Sample environment development and “sample” environment

Paul Henry

Instrument Scientist – ISIS/STFC, UK

Adj. Prof. in Neutron Scattering – CTH, Göteborg, Sweden

SoNS Neutron School
Erice, 4-13th July 2018

Outline

- Specialised sample environments for *in situ* chemistry applications
- “sample” environment – the pitfalls and opportunities with H containing materials
- Applying for beamtime
- Examples to illustrate differences between neutron and X-ray scattering

Specialised sample environments for *in situ* chemistry

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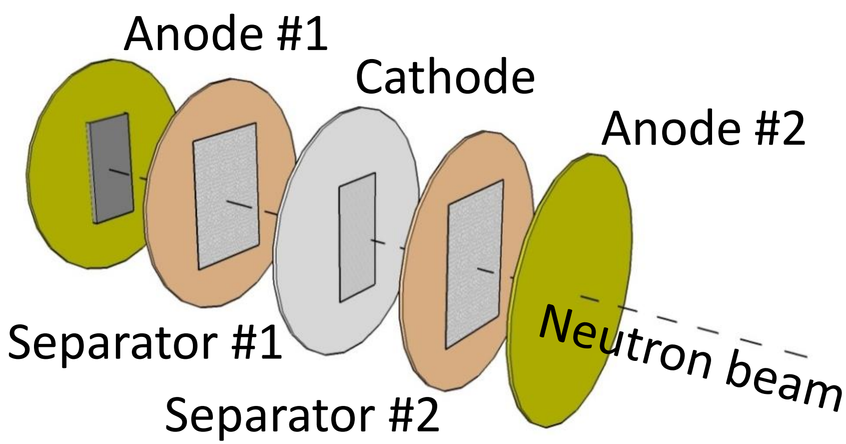
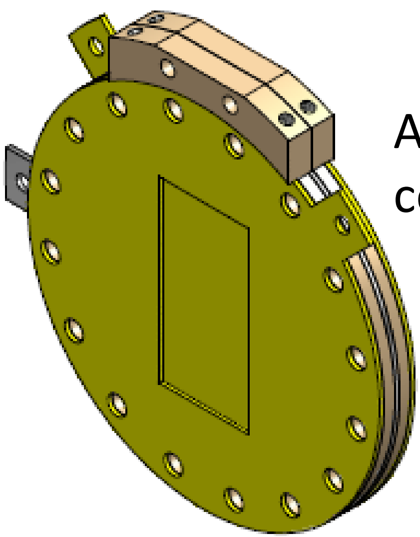
In situ battery cells

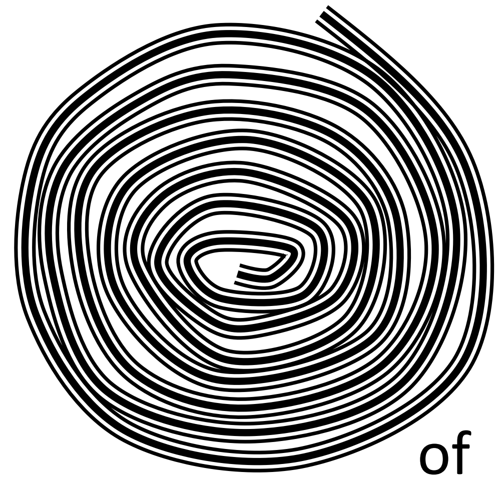
- Modular 'coin cell' design, collaboration with Sheffield and Stockholm Universities.



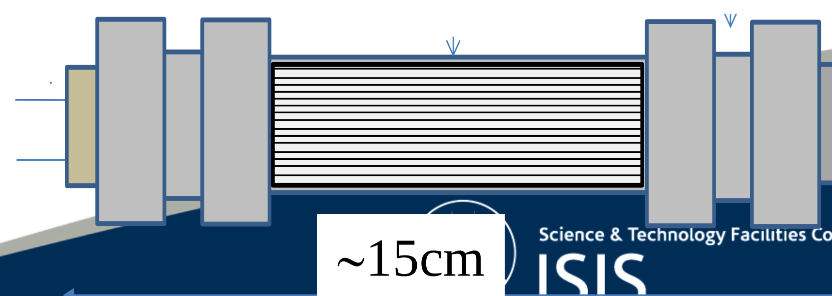


Assembled cell

- Wound 'Swiss Roll' design, collaboration with Oxford and Uppsala Universities.

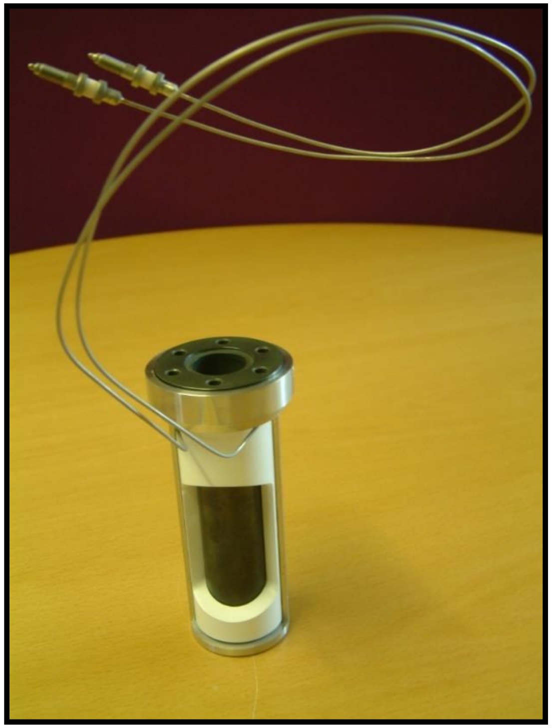


Wound laminate of cathode, anode, current collectors and porous separator.

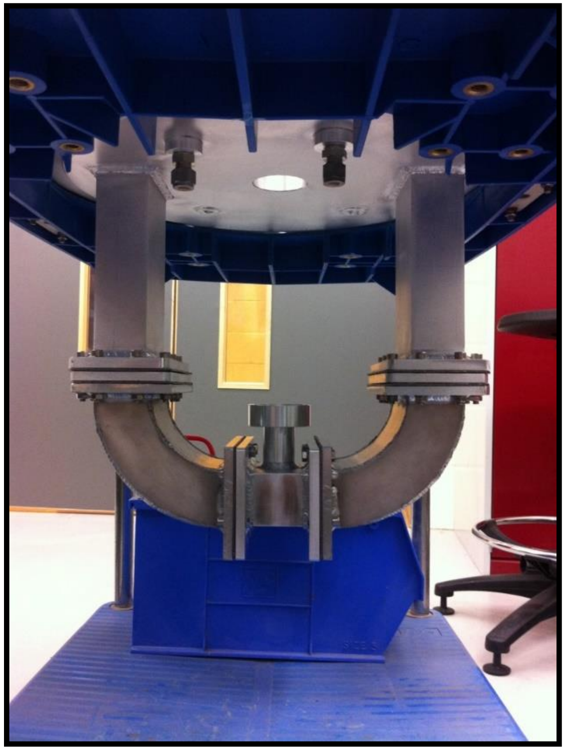


In situ chemical reaction cells

A number of the development projects have been designed to exploit the high countrate of GEM and Polaris to monitor chemical reactions in-situ.....



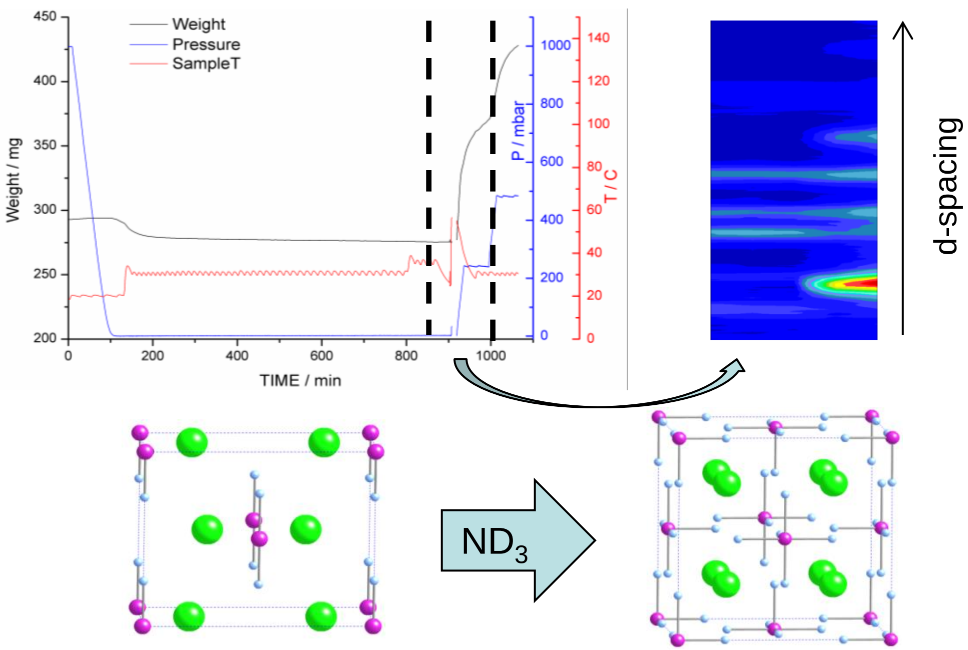
Supercritical hydrothermal cell (Korea+ISIS+Oxford).



In-situ microwave synthesis (Glasgow+ISIS).

In situ gravimetric analysis

The IGAn enables the mass of a sample to be measured during a chemical process while collecting in-situ neutron powder diffraction data. The temperature and gas environment around the sample can be controlled remotely.



Temperature range: -170 to 480°C
Pressure range: 0 to 20 bar
Example gases: H_2/D_2, NH_3/ND_3, O_2, CO_2...

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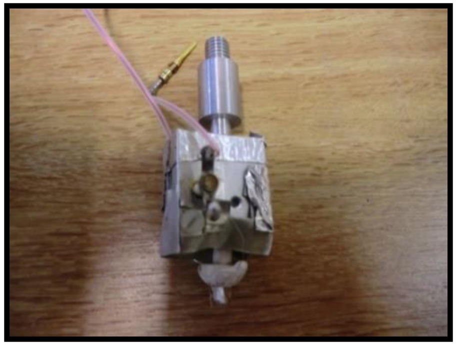
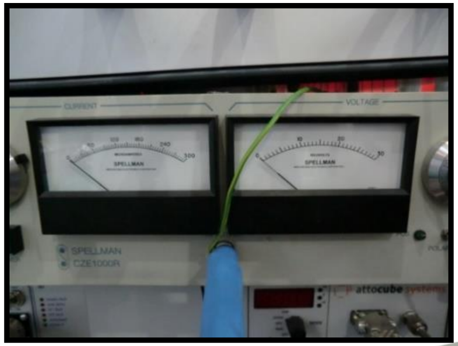
In situ electric fields

Centrestick to allow diffraction studies to be performed under applied electric field.....

- $4 \leq T(\mathrm{K}) \leq 500$K (approx.)
- Maximum 30kV.
- Switchable polarity
- Current limiter.
- Future development of computer control and waveform generator.





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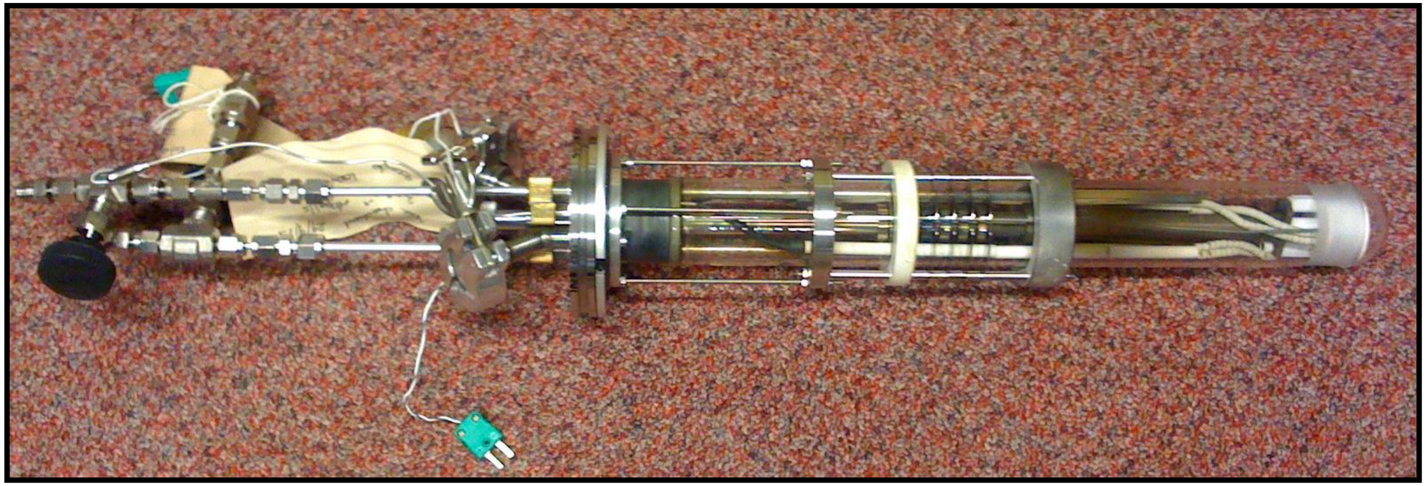
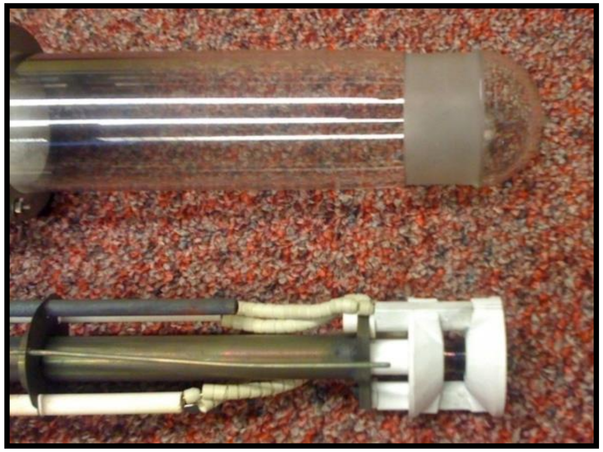
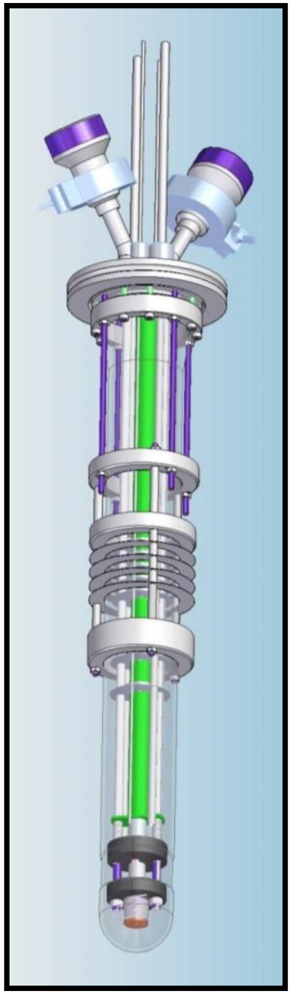
In situ conductivity measurements

In-situ cell to allow the simultaneous monitoring of electronic/ionic conductivity during powder diffraction measurements up to high temperatures (~1200K).







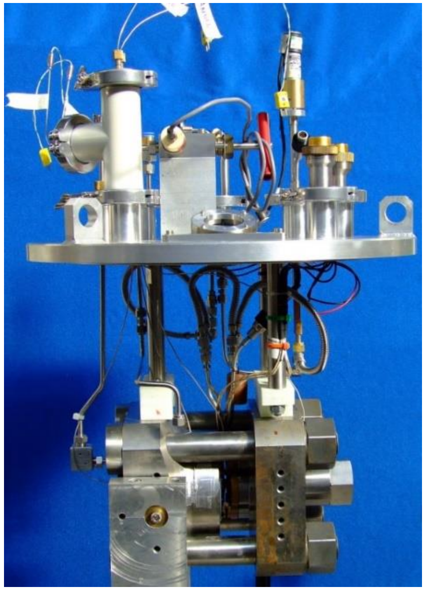
Extension of this project to allow measurement of conductivity and Seebeck coefficient for diffraction studies of thermoelectric materials →

High pressure developments

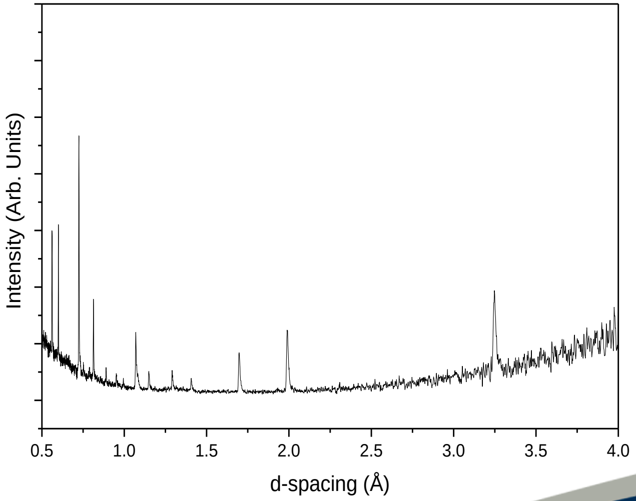
Current high pressure programme uses versions of the Paris-Edinburgh cell (~80mm^3, p_{max}~10GPa).

Programme of developments to extend temperature range (high and low) accessible at high pressures.

Also exploring the use of Diamond Anvil Cell (DAC) technology - potential to reach ~50GPa.



Demonstration using <0.1 mm^3 of Ge within a large DAC.....

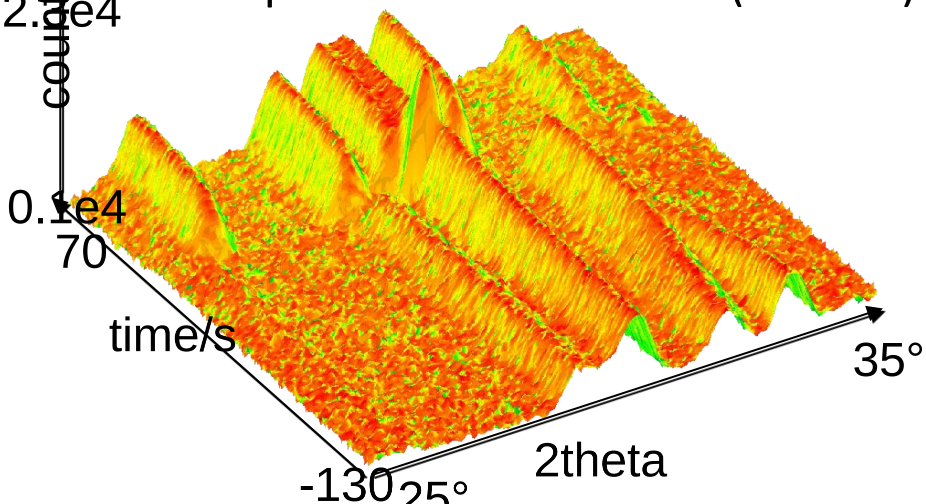


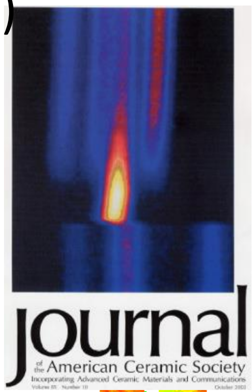
Collaboration with :

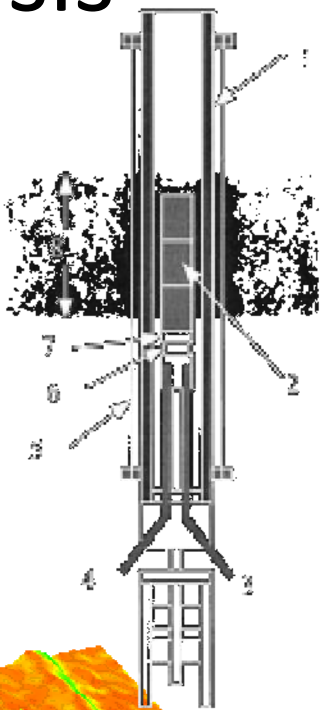
- CSEC, Edinburgh. Univ.
- Geophysical Lab., Washington.
- Université P. et M. Curie, Paris
- ESS, Lund

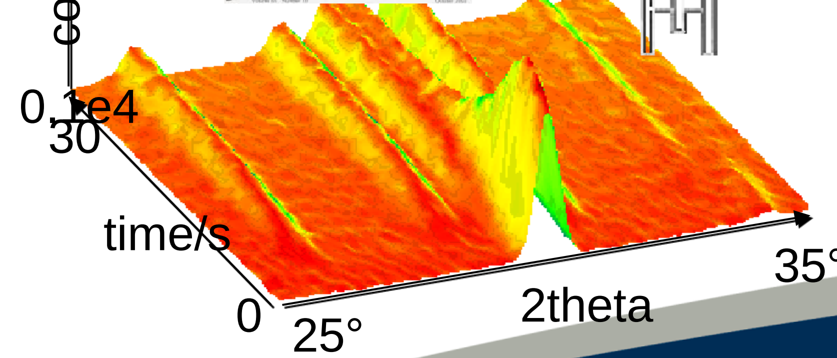
Self-propagating high T synthesis

- Titanium silicon carbide Ti_3SiC_2
  - Hot isostatic pressing expensive
- Self-propagating High-temperature Synthesis (SHS)
  - here: *Thermal Explosion Synthesis*, *TES*
  - 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)





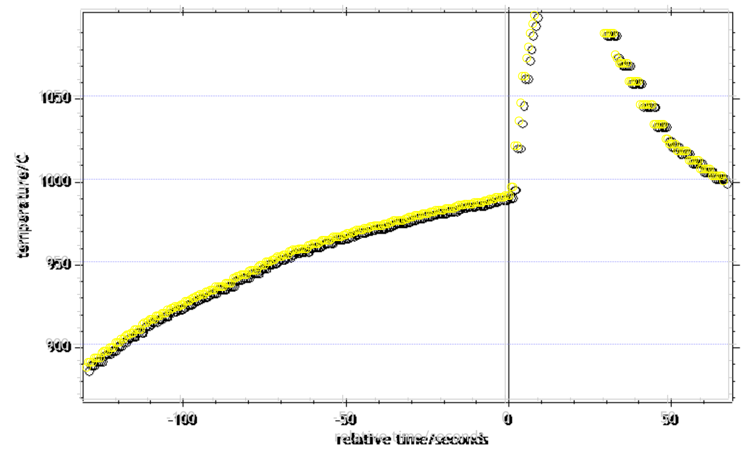


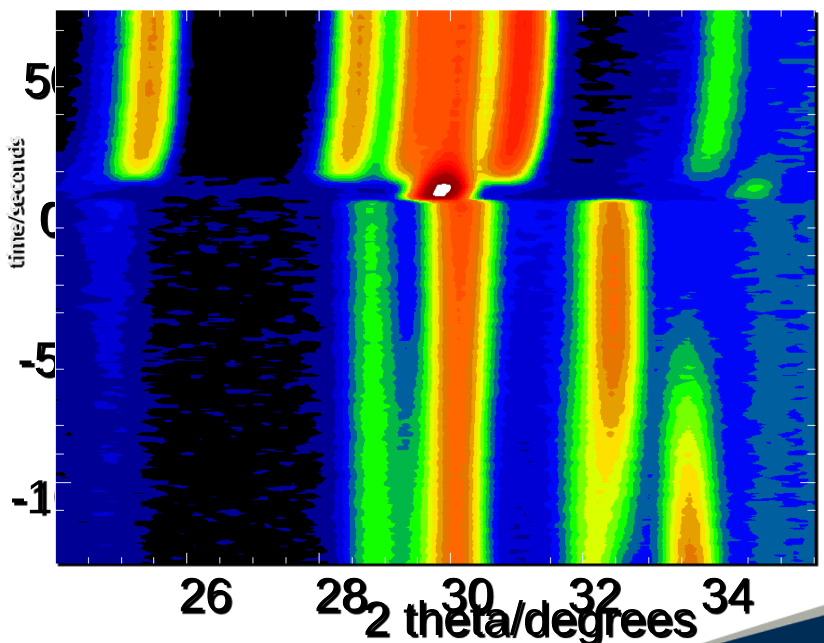


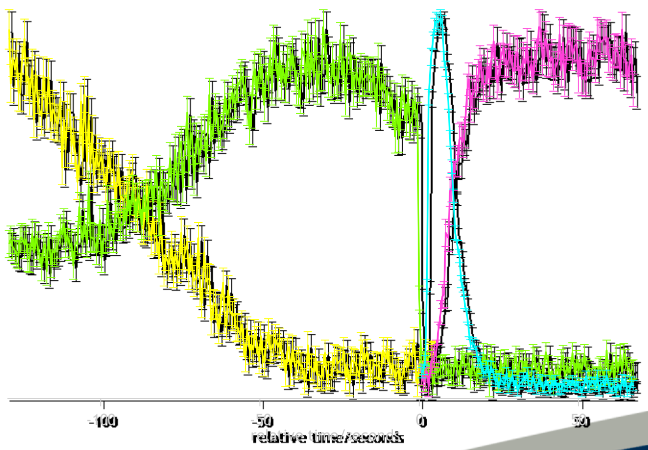
D.P. Riley, E.H. Kisi, T.C. Hansen, A. Hewat, *J. Am. Ceramic Soc.* **85** (2002) 2417-2424.

SHS pre-ignition

- Ti α-β transition
  - starting at 870 C
- Pre-ignition:
  - TiC_x growth during 1 min
- Melting (?) in 0.5 s







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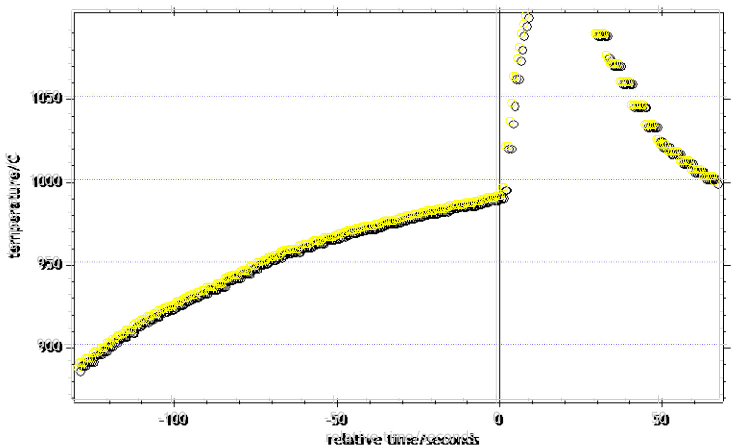
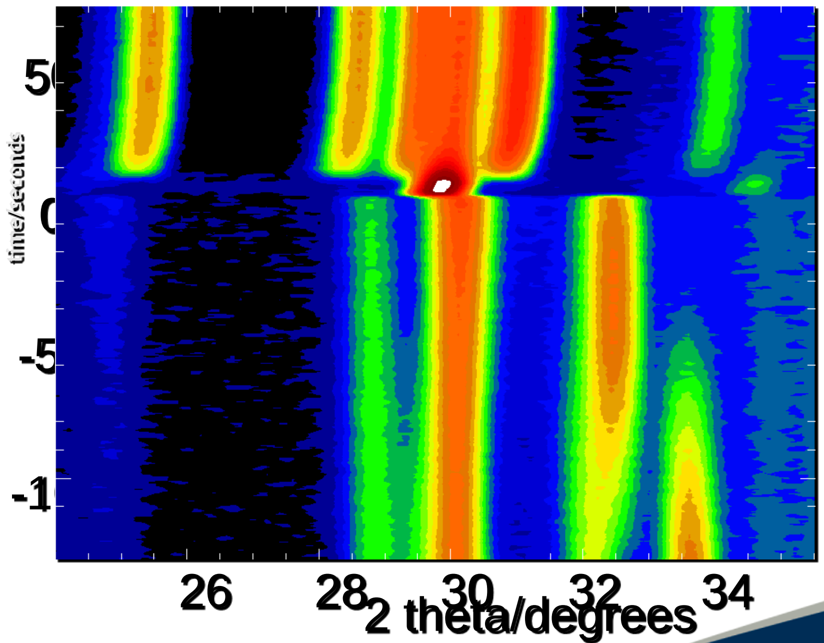
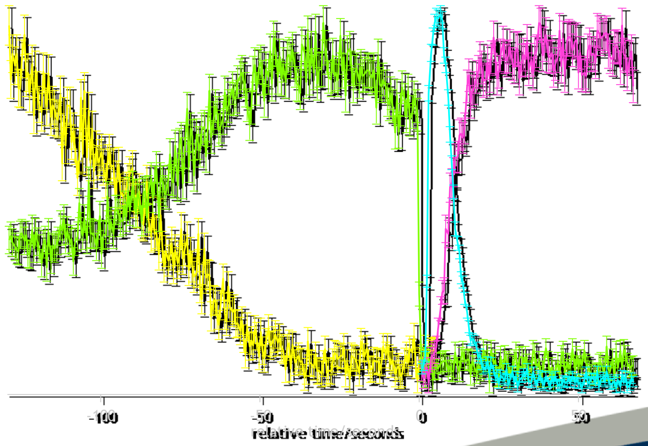
SHS intermediate phase

- Intermediate phase
  - TiC, Si substituted
  - formed in 0.5 s, 2s delay
  - Heating up to 2500 K
  - afterwards decay in 5 s







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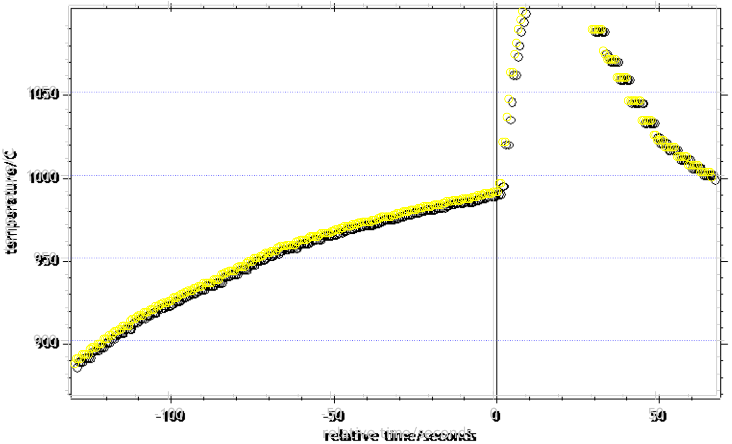
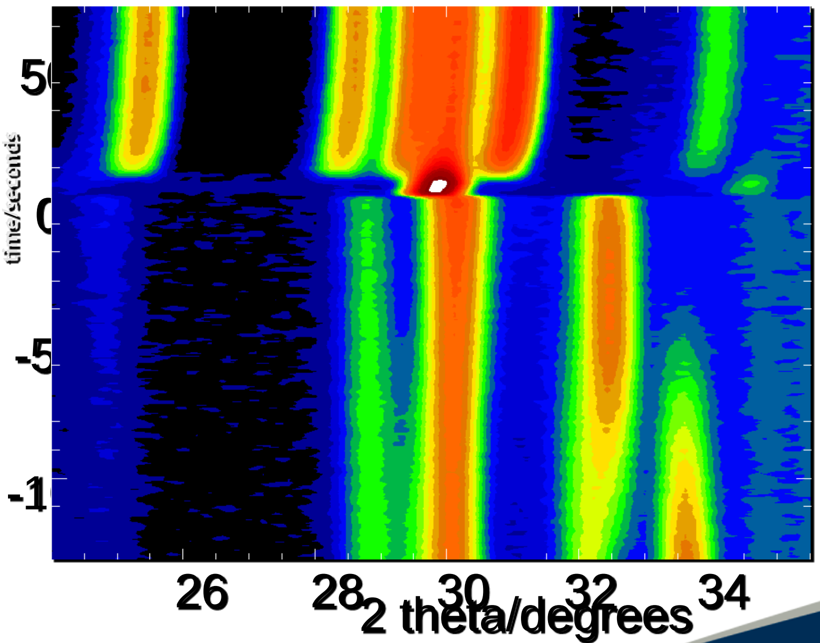
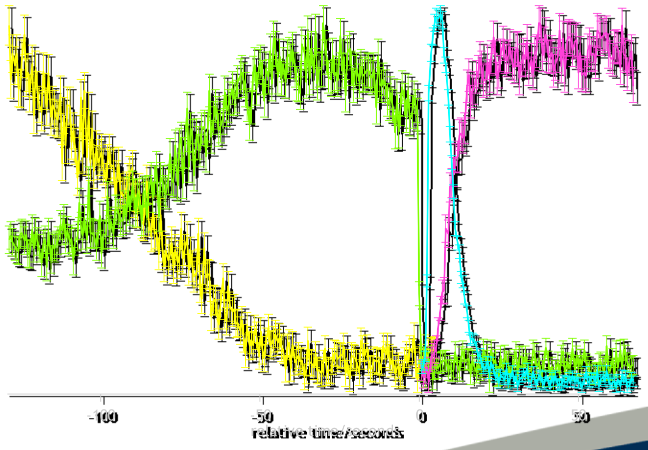
SHS intermediate phase

- Product Ti_3SiC_2
  - starts after 5 s incubation
  - time constant about 5 s

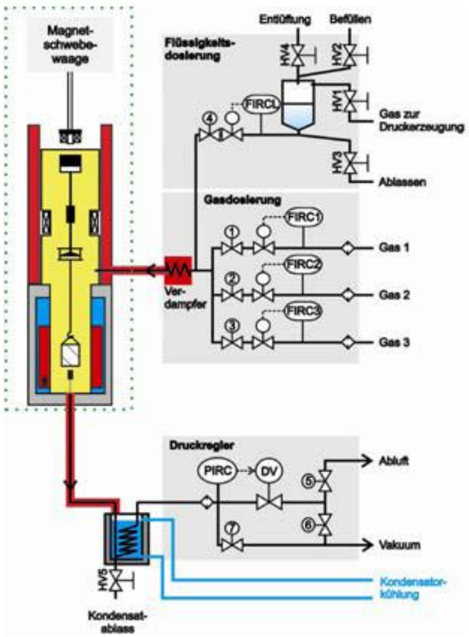






Long term development of sample environment

- Technology transfer with X-ray sources as sample sizes approach those routinely used in X-ray experiments (< 10 mm^3)
- Integrate with data acquisition software
- Event-mode counting the ideal match for in-situ experiments



"sample" environment – the pitfalls and opportunities with H containing materials

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Acknowledgements

University of Glasgow

Centre for Sustainable Chemical Technologies

Universität Leipzig 1409 2009 Alma Mater Lipsiensis

HZB Helmholtz Zentrum Berlin

University of Bath

European Spallation Source

Royal Society of Chemistry

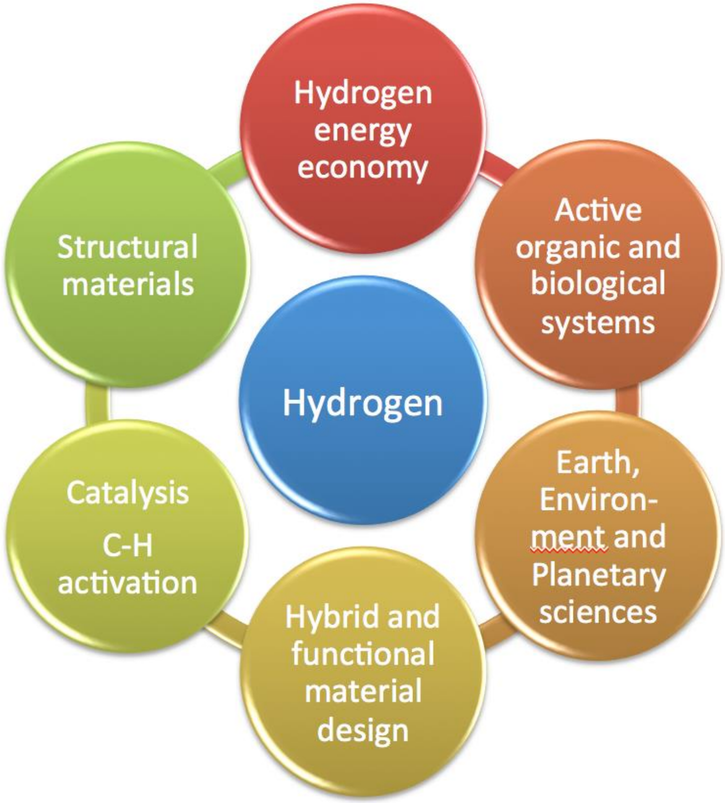
ILL Neutrons for Science

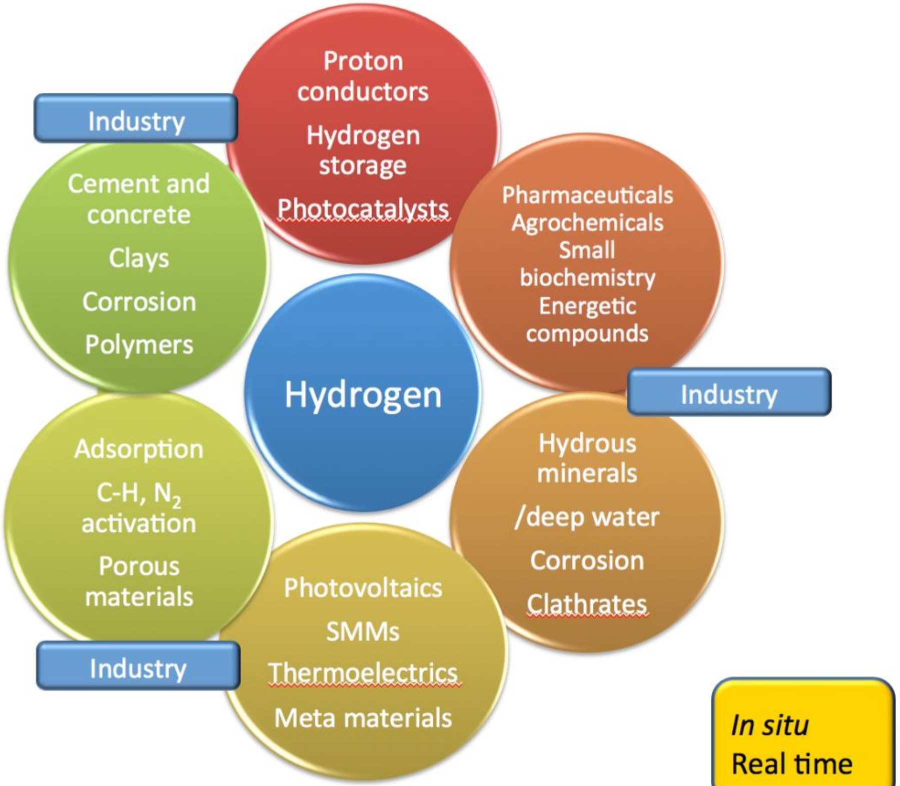
Science & Technology Facilities Council Rutherford Appleton Laboratory

EPSRC Engineering and Physical Sciences Research Council

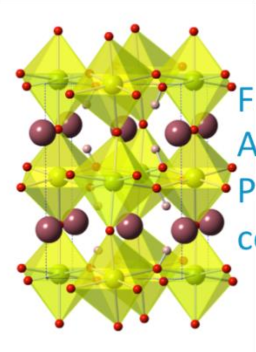
Science & Technology Facilities Council ISIS

Why is hydrogen important?



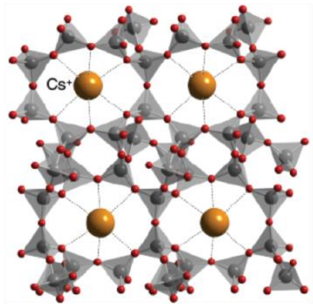


Hydrogen-containing materials feature in nearly all the major global challenges, which is reflected in National Research Council and EU research spending.

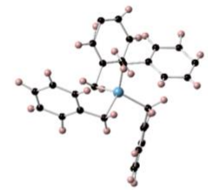


Fuel Cells
Acid salts
Proton conductors

Zeolites/porous frameworks

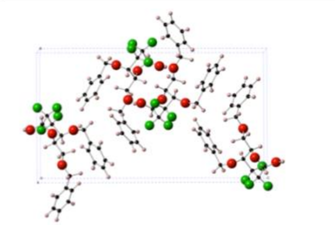


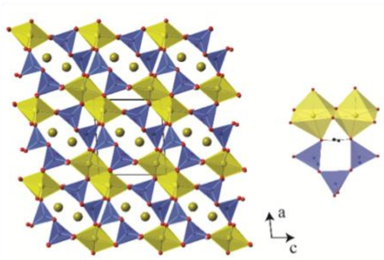
Inorganic ferroelectrics



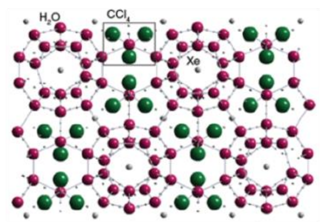
Organometallics

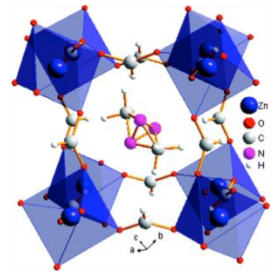
Pharma-/agrochemicals



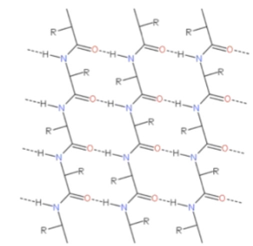


clathrates

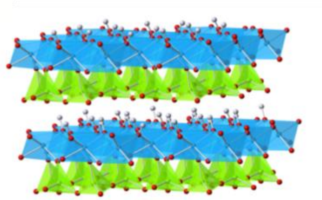


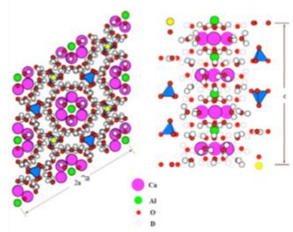


Small biomolecules, sugars, amino acids

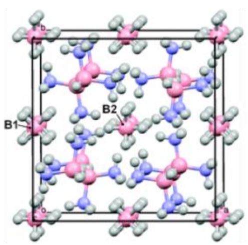


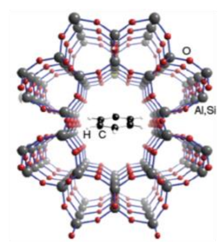
Minerals, deep water





Non-linear optics
Organic PV

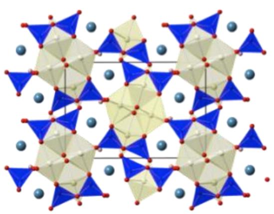




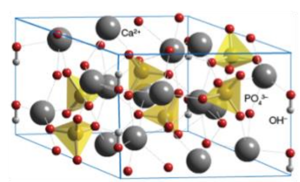
Adsorbates/ separation

Build materials; clays cements,biopolymers

Hydride storage



Magnetic/
M-I materials



biominerals

Also MOFs, ZIFs, flexible polymers, thermoelectrics – rattling organics, proton-shift/colour change meta-materials, etc…

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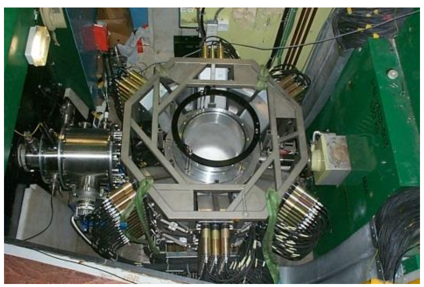
Structural investigation of hydrogenous systems

- Single Crystal X-ray Diffraction (SCXD)

  Excellent for light elements and well defined geometries – e.g. organics, and where H atoms less important or less well-defined

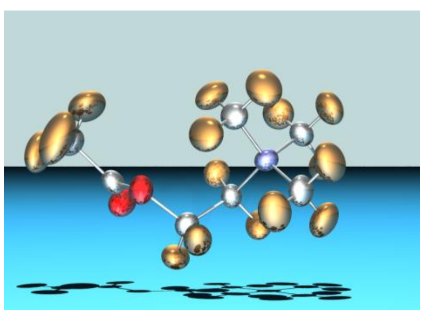
  Less good for heavier atom systems (materials), “unusual” hydrogen bonds (even multi-condition SCXD)



- Single crystal neutron diffraction (SCND)

  Good for H positions in complex crystal structures

  Requirement for large crystals, fairly long counting times, phase transformations can cause problems



- Deuteration and powder neutron diffraction (PND)

  Potentially of wide application

  Often chemically challenging, sometimes incomplete, can alter properties

Scattering properties of H and D

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

+ive v -ive scattering length ✔

Low absorption cross sections ✔

Coherent scattering cross sections ✔

^{1}H has large σ_{inc} ➔ background ✗

^{2}H low in abundance ➔ expensive ✗

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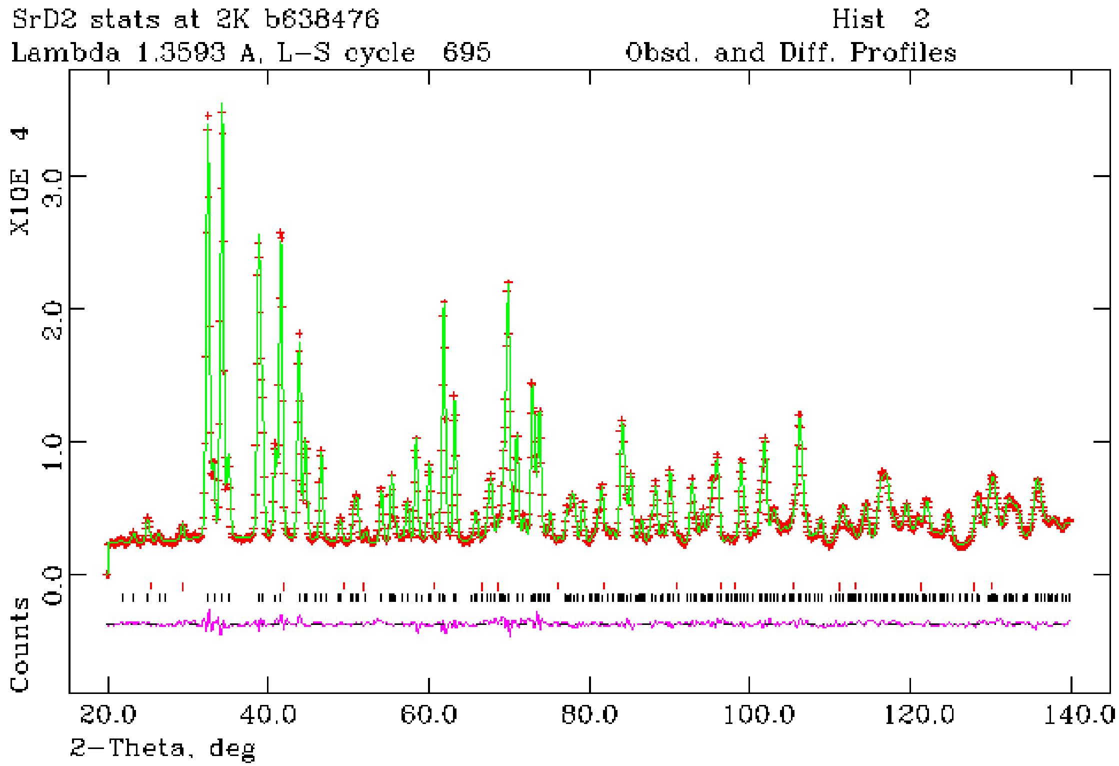
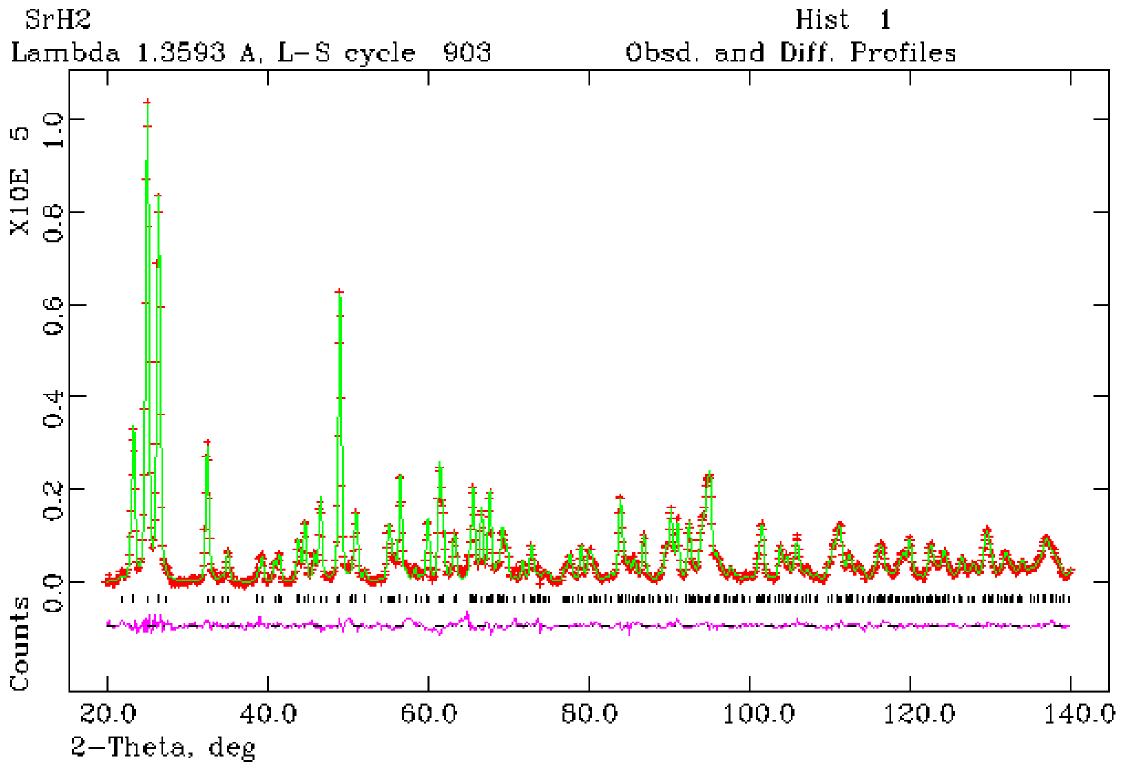
H v D in neutron powder diffraction



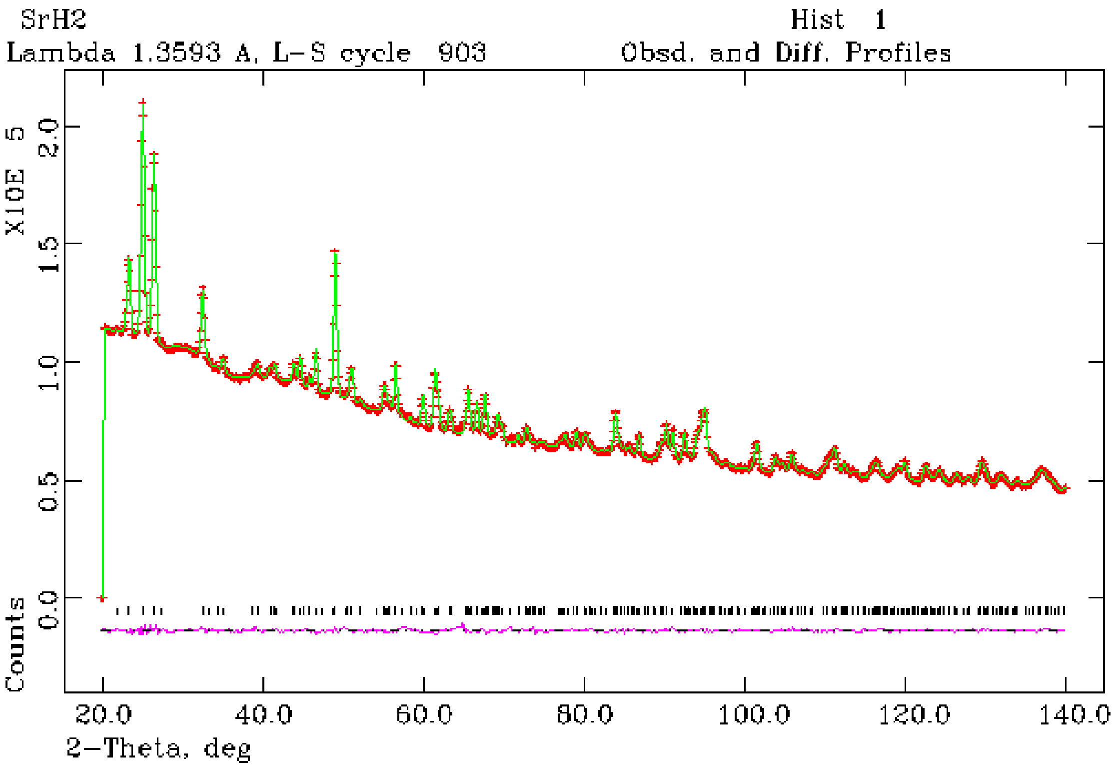
SrD_2

H v D in neutron powder diffraction



SrH_2

H v D in neutron powder diffraction



SrH_2

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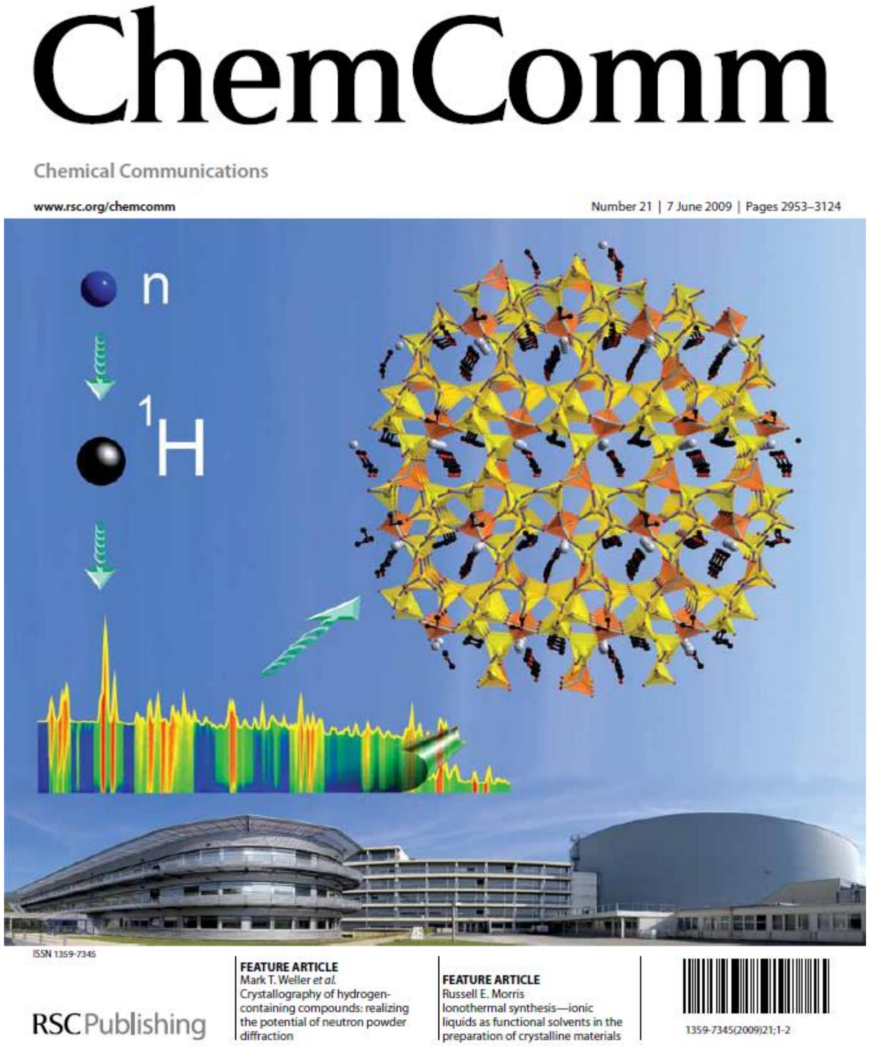
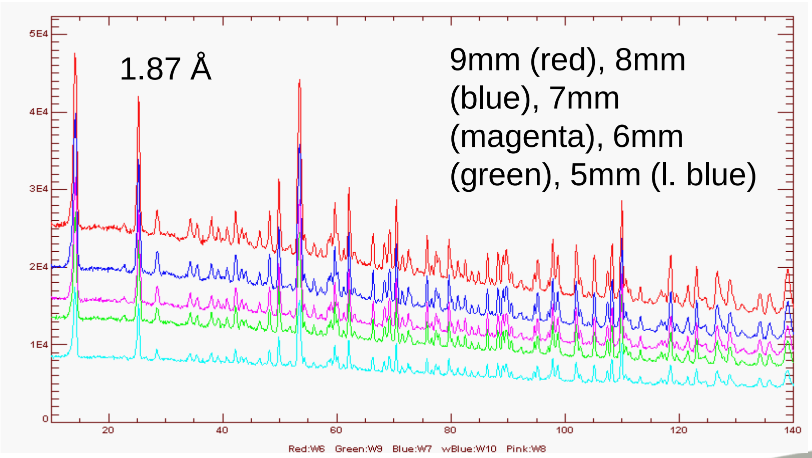
H Groundwork 2007-2009



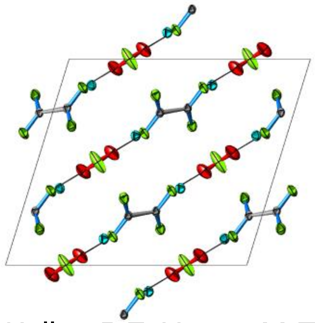
- Sample size
- H content: up to 70 at.%
- Instrument at ILL
- Counting time
- Data collection strategies



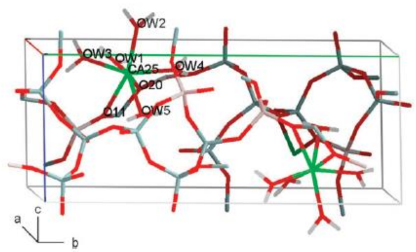
P. F. Henry, M. T. Weller, C. C. Wilson. *J. Appl. Cryst.* 2009, **42(6)**, 1176-1188

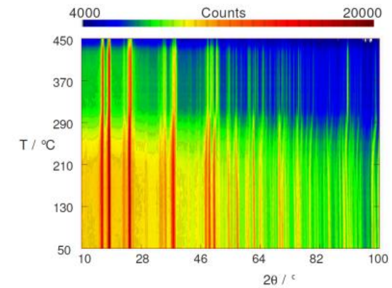
M.T. Weller, P.F. Henry, V.P. Ting, C.C. Wilson. *Chem. Commun.* 2009, 2973-2989

Examples of published work

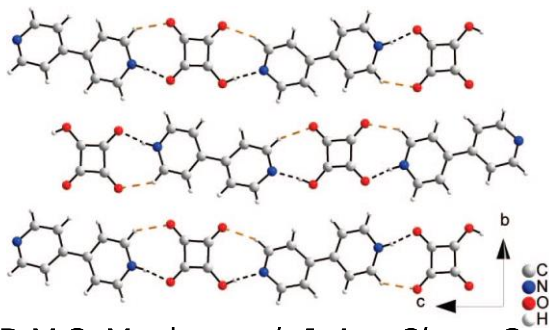


M.T. Weller, P.F. Henry, M.E. Light. *Acta Cryst. B* 2007, **63(3)**, 426.

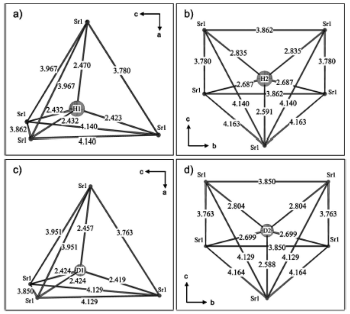




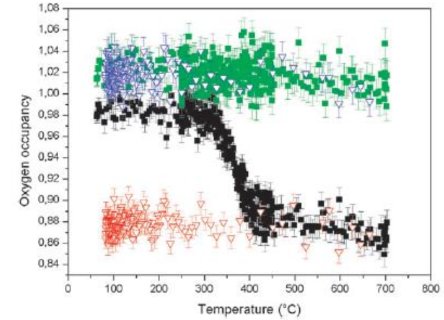
P.F. Henry, M.T. Weller, C.C. Wilson, *Chem. Commun.* 2008, 1557.
J.A. Armstrong *et al. Am. Mineral.* 2010, **95(4)**, 519.



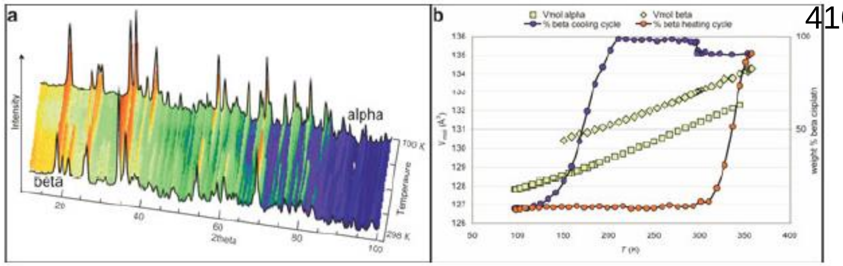
D.M.S. Martins *et al. J. Am. Chem. Soc.* 2009, **131(11)**, 3884.



V. P. Ting *et al. Phys. Chem. Chem. Phys.* 2010, **12(9)**, 2083.



F. Tonus *et al*. Chem. Commun. 2009, 2556.
F. Tonus,*et al. J. Mater. Chem.* 2010, **20(20)**, 4103.



V.P. Ting *et al. Angew. Chemie 2010, **49(49)**, 9408.*

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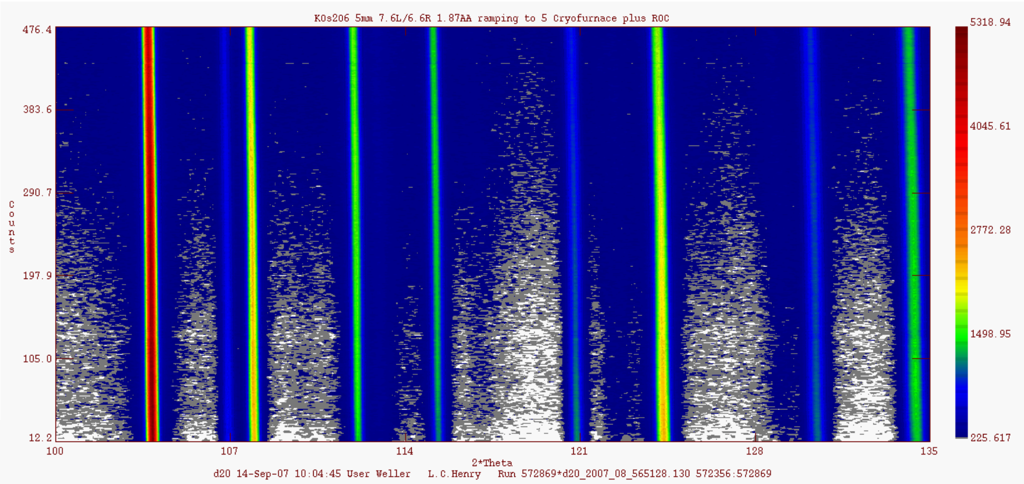
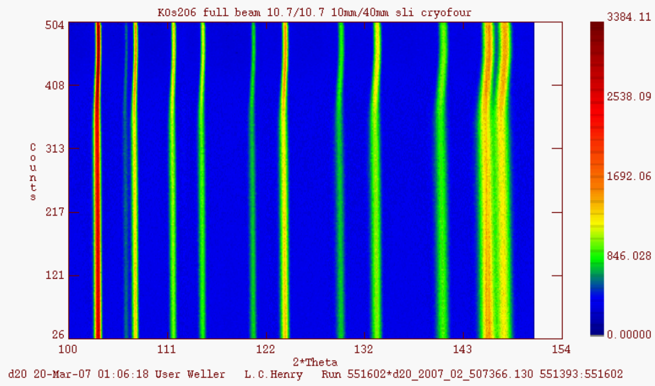
KOs_2O_6 high scattering angle vs. T



Cycled sample



As prepared

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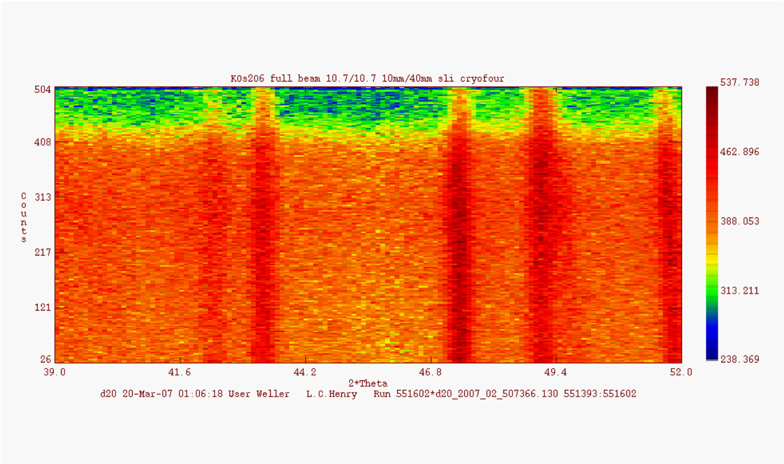
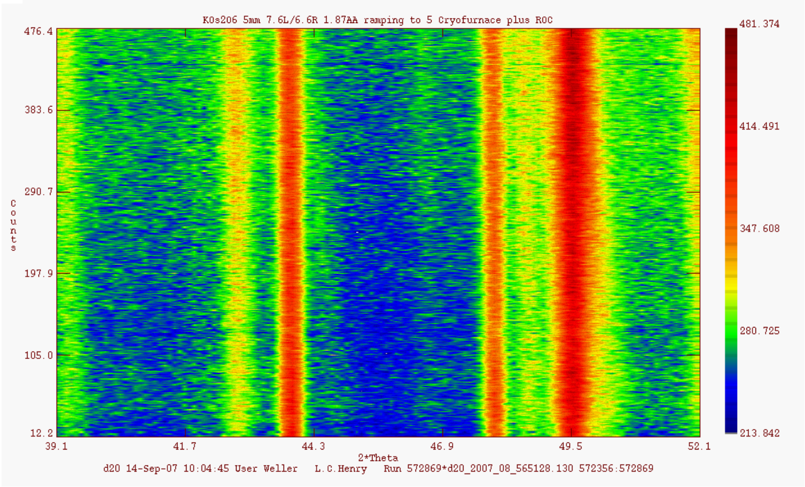
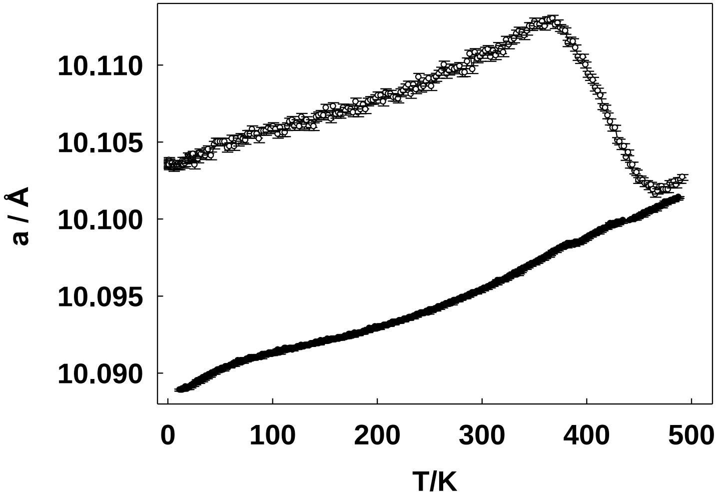
$KOs_2O_6.nH_2O$ incoherent contribution



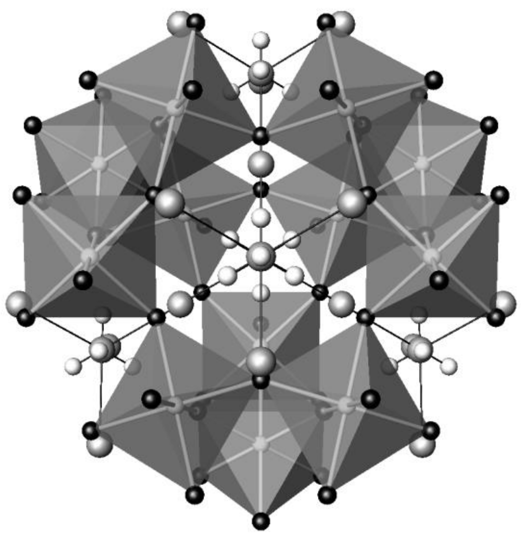


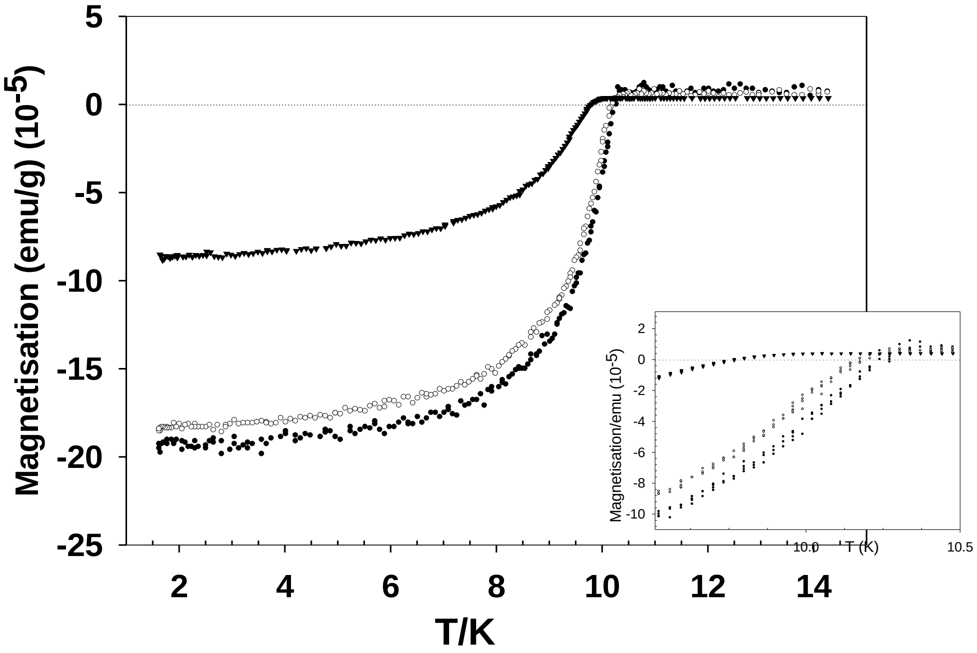


- R. Galati, R.W. Hughes, C.S. Knee, P. F. Henry, M.T. Weller. *J. Mat. Chem.* 2007, 17(2), 160-163.
- R. Galati, C. Simon, C.S. Knee, P.F. Henry, B.D. Rainford, M.T. Weller. *Chem Mater.* 2008, 20, 1652-1659.
- R. Galati, C. Simon, P. F. Henry, M. T. Weller. *Phys. Rev. B* 2008, 77, 104523.

Alkali metal pyrochlore Osmates

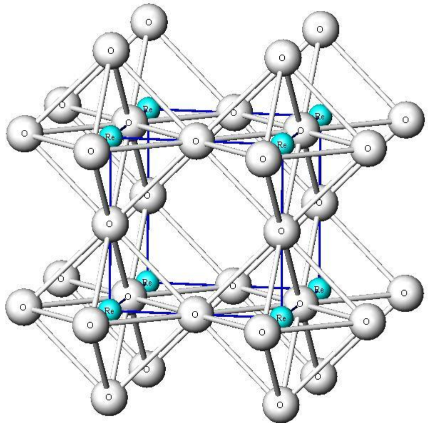
Osmate β-pyrochlores found to be superconducting but T_c variable with sample preparation with TGA showing 0.1 H_2O content responsible for 0.5K fall in T_c.

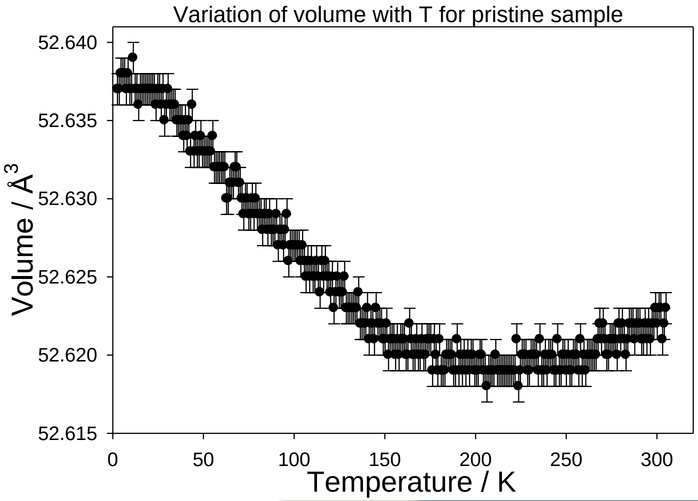




NTE in ReO_3

- Simple cubic structure
  - DO_9 type
  - *Pm-3m*
  - *a* = 3.74 Å
- Based on a perovskite with empty A-site
- Phonon modes should give rise to NTE
- Mixed literature
- Calculations predict NTE to 300K+
- Re-investigation using PND





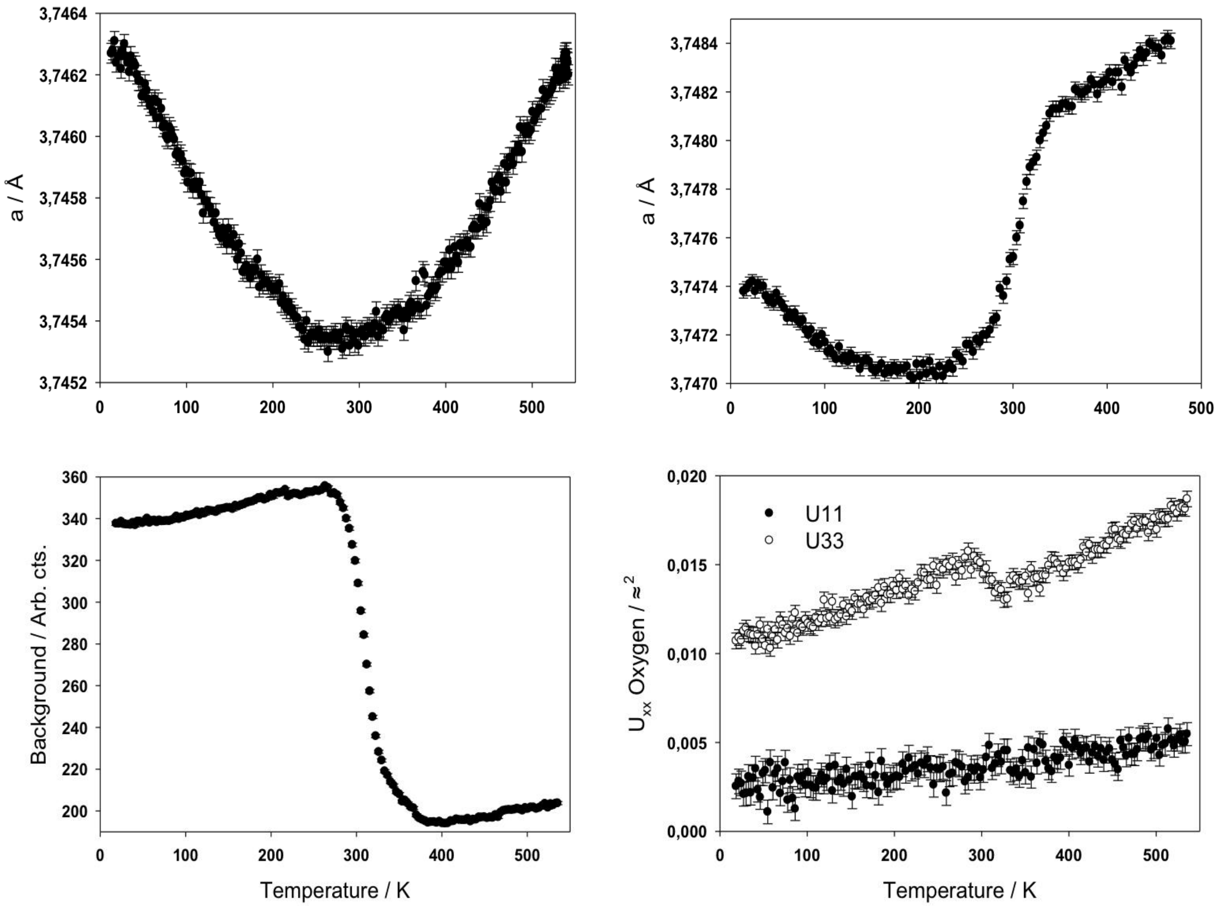
T. Chatterji, P.F. Henry, R. Mittal, S.L. Chaplot. *Phys. Rev. B* 2008, **78**, 134105.

ReO_3 sample preparation dependence

Vacuum dried sample

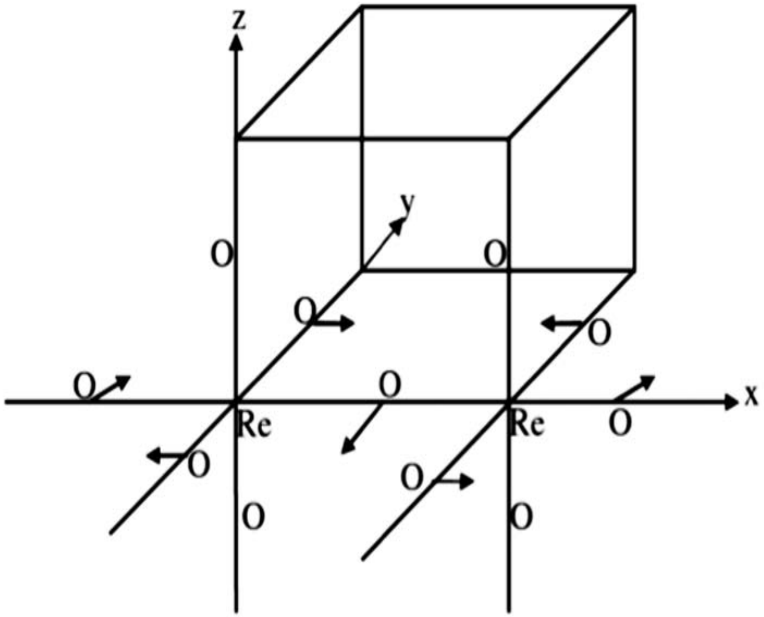
Left in a H_2O atmosphere

Background and ADP change (water loss?)



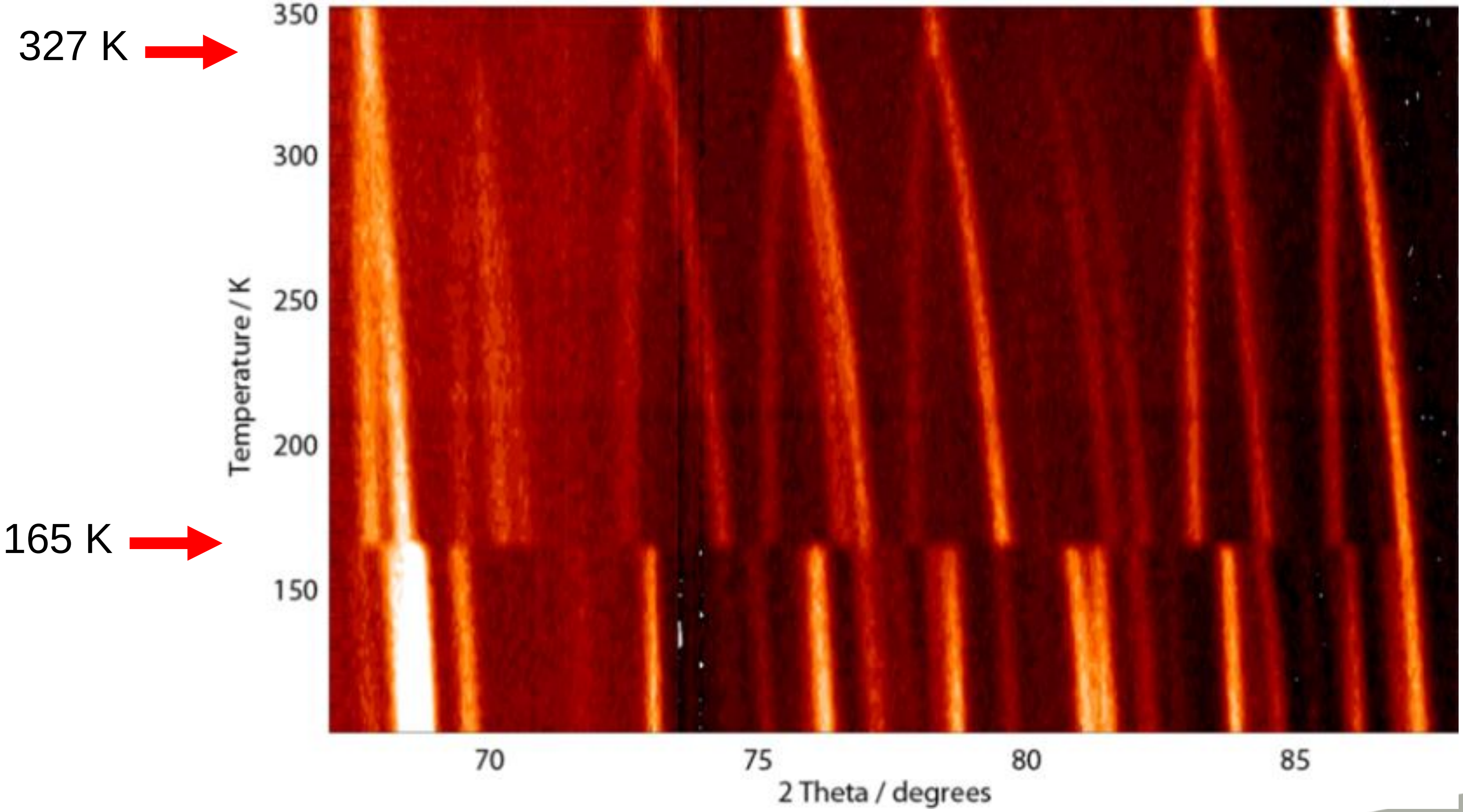
Interpretation

- Hydrogenous species disrupt M_3 phonon mode
  - Known in Prussian Blues
- Most water is surface water
- Actual intercalated species unknown
  - Raman
  - Infra-Red
- Role of static oxygen disorder?
  - Reported in Rodriguez et al. *J. Appl. Phys.* 2009, **105**, 114901.
- Bronzes can be formed
  - Metallic
  - High lustre
  - Cubic or orthorhombic



Results show even 'simple' systems are not well understood and small amounts of intercalants can have large effects on observed properties.

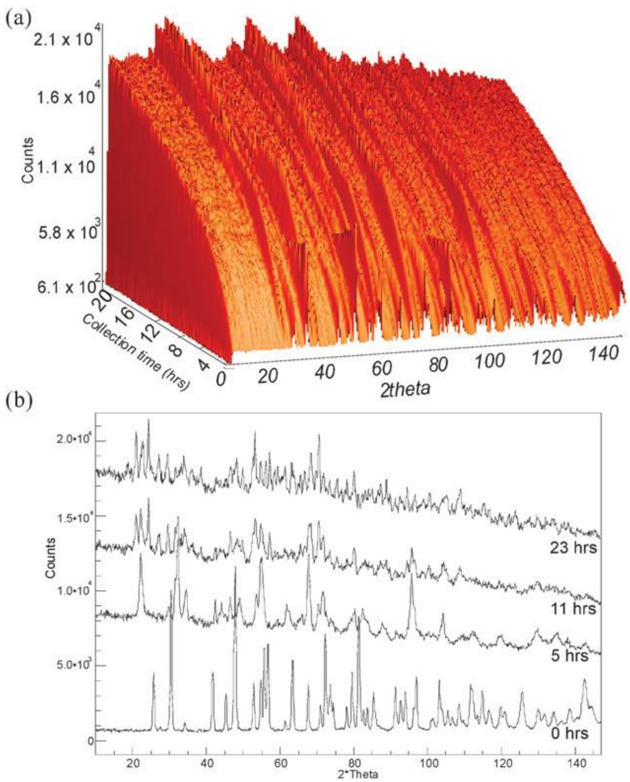
Data quality / counting time



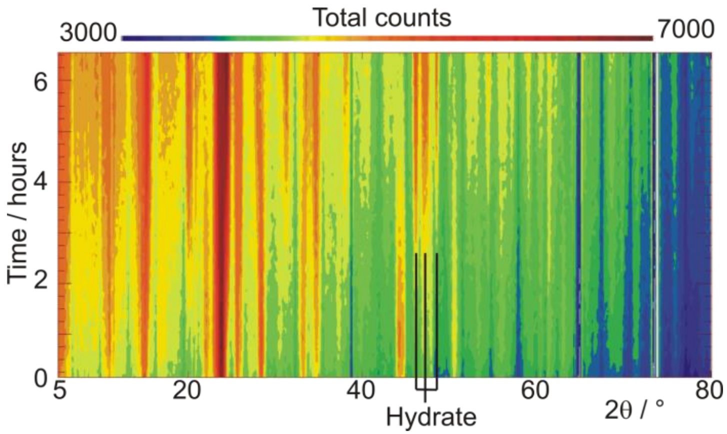
M. T. Weller, O. J. Weber, P. F. Henry, A. M. Di Pumpo, T. C. Hansen, *Chem. Commun.*, 2015, **51**, 4180-4183

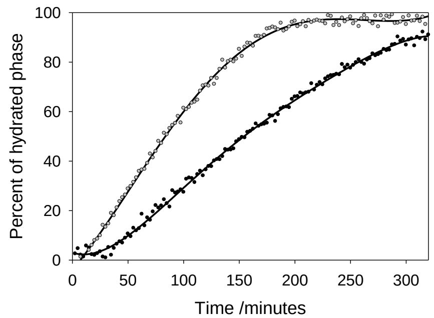
Use incoherent scattering as a direct probe

V.P. Ting, P.F. Henry, M. Schmidtmann, C.C. Wilson, M.T. Weller. *Chem. Commun.* 2009, 7527.

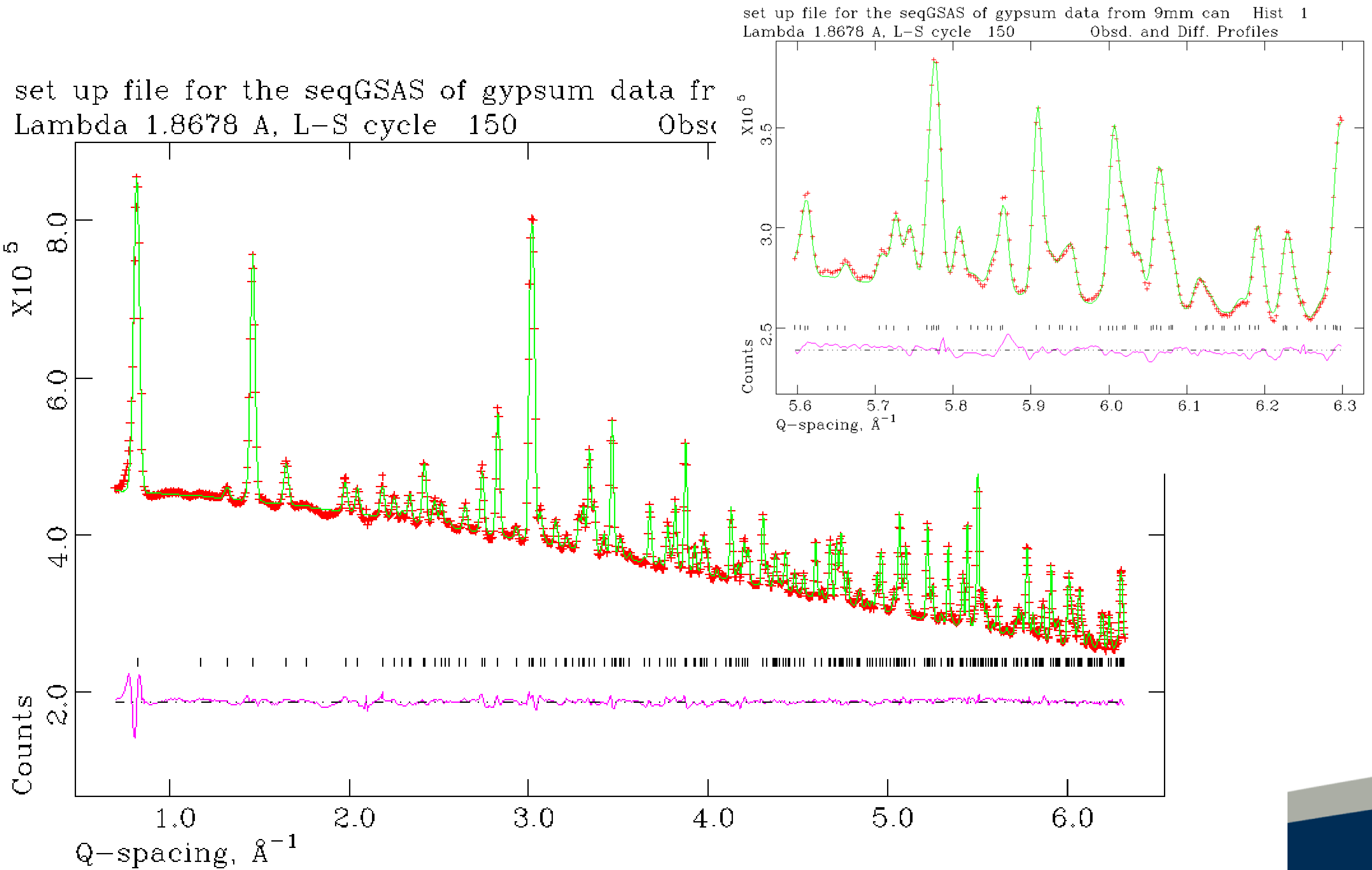


V.P. Ting, M. Schmidtmann, P.F. Henry, S. Dann, C.C. Wilson, M.T. Weller. *Med. Chem. Commun* 2010, 1(5), 345.

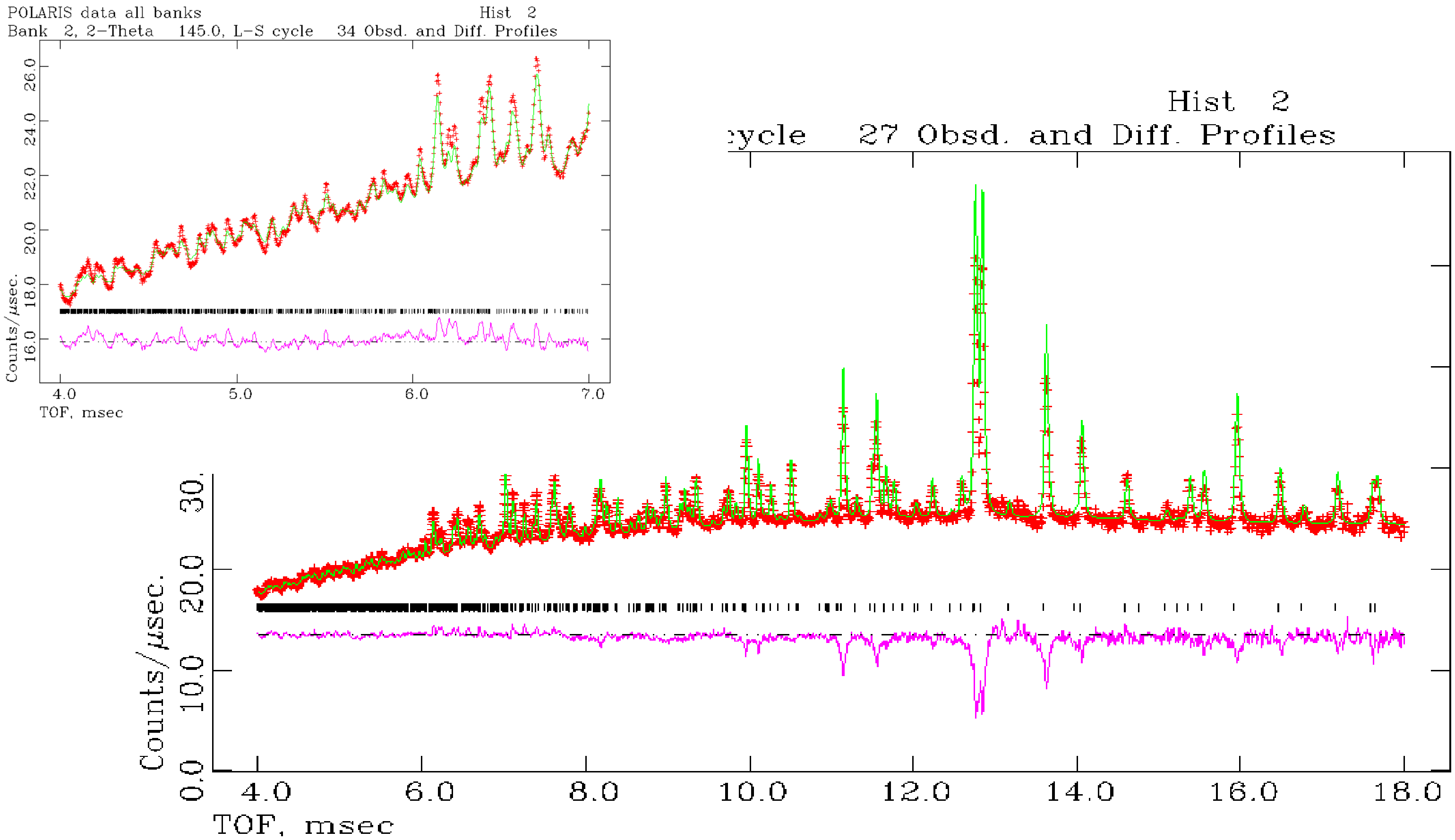




Gypsum: Monochromatic



Gypsum: t.o.f. ISIS



Effect is similar to that seen for an absorbing sample

Variation of $\sigma_{inc}H$ with λ

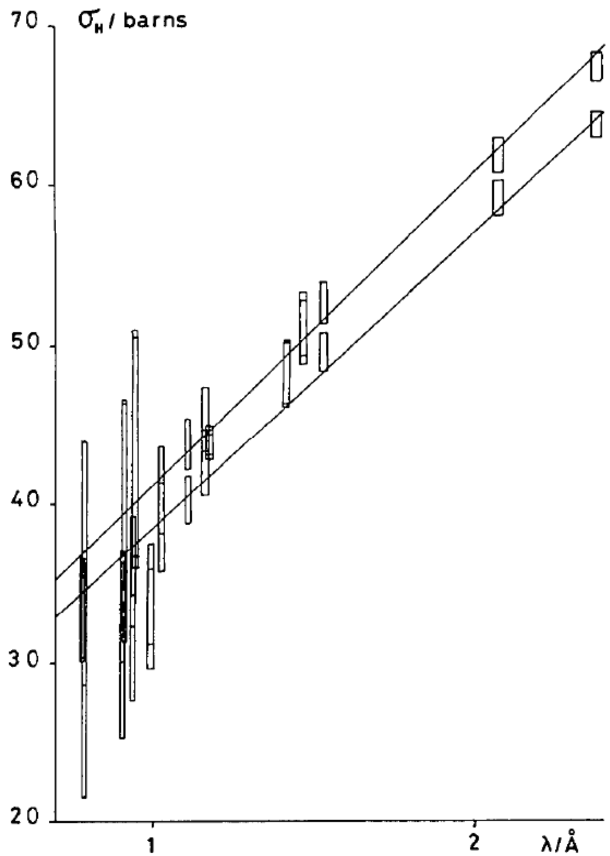


Fig. 1. Plot of σ_H *vs* λ for the Re crystal. Error bars on points incorporate e.s.d.'s in both σ_H and λ.

Neutron scattering lengths and cross sections							
Isotope	**conc**	**Coh b**	**Inc b**	**Coh xs**	**Inc xs**	**Scatt xs**	**Abs xs**
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

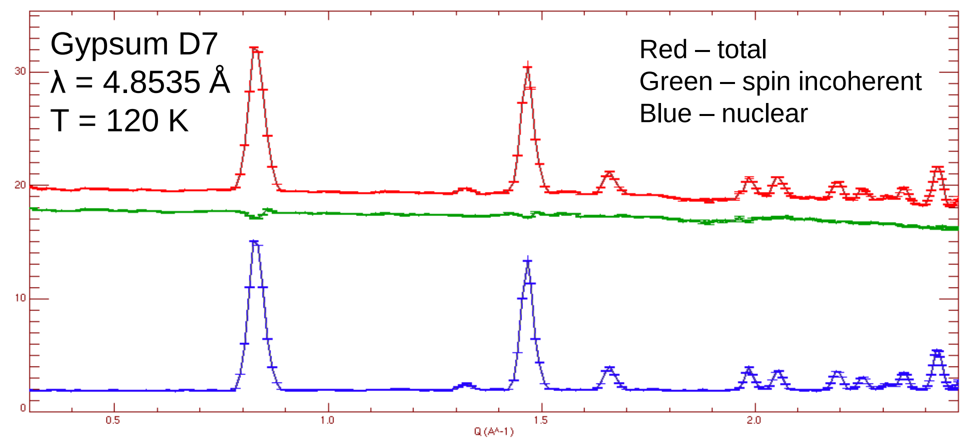
- Large change with incident wavelength
  - Is it linear?
  - Chemical environment contribution?
  - Implications for t.o.f. instrument

Howard et al. J. Appl. Cryst (1987) **20**, 120-122.

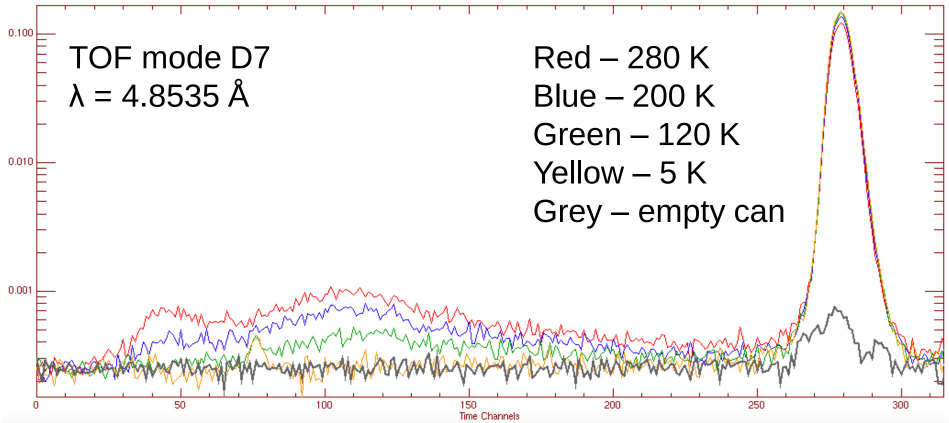
Koetzle & McMullan (1980) research memo C-4. Brookhaven national laboratory

Frost (1989) ILL 'stage' (unpublished)

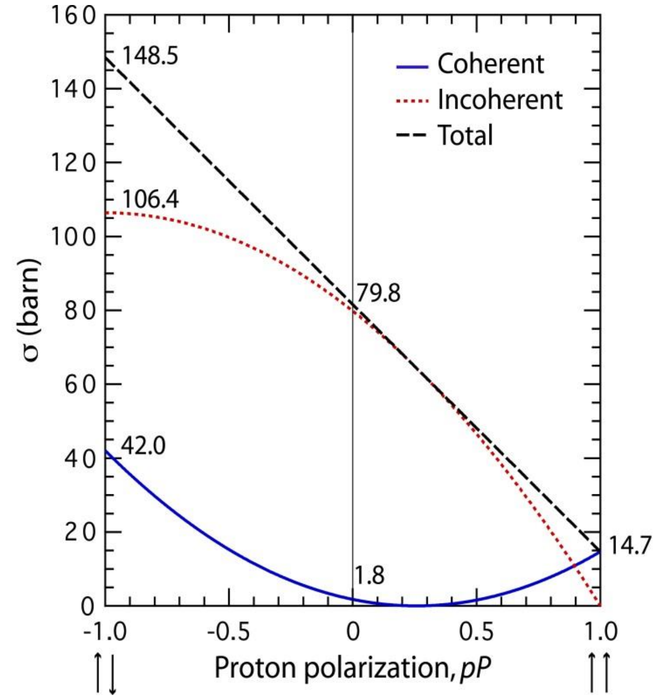
Suppress / remove incoherent scattering



Polarisation analysis



TOF energy discrimination



Dynamic Nuclear Polarisation

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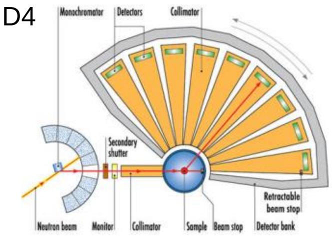
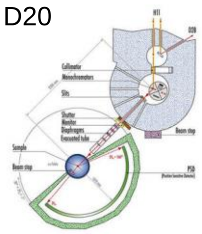
Empirical correction as a function of E(λ)

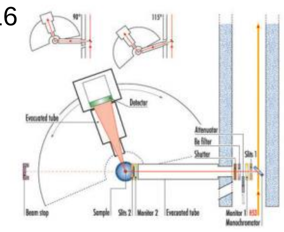
D4



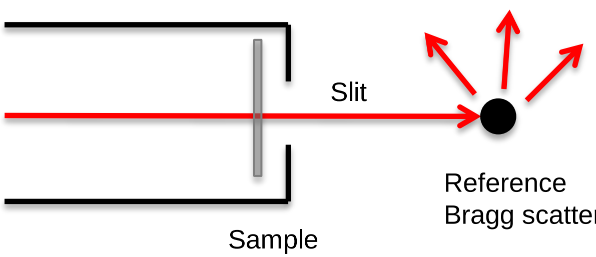
D20



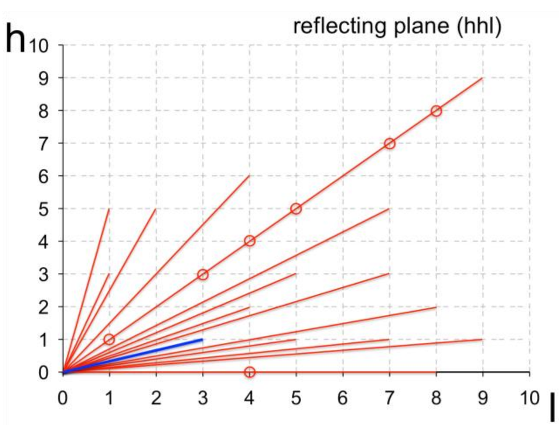
D16

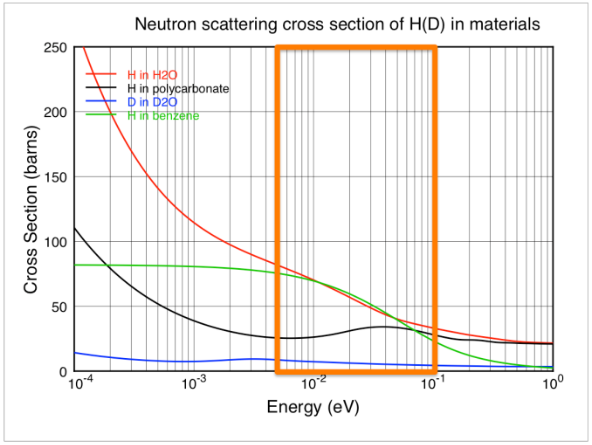


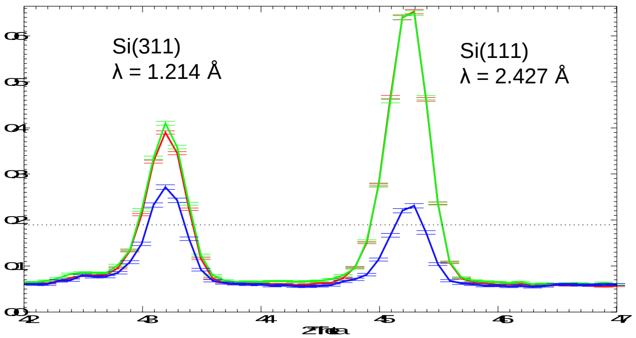
Hot	Thermal	Cold
<0.7 Å	0.8 - 3 Å	4.5 - 6 Å



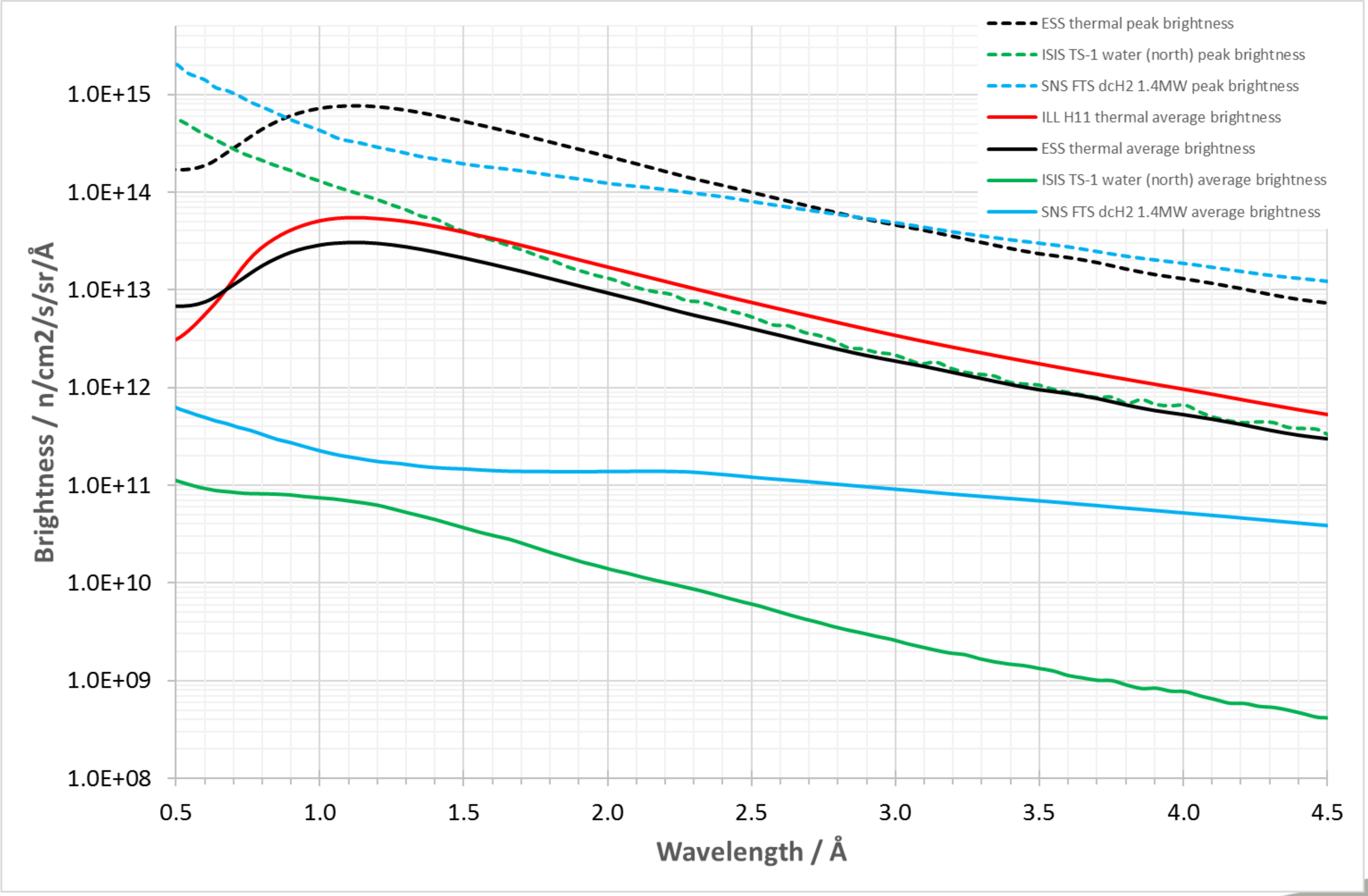
Top view







H diffractometer for ESS



High peak brilliance good for TOF but also
High time-average brilliance good for CW

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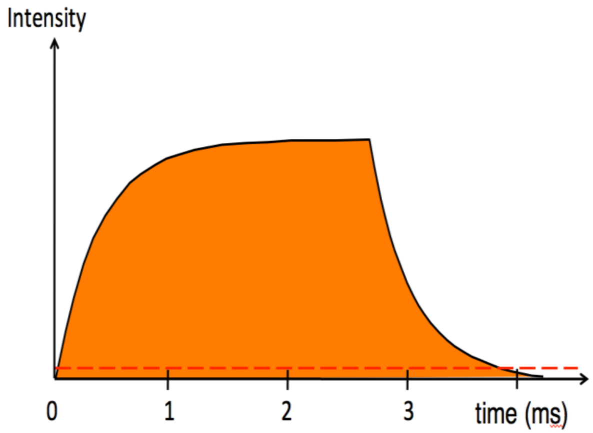
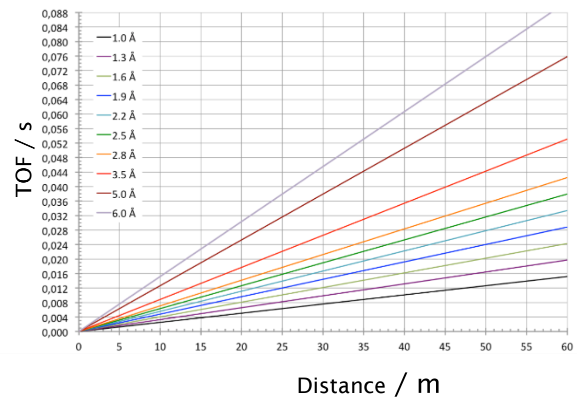
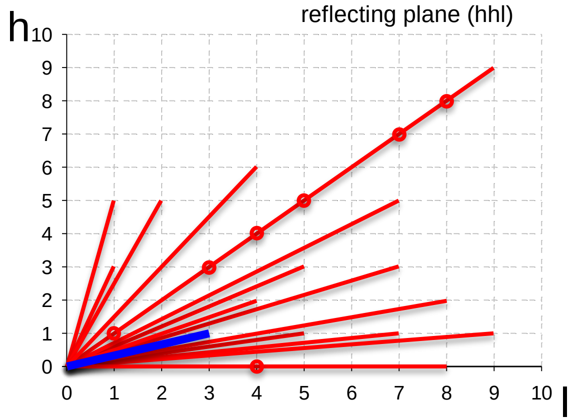
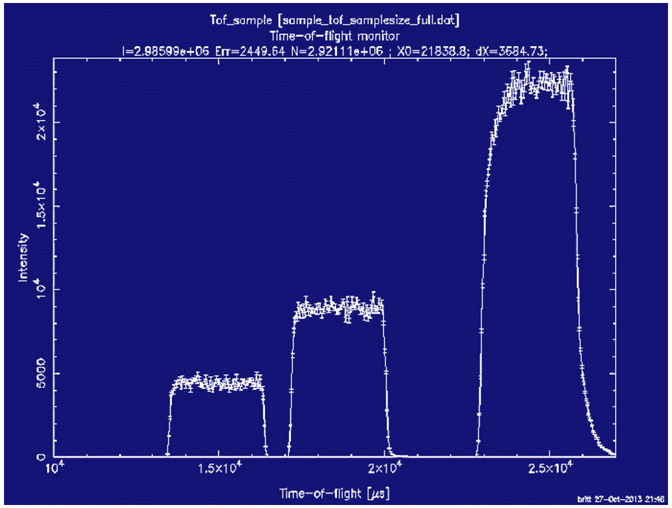
H diffractometer for ESS









- Use distance to separate higher order monochromator reflections in TOF at the detector
- Develop new monochromator materials
- Access wider Q range
- Tune Q resolution

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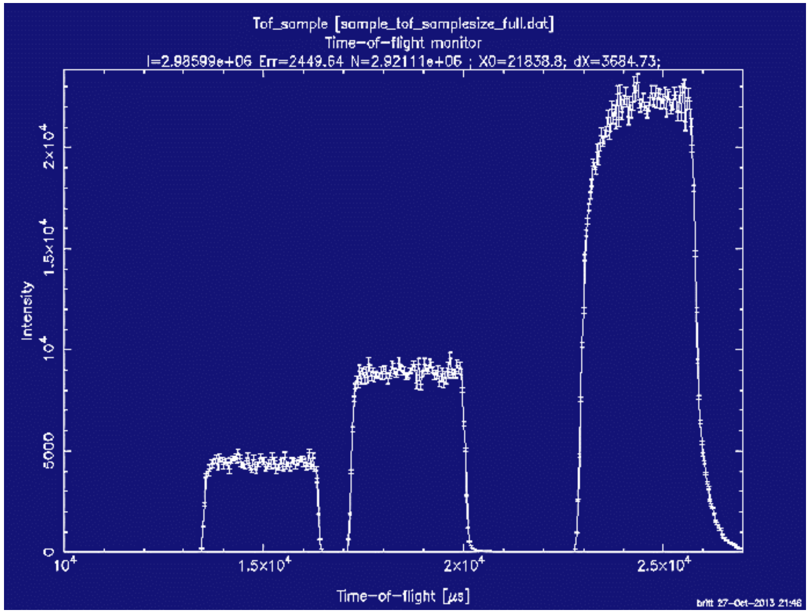
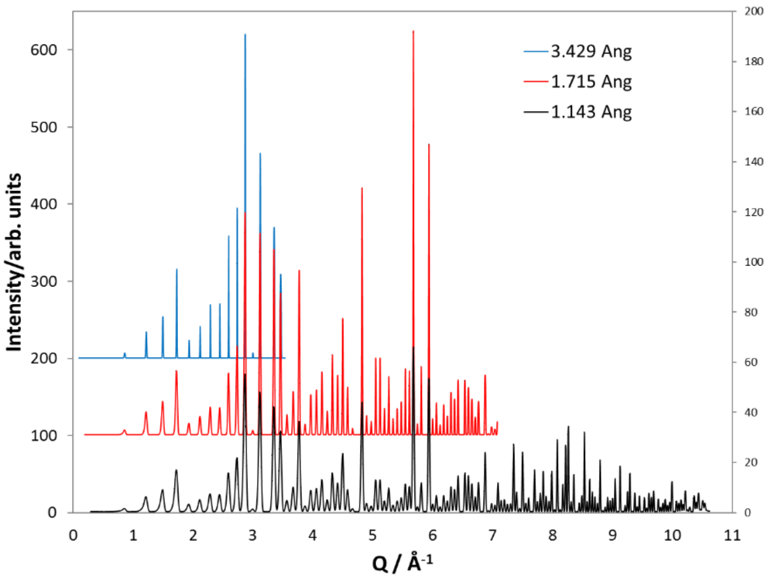
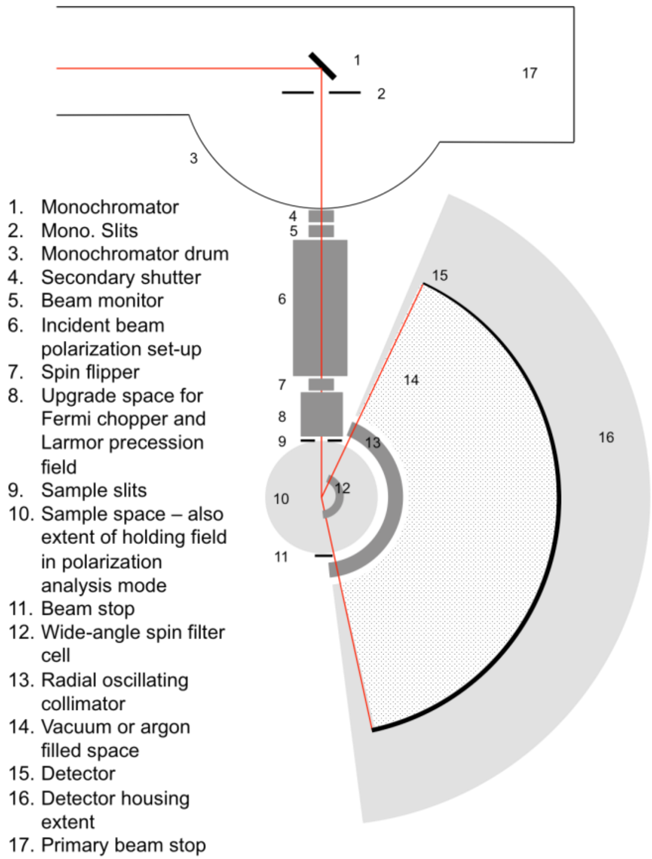
H diffractometer for ESS

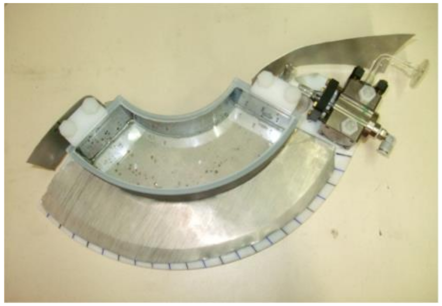




- Combine several current CW instrument capabilities in one simultaneous measurement
- No wavelength contamination
- Lower instrument background
- New science possibilities

H diffractometer for ESS





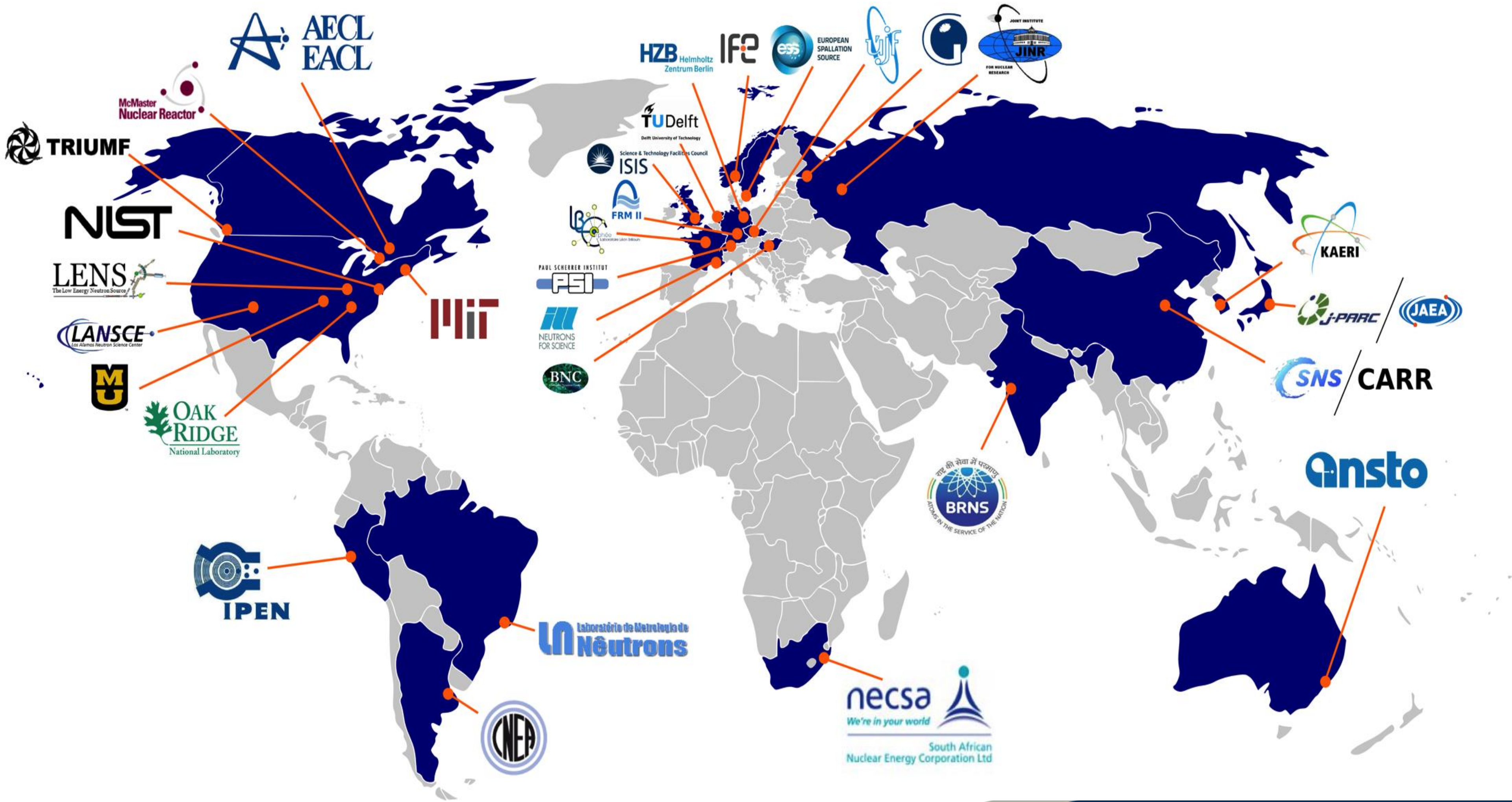
- Polarisation analysis to remove incoherent background

To deuterate or not to deuterate?

- If you are *sure* that deuteration changes nothing – deuterate
- ^{1}H v ^{2}H scattering length contrast ideal – deuteration is an essential tool here (selective and complete)
- Partial site deuteration is worse than using ^{1}H sample
- ^{1}H v ^{2}H when looking at kinetics, dynamics or structure/phase transitions in H-bonded systems is non-trivial as an 'equivalence' issue
- Beware the 'costs' of deuteration
  - Expensive
  - Smaller samples
- Prefer to spend time and money on
  - Optimising existing neutron instrumentation + counting strategies
  - Building new, optimised neutron instrumentation
  - Optimising sample geometry and sample environment

Applying for beamtime

Neutron sources worldwide



Major neutron sources in Europe

How to apply for beam time in Europe

Large Neutron user facilities in Europe with open user programmes

- ILL: https://www.ill.eu/users/applying-for-beamtime/
- ISIS: http://www.isis.stfc.ac.uk/apply-for-beamtime/apply-for-beamtime2117.html
- FRM-II (MLZ): http://www.mlz-garching.de/englisch/user-office/getting-beam-time.html
- PSI: https://www.psi.ch/sinq/beamtime-applications
- LLB: http://www-llb.cea.fr/en/Web/avr2000_e.php
- HZB: https://www.helmholtz-berlin.de/user/beamtime/index_en.html

AEKI, IFE, TU Delft, NPI, PIK and Dubna offer user access

Most smaller sources are open for direct contact with instrument team to arrange beam time. However, no travel or subsistence support is available

Major neutron user facilities outside Europe

Australia

- ANSTO: http://www.ansto.gov.au/ResearchHub/Bragg/Users/Requestingbeamtime/index.htm

Americas

- SNS/HFIR: https://neutrons.ornl.gov/users
- NIST: https://www.ncnr.nist.gov/call/current_call.html

Japan

- J-PARC: https://j-parc.jp/researcher/MatLife/en/applying/index.html

Non-European sources tend not to have travel support for experiments

All sources base beam time on scientific merit (with some national balancing)

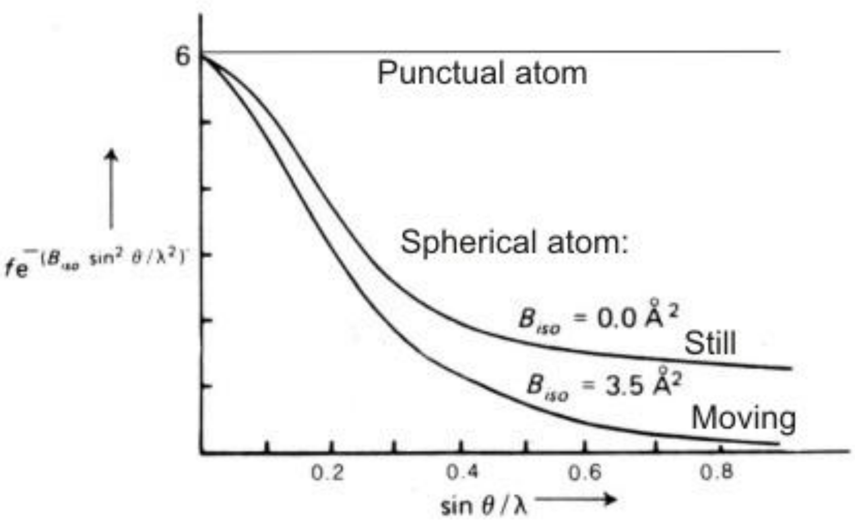
Examples to illustrate differences between neutron and X-ray scattering

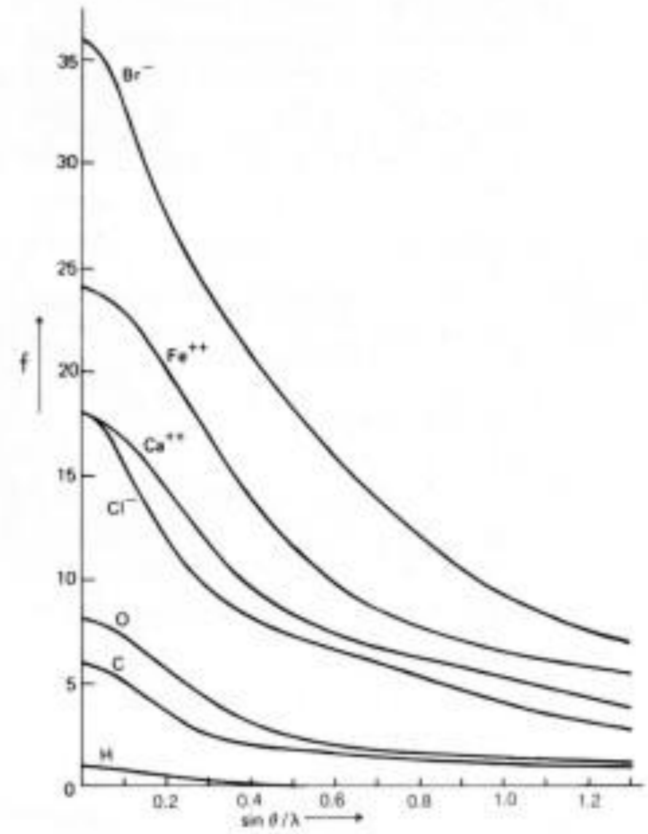
X-ray cf. neutron for diffraction

X-rays	Neutrons
Small samples	Large samples
Strong sample absorption	Low sample absorption
High energy (1 Å = 12.4 keV)	Low energy (1 Å = 81.81 meV)
Low penetration depth	High penetration depth
Light elements hard to detect	Light elements scatter well
Scattering power highly Q dependent	Scattering power almost Q independent
Neighbouring elements cannot be discriminated	Neighbouring elements can be discriminated
High availability (lab)	Low availability (large scale facility)
Cannot distinguish isotopes	Isotopes can be distinguished
Magnetic structures not easily probed	Magnetic structures easily probed

X-ray and electron scattering form factor

- Scatter from electrons
- Larger z elements have higher scattering power
- Atoms vibrate leading to lower scattering power at high Q





Neutron form factor

- Neutrons scatter primarily from the nucleus and form factor is almost Q-independent
  - Atom vibrations still reduce scattering at high Q
- The neutron can also interact with unpaired electrons to probe magnetism
  - Q-dependent form factor
  - Magnetic reflections are most intense at low Q

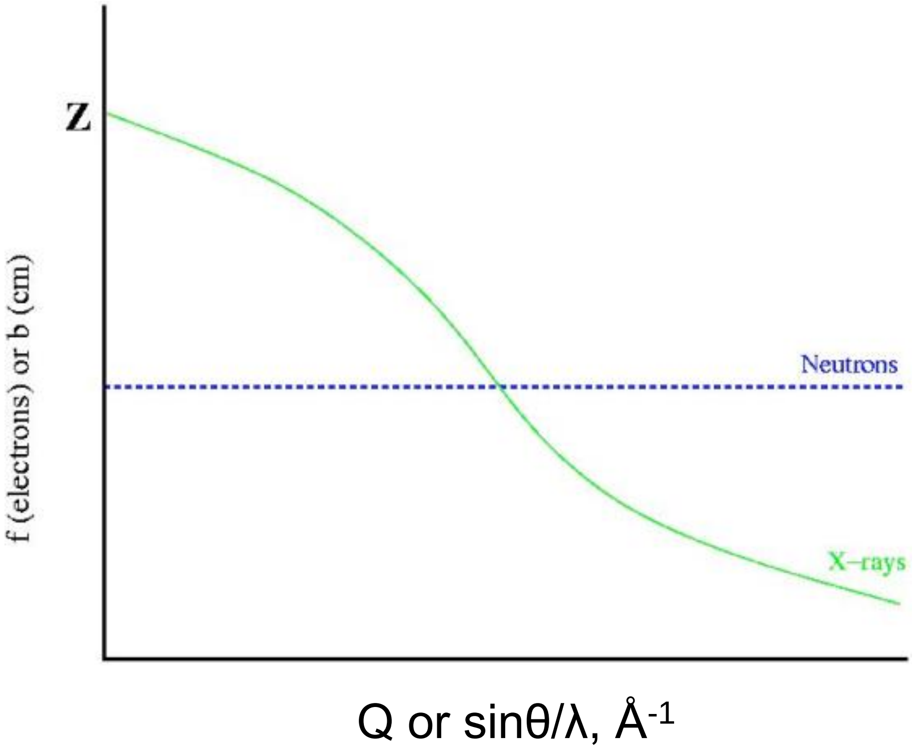
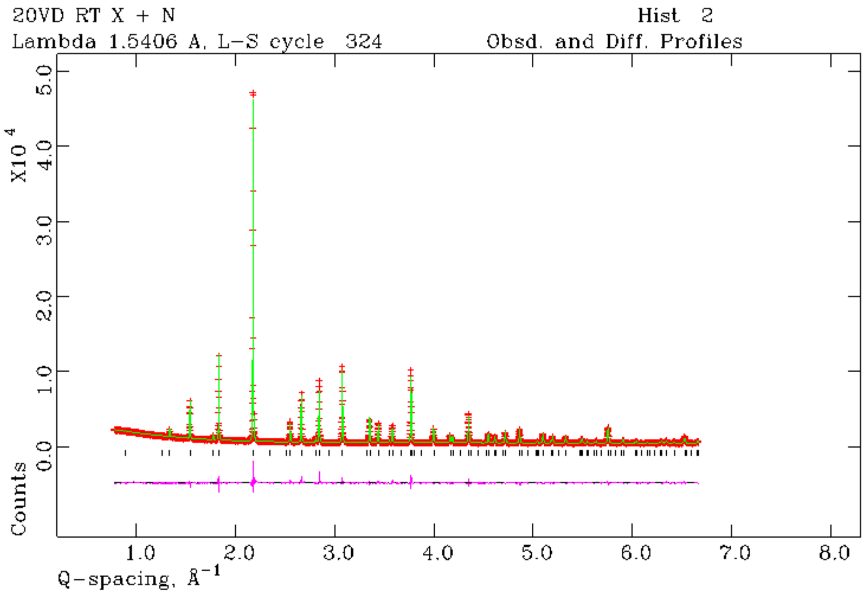
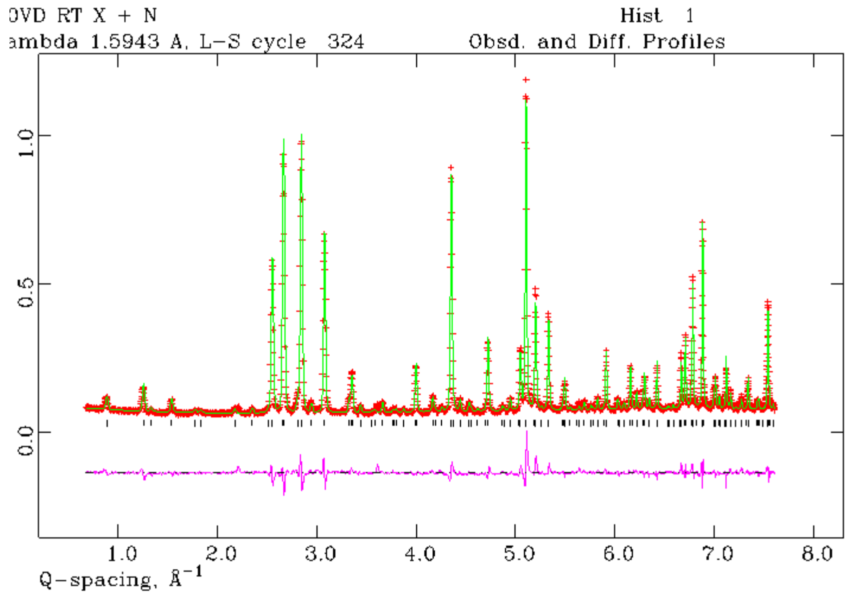


Illustration of X-ray and neutron Q dependent scattering





Note peak intensity differences – complementary information
Main peak in X-ray data (left) almost zero intensity in neutron pattern (right)
Scattering to higher Q in neutron data (form factor)
NB. Sample for X-ray and neutron from same synthesis batch

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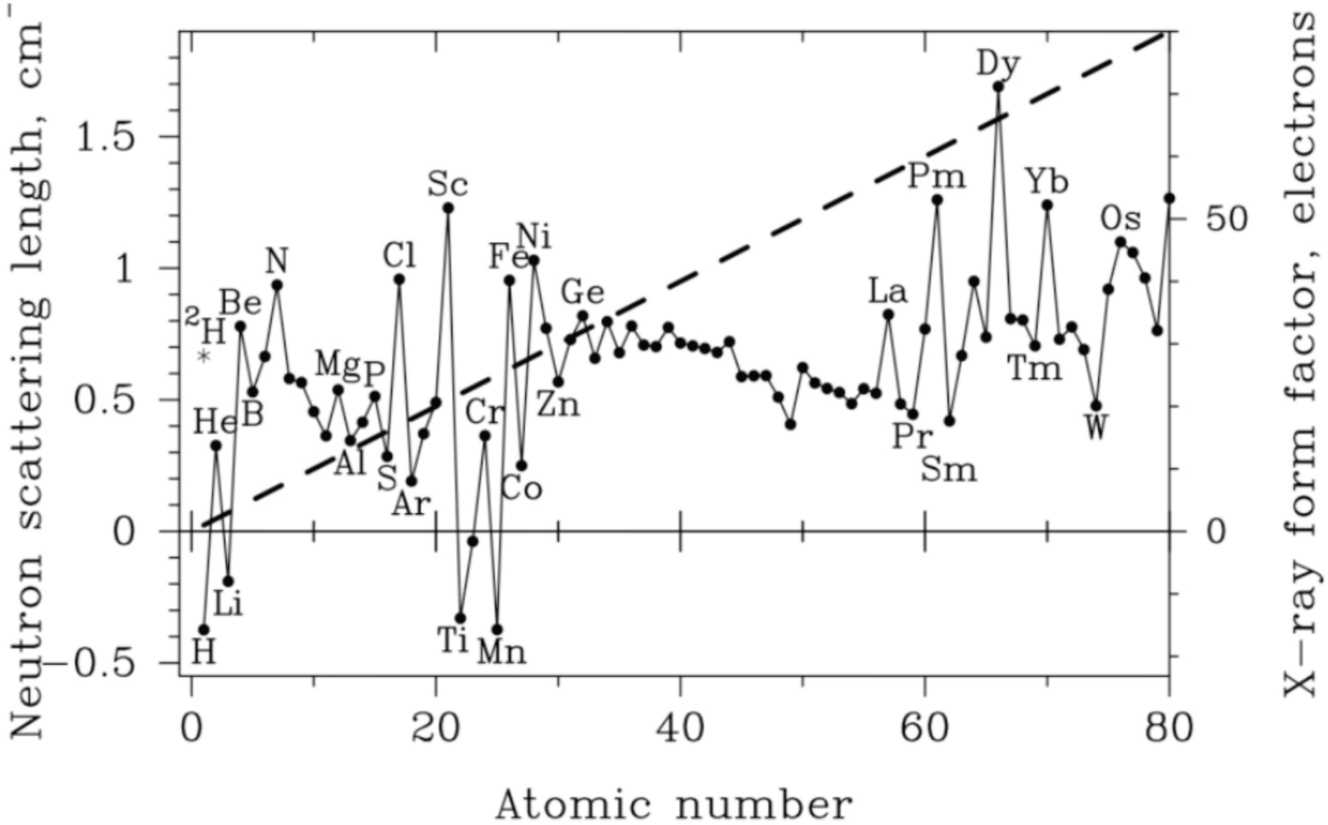
X-ray vs neutron scattering power



https://www.ncnr.nist.gov/resources/n-lengths/

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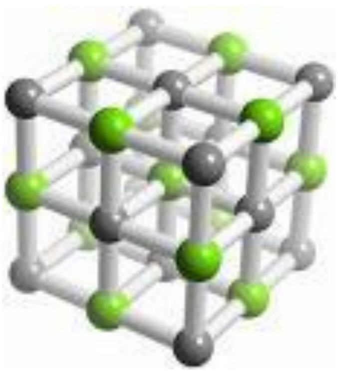
Neighbouring Element Discrimination



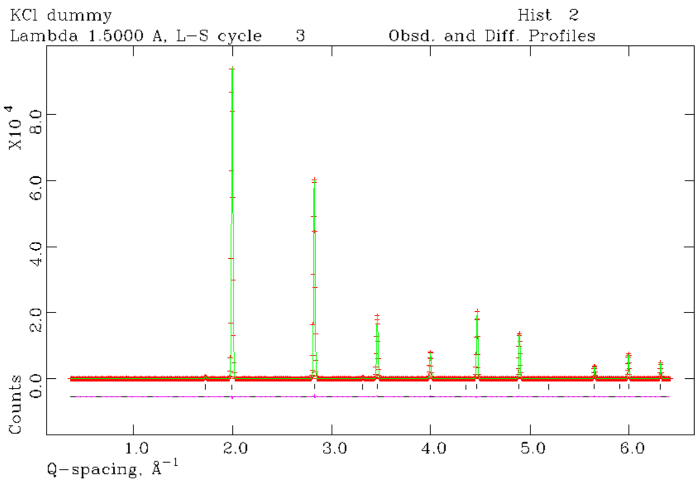
KCl

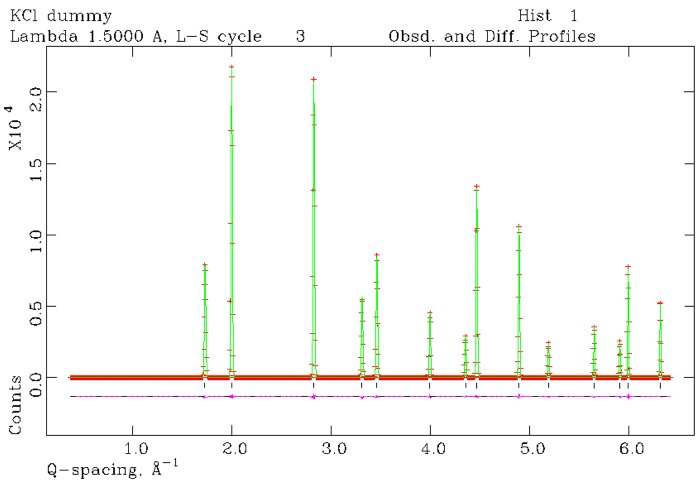
Fm-*3*m *a* = 6.29 Å

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 as elements are identical to X-rays as both have 18 e^-

The non-linear relationship of neutron scattering length between neighbouring elements is crucial

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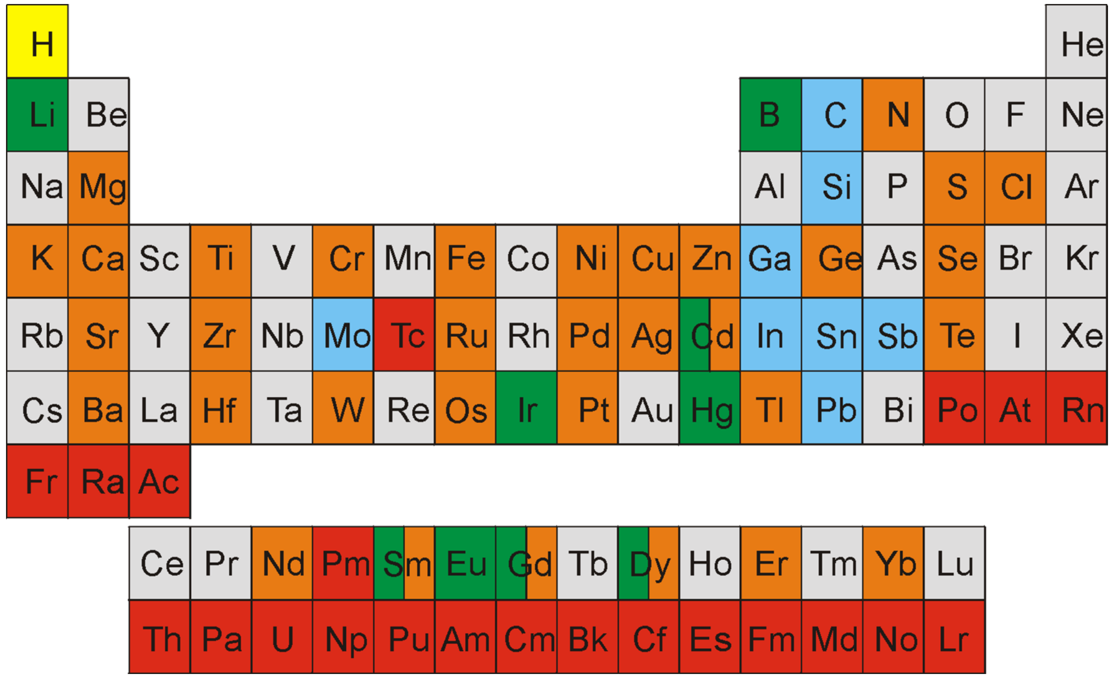
Scattering contrast isotopes



- > 20% scattering length contrast isotopes
- 5-20% scattering length contrast isotopes
- Non-absorbing isotopes available
- Non-incoherent scattering isotope available
- Mono-isotopic elements
- Radioactive elements

Isotopes have different scattering properties for neutrons

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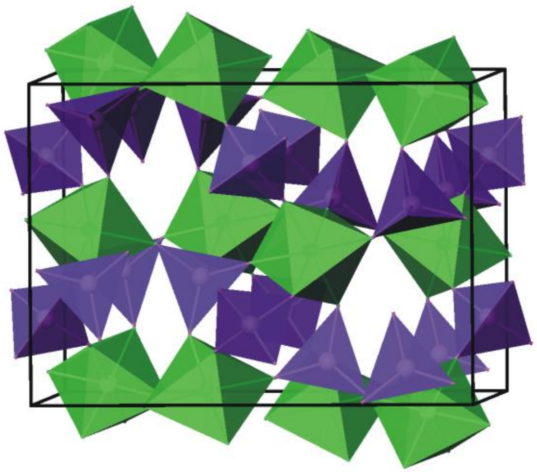
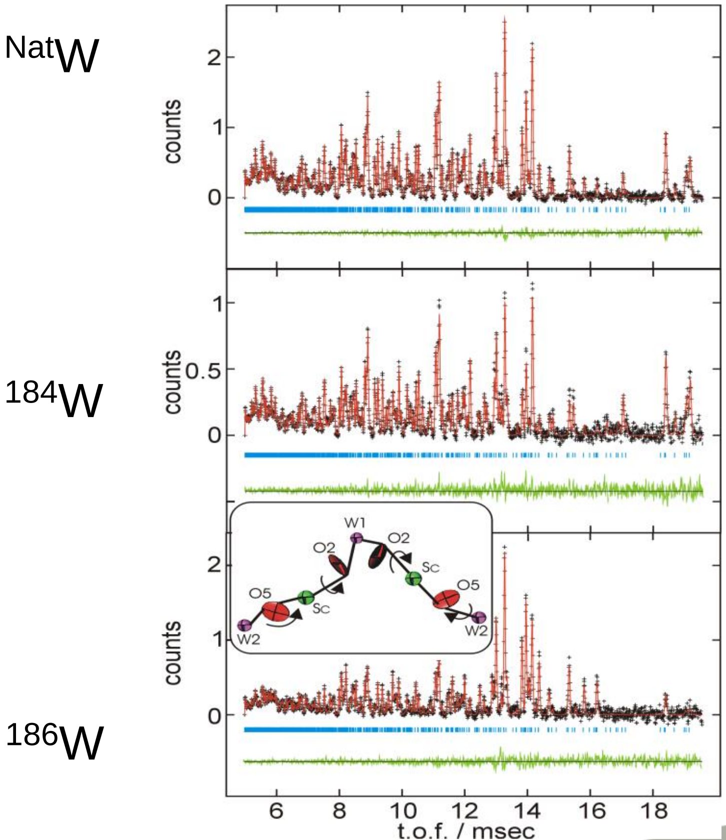
Example: Origin of Negative thermal expansion in $Sc_2(WO_4)_3$



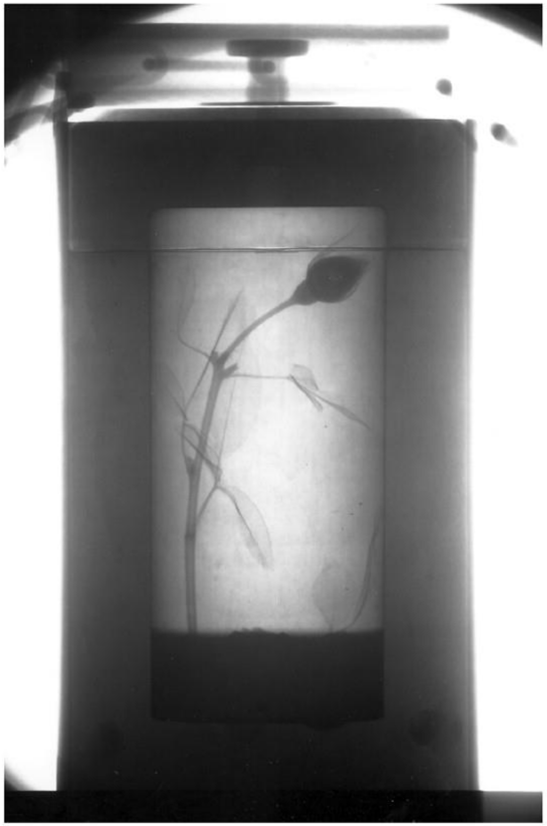


- Resolved co-operative atomic displacements
- First example using PND
- 10 years later same experiment possible without ISND on upgraded instrument HRPD

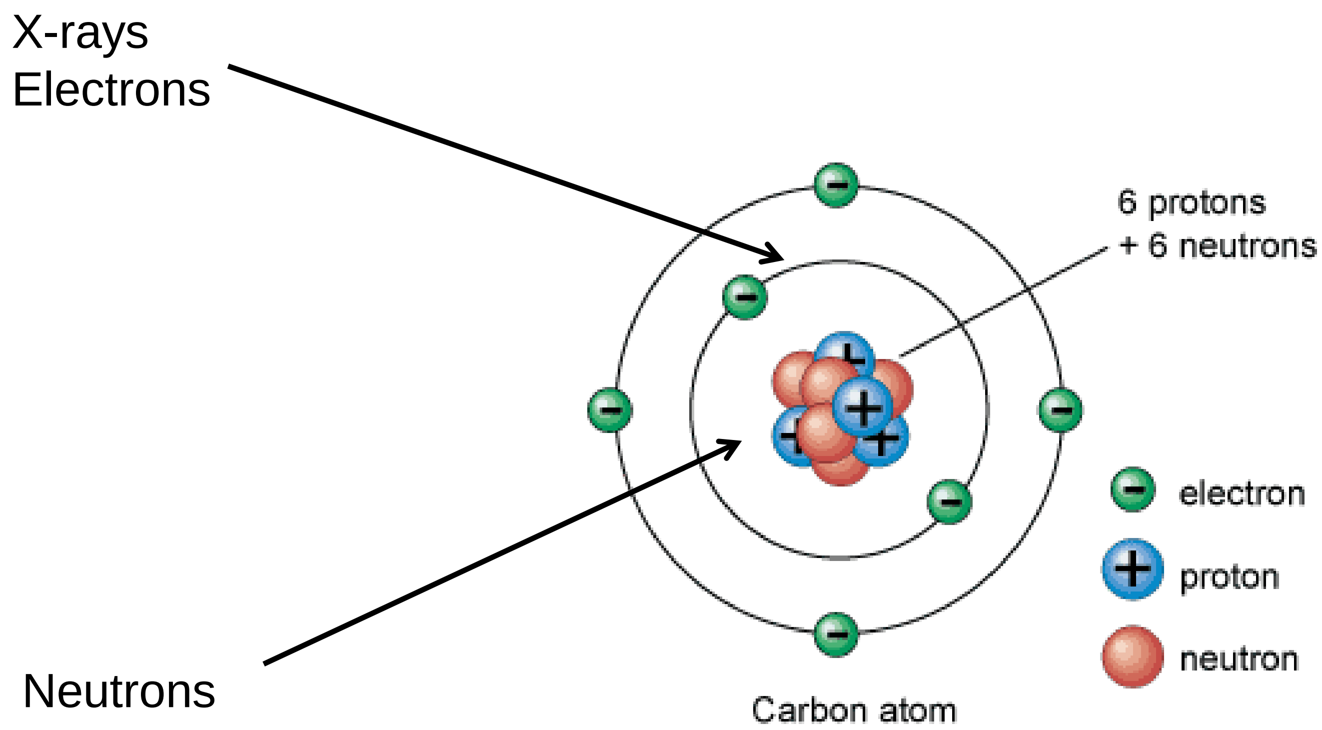
M.T. Weller, P.F. Henry, C.C. Wilson. *J. Phys. Chem. B* 2000, **105(51)**, 12224-12229

Penetration depth (neutrons)

A rose in a lead box
X-rays cannot penetrate the box
Neutrons pass through the lead and scatter from hydrogenous materials in the flower

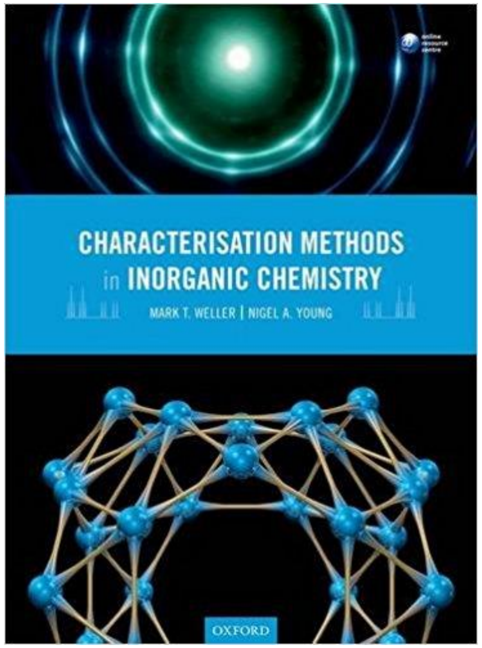


X-rays and Neutrons are Complementary Probes for Diffraction

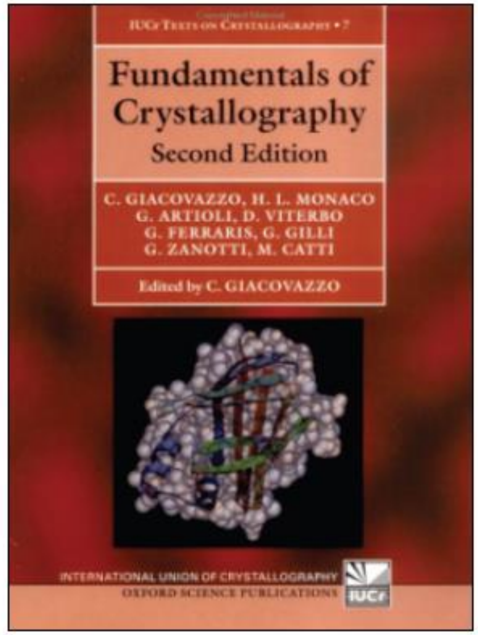


Neutron diffraction is used for problems that X-rays cannot address or inadequately address

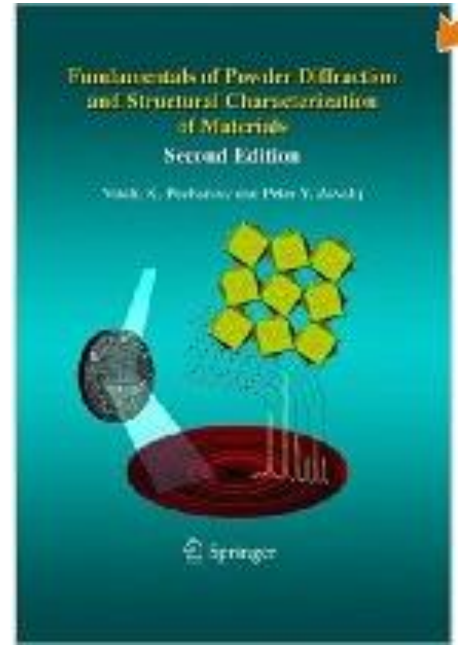
Summary: further reading



Weller & Young
Chapter 2



Giacovazzo *et al.*
Chapter 1



Pecharsky & Zavalij
Chapters 1-9