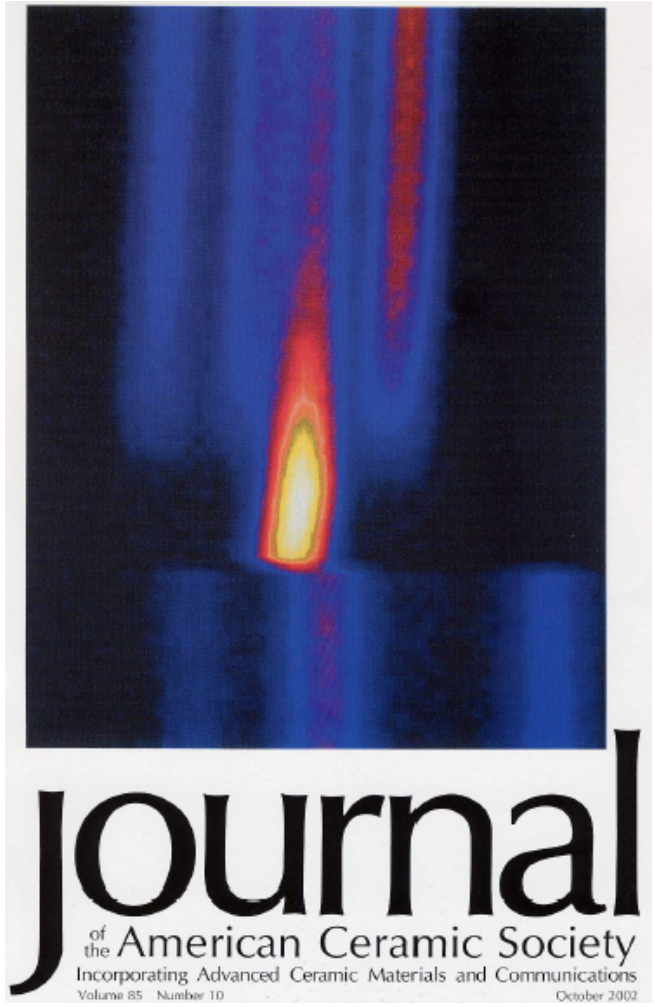






Identify T_{mag}
Get order parameter
Relate structure to magnetic properties

Self-propagating high-T synthesis



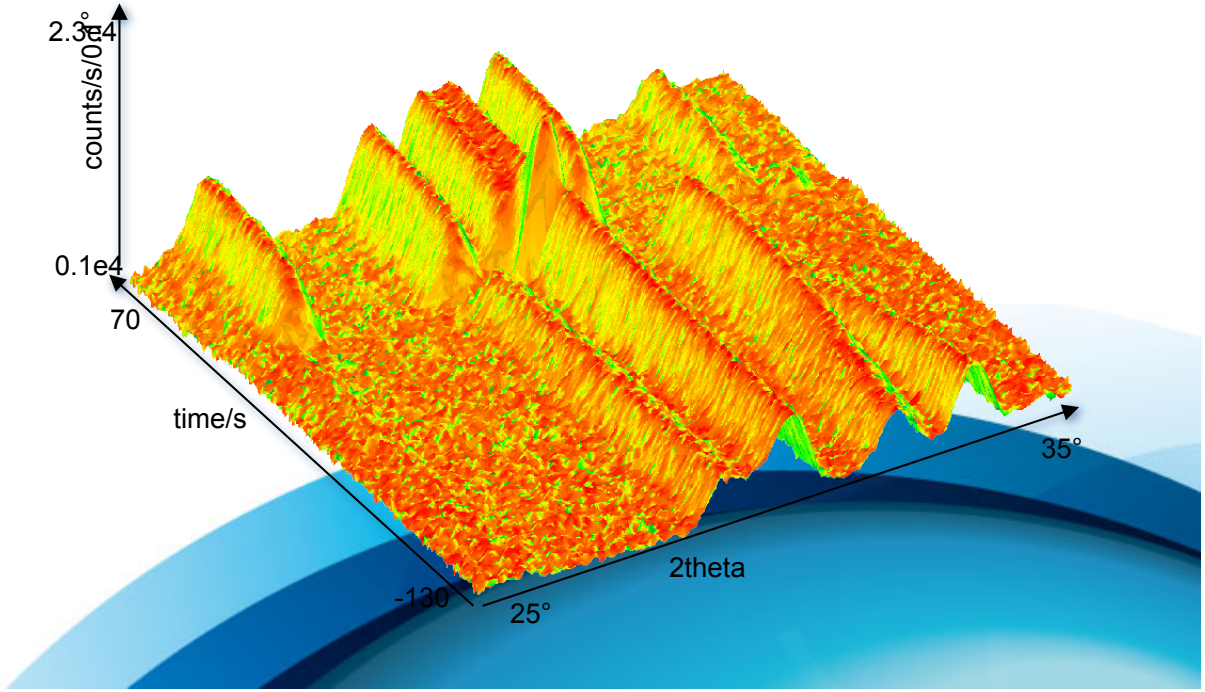
D.P.Riley et al. *J. Am. Ceramic. Soc.* 2002, 2417-2424.

Ti_3SiC_2 made by hot isostatic pressing is expensive

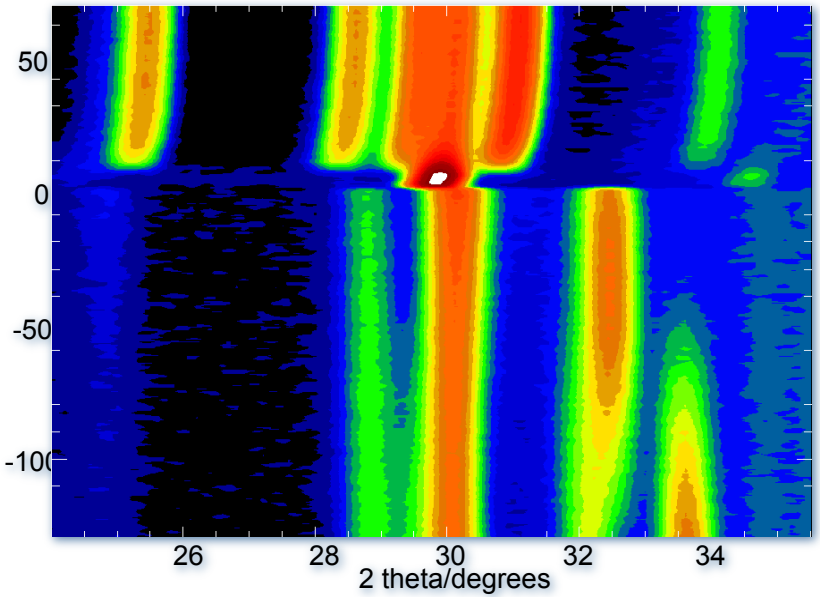
In-situ investigation of thermal explosion synthesis (TES)

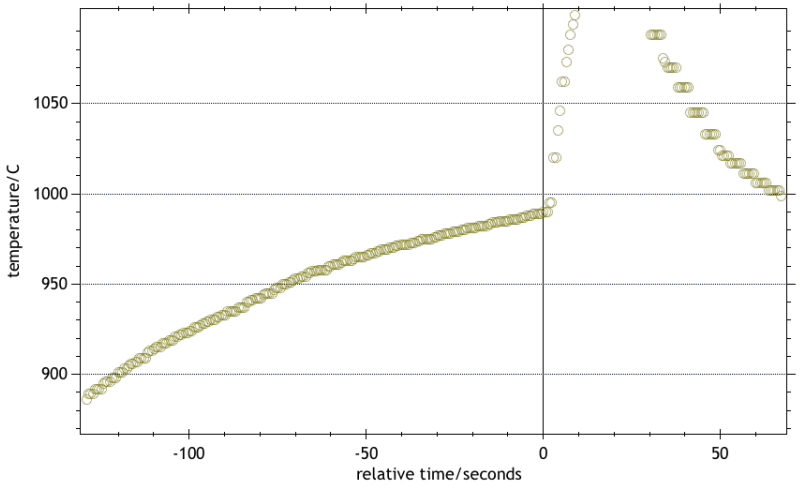
Initiate by heating from 850-1050 °C at 100 °C/ min

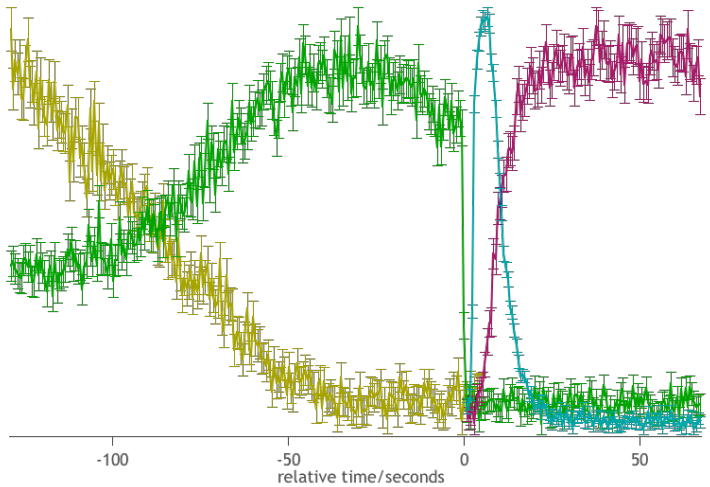
Acquisition time 500 ms (300 ms deadtime)



Self-propagating high-T synthesis







α→βTi at 870°C

TiC_x growth

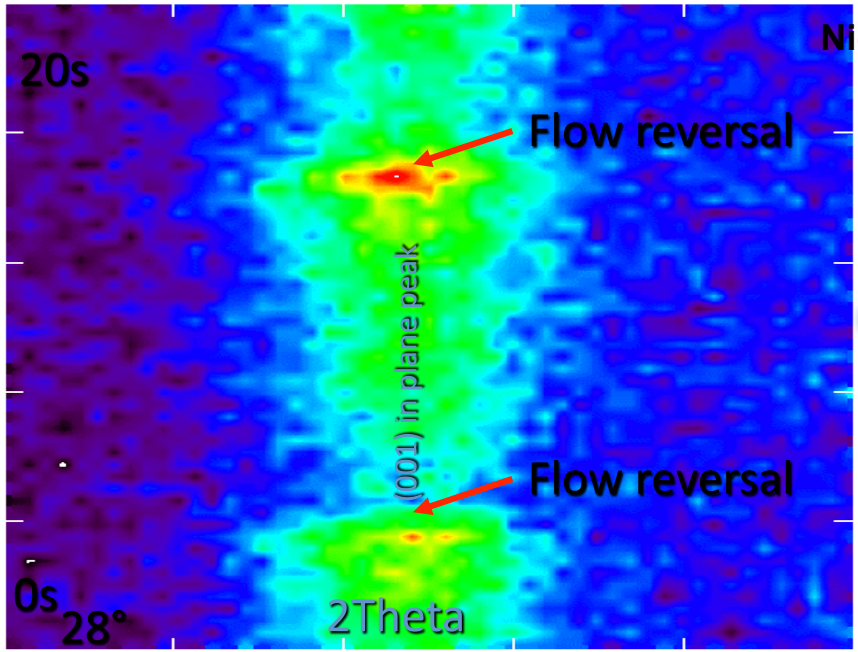
Ignition + melting T ↑<2000°C

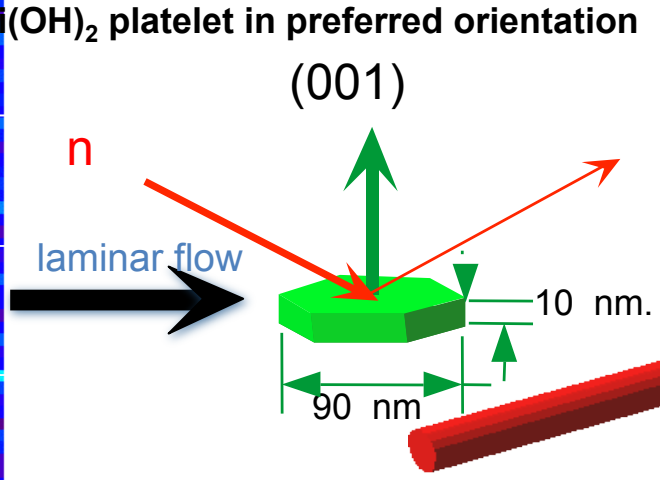
Si substituted TiC formed

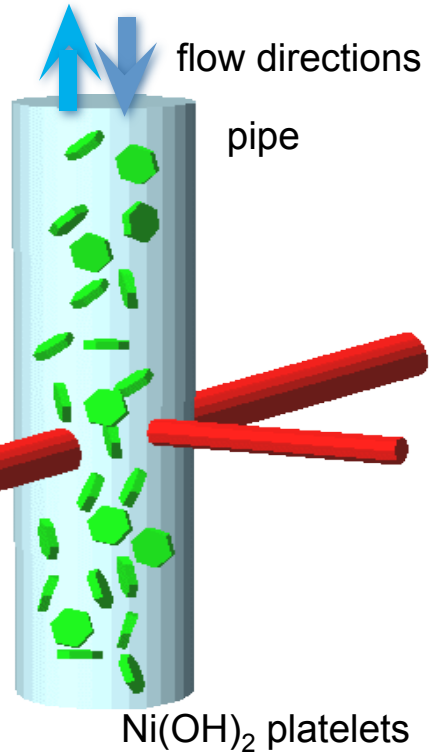
Ti_3SiC_2 precipitates after 5s

Complete after further 5s

Rheology







Rennie, Clarke, Brown on D20 at ILL
Flow properties of platelets in D_2O / NaCl dispersion
Stroboscopic measurement
17 cycles, 54 time slices (390ms)
In-plane peak shows degree of orientation

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Current neutron landscape

OPAL - Australia

ILL - France

HMI - Germany

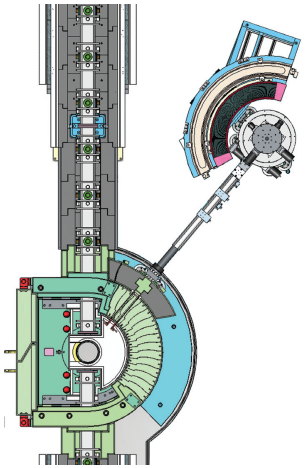
SNS - USA

ISIS - UK

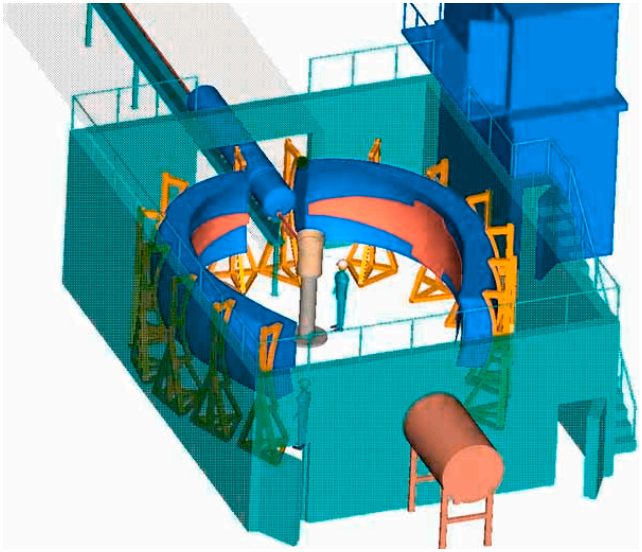
JPARC - Japan

Plus others….

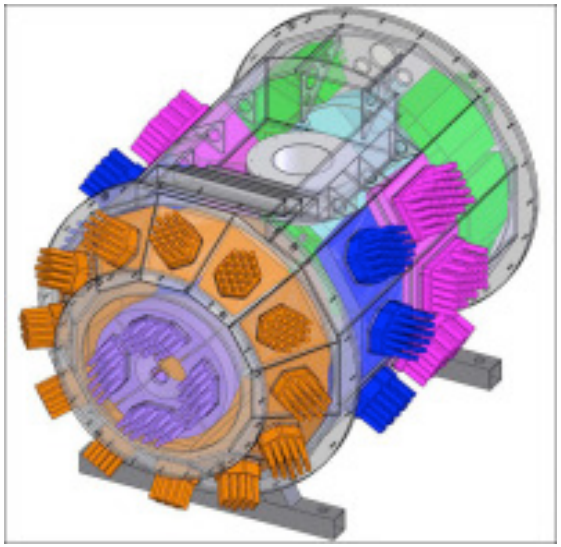
More powerful instruments



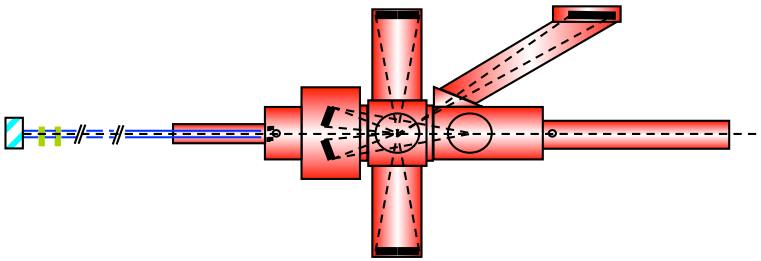
WOMBAT



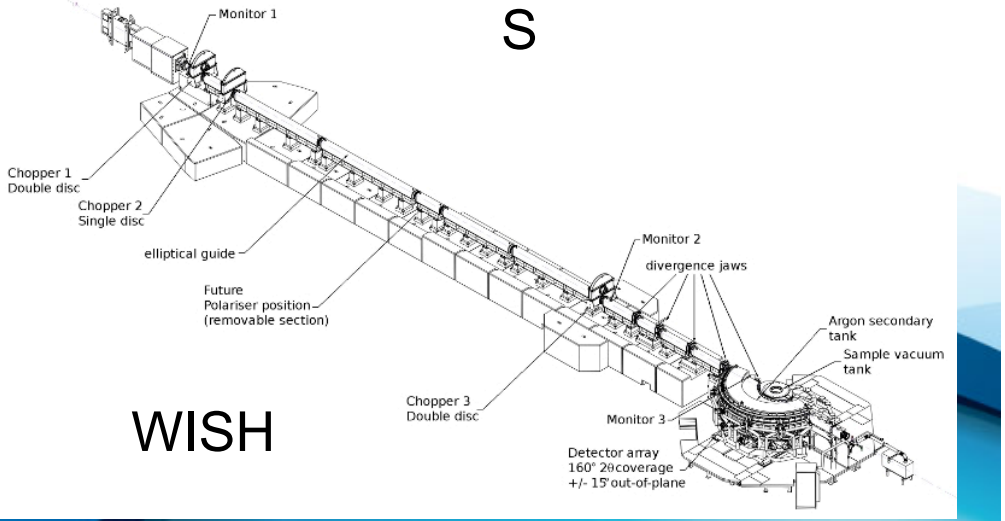
POWGEN3



newPOLARIS



newHRPD



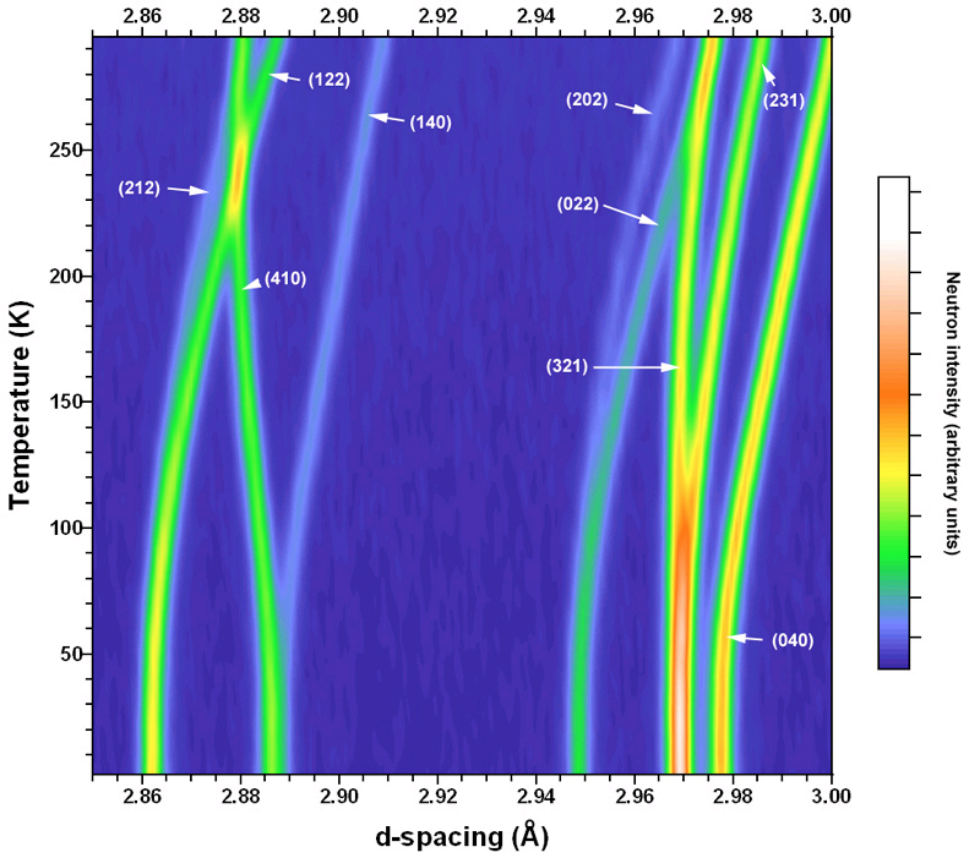
WISH

Where next?

- Specialised instruments for extreme environments (T, P, H)
- Faster data collection
- Complex sample environments
- More than just diffraction: combined methods

- Linking time-stamped detection in detector technology to sample environment control and experiment optimisation.
- Intelligent / semi-intelligent instrument control software

Old adage: bigger, better, faster, more!



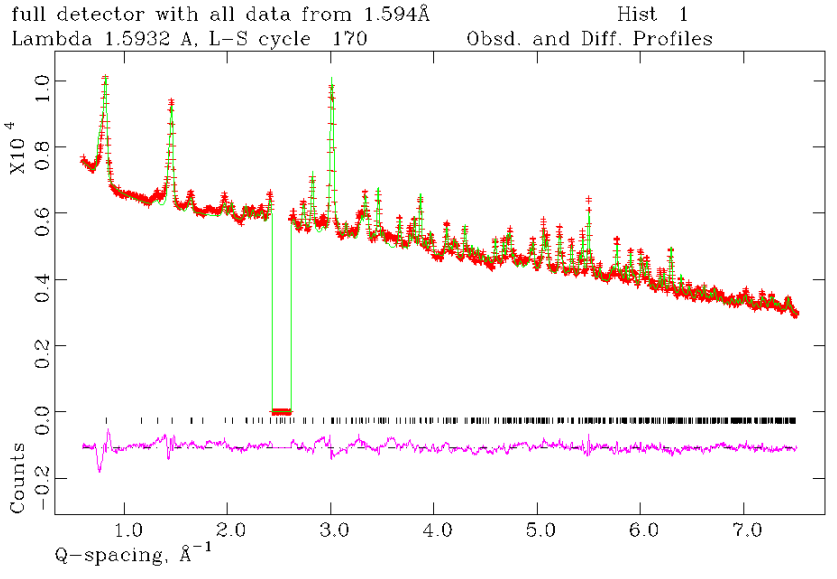
My Interest: hydrogenous materials

- Hydrogen is the most abundant element in the Universe
- Many uses

  Hydrates, geomaterials, zeolites, ferroelectrics, SOFCs, proton conductors, hydrogen storage, MOFs, molecular materials and proton transfer etc...

Problems?

- Incoherent scattering from Hydrogen
- Low incident neutron fluxes
- Low detector efficiency



Solutions / work arounds

- Deuterate
- Use single crystals
- Use other techniques: PXD, SXD, NMR, Raman

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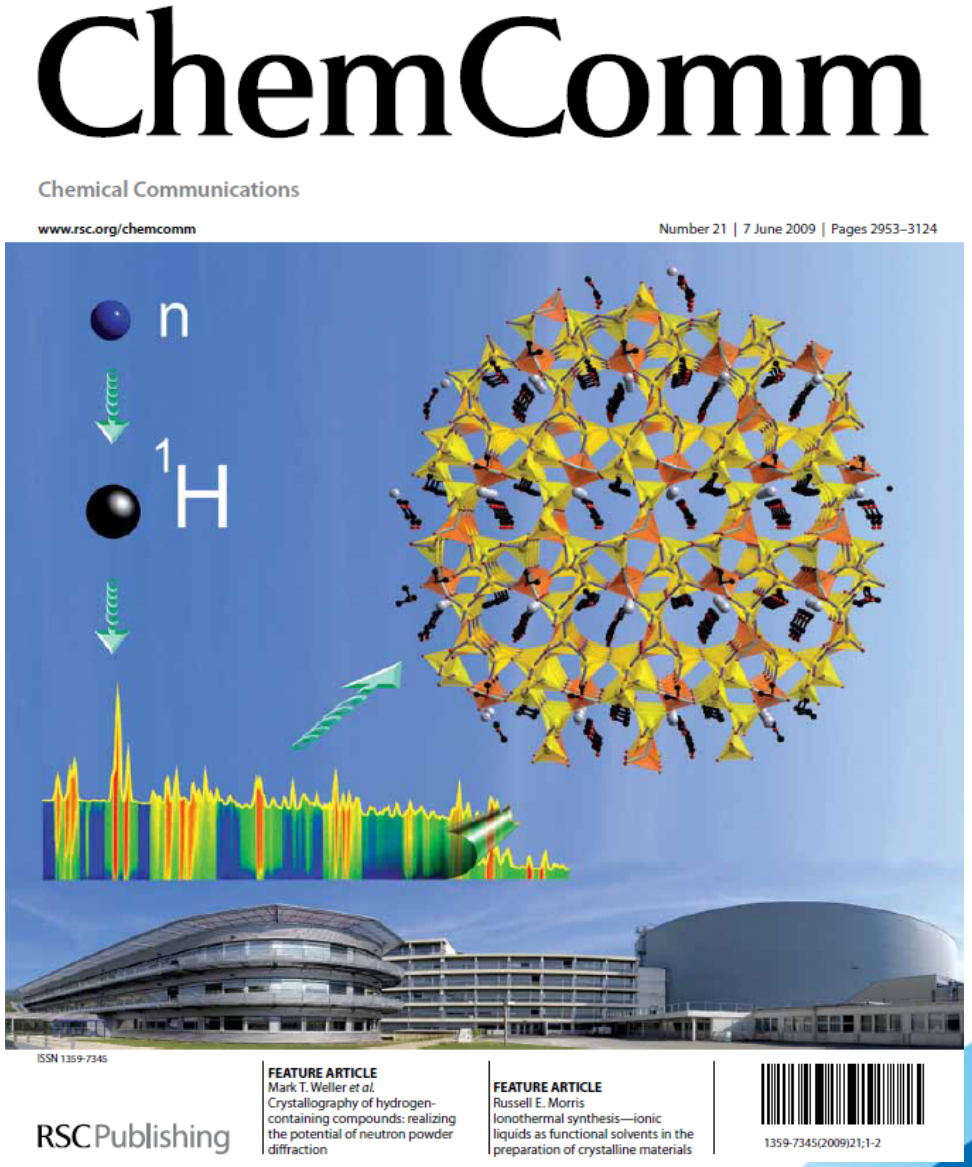
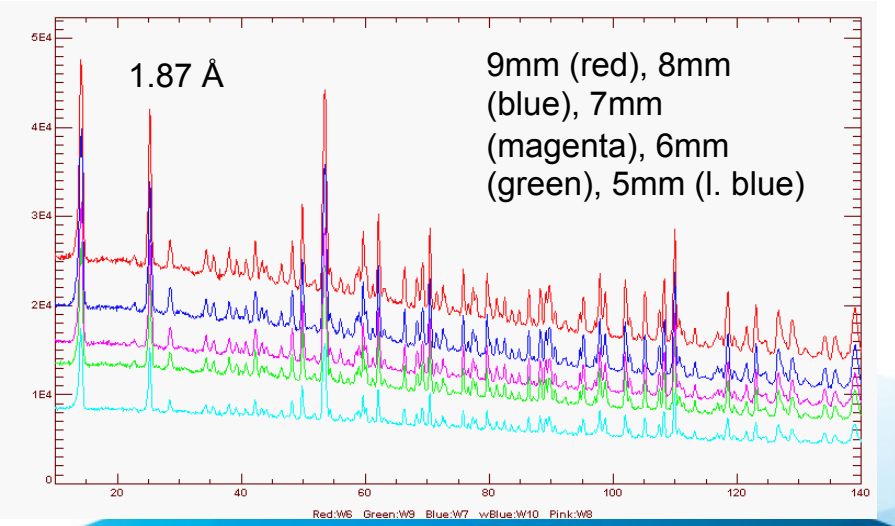
Groundwork 2007-2009



- Sample size
- H content: up to 70 at.%
- Instrument at ILL
- Counting time
- H type: ionic, covalent
- Data collection strategies



P. F. Henry, M. T. Weller, C. C. Wilson. *J. Appl. Cryst.* 2009, **42(6)**, 1176-1188

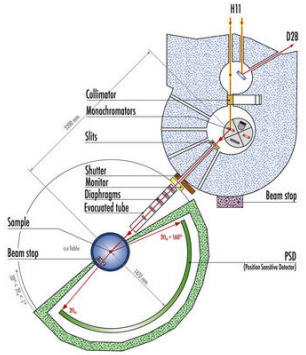
M.T. Weller, P.F. Henry, V.P. Ting, C.C. Wilson. *Chem. Commun.* 2009, 2973-2989

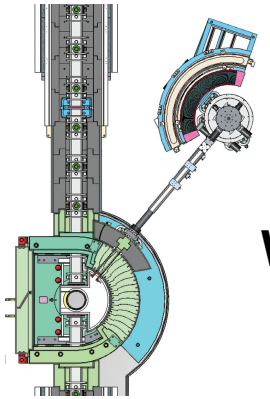
Instrument characteristics

- High incident flux
- Large area detectors
- Low background
- Medium to high resolution ($\Delta d/d < 5 \times 10^{-3}$)
- Stable detector to high count rates
- Many incident wavelengths to access different d-ranges
- Efficient beam transport to sample

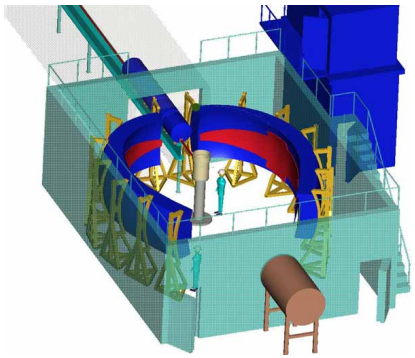
→ **Reproducibility, fast counting, flexibility**

D20

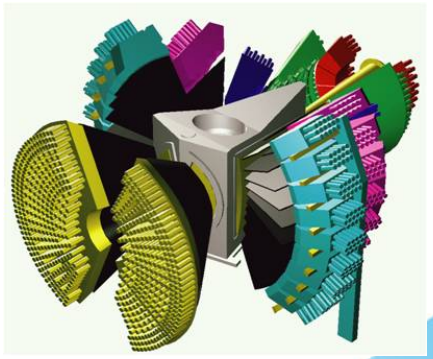




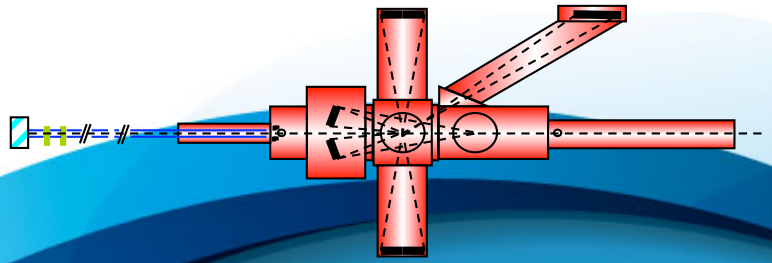
WOMBAT



POWGEN

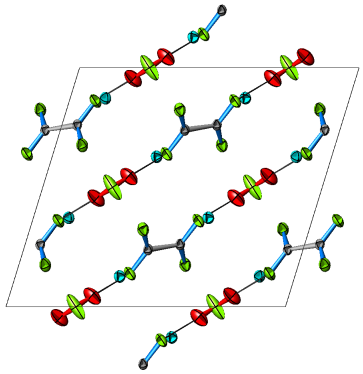


GEM



newHRPD

Examples of published work



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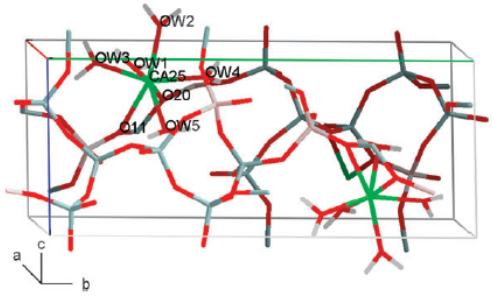

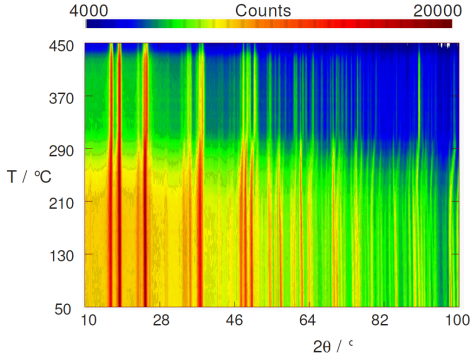

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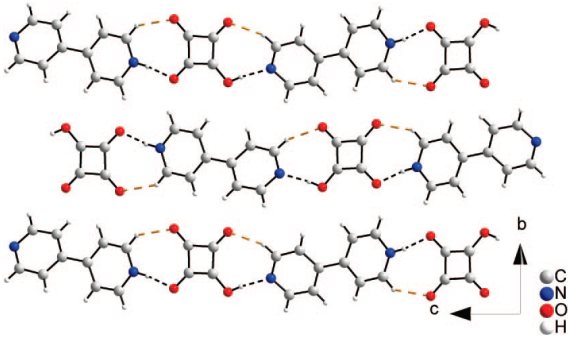

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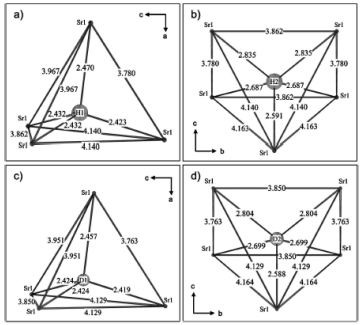

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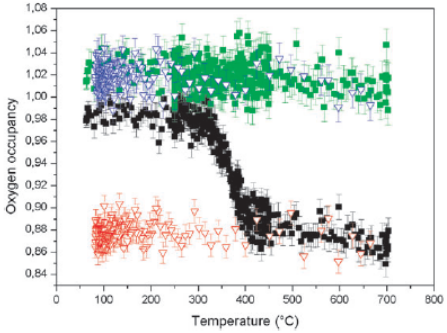

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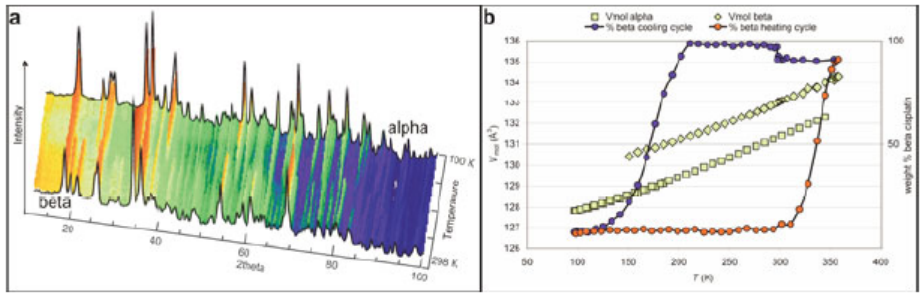

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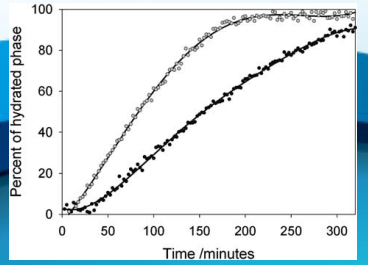

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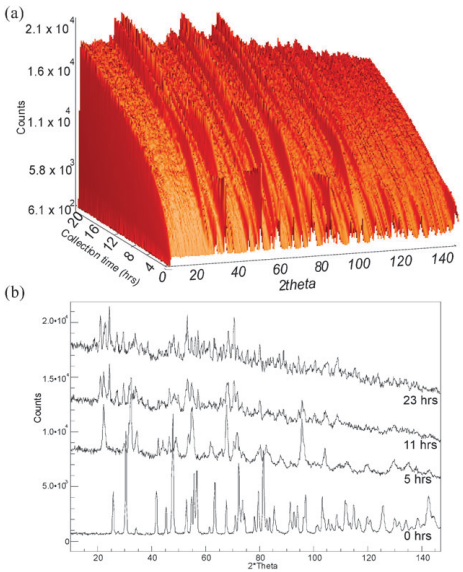
Sample environment development



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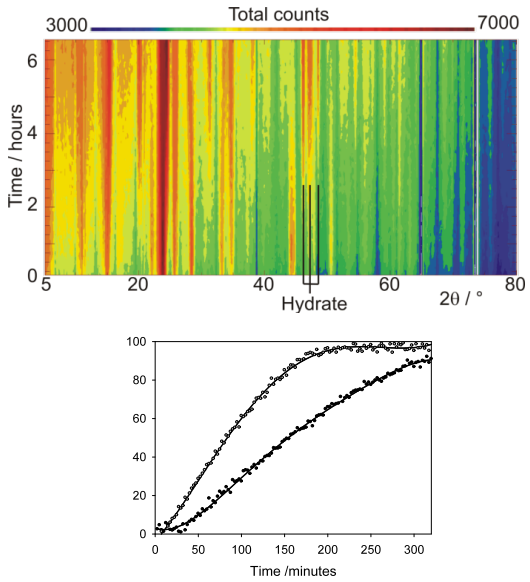

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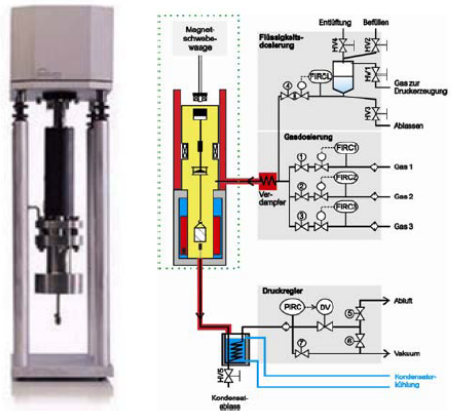
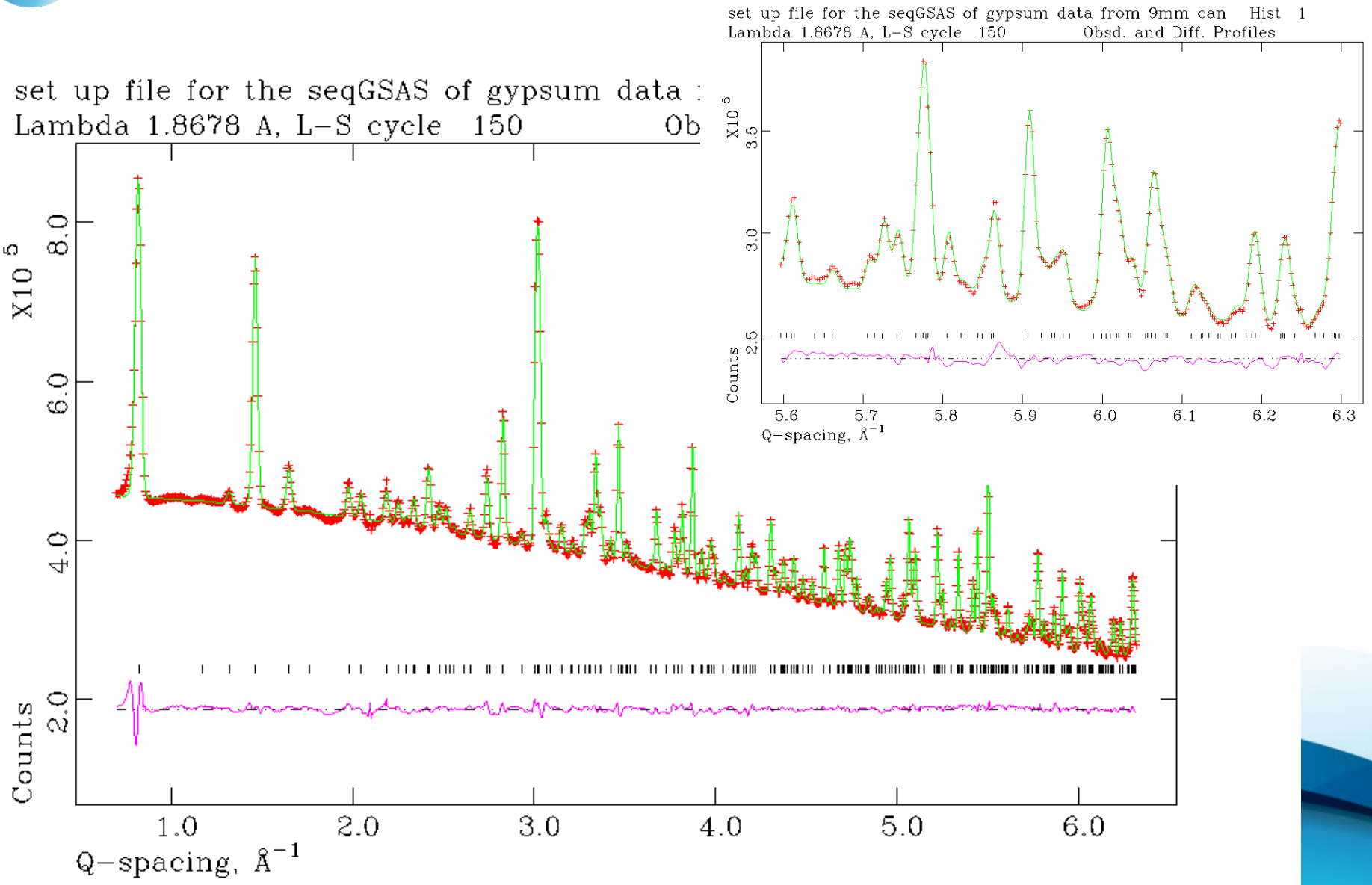
Requirement: dedicated sample environments that allow users to perform experiments *in-situ* at neutron facitilites easily – i.e. Based on-site with appropriate back-up and characterisation facilities that match laboratory and / or working conditions.

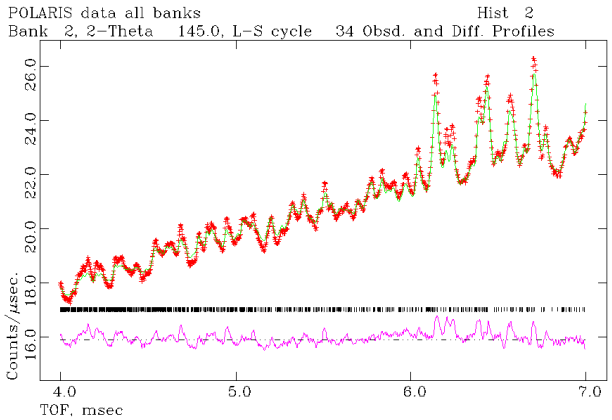
- Bulk humidity cell
- Gas flow rigs
- Pressure cells
- TGA with mass spectroscopy
- Reaction chambers

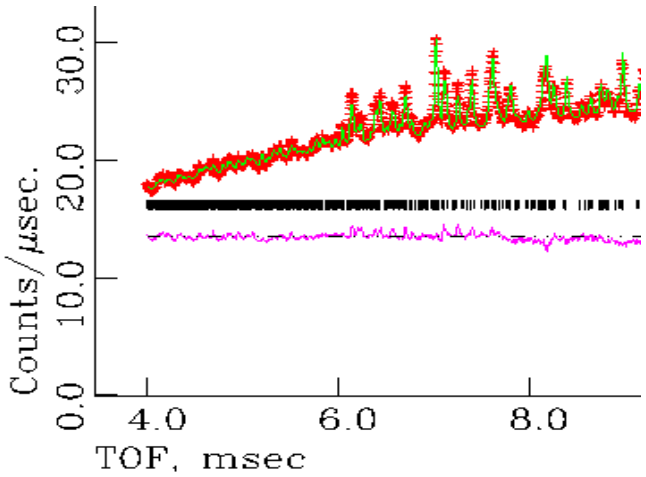


Monochromatic v t-o-f data



σ_{inc} Hydrogen for t-o-f instruments





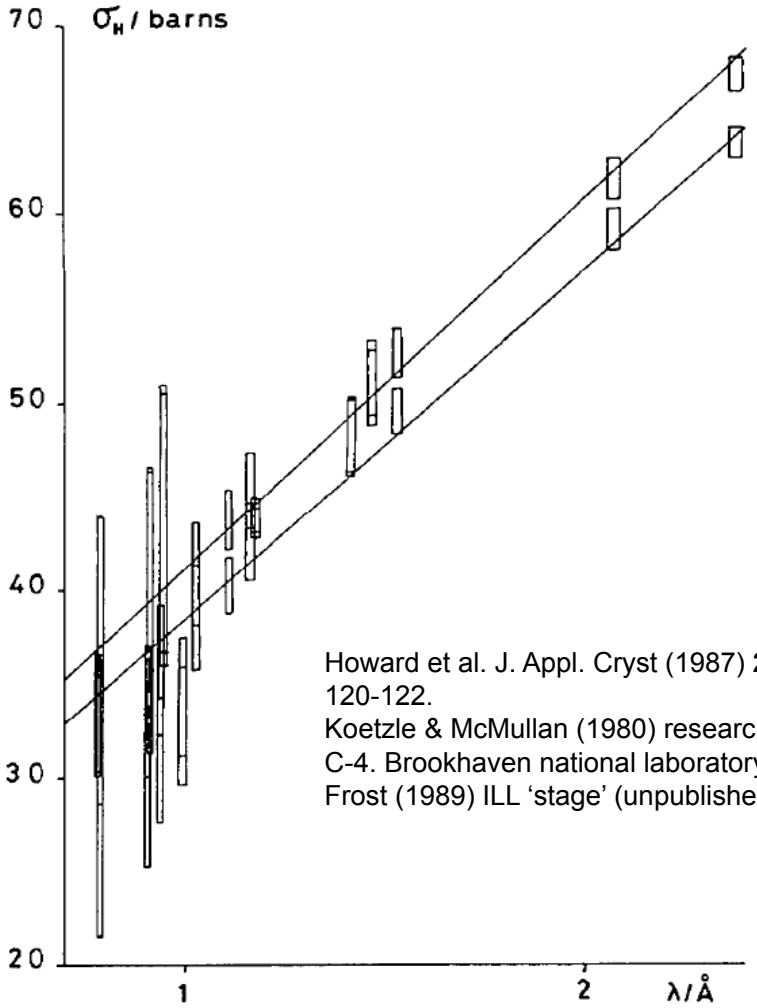


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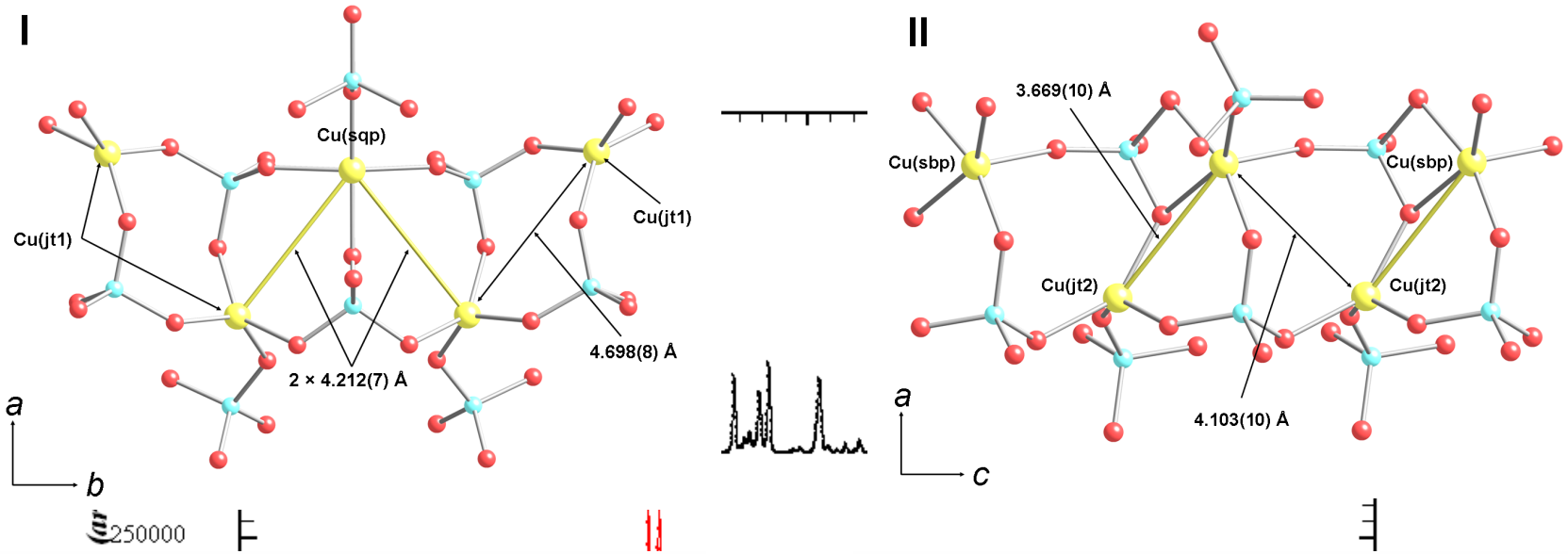
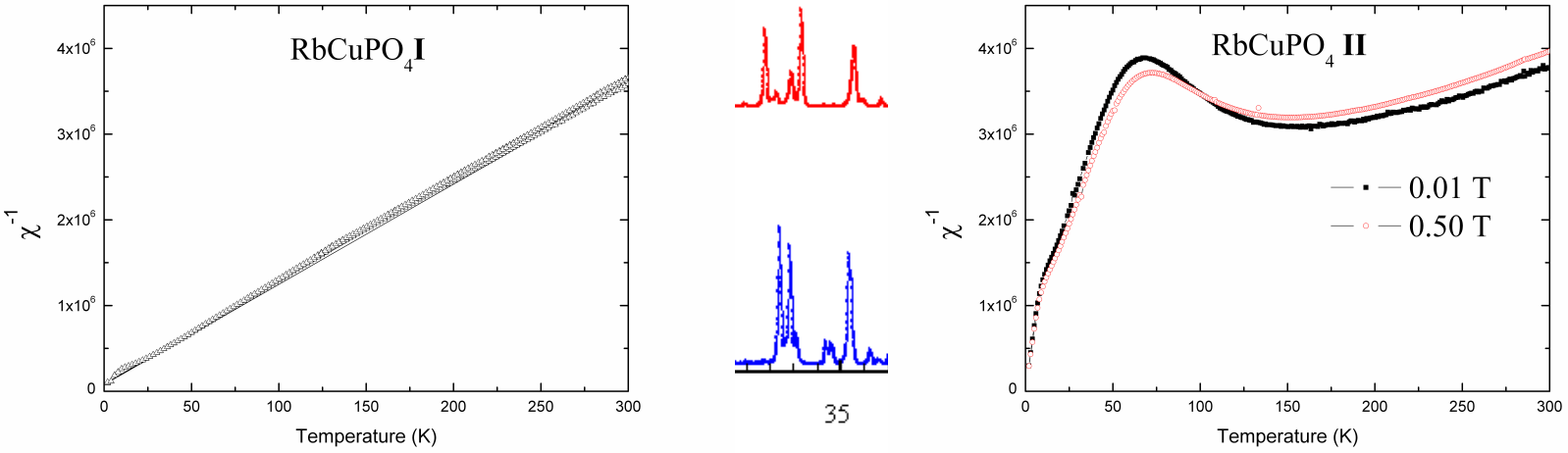
Fig. 1. Plot of σ_H *vs* λ for the Re crystal. Error bars on points incorporate e.s.d.'s in both σ_H and λ.

Transition metal phosphates





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Conclusions

- Powder diffraction has changed markedly over the last 15 years
  - New and upgraded instruments
  - New sources
  - New sample environment
  - New scientific focus
- Powder diffraction remains the cornerstone of materials characterisation
- New instrument capabilities will expand and drive the user community
- ESS will be a large part of that future!