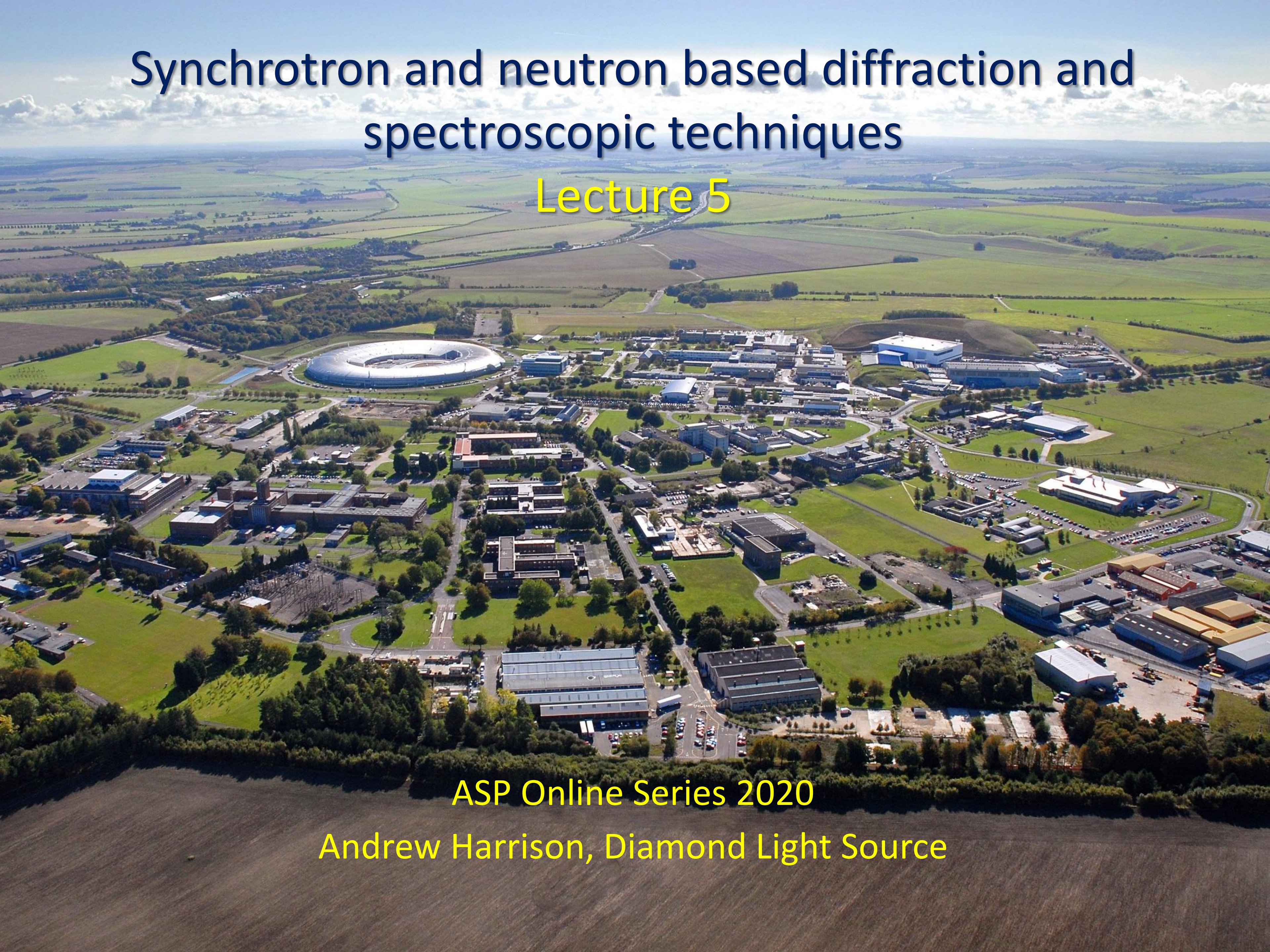


Synchrotron and neutron based diffraction and spectroscopic techniques

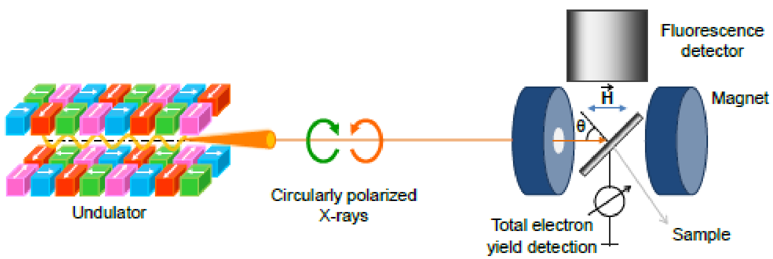
Lecture 5

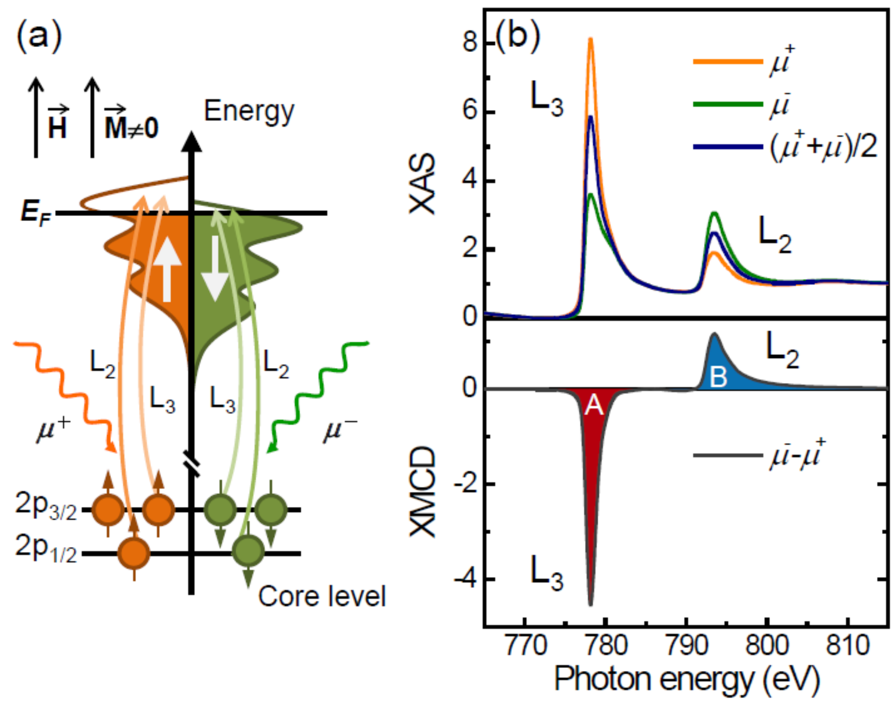
ASP Online Series 2020

Andrew Harrison, Diamond Light Source

Mapping magnetism

- Electronic transitions may also involve changes in spin/magnetic state (m)
- Probe by XAS with CD: LCP-RCP reveals $\Delta m = +/- 1 \rightarrow$ XMCD

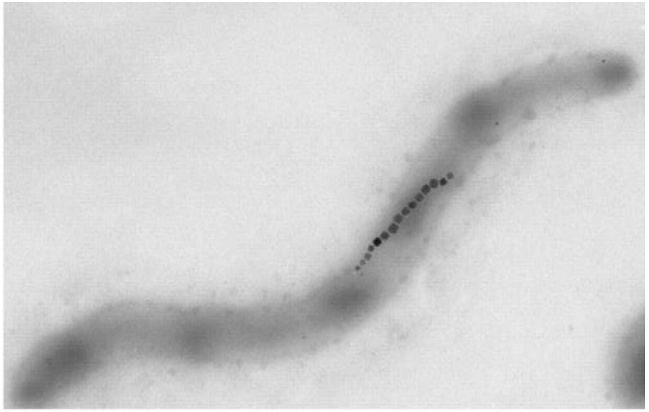


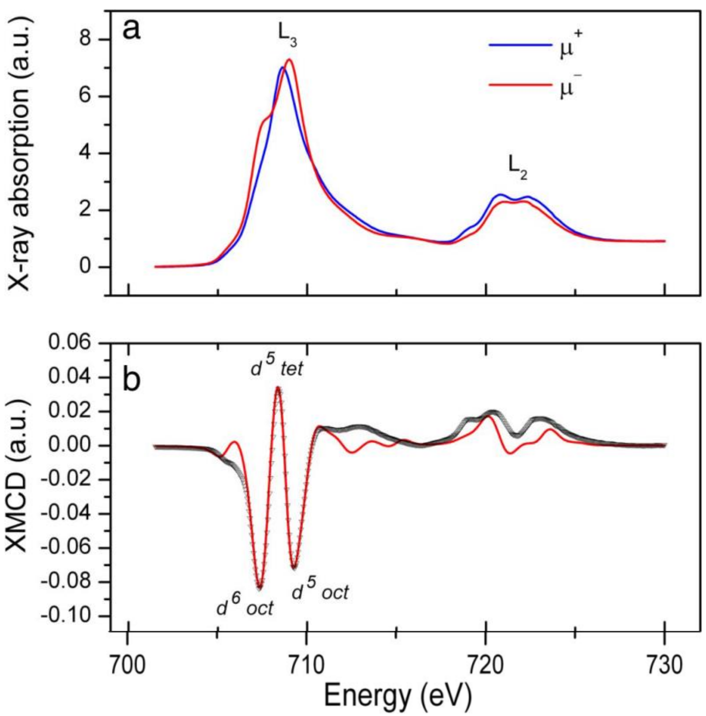


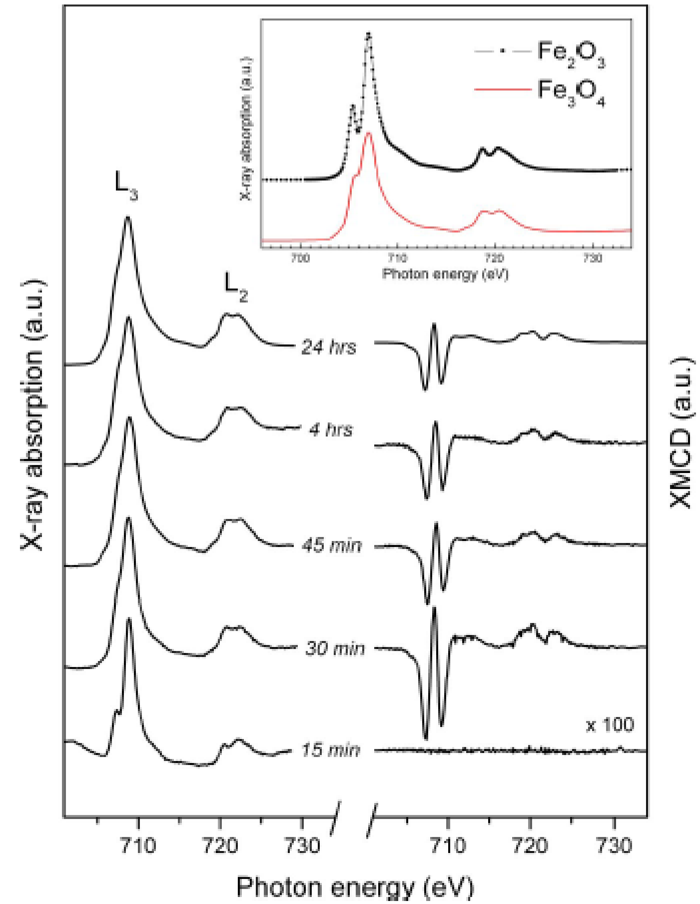
- XAS with LP radiation: Δ ($\perp$-//) ~ $\langle M^2 \rangle \rightarrow$ XMLCD

G van der Laan and A.I. Figueroa, Coord. Chem. Reviews 277-278 (2014) 95

Magnetic bugs





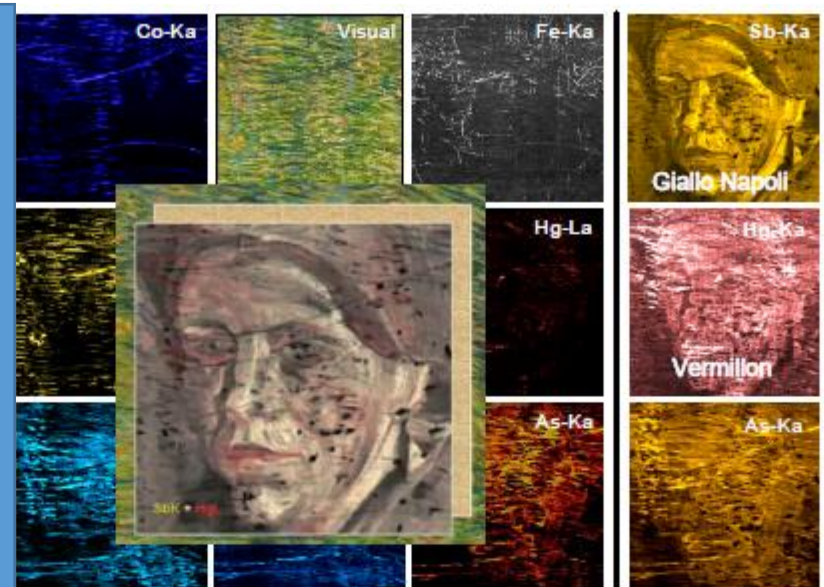


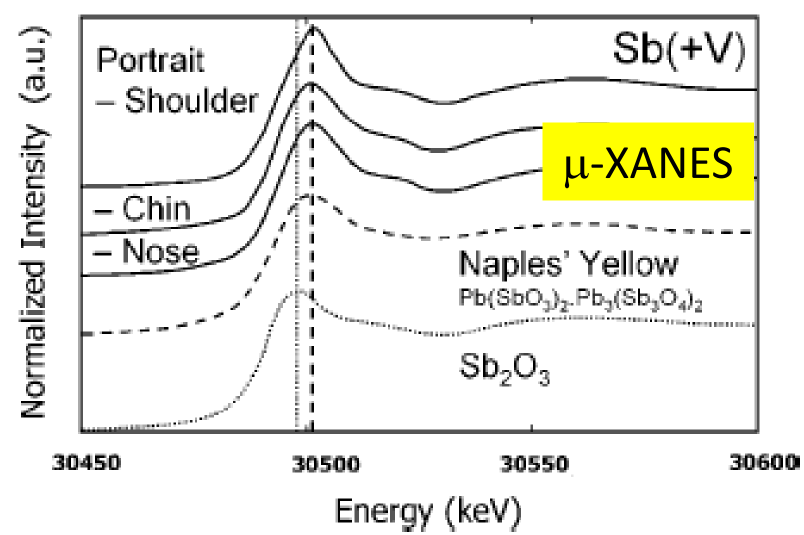
Follow growth of magnetic particles in situ by XMCD

Staniland et al, PNAS, 104 (2007) 19525

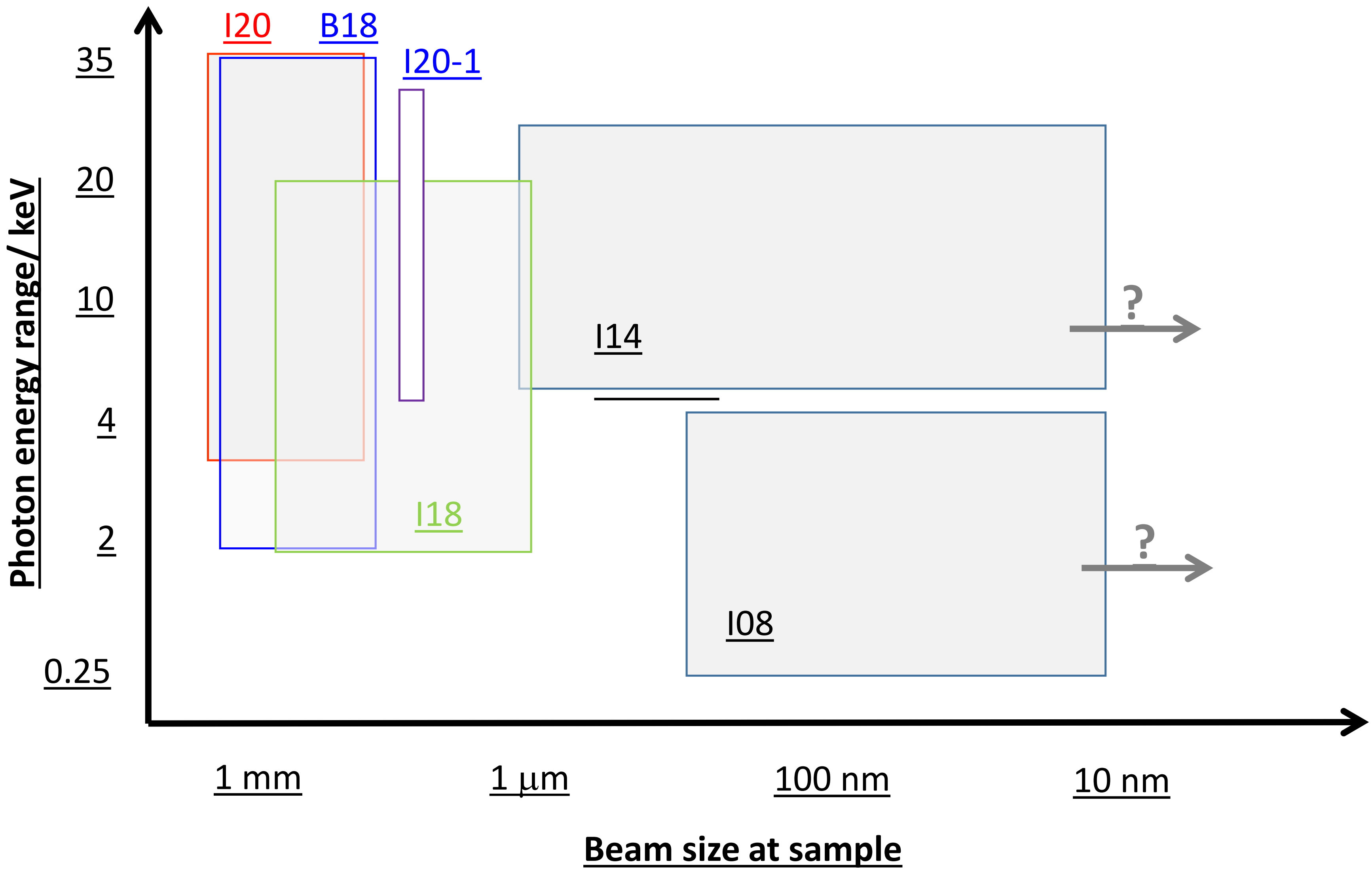
XRF

- Highly sensitive, element-sensitive probe with high spatial resolution



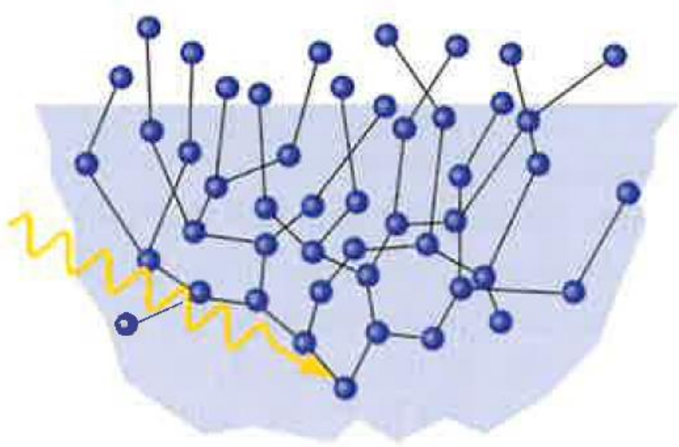


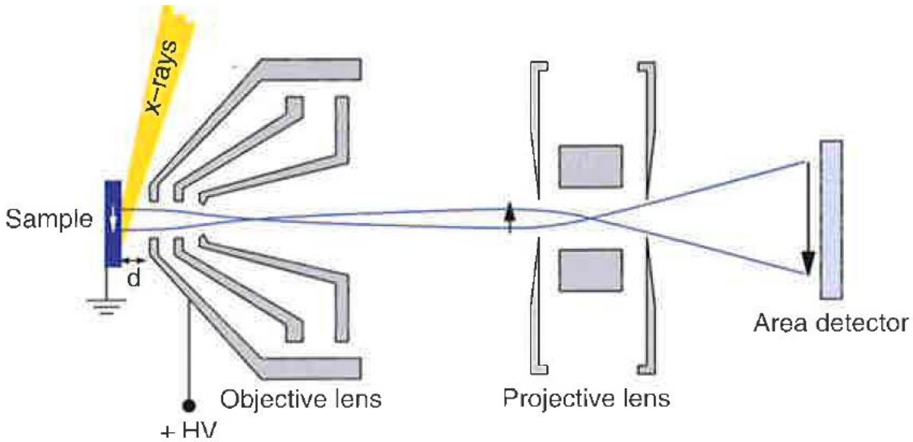
Micro- and nanoprobe suite



XAS Nanoprobes

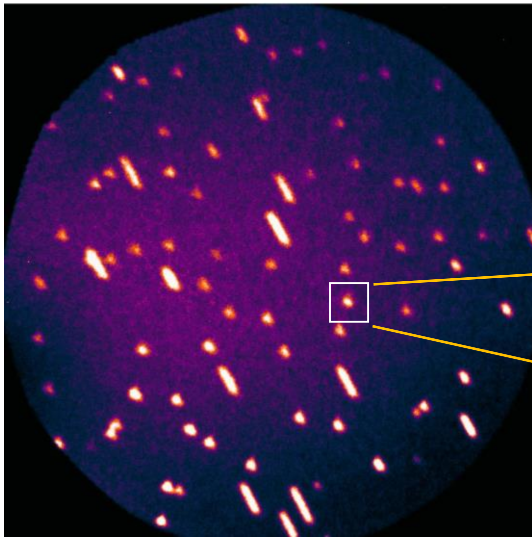
- Resolution to 50 nm with Photoemission Electron Microscopy (PEEM)
- XAS in XANES region produces photoelectrons which create secondary, low-energy (eV) photoelectrons with longer mean-free path. Spatial resolution for imaging these e^- is 10’s of nm
- Exploit to make nanoscale maps of chemical or magnetic character



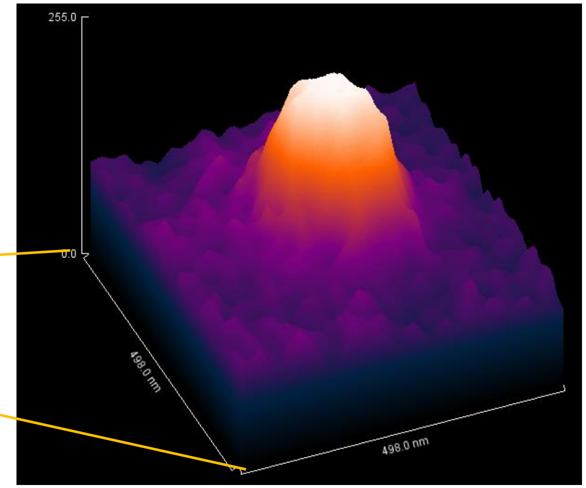


XAS Nanoprobes

- Exploit to make nanoscale maps of chemical character

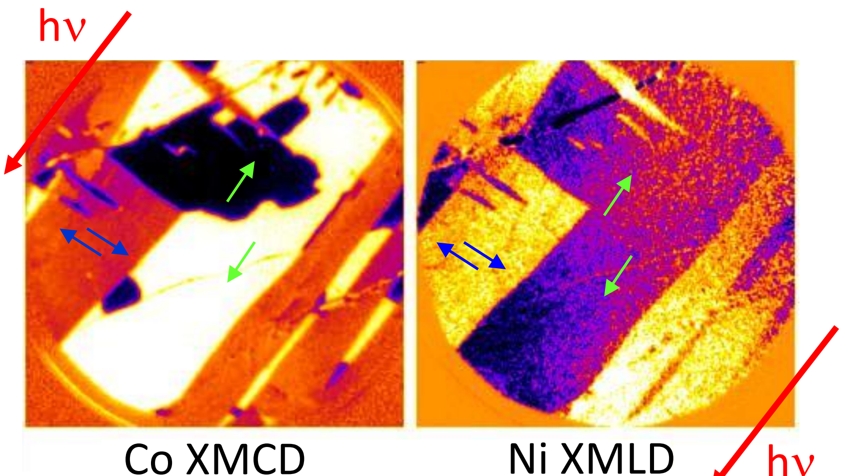


Thornton et al, UCL



Pd nanorods on TiO_2 recorded using hν = 450eV, FOV = 10 μm

- PEEM plus XMCD, XMLD to map magnetic domains to nm lengthscales



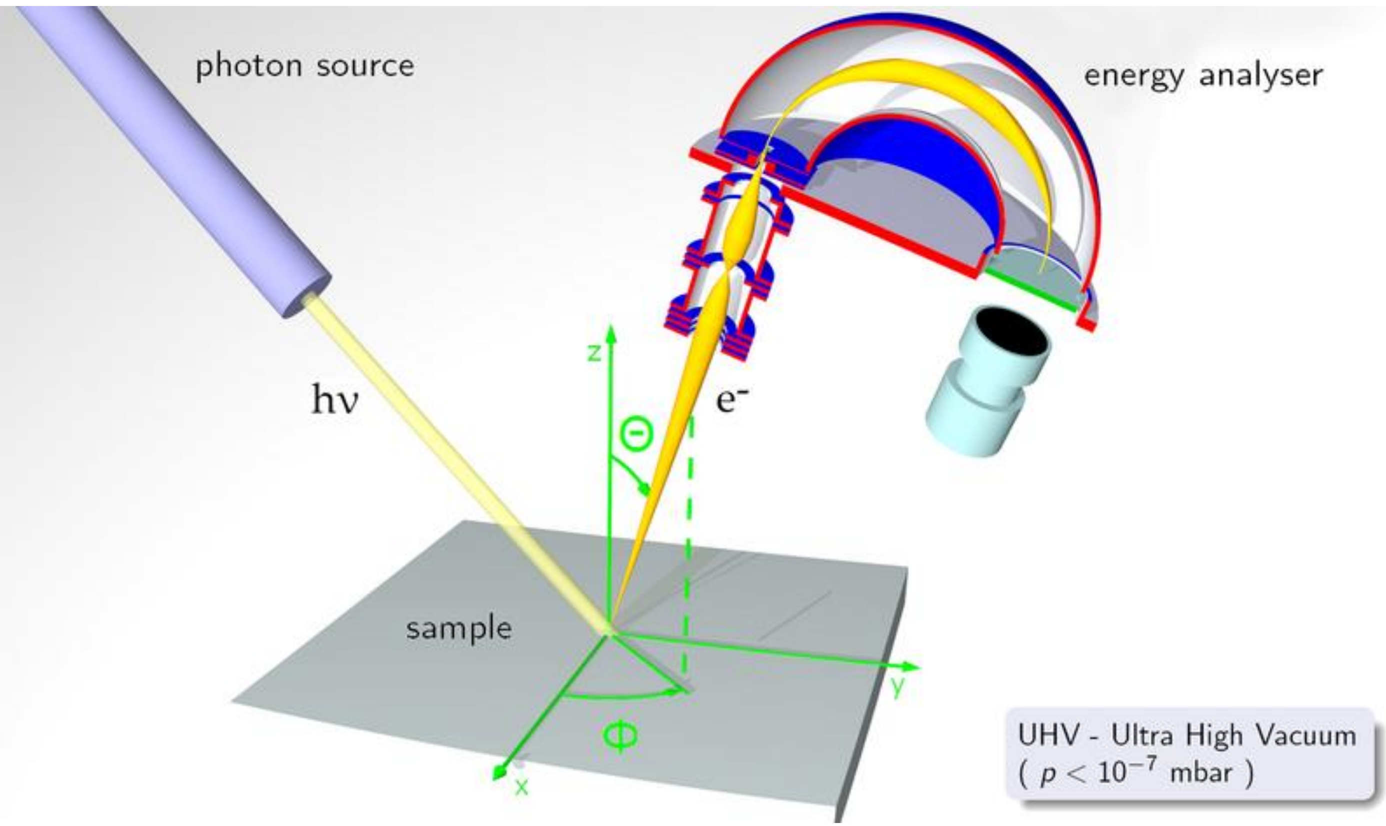
Co XMCD Ni XMLD

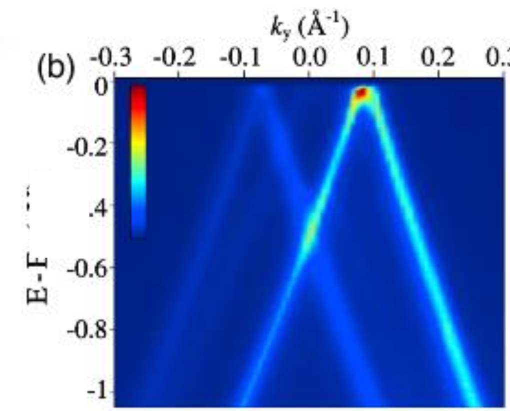
XMCD for (FM) Co L3 and XMLD for (AFM) Ni L2 shows orientation of the two types of moments at the interface is perpendicular – opposite of what was inferred from less precise measurements, crucial for device function

Van der Laan et al, Diamond

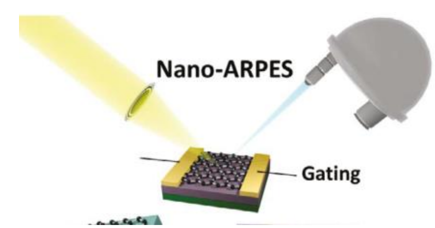
ARPES – Angle-Resolved Photoemission Spectroscopy

- Measure energy and momentum of valence electrons to map out band properties of surfaces
- Now with nano-ARPES can map behaviour to < < 1μm, e.g. in heterogenous materials and devices





Graphene on SiC



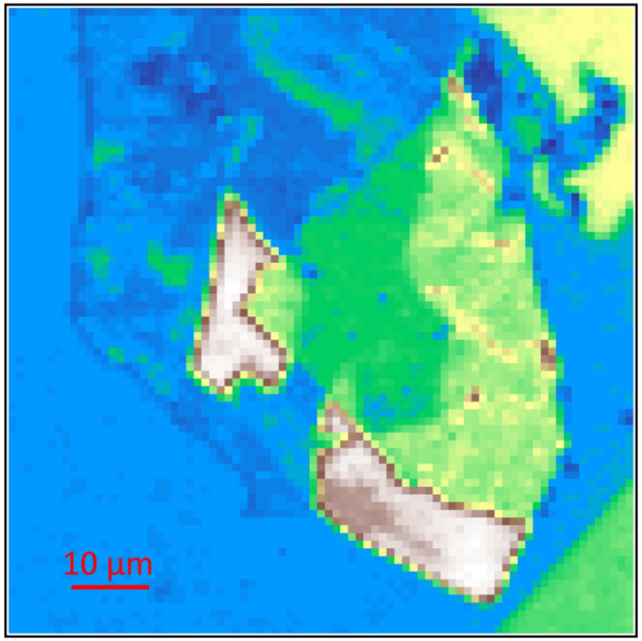
Nano-ARPES imaging device components

ARPES and nano-ARPES

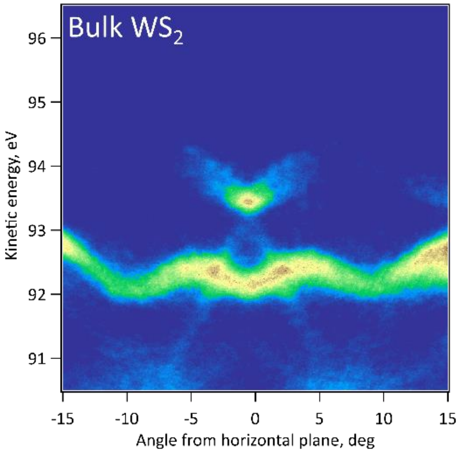
Synchrotrons enable ARPES to be measured with spatial resolution < 1μm

Map out electronic properties of heterogenous materials, devices….

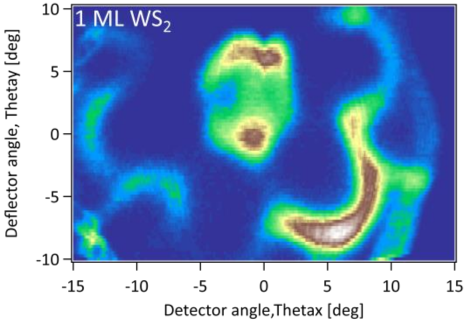
Spatially resolved ARPES image from first user experiment –
Graphene on 1 ML WS_2/BN, Wilson and Teutsch (Warwick)
(integrated over 30° angle and 7 eV energy band)



ARPES from image



Energy cut of 3D ARPES scan from micro-spot

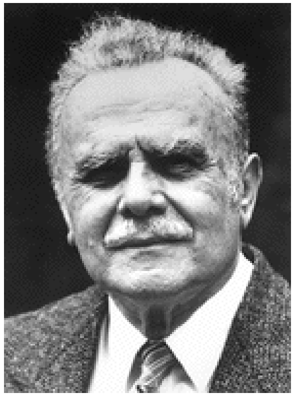


Neutron scattering

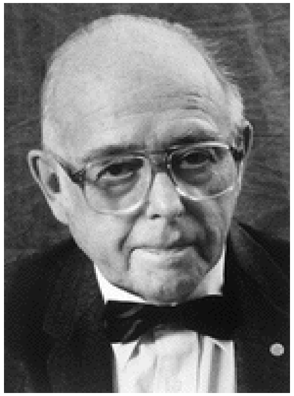
Neutron scattering

- A unique probe of ‘where atoms are and what atoms do’

to paraphrase the citation for the Nobel Prize in Physics awarded to Brockhouse and Shull in 1994



Bert Brockhouse



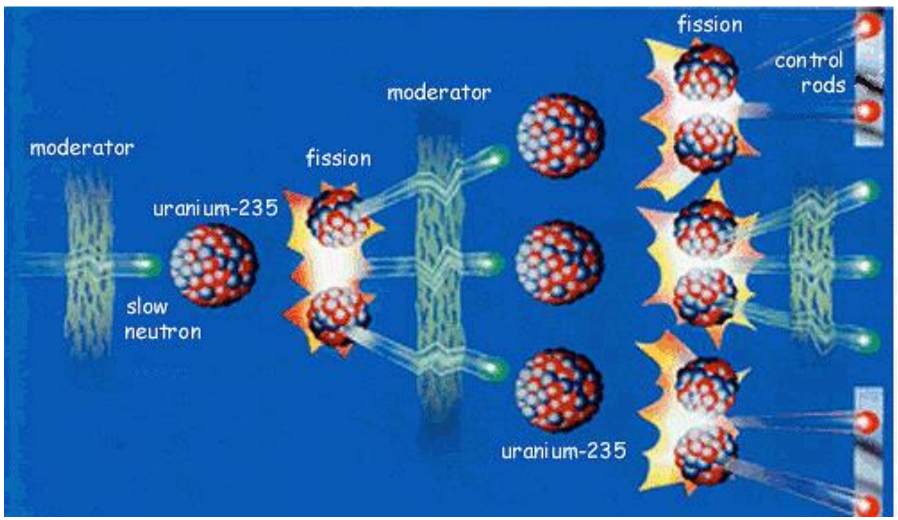
Cliff Shull

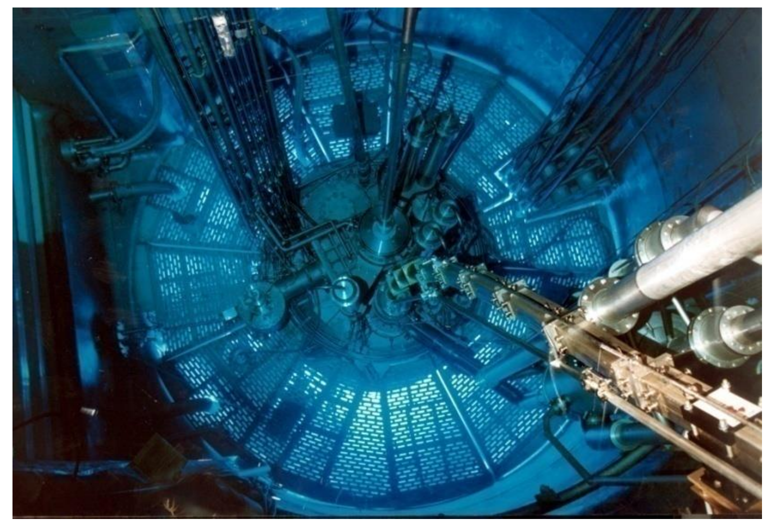
Properties of neutrons

- Uncharged, subatomic particles found in atomic nuclei
- Approximately mass of proton
- Can be produced as free particles in beams as a consequence of nuclear fission or spallation

  Fission - e.g. $^{235}U + {}^{1}n$ = fission fragments + 2.4 ^{1}n + 192.9 MeV

  Spallation – high energy protons + heavy metal target (W, Hg) = high energy neutrons

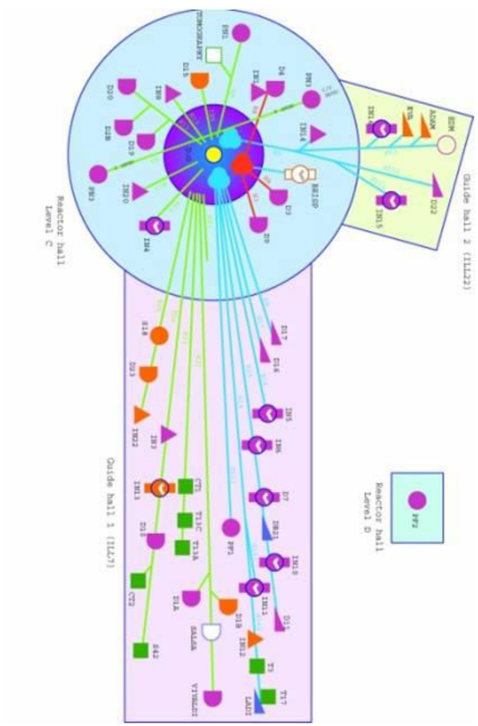


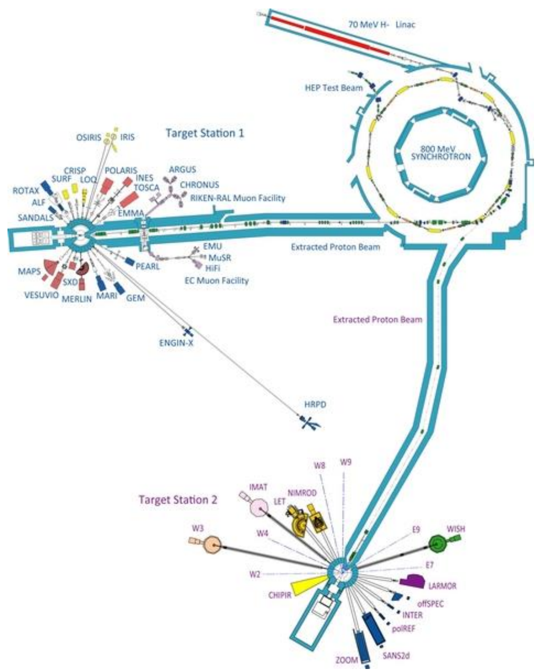


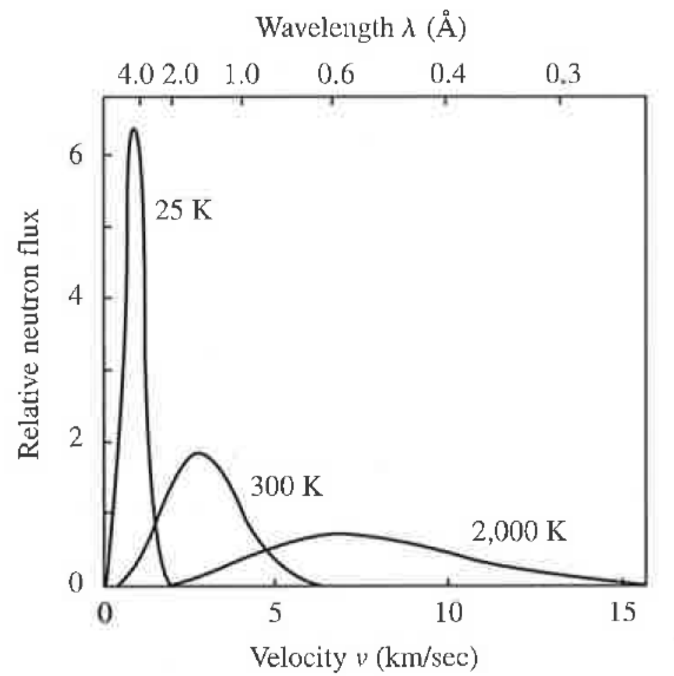
- Wave-particle duality: $\lambda \cong 1.8$ Å at room temp (~2 km/s)) – diffraction
- Possesses a small magnetic moment equivalent to s = ½ - magnetic probe

Harnessing neutrons in facilities

- Neutrons generated at a reactor or spallation sources have high energies, which are moderated by passing through a medium such as water to produce a Maxwellian distribution. Cold or hot sources (liquid H_2, solid CH_4 at 20-25K on one hand, graphite at 2400 K on the other) produce other distributions.
- Neutrons can be ‘piped off’ in beams using tubes with reflective inner surfaces called guides and delivered to instruments

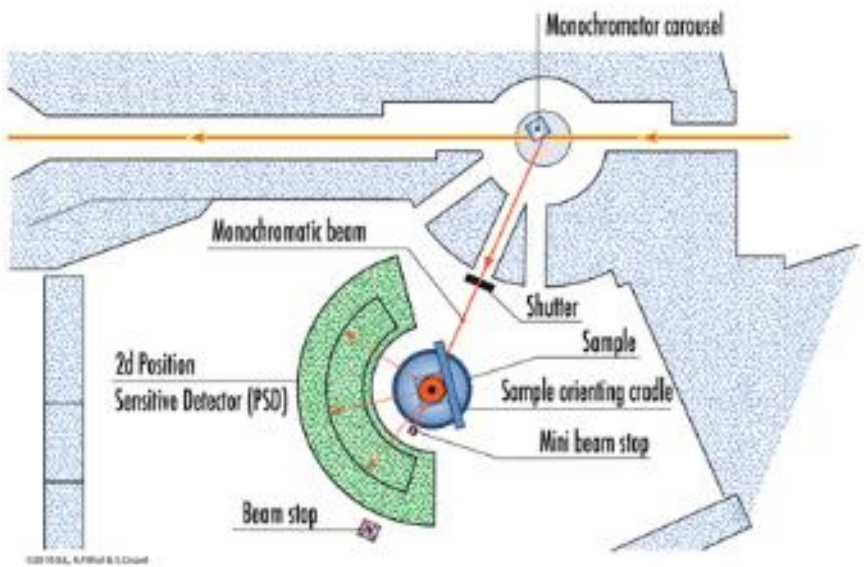


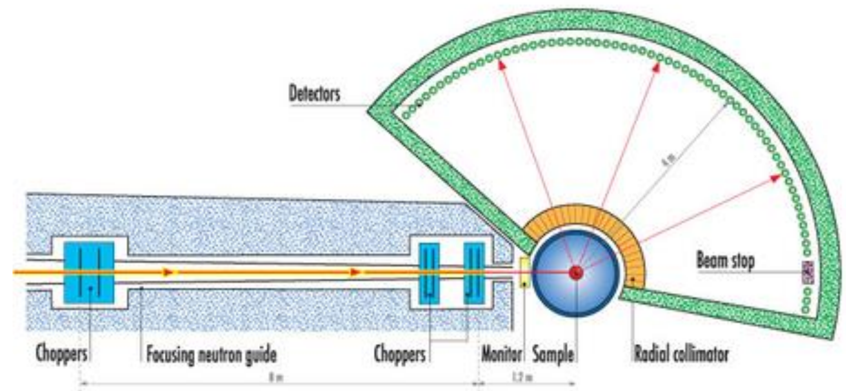




Harnessing neutrons in facilities

- Further selection of energy or wavelength can be made using either a monochromator crystal or some form of rotating shutter or chopper that only lets neutrons within a certain range pass.
- Guides are usually slightly curved to avoid direct line of sight of higher-energy neutrons from the source
- Neutron instruments – particularly at reactor sources – have some features in common with X-ray instruments (diffractometers, SANS and reflectometry, imaging instruments), but also some distinct differences, mainly because of important differences between neutrons and X-rays





Neutron –Matter Interactions

- Why build expensive neutron sources if they probe in a similar way to X-rays ?
- Neutrons reveal the properties of materials in complementary ways to X-rays

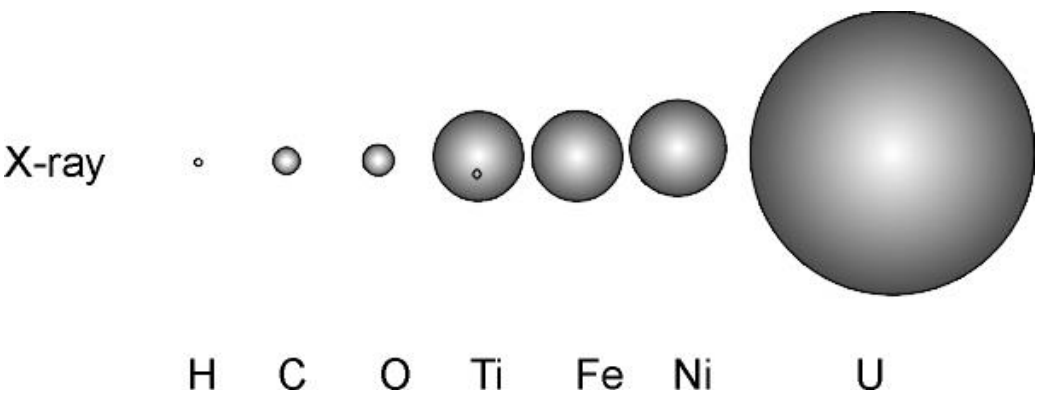
1 – Deeply penetrating and reveal position of light elements such as H or Li

2 – The magnetic structure of materials regardless of magnetic element

3 – Low-energy excitations – diffusion, rotation, low-energy vibrations and magnetic excitations

Neutron-matter interactions (1)

- Neutrons are scattered primarily by the nucleus of atoms, and the scattering length b (or cross-section, $\sigma=\pi b^2$) rises on average with Z much less steeply than for X-rays, as well as having some very distinct deviations from a smooth dependency.



Dependence of scattering strength on Z

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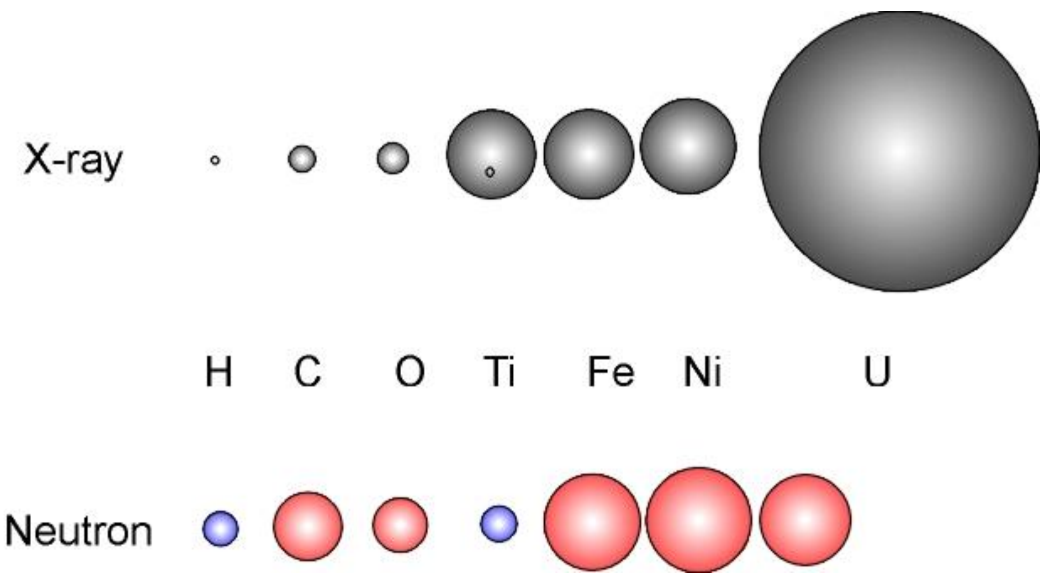
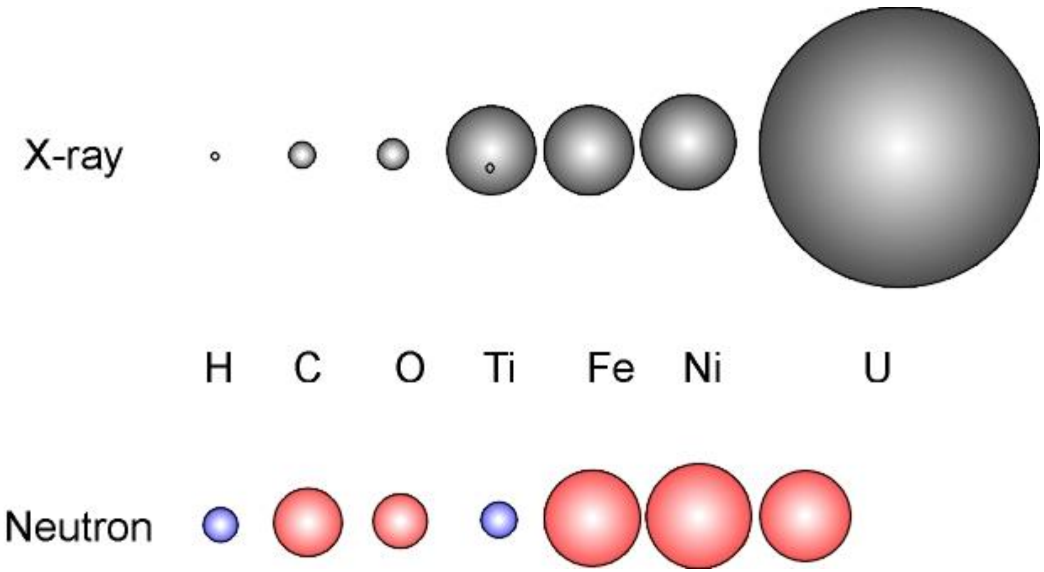


Dependence of scattering strength on Z

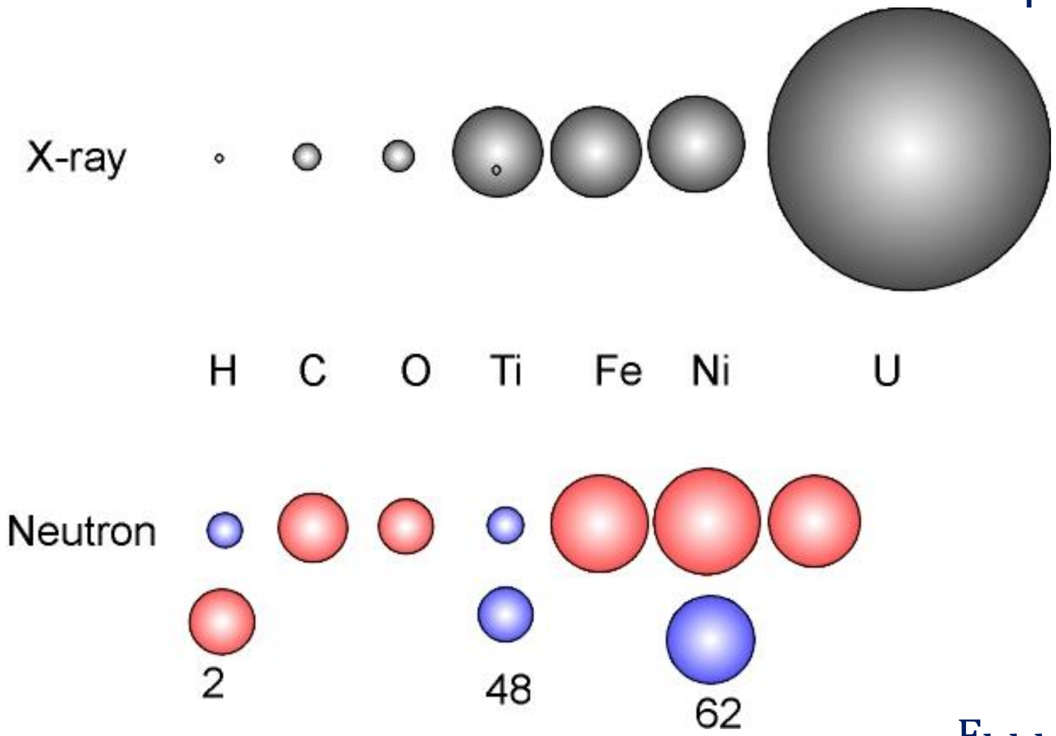
- Neutrons are scattered primarily by the nucleus of atoms, and the scattering length b (or cross-section, $\sigma=\pi b^2$) rises on average with Z much less steeply than for X-rays, as well as having some very distinct deviations from a smooth dependency
- Can look deeper inside dense engineering materials with neutrons



Al almost transparent, much less absorbing than H in coffee pot

Isotopic interactions

- Neutrons are scattered primarily by the nucleus of atoms, and the scattering length b (or cross-section, $\sigma=\pi b^2$) rises on average with Z much less steeply than for X-rays, as well as having some very distinct deviations from a smooth dependency.
- Different *isotopes* can have very different scattering cross-sections because of different nuclear-neutron interactions – particularly H and D

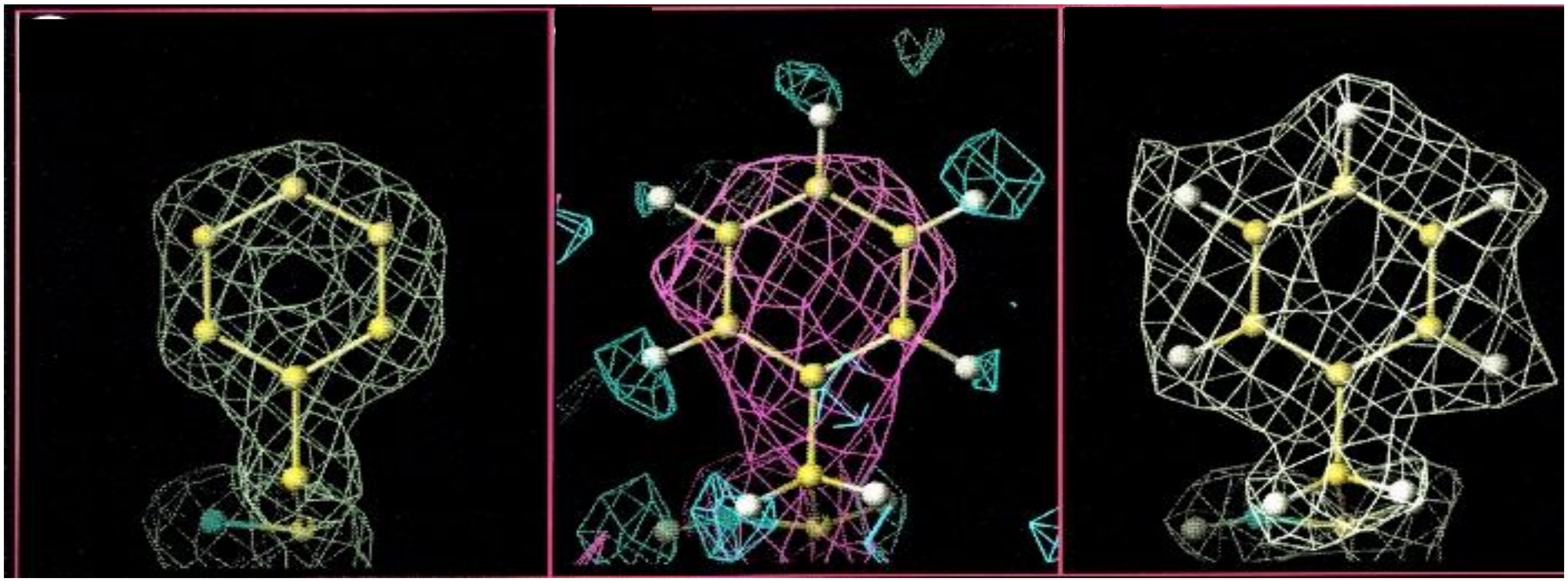


Different colours correspond to different signs for b: positive (red) and negative (blue)

$$F_{hkl} = \sum_j b_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

Pinning down light elements

- Neutron diffraction is particularly effective at finding light elements in diffraction experiments, and we can also exploit contrast between isotopes such as H and D



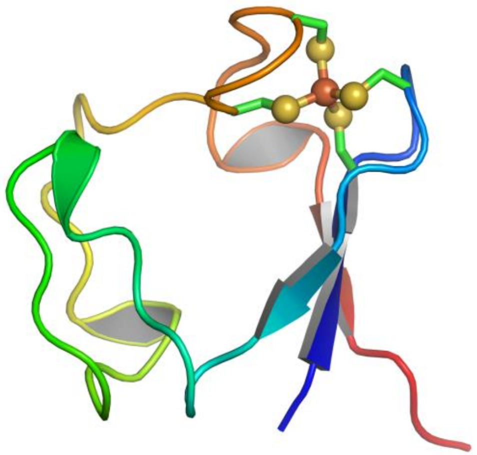
X-ray map   Neutron map (H)   Neutron map (D)

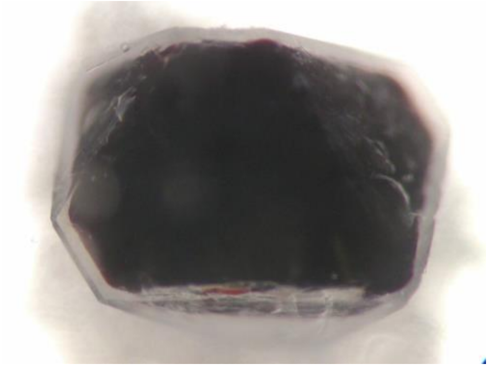
Though we could infer position of H’s knowing where the other atoms are and using chemical intuition…

Pinning down light elements

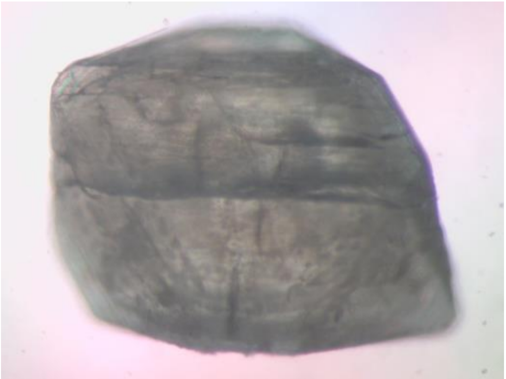
- Location of H atoms when X-rays/chemical 'rules' don't help
- Study of samples susceptible to radiation damage
- Study of Rubredoxin structure illustrates both

  - Small (~6kD) iron-sulphur containing redox protein – important model system to understand electron transfer processes using redox systems – here Fe^{3+} - Fe^{2+}
  - Fe^{3+} form very easily reduced in the X-ray beam





Fe^{3+}

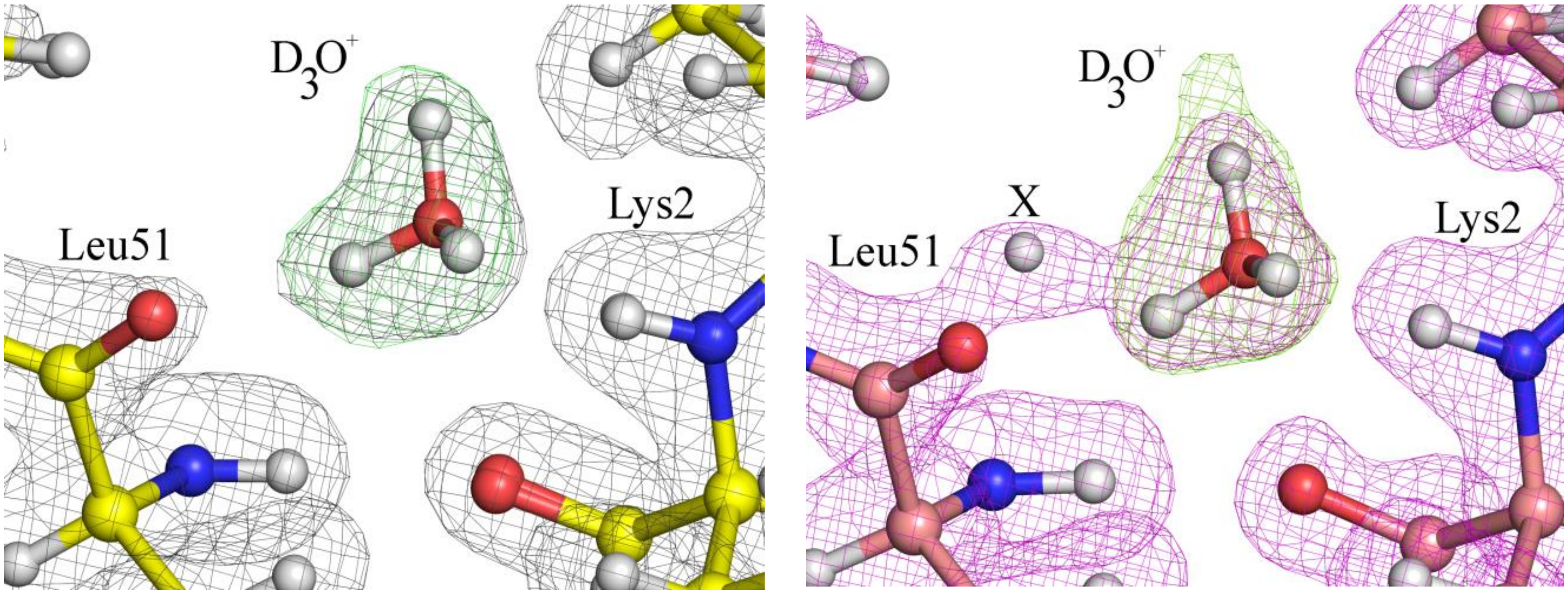


Fe^{2+}

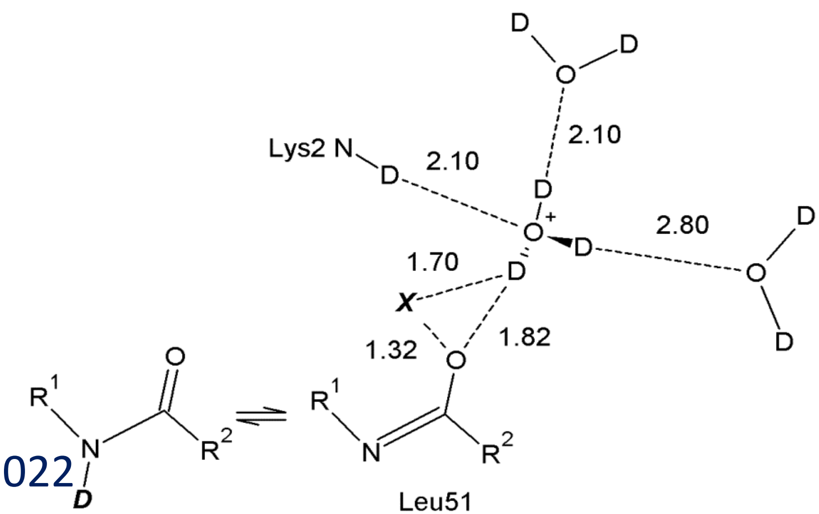
Max Cuypers *et al*, *Angewandte Chemie 52* (2013) 1022

Pinning down light elements

- Structure of reduced and oxidised form measured on D19 at ILL



Observation of hydronium (D) ions and of tautomeric shifts following the change from the oxidised form to the reduced form

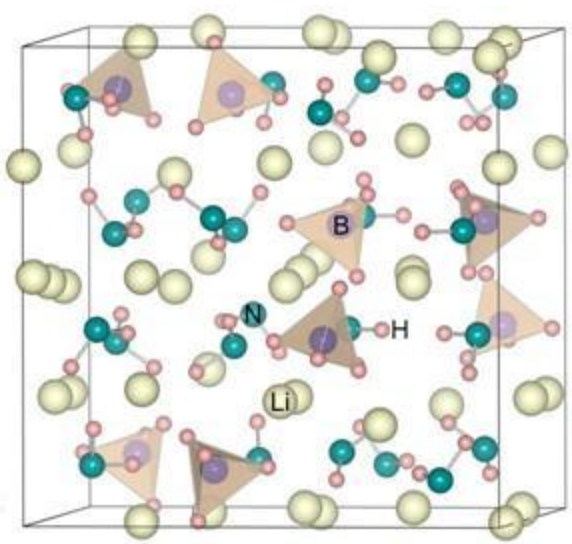


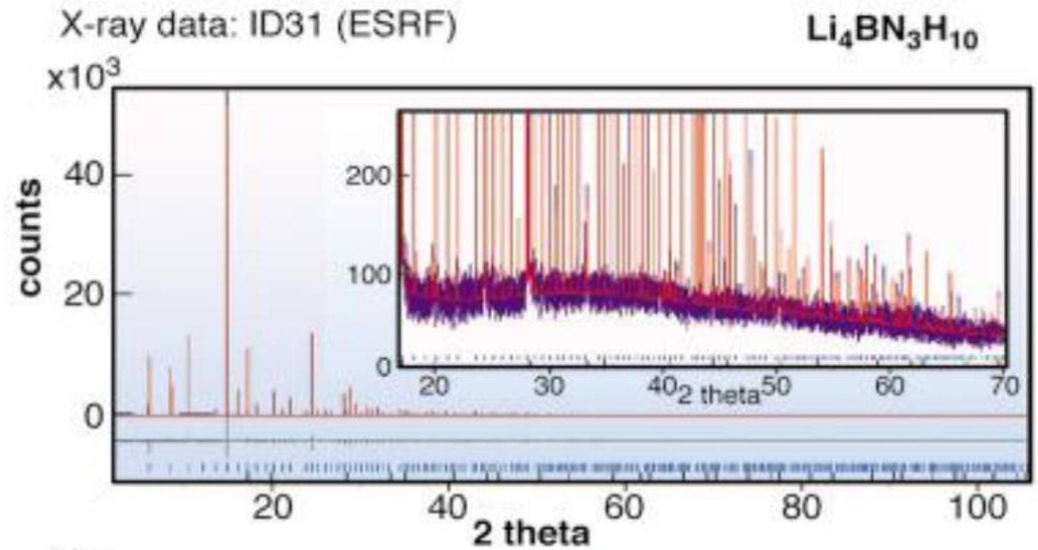
Max Cuypers *et al*, *Angewandte Chemie 52* (2013) 1022

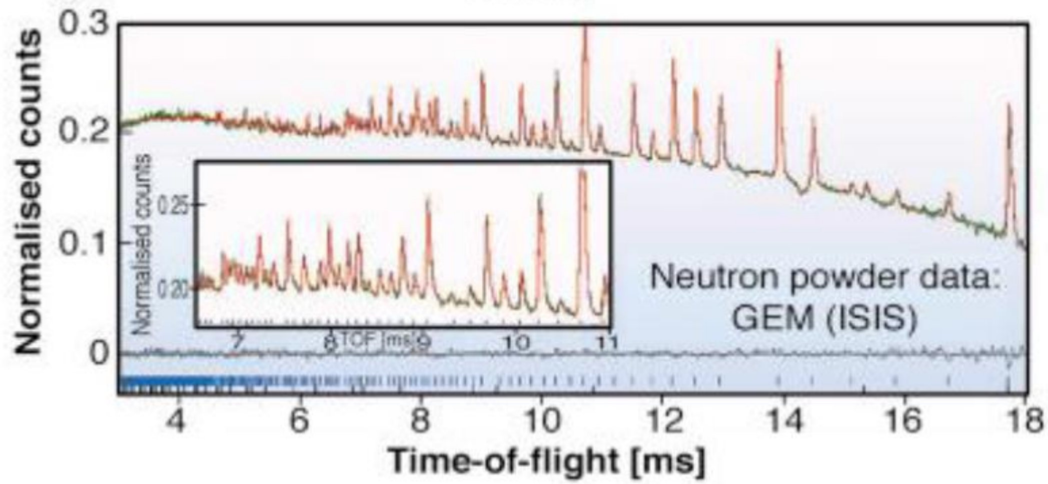
'Hard' materials

- Many important materials contain hydrogen or other light atoms that are crucial to function – e.g. for hydrogen storage materials

- Combine X-rays for rapid, high-resolution survey/ study then neutrons to locate H, Li, etc….

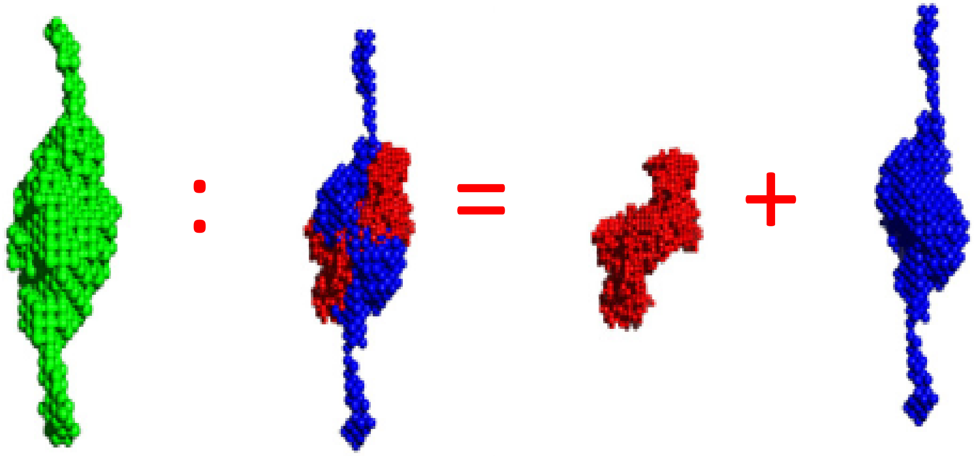


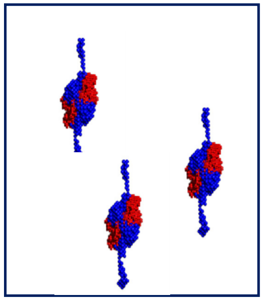




Contrast variation

- H and D have very different neutron scattering cross-section - H is negative and D is positive so mixtures of the two have a very variable average that can be used to tune the contrast between a scatterer and the medium it is in – exploit in SANS $(n \lambda = 2d \sin \theta)$
- e.g. Enzyme with two distinct parts (genes) to select then act (methylate) a specific DNA sequence to protect it. Deuterate one and not the other then suspend in media with variable H/D (H_2O/D_2O)





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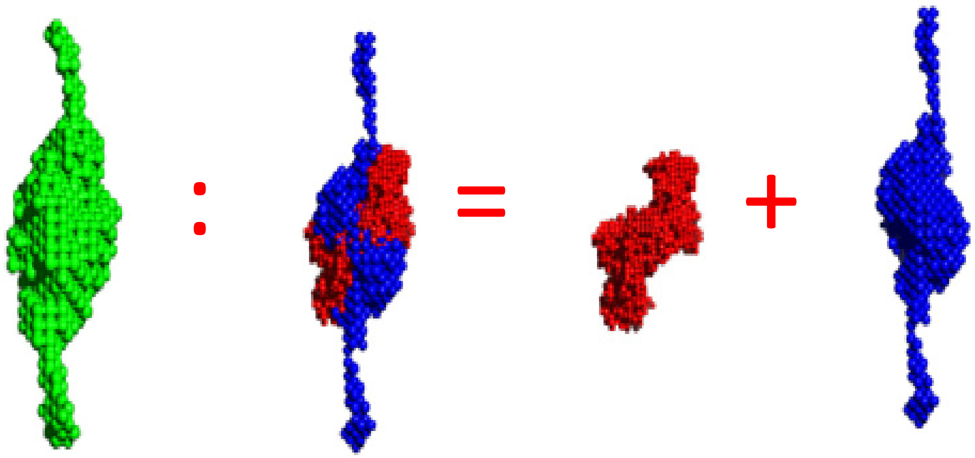

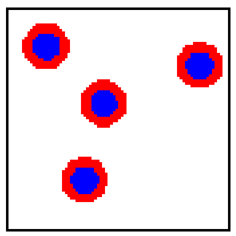

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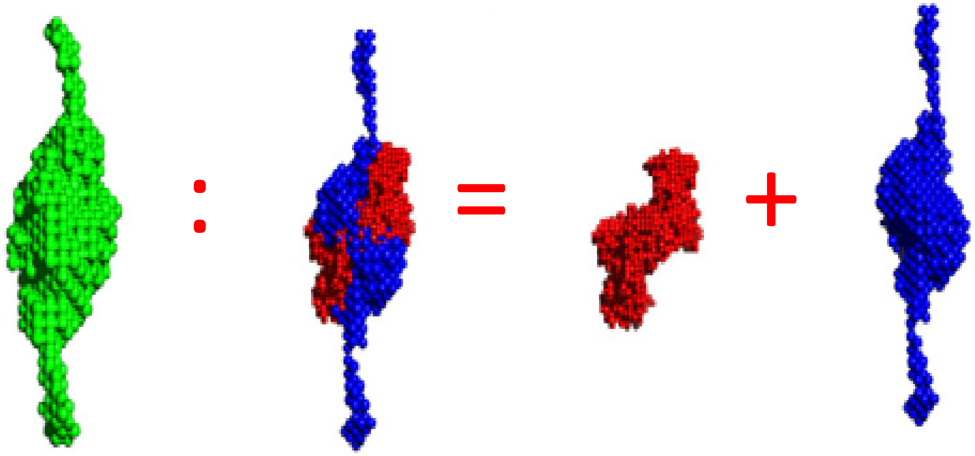

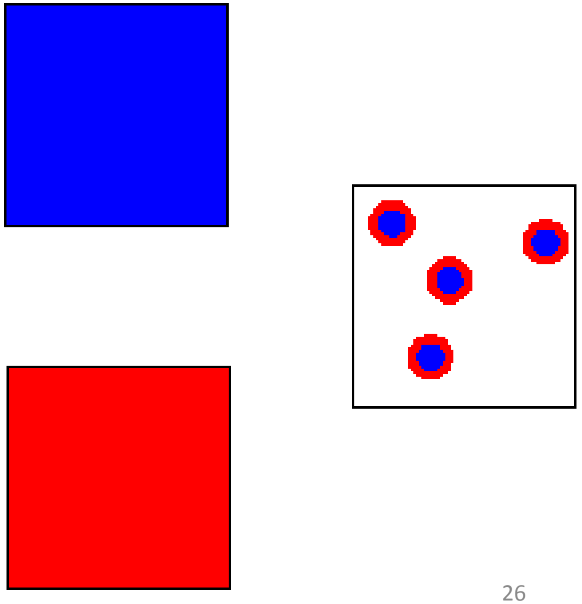

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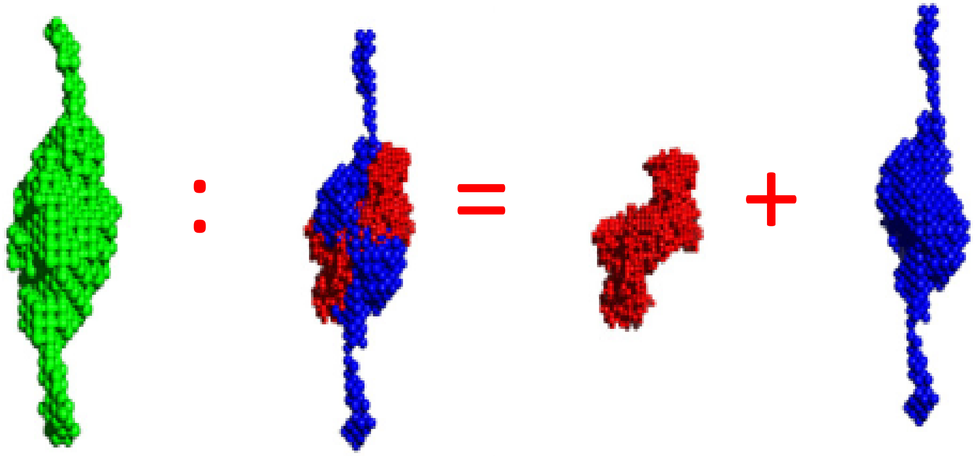

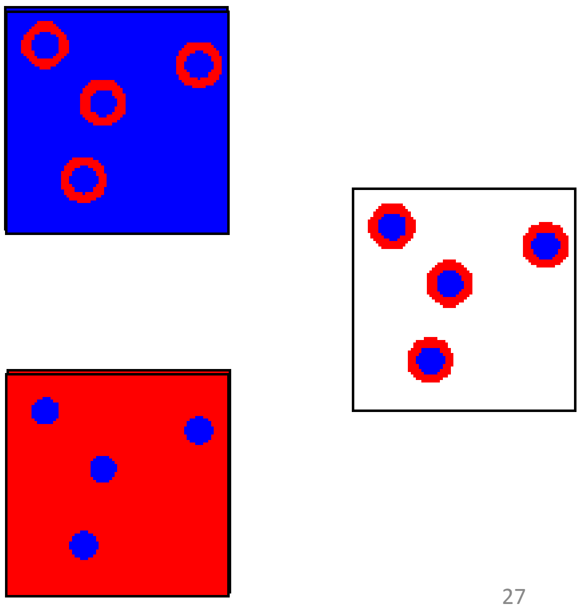

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