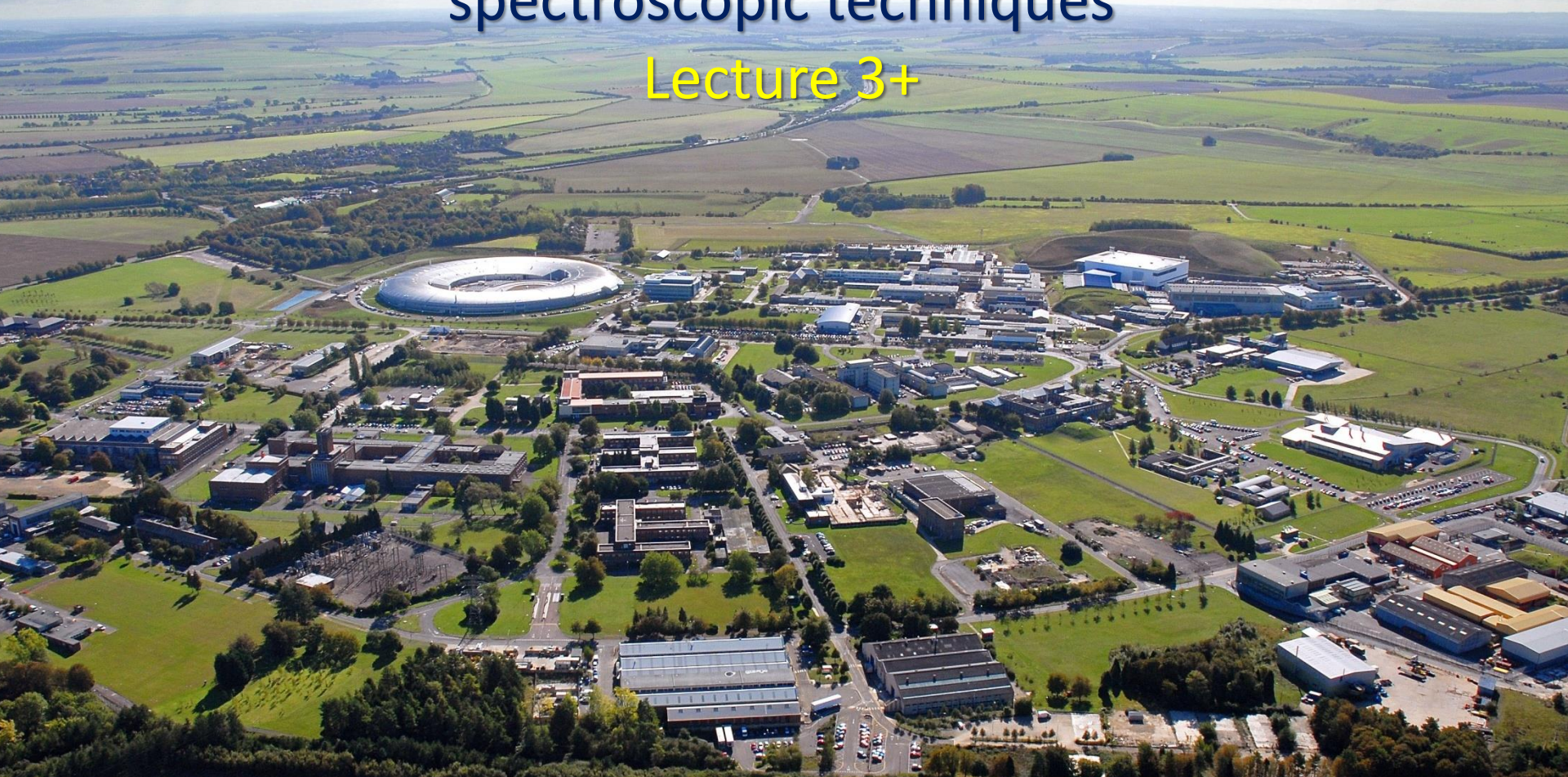


Synchrotron and neutron based diffraction and spectroscopic techniques

Lecture 3+

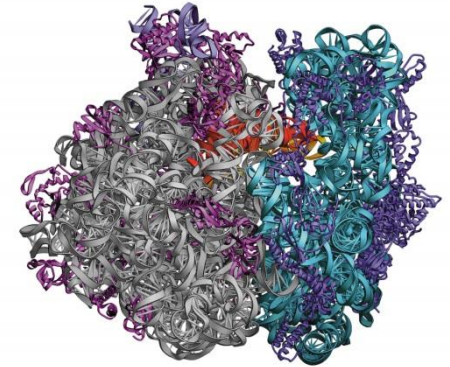
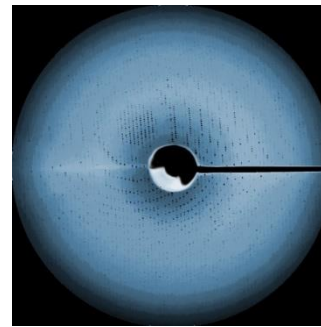


ASP Online Series 2020

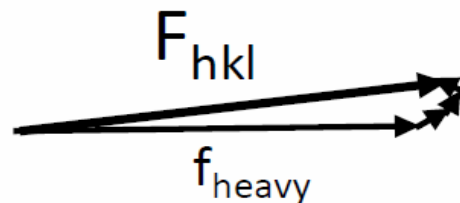
Andrew Harrison, Diamond Light Source

Failure of direct methods

- Direct methods do not work for the large macromolecules that govern life and are implicated in disease and drug discovery and can contain 100's of thousands of atoms – e.g. the work on the structure of the ribosome which was recognised by the award of the 2009 Nobel Prize in Chemistry to Ada Yonath, Venki Ramakrishnan and Thomas Steitz



- Note that scattering from an individual atom $\propto Z^2$ so heavy atoms can dominate scattering. If a natural atom such as S is substituted in the structure by Se this can help us determine the phase.

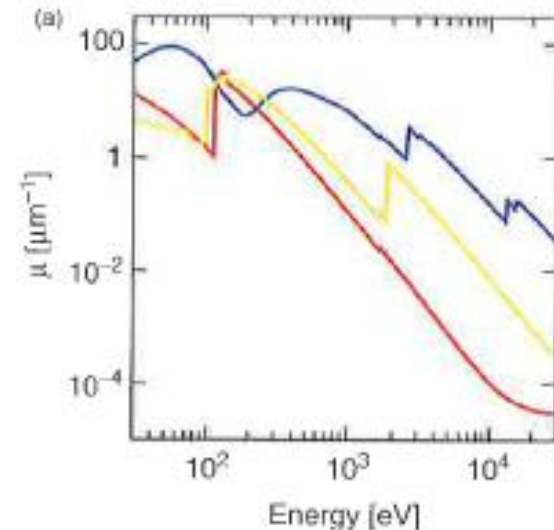
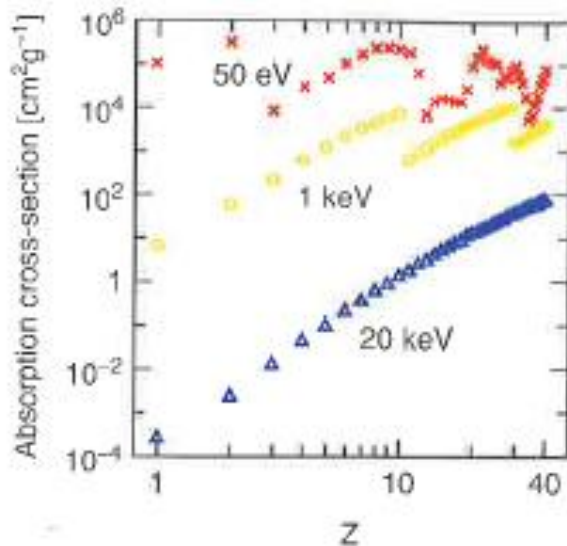


Multiple Isomorphous Replacement (MIR)

- This technique of chemical substitution is known as Multiple Isomorphous Replacement (MIR)
- MIR assumes/requires:
 - The structure is not otherwise disrupted by the substitutions
 - At least two substitutions to solve structures unambiguously e.g. S by Se, binding Hg to thiols or uranyl to carboxyl groups – this may be non-trivial and very time consuming
- Synchrotron radiation provides a very powerful alternative to MIR on account of the tenability of its energy and the way that the scattering changes around an absorption edge

Variation in atomic scattering factor with E

- Already noted that Thomson scattering is modified through photoabsorption effect.
- This is not very significant for high energy X-rays and here the scattering factor f of an individual atom in the expression for F_{hkl} is essentially the same as predicted for Thomson scattering, f_0

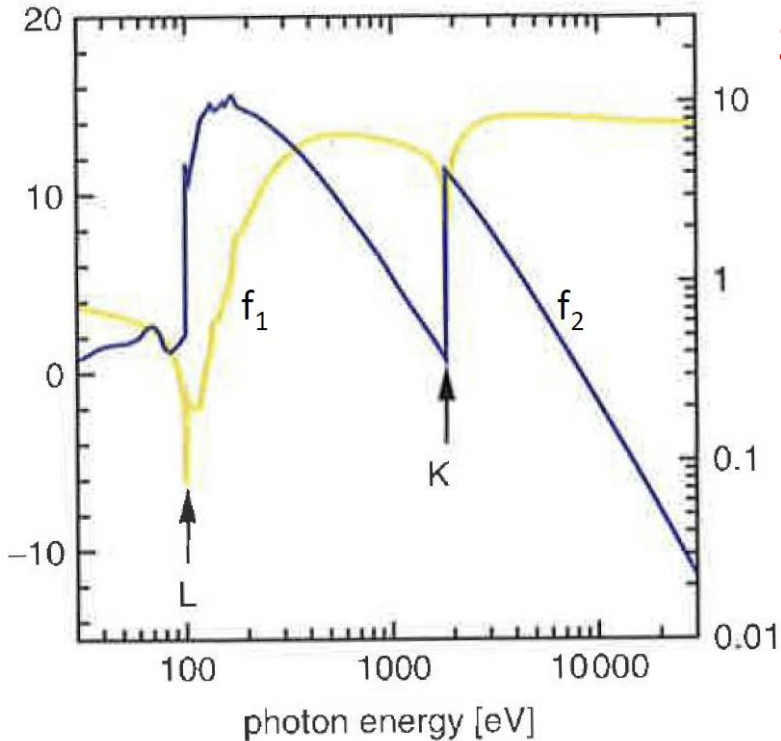


Variation in atomic scattering factor with E

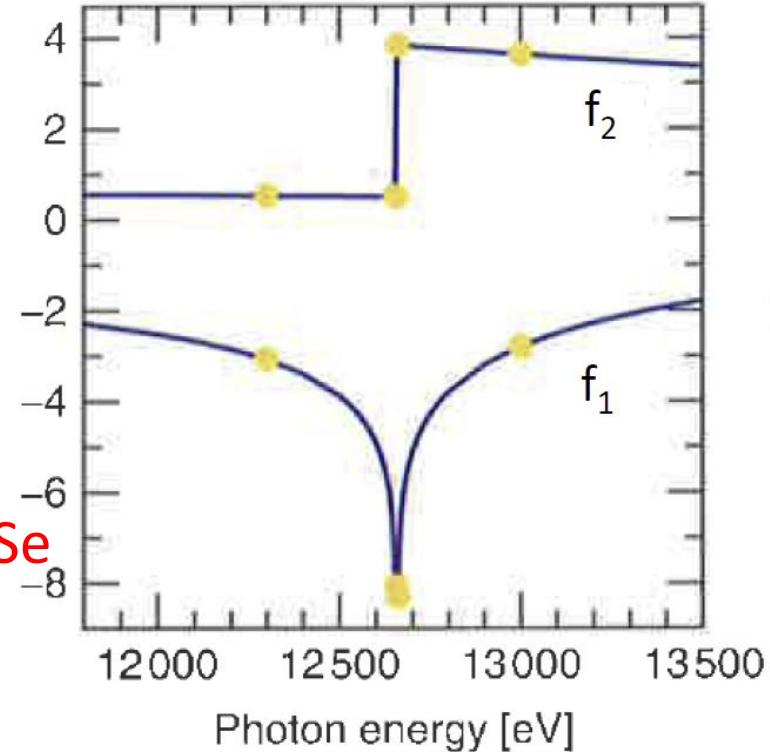
- Already noted that Thomson scattering is modified through photoabsorption effect.
- This is not very significant for high energy X-rays and here the scattering factor f of an individual atom in the expression for F_{hkl} is essentially the same as predicted for Thomson scattering, f_0
- At lower energies, particularly around an absorption edge, the amplitude of the X-rays generated through the Thomson effect is damped significantly, and the scattered wave is no longer in phase with the driving field. As consequence, f must be modified with a real component f_1 representing the damping of the amplitude of the scattered wave, and a imaginary component f_2 that is proportional to the photoabsorption cross-section: $f = f_0 + f_1 + if_2$

Multiwavelength Anomalous Dispersion (MAD)

- f_1 and f_2 change particularly strongly near an absorption edge



Si

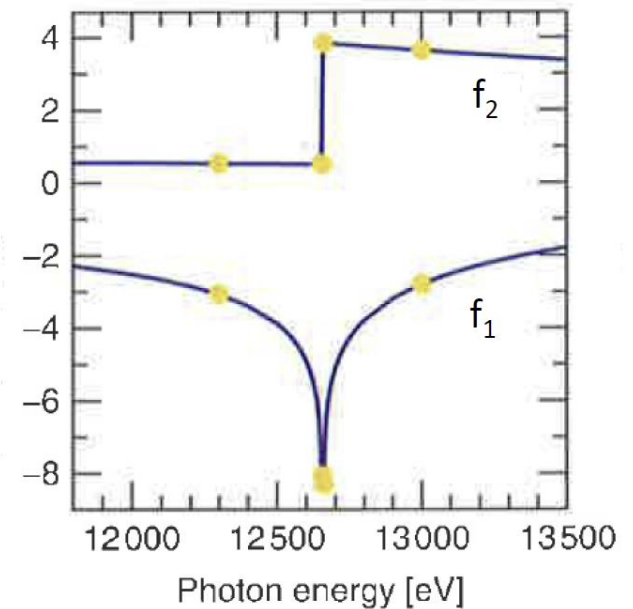


K edge of Se

- This provides the opportunity to tune f for a particular atom strongly without needing to do MIR. In practice about 3 measurements are made around the absorption edge - Multiwavelength Anomalous Dispersion (MAD) - no multiple substitution + crystal growth needed

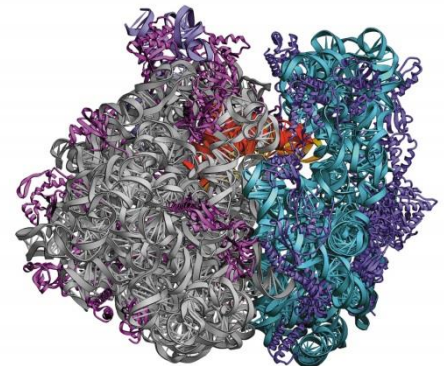
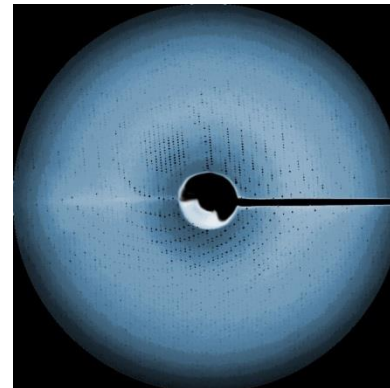
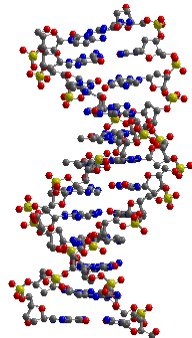
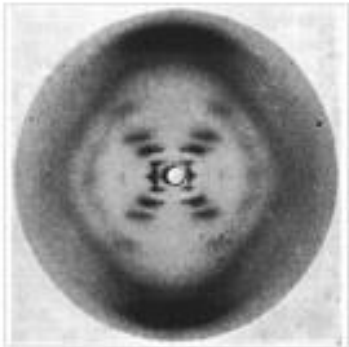
Multiwavelength Anomalous Dispersion (MAD)

- Common method in modern macromolecular crystallography
- Requires an element with an edge at an energy that is suitable for diffraction. If the energy is too low, λ may be so long that there are very few observable reflections for $\theta < 180$ ($\lambda=2d\sin(\theta)\rightarrow d \geq \lambda/2$)
- Further, as the energy drops so the absorption by air becomes very significant and can dominate the signal.
- In practice therefore atoms such as S are substituted for Se, moving the K edge from 2470 eV to 12600 eV

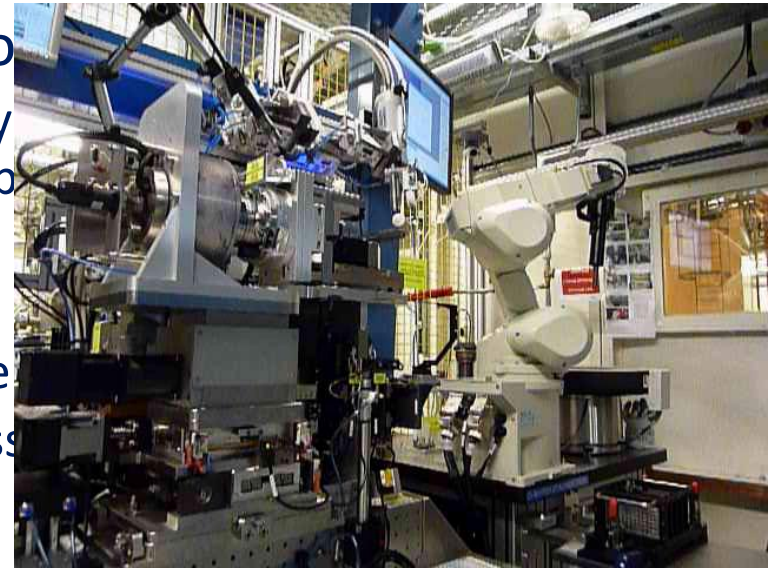


Modern Macromolecular Crystallography (MX)

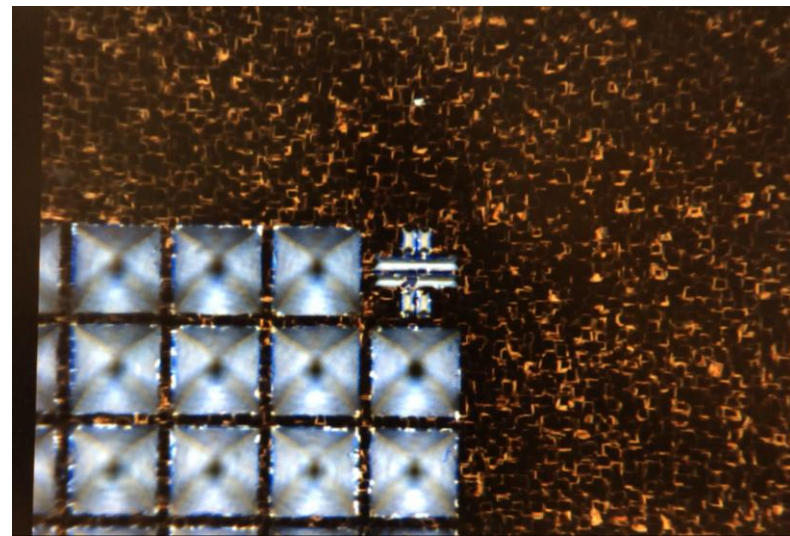
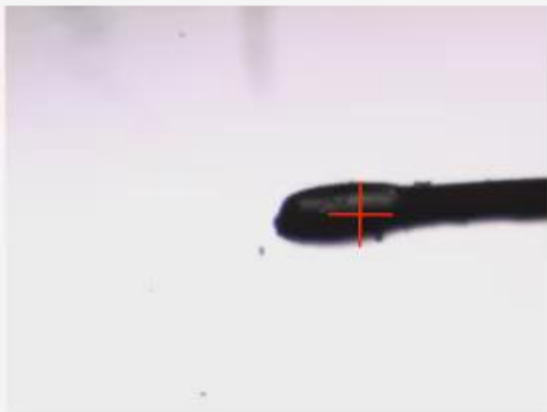
- Complete transformation since the time of Rosalind Franklin
 - Far brighter beams reduce exposures from days to seconds – though care with radiation damage – reject data when crystal appears to fail, which needs rapid refresh rate on detector
 - MAD techniques, which, combined with high-power computing rather than slide rules solves structure in minutes
 - Automation (robotics) facilitates remote access and 100's samples/24 hrs



Modern MX



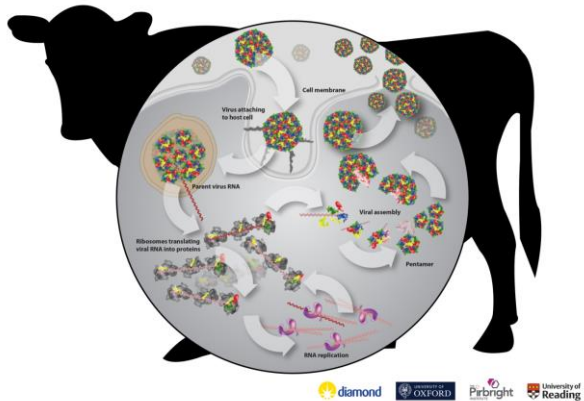
OAV



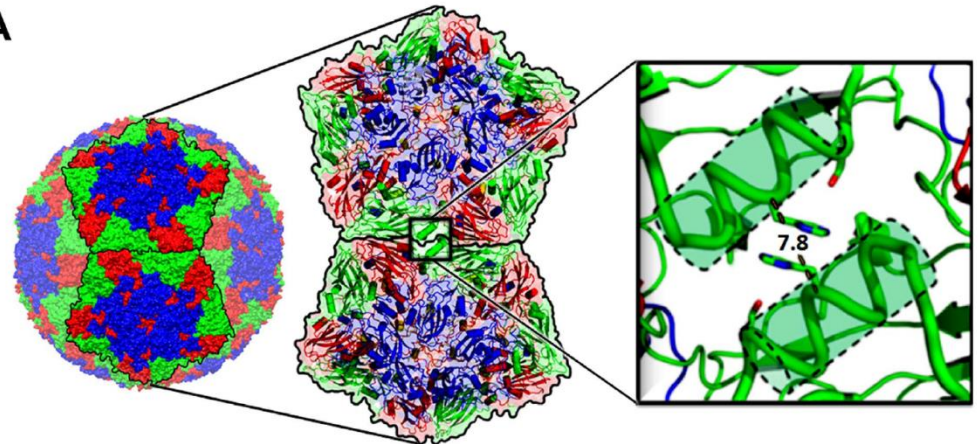
Unpicking virus structures

- FMDV causes huge economic impact, not to mention suffering of cattle
 - Synthesised virus capsid without live genetic material inside, so much safer but less stable thermally than natural virus so less stable in the field e.g. Africa
 - Identify by MX bond that could be strengthened to keep shell together and engineer modified compound that is now thermally stable

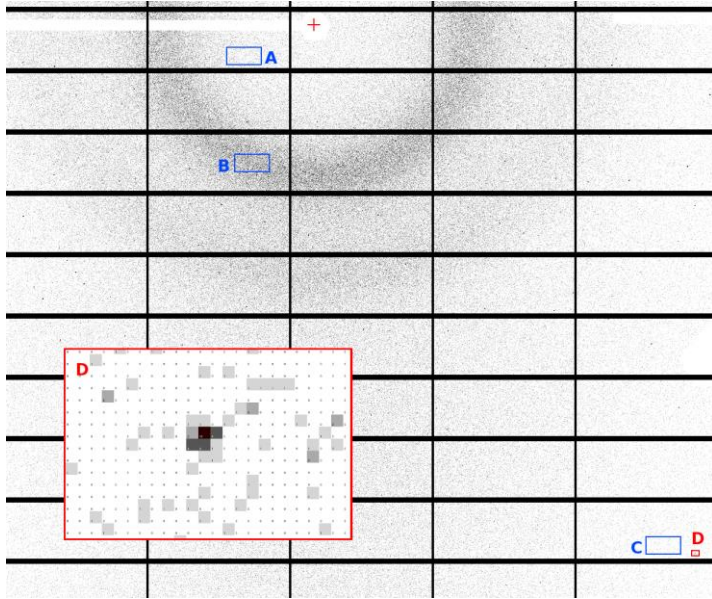
Foot and Mouth disease virus lifecycle



A

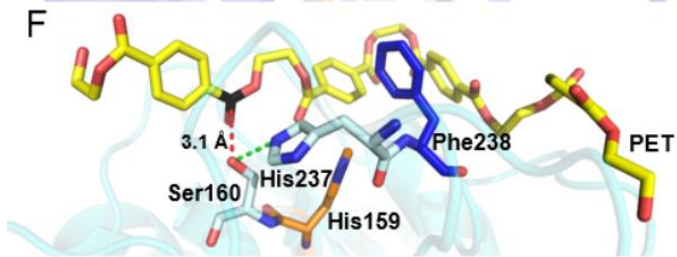
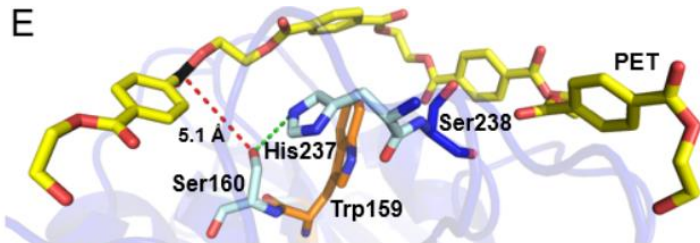
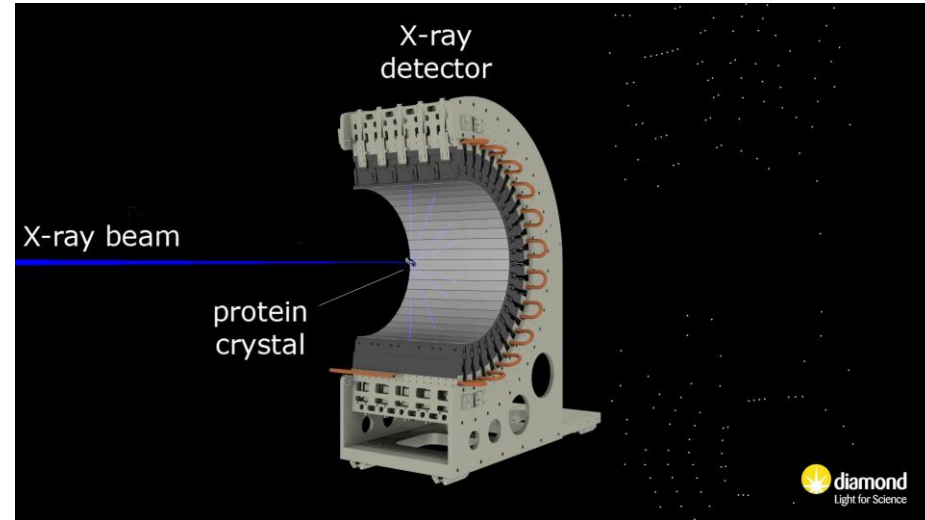
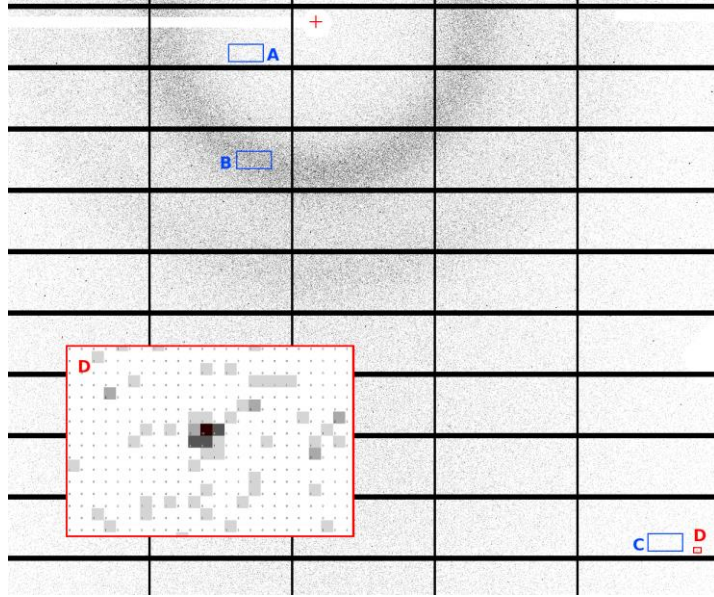


Beyond MAD ? Looking at native proteins



- Scattering from air need the K-edge of S produces unacceptable background
- Develop an *in vacuo* diffractometer (I23)
- Now access 'native' proteins directly

Developing PET-eating enzymes

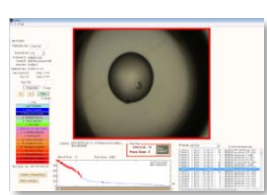


© David Jones

Characterization and engineering of a plastic-degrading aromatic poly(esterase), *PNAS* (2018), Harry P. Austina,¹ Mark D. Allena,¹ Bryon S. Donohoeb,¹ Nichola Rorrerc,¹ Fiona Kearnsd,¹ Rodrigo L. Silveirab,^e Benjamin Pollardd, Graham, Dominickc, Ramona Dumanf, Kamel El Omarif, Vitaliy Mykhaylykf, Armin Wagnerf, William E. Michenerc, Antonella Amoreb, Munir S. Skafe, Michael F. Crowleyb, Alan W. Thornea, Christopher W. Johnsonc, H. Lee Woodcockd*, John E. McGeehana*, and Gregg T. Beckha

Needles in haystacks

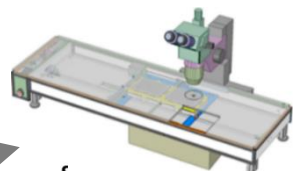
Fragment screening for drug discovery: XChem – 500 samples/24 hrs



Crystal targeting
(TeXRank)



Crystal soaking
(ECHO)



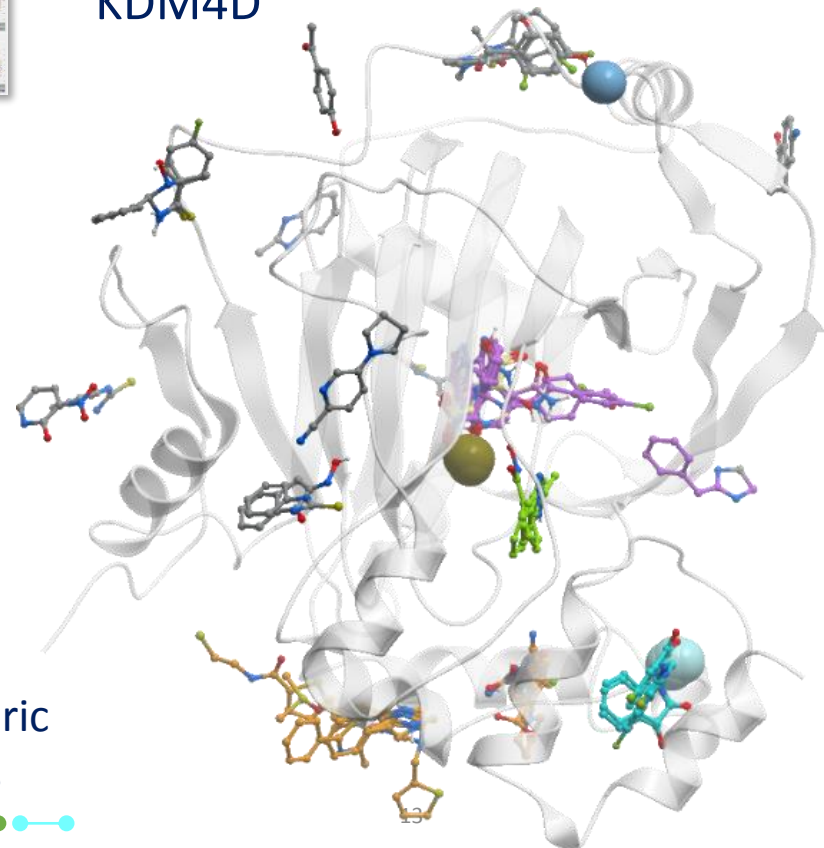
Crystal harvesting
(Shifter)



Automatic data collection
(I04-1)



Outcome of high concentration
soak on Protein coding gene
KDM4D

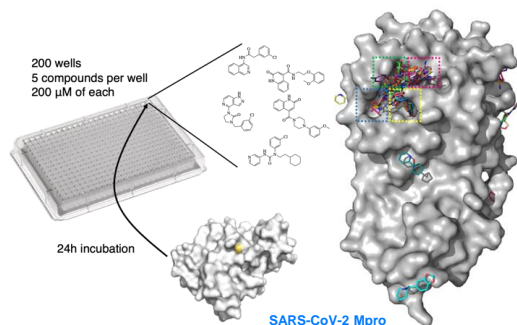


The COVID-19 moonshot

PHASE 0: 1500 fragment soak and X-ray crystallography produces 71 fragment structures [6 Mar 2020]

PHASE 1: IDEATION: 10,000 crowdsourced compound designs submitted [2 Apr 2020]

PHASE 2: OPTIMIZATION [now]



COVID Moonshot
Help us Fight Coronavirus
Contribute your expertise to design inhibitors of the SARS-CoV-2 main protease.

Design a Compound, We Will Make It
We will produce compounds and screen them. You will receive the chemical structures of the compounds that we will make.

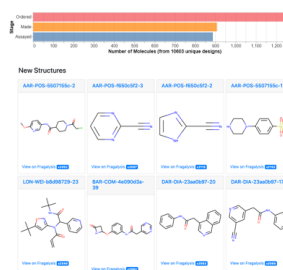
Submissions

New Structures

1072 compounds made and assayed

66 compounds IC50 < 10 μM

188 X-ray structures



DESIGN

med chem strategy review
ENUMERATE
virtual synthetic
library enumeration
PRIORITIZE
structure-enabled
free energy
calculations
MAKE
+ assay cascade
CRO-aware synthesis delegation
to minimize synthesis time and cost

ANALYZE
COVID Moonshot
data exploration
TEST portal
simultaneous X-ray
and biochemical data
(<1 week)

Many small steps towards a COVID-19 drug

Daniel A. Erlanson

Nature Communications **11**, Article number: 5048 (2020) | [Cite this article](#)

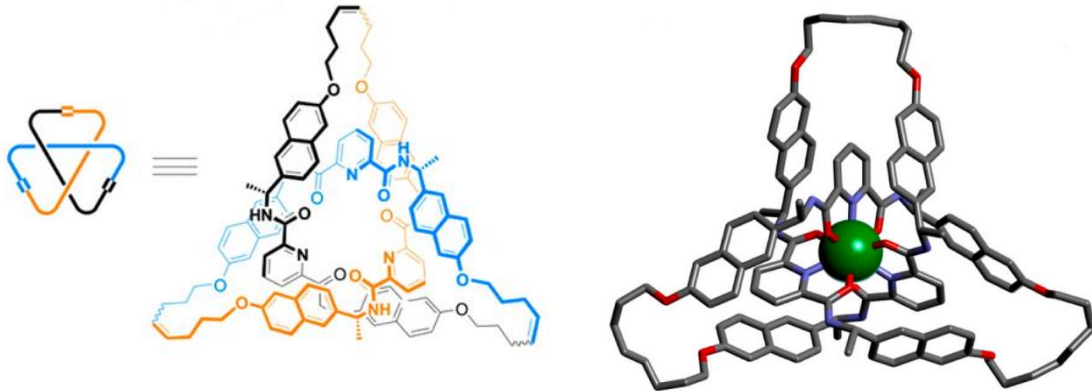
118 Accesses | 32 Altmetric | [Metrics](#)

The speed with which this was done is breathtaking: protein crystals were first obtained on 13 February 2020, and all experimental data were collected by 7 March. The first crystal structures were made public only three days later, and by the beginning of April 2020 all final structures were released in the midst of the evolving pandemic. If a picture is worth a thousand words, Douangamath et al. have published a novel.... Another impressive aspect of the work is the researchers' dedication to open science

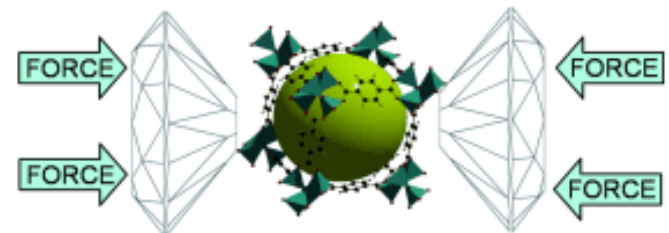
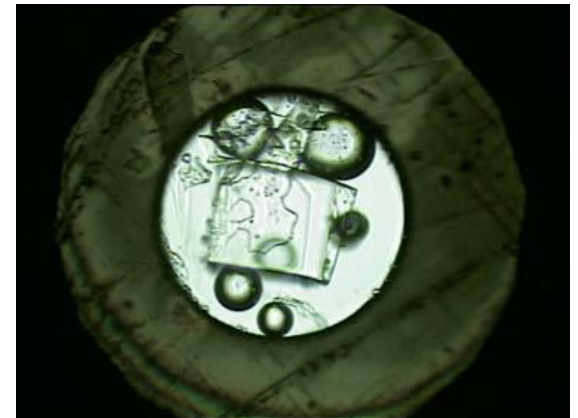
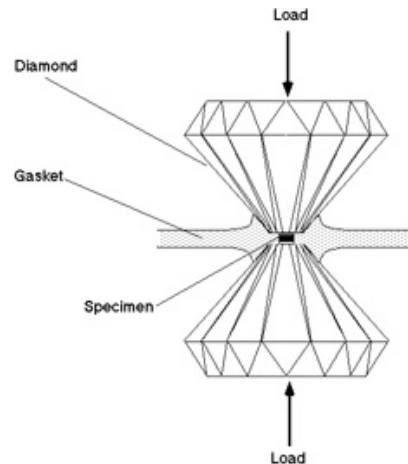
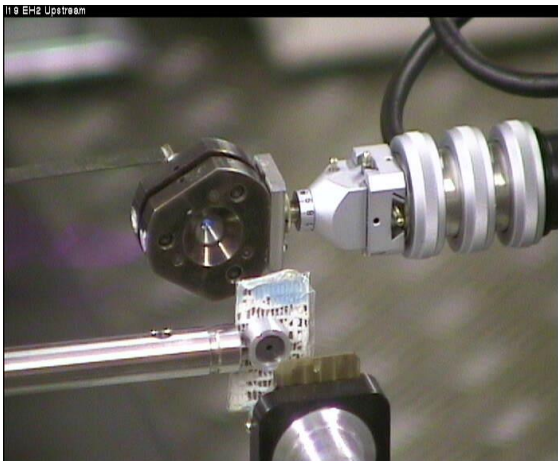


Not everything is organic...

- Complex inorganic structures (Lee Group)

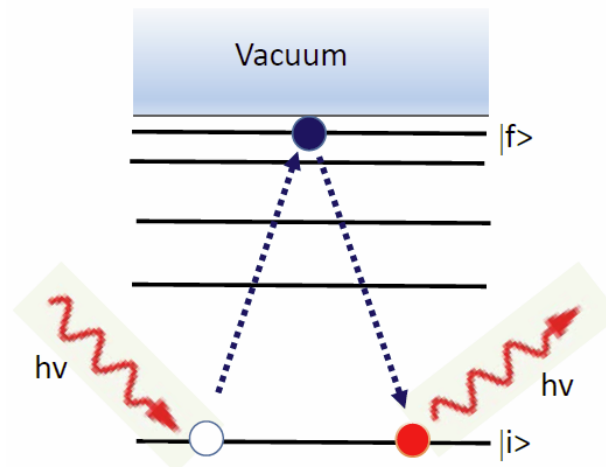


- Materials under extreme conditions – millions of atmospheres on the beamline



Resonant X-ray Scattering - RXS

- Tune SR energy to match transition from core to unoccupied valence state of a selected atom in the structure – exciting electron with prompt relaxation so that overall process is elastic
- This **resonant X-ray scattering (RXS)** enhances diffraction (amplifies intensities) in a manner that is sensitive to the character of the particular valence orbitals on the particular element – reveals information about oxidation state, orbital occupancy and magnetism
- Most commonly applied to TM – mostly 3d – and lanthanide ions (4f) because of interesting and useful magnetic and electronic properties



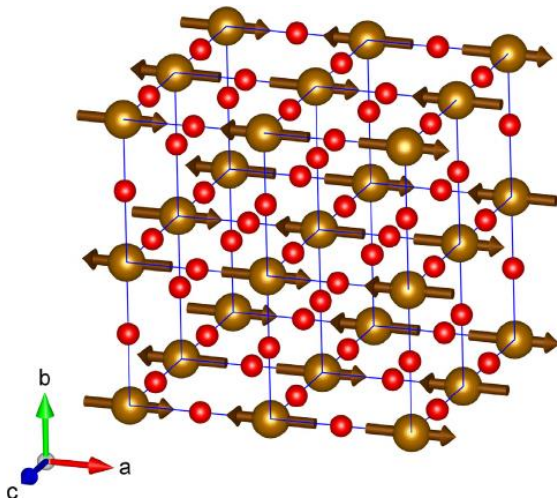
Resonant X-ray Scattering - RXS

- Selection rules apply: dipole transitions ($\Delta l = \pm 1$) generally much stronger than quadrupole transitions ($\Delta l = \pm 2$) so from s state this component of the process is stronger if final state is p, not d or f
- However, magnetism and electronic properties mostly determined by 3d, 4f states – probe through mixing of these states with p-states through orbital mixing (plus some weaker quadrupole transitions)
- Energies relatively low, wavelengths are less suitable for diffraction, so only a few reflections observed ($n\lambda = 2d\sin\theta$ – only largest d seen)

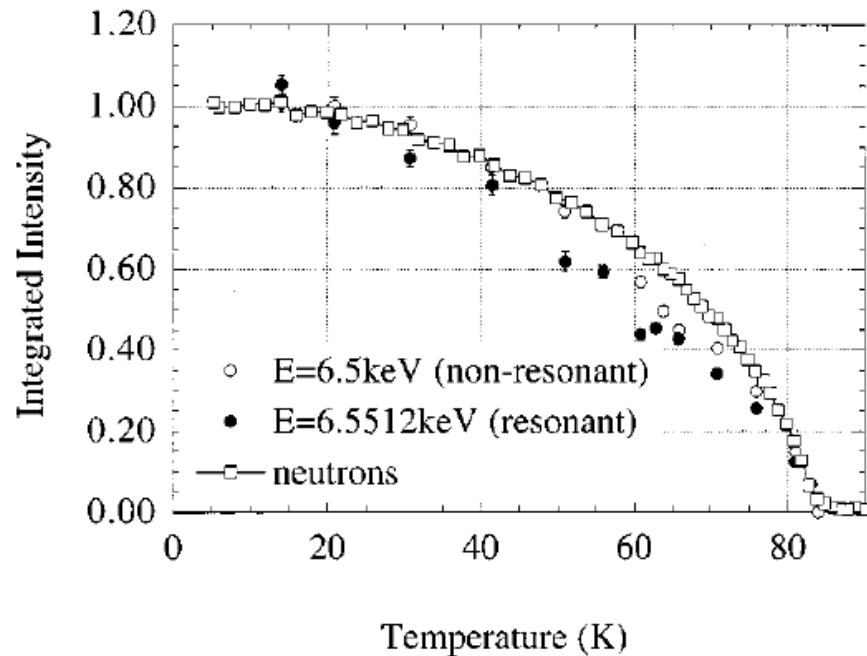
elements	edge	transition	energy range [keV]	resonance strength	comment
3d	K	1s → 4p	5 - 9	weak	small overlap
3d	L _I	2s → 3d	0.5 - 1.2	weak	small overlap
3d	L _{II} , L _{III}	2p → 3d	0.4 - 1.0	strong	dipolar, large overlap, high spin polarisation of 3d
4f	K	1s → 5p	40 - 63	weak	small overlap
4f	L _I	2s → 5d	6.5 - 11	weak	small overlap
4f	L _{II} , L _{III}	2p → 5d 2p → 4f	6 - 10	medium	dipolar quadrupolar
4f	M _I	3s → 5p	1.4 - 2.5	weak	small overlap
4f	M _{II} , M _{III}	3p → 5d 3p → 4f	1.3 - 2.2	medium to strong	dipolar quadrupolar
4f	M _{IV} , M _V	3d → 4f	0.9 - 1.6	strong	dipolar, large overlap, high spin polarisation of 4f
5f	M _{IV} , M _{II}	3d → 5f	3.3 - 3.9	strong	dipolar, large overlap, high spin polarisation of 5f

Resonant X-ray Scattering - RXS

- Commonly used to determine the nature of magnetic ordering, for which unit cells can be relatively large e.g. transition to antiferromagnet ordering for cubic cell doubles lattice parameter so reflections may start to be observed at half-integer values of (hkl)
- Note there is also a non-resonant magnetic contribution to the scattering, but it is very weak and neutrons usually more insightful



Rb and Mn ions in cubic perovskite RbMnF₃ showing antiferromagnetic order of moments on Mn²⁺

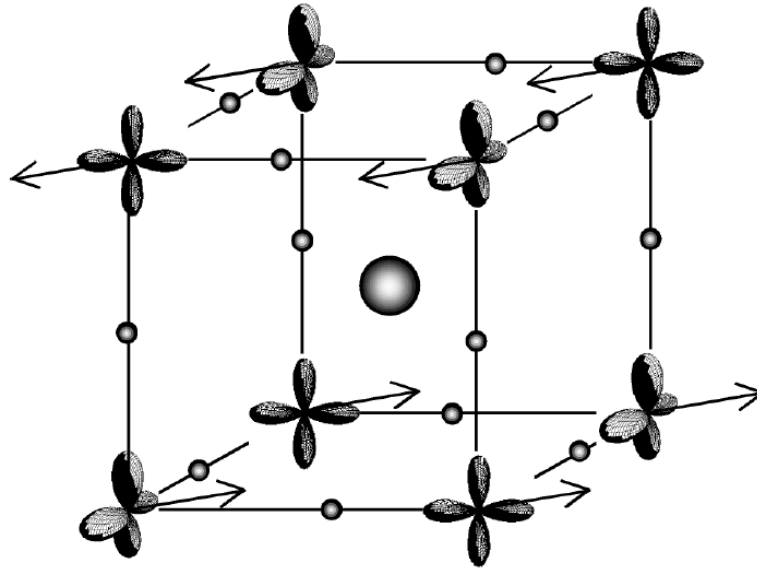


Revealing orbital and magnetic ordering by RXS

- Certain TM ions are Jahn-Teller active and display distinct anisotropy of local bonding in complexes and extended crystalline solids
- These distortions can have a profound effect on the electronic and magnetic character often interlinked e.g. in magnetoresistant materials whose conductivity can be controlled by the application of a magnetic field, and very likely involved in high- T_c superconductivity
- E.g. (though not conducting) Cu^{2+} in KCuF_3 has a $3d^9$ configuration in which the hole is in the $d_{x^2-y^2}$ orbital so there is elongation along the z-axis (ABO doubly occupied). The ion also has an unpaired electron spin which gives rise to a spin-only moment.

Revealing orbital and magnetic ordering by RXS

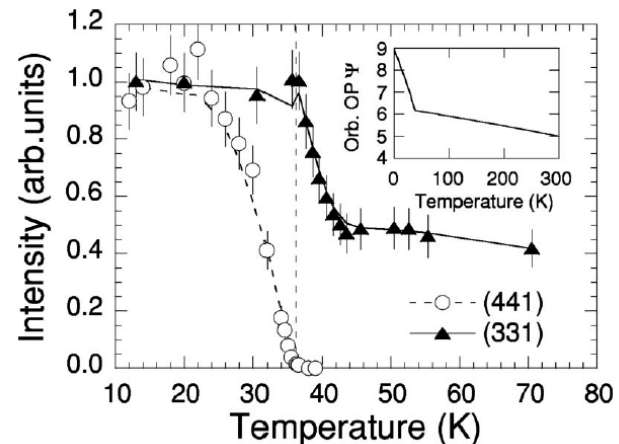
- The structure of KCuF_3 is based on cubic perovskite but closer inspection at low temperature reveals more detail.
 - JT-distorted Cu^{2+} centres are ordered in the crystal such that the local axis of elongation alternates along any cubic edge
 - The magnetic moments interact weakly with their neighbours, freezing into an ordered array on cooling to 38 K



Revealing orbital and magnetic ordering by RXS

- As the energy is tuned below the Cu K edge two types of resonant transition might be brought into play.
 - $1s \rightarrow 3d$ is dipole forbidden but probes the spin states and orbital occupancy directly
 - $1s \rightarrow 4p$ is dipole allowed but only probes the spin states and orbital occupancy indirectly through (weak) 3d-4p mixing
- Both factors contribute and reveal the orbital and magnetic order through new diffraction peaks that are forbidden in the simple cubic structure

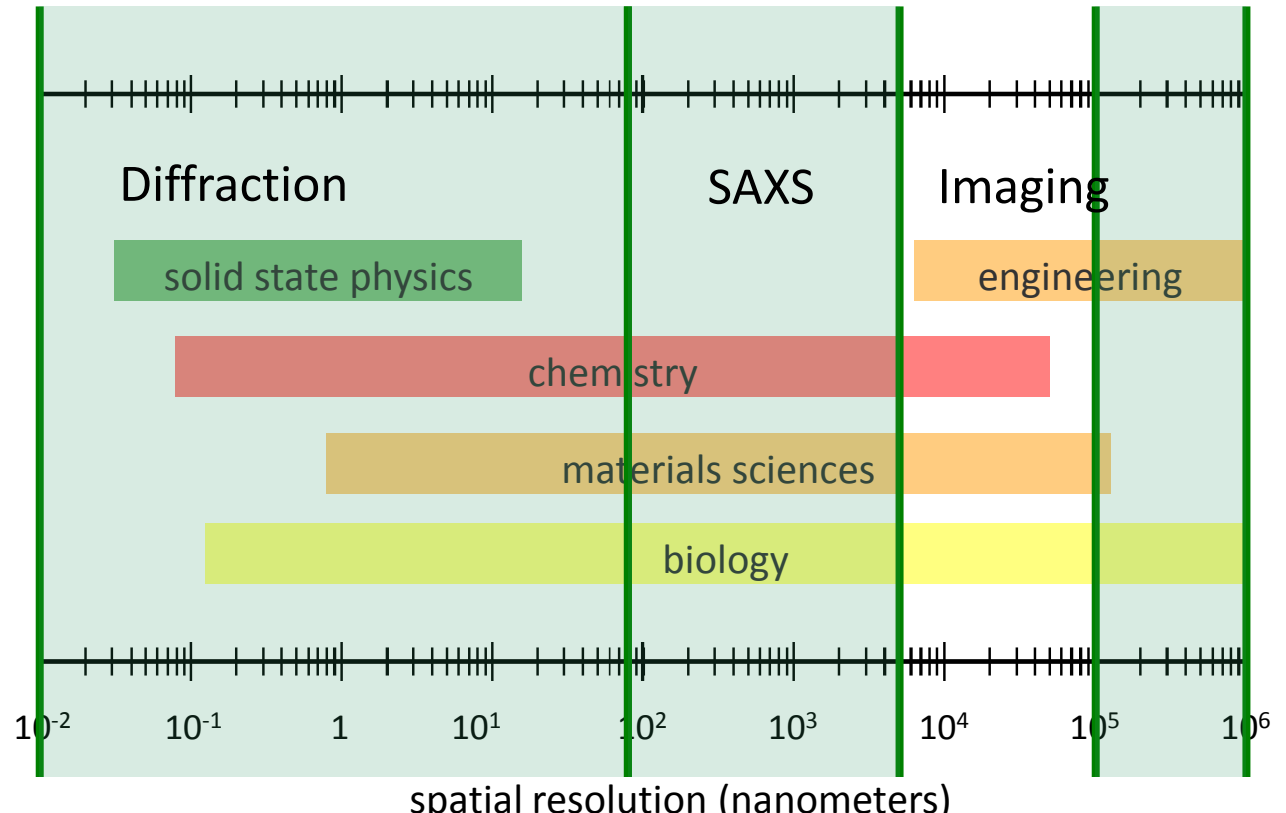
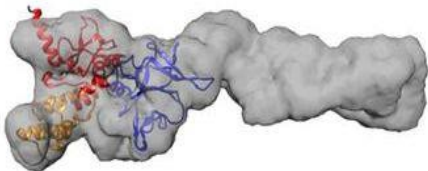
Measurement of intensity of reflections characteristic of orbital order (331) and magnetic order (441) at 8.922 keV, $1s \rightarrow 4p$
Caciuffo et al, Phys. Rev. B65 (2002) 174425



Other forms of diffraction

- Small-angle scattering (SAXS) to probe the size and shape of large objects e.g. macromolecules in solution, material pores and defects

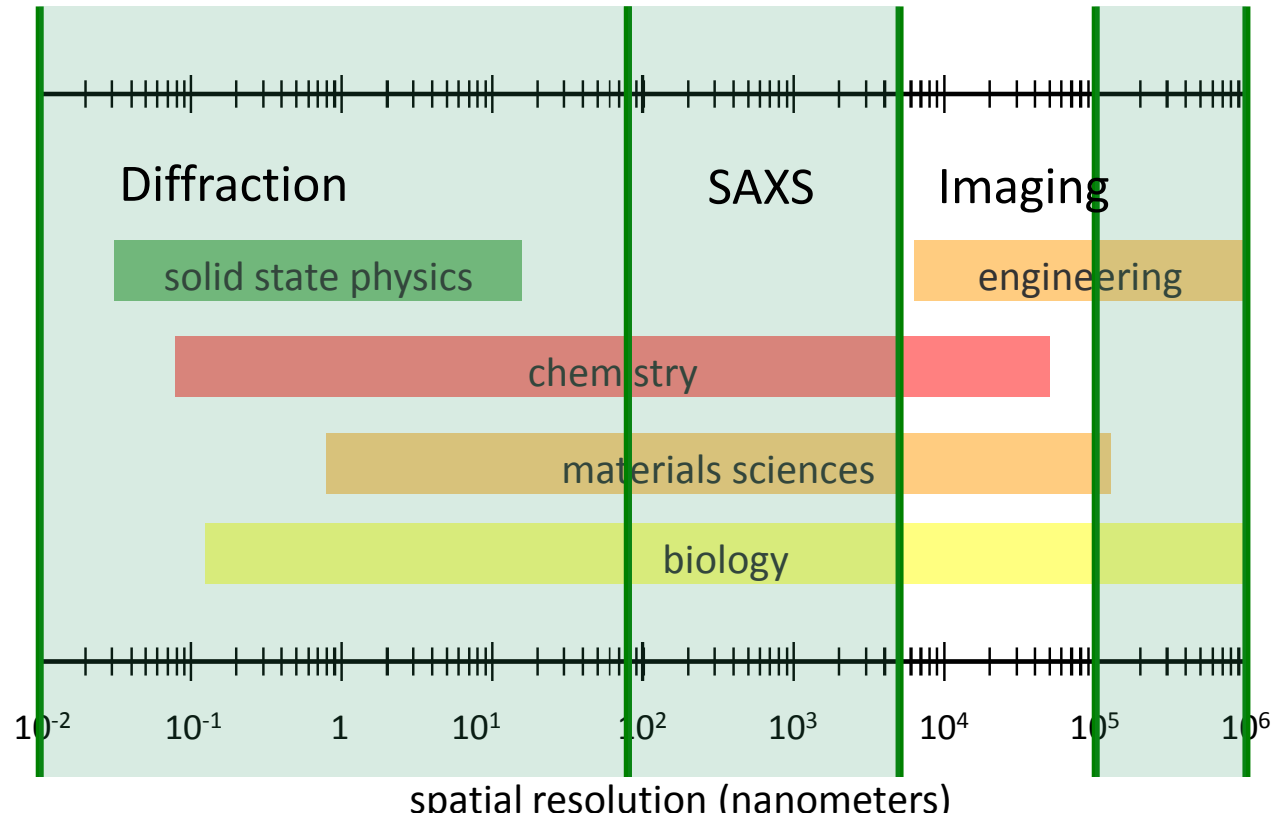
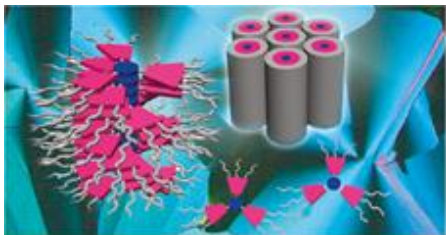
$$n \lambda = 2d \sin \theta$$



Other forms of diffraction

- Small-angle scattering (SAXS) to probe the size and shape of large objects e.g. macromolecules in solution, material pores and defects
- Reflectometry to study surfaces, interfaces and depth profiles

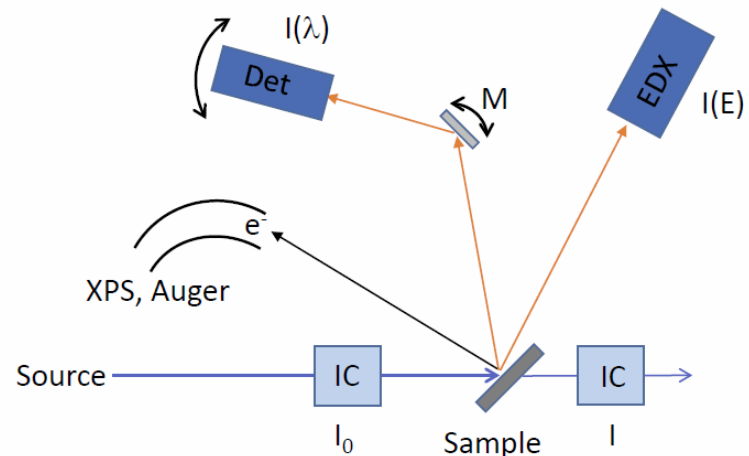
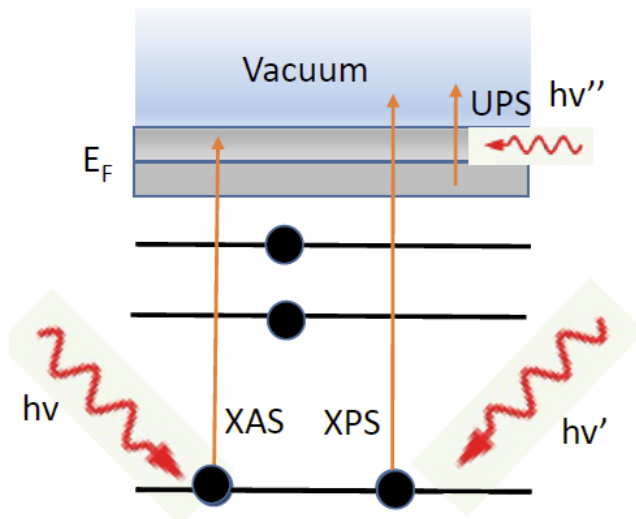
$$n \lambda = 2d \sin \theta$$



Spectroscopy

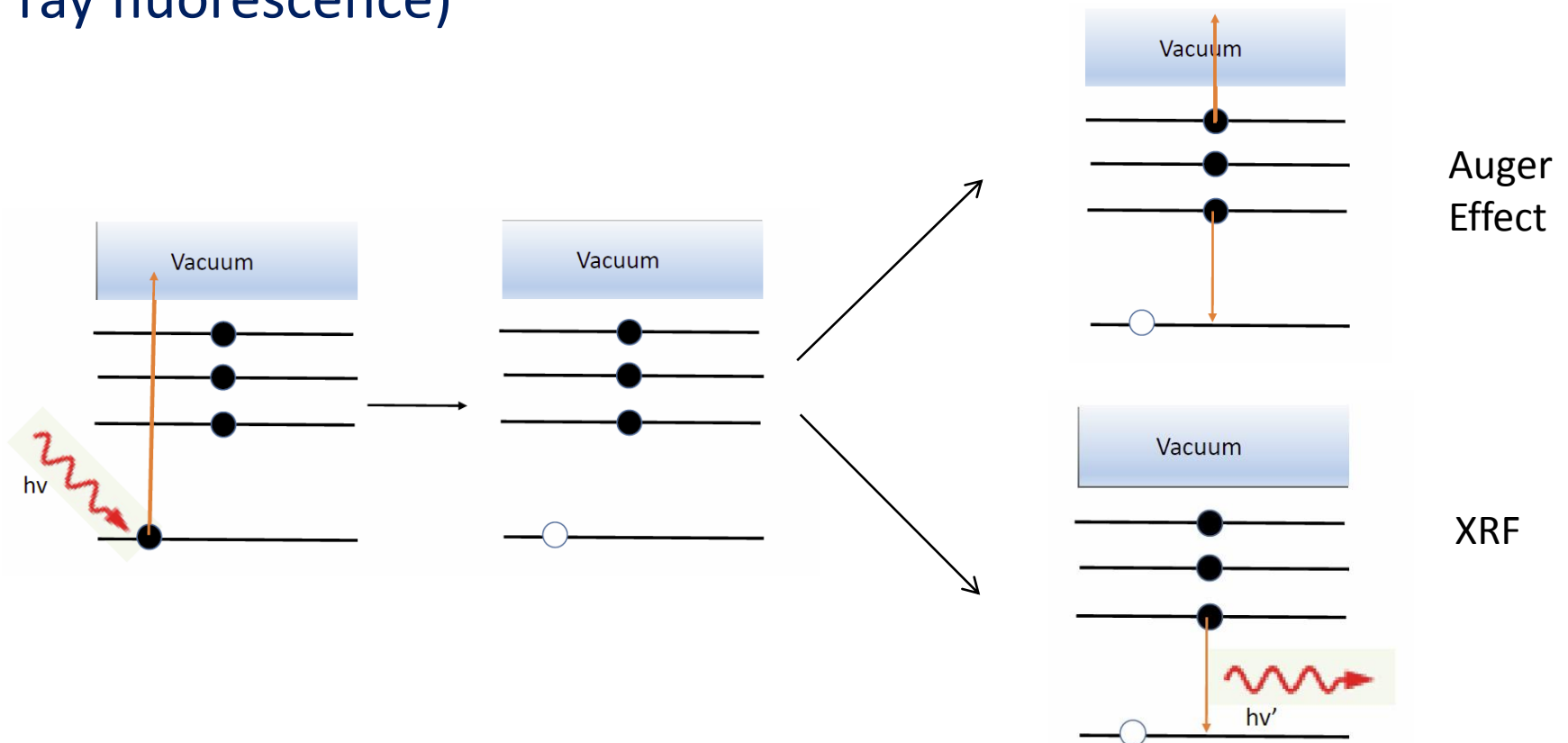
Spectroscopy

- Both X-ray Absorption and Fluorescence spectroscopies - XAS and XRF - are used as very sensitive probes of chemical character, with spatial resolutions of the order $1\ \mu\text{m}$ or less
- Energy of photoelectrons may also be analysed as chemical probe – of valence (UPS) and more tightly bound (XPS) electrons
- General experimental set-up



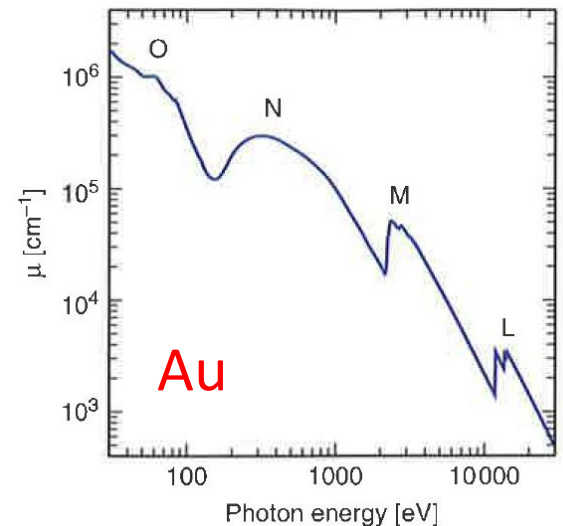
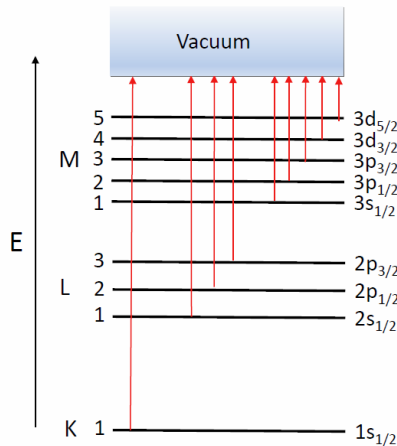
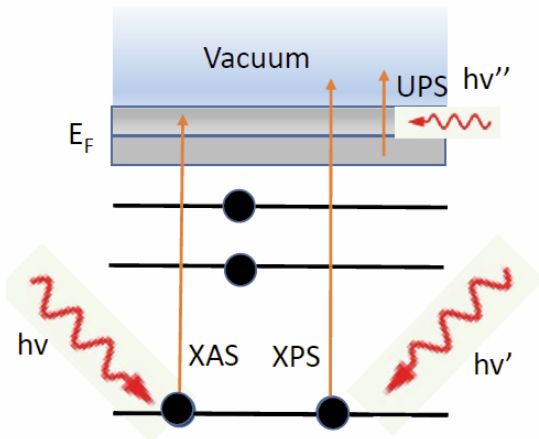
Relaxation after photoionisation ?

- Photoionisation leaves a hole behind which is electronically unstable and is rapidly filled by relaxation of higher-energy electrons and the additional energy is carried away either by a secondary photoionisation event (Auger effect) or photons (X-ray fluorescence)



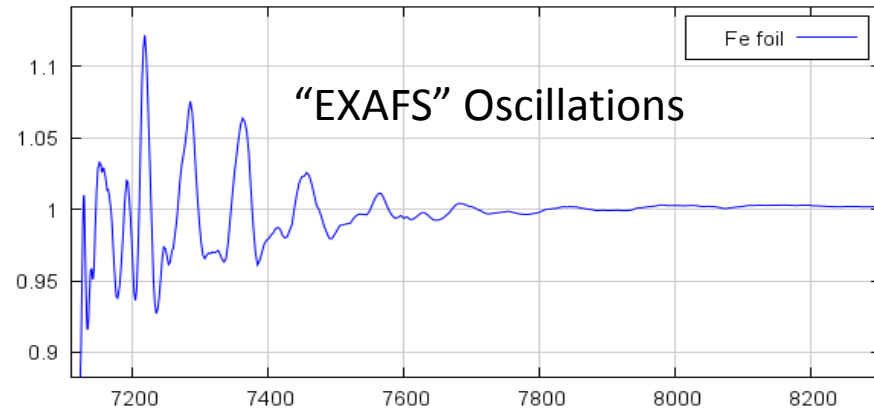
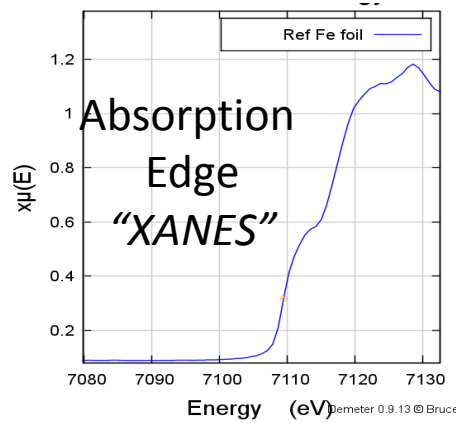
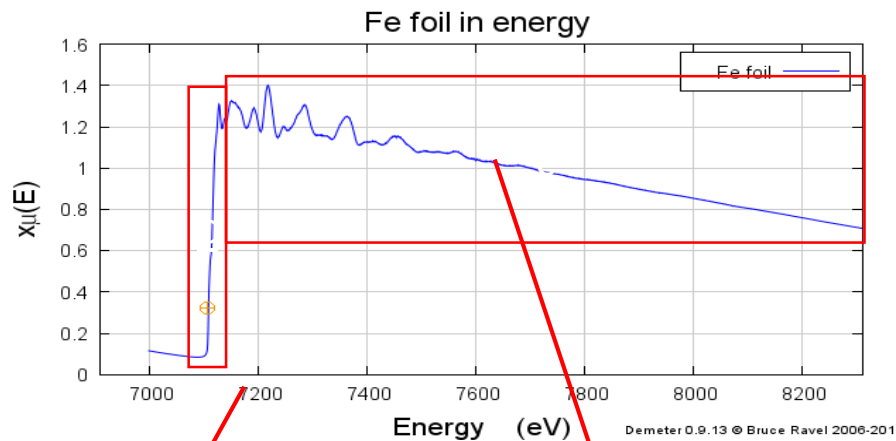
XAS

- Recall that X-ray absorption edges are observed for photoionisation from bound states with successively higher values of n , l and j . Edges get broader with n (more states with higher l , e.g. below Au)
- For atoms bound in a molecule or extended solid the transitions from core levels are similar to those in atoms, while transitions from valence orbitals can change markedly – particularly for metals and semiconductors where there is generally a continuum of states (band) with empty levels below the photoionisation threshold



XAS and fine structure

- Closer study of an absorption edge reveals fine structure
 - XANES – X-Ray Absorption Near Edge Spectroscopy
 - EXAFS – Extended X-Ray fine structure – 50-100's eV above edge



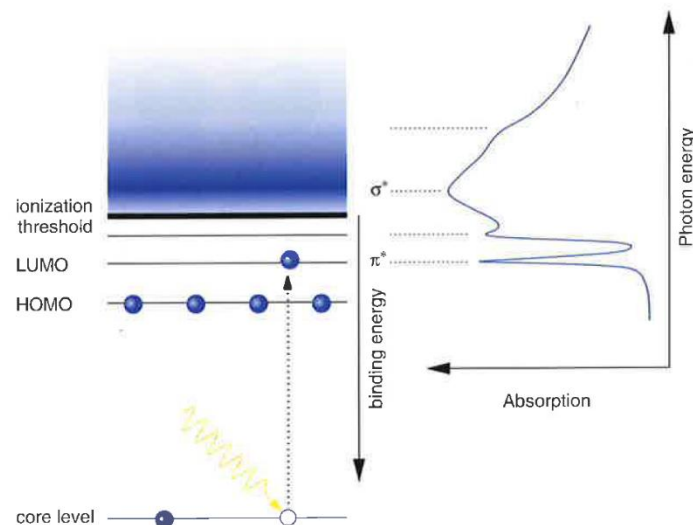
XANES— X-Ray Absorption Near Edge Spectroscopy

- Closer study of an absorption edge reveals fine structure corresponding to excitation of electrons to empty bound states and to low-lying states in the unbound continuum
- Intensity of transition $i \rightarrow f$ given by Fermi's Golden Rule:

$$P_{if} \sim |\langle f | H' | i \rangle|^2 \rho$$

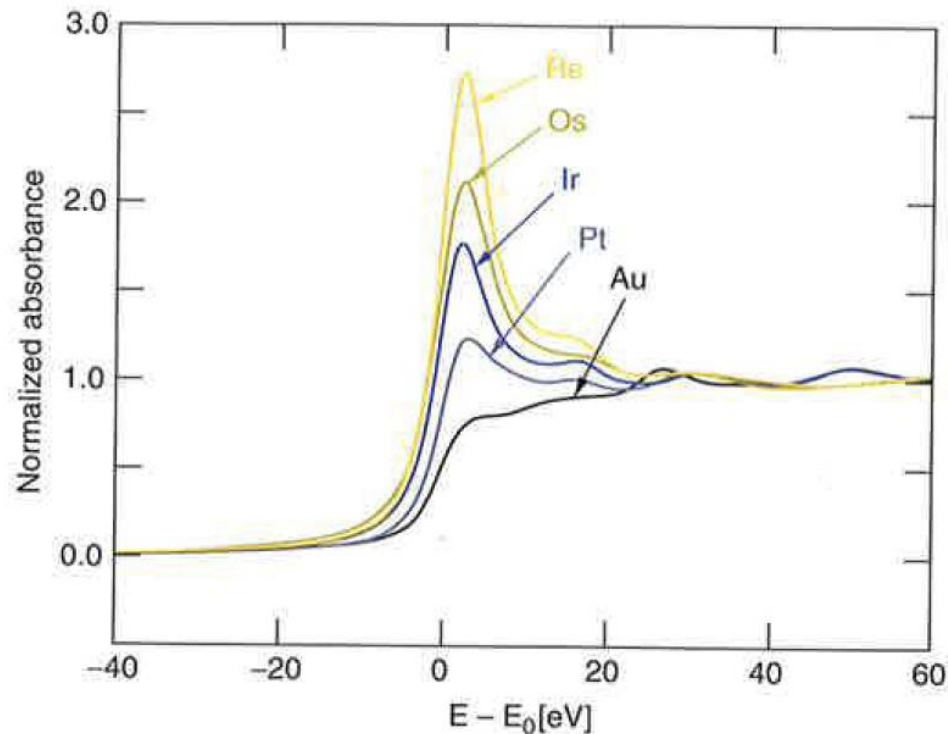
ρ is density of states for f , and H' is the operator representing the effect of the light – dipole nature – so $\Delta l = \pm 1$ when f is a bound state

In practice this often breaks down because s-p, p-d mixing is allowed, particularly when the atom at the centre of the study is non-centro-symmetric so can occur for isolated atoms and also molecules



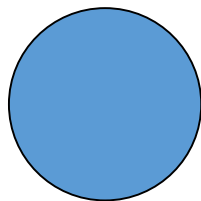
XANES— X-Ray Absorption Near Edge Spectroscopy

- Dependence of P_{if} illustrated by XAS for series of elements from Re to Au - $[\text{Xe}] 4f^{14}5d^56s^2$ to $[\text{Xe}]4f^{14}5d^{10} 6s^1$ - changes as 5d fills up
- All of these features may be modelled and then the model refined to optimise the goodness of fit to the data to determine the local binding and thus the local structure around the absorbing centre

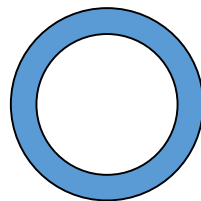


Mapping chemistry with μ -XANES

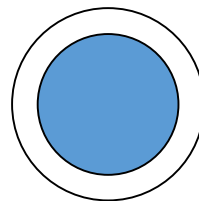
- Effectiveness of heterogenous catalysts depends *inter alia* on physical state/distribution and nature of active centres
- E.g. commercial BASF catalyst for hydrogenation of nitrobenzene to aniline using colloidal Pt-containing catalyst (0.8wt %) supported on carbon particles with Mo-containing promoter (0.3wt %)



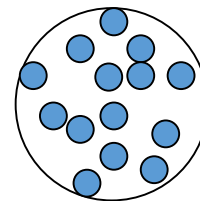
Even
distribution



Egg-shell
distribution

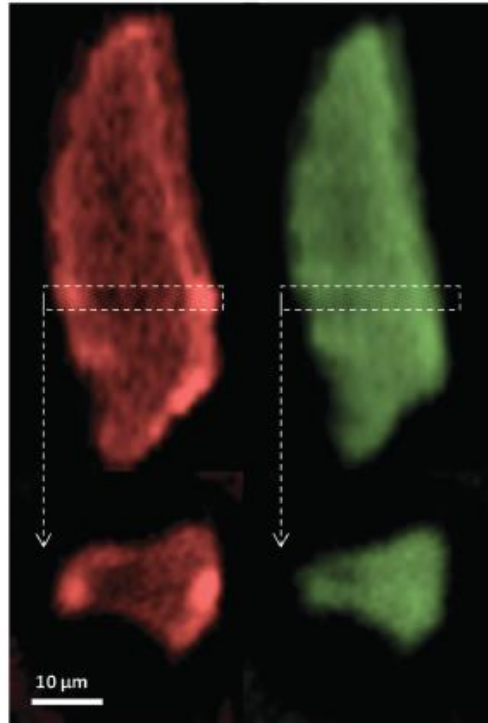


Egg-yolk
distribution

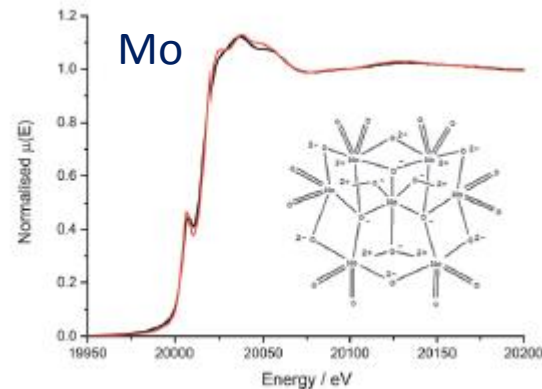


Uneven
distribution

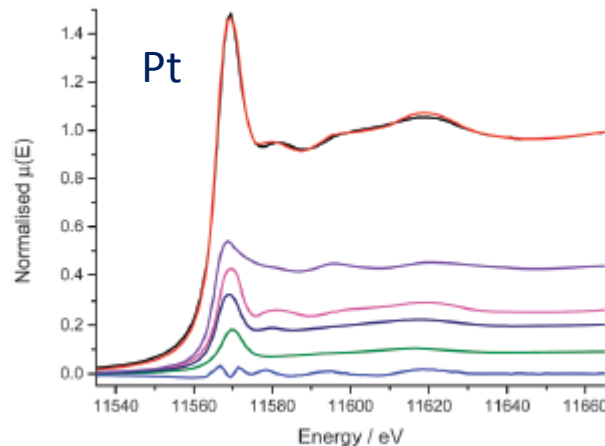
Crafting catalysts



XRF tomography –
Mo (green) and Pt (red)

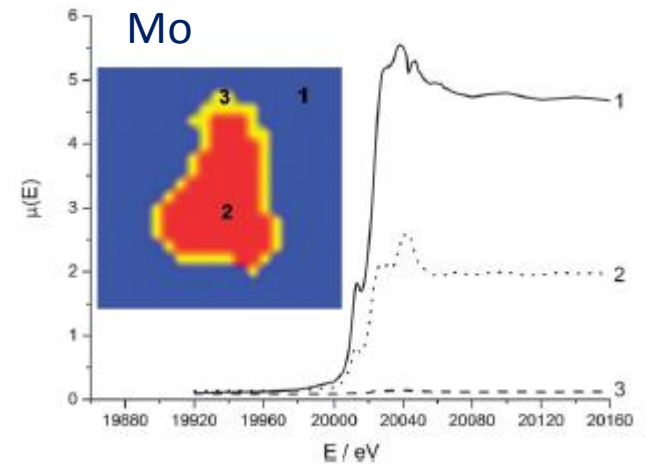


Species identification

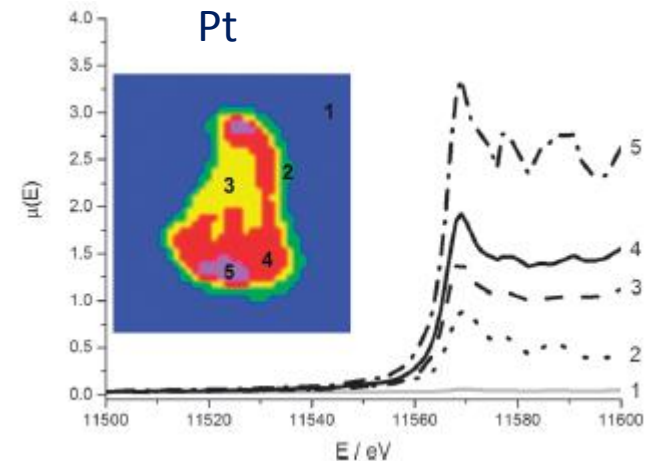


Price et al, PCCP, Phys. Chem. Chem. Phys., 17 (2015) 521

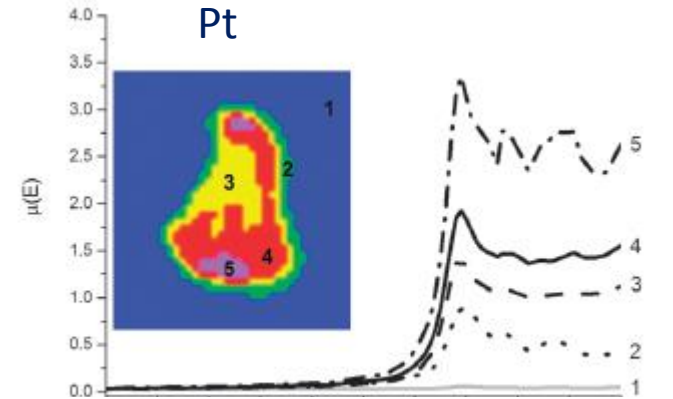
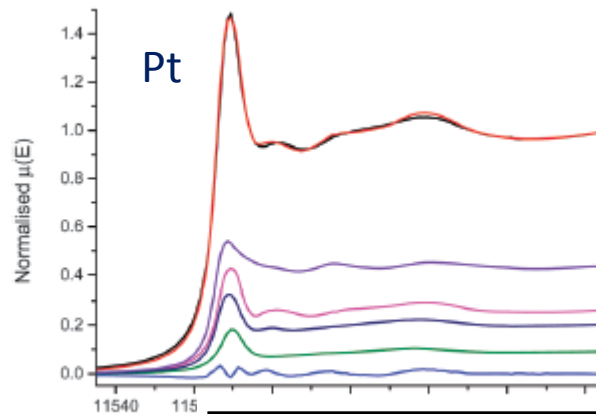
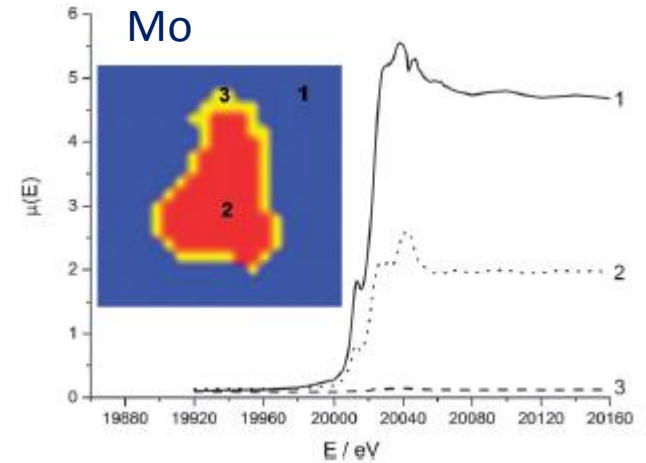
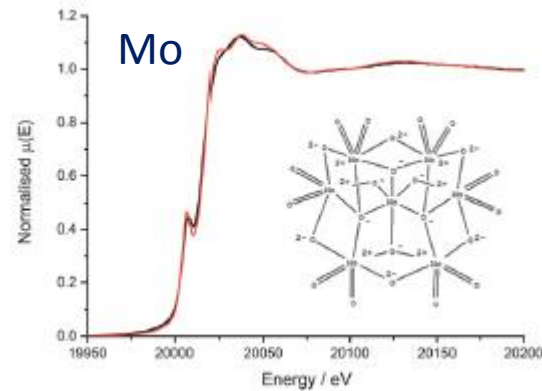
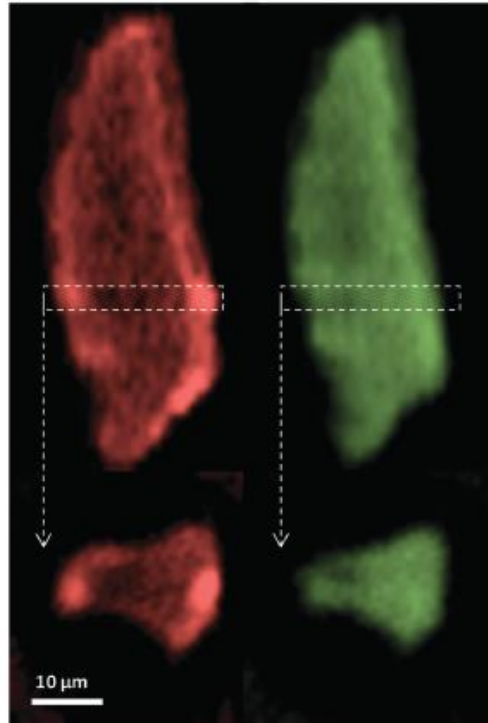
Now *in operando* (XRF, XRD) Price, et al., *Angewandte Chemie International Edition* **2015**, 54, 9886-9889



Species mapping



Crafting catalysts



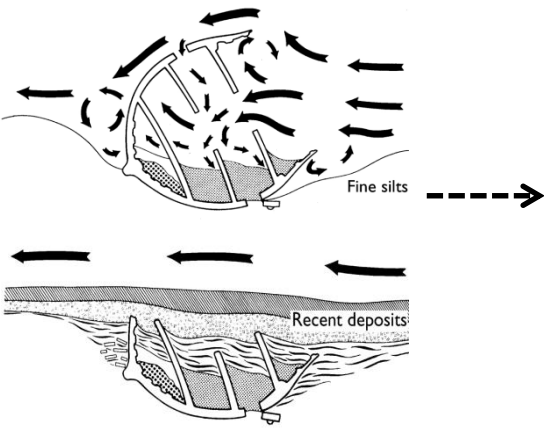
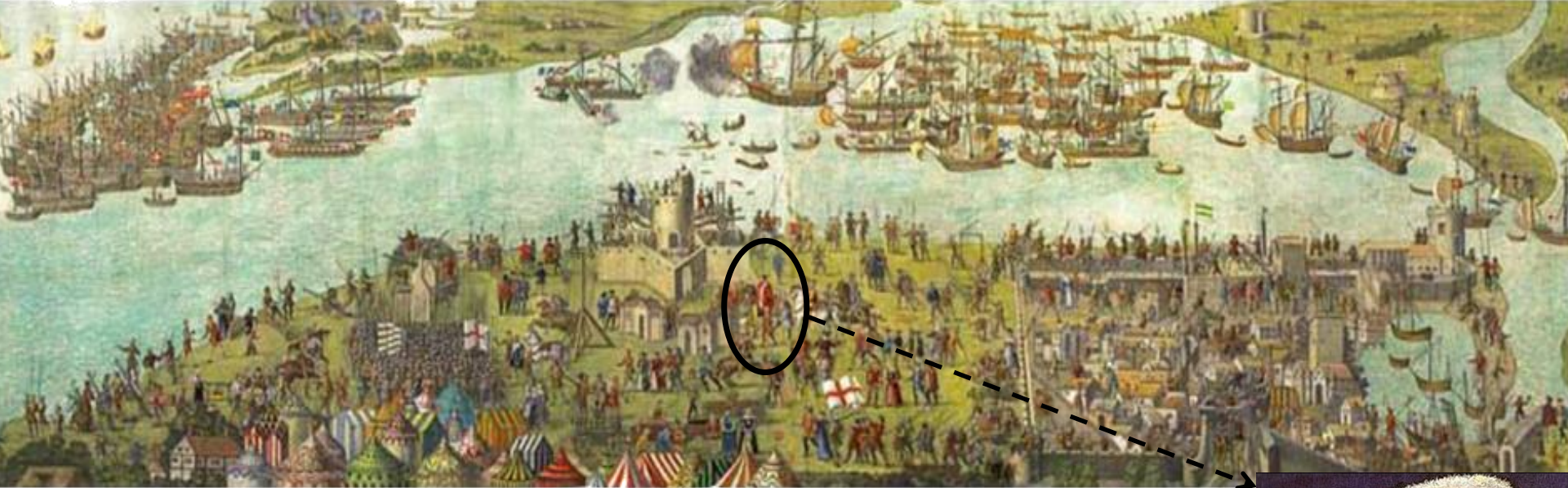
XRF tomography –
Mo (green) and Pt (red)

Spec

Component	Weight/%	R_f	Reduced χ^2
Pt/C nano	44 (2)	0.0007	0.0001
PtO ₂	9 (5)		
PtCl ₂	21 (3)		
K ₂ PtCl ₆	26 (3)		

Price et al, PCCP, Phys. Chem. Chem. Phys.
Now *in operando* (XRF, XRD) Price, et

Preserving the past with X-ray spectroscopy



Sank 1545

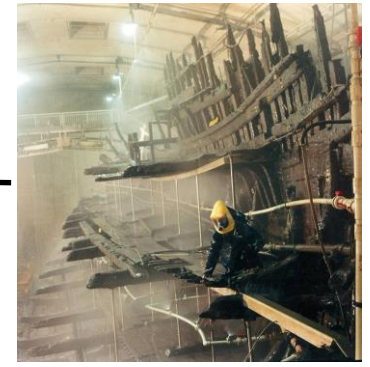
Hull conservation



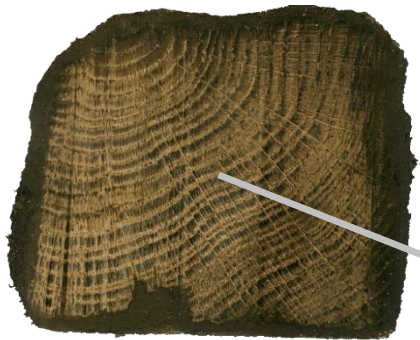
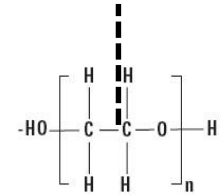
Raised 1982



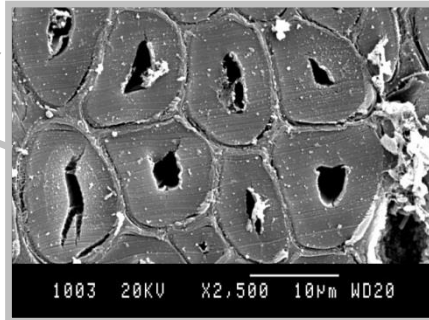
1982 – 1994: Cold water



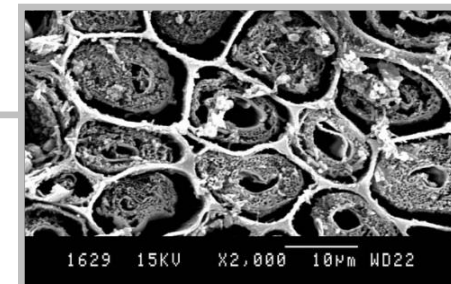
1994 – 2013: PEG



1994 – 2006



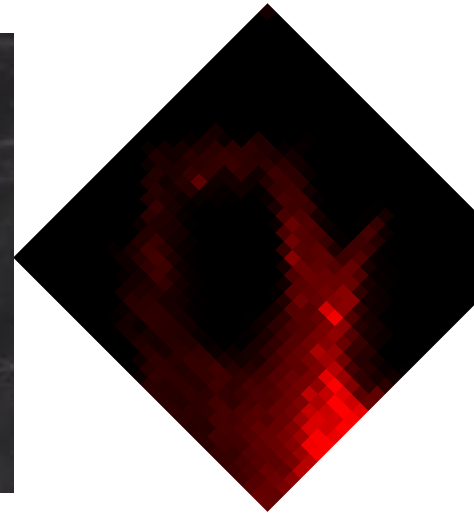
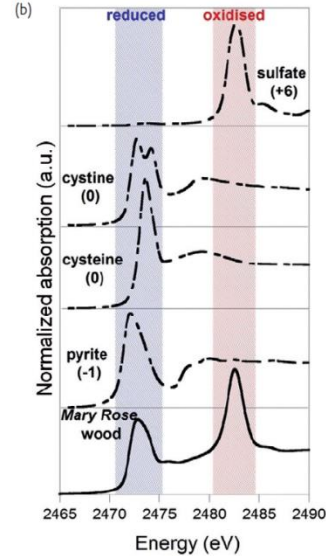
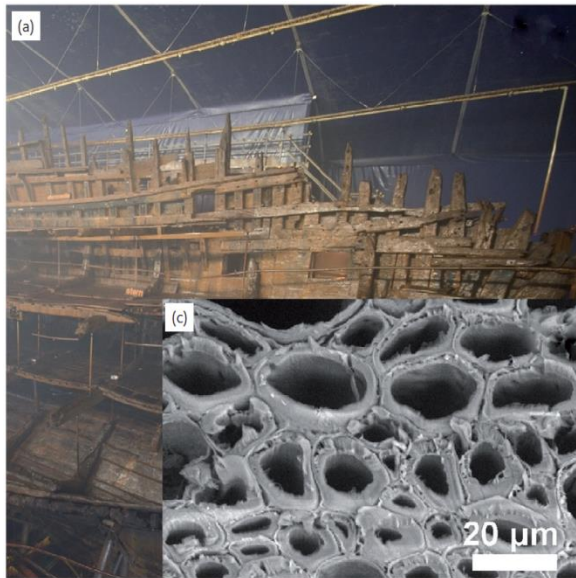
2006-2013



The sulfur problem

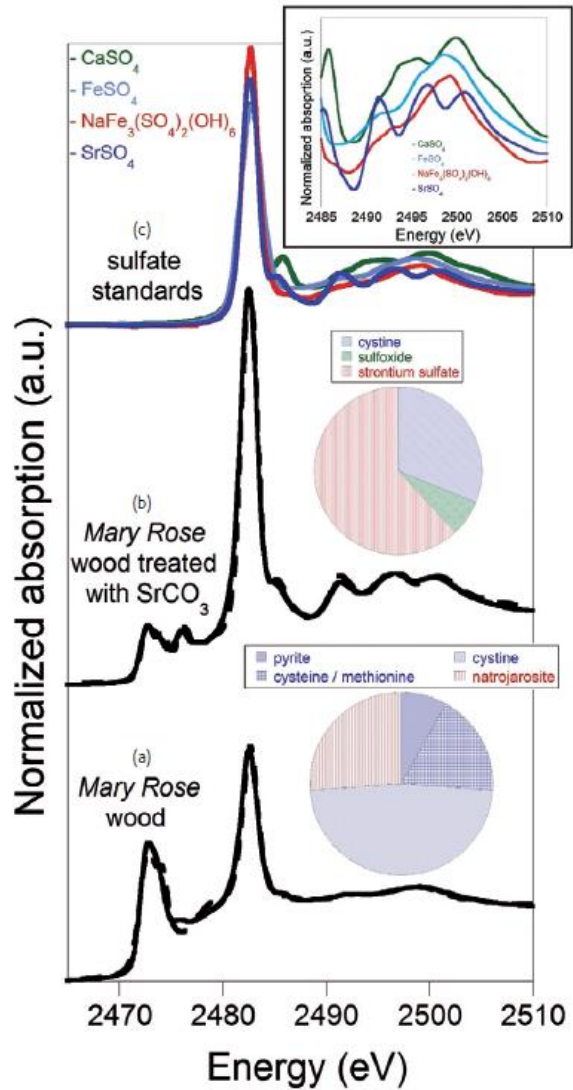


Sulfate salts



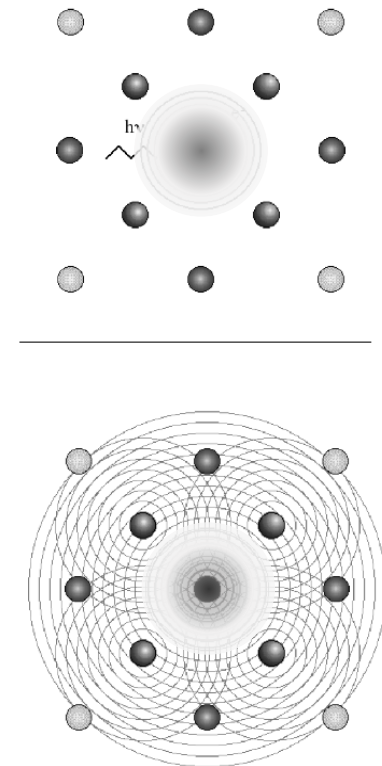
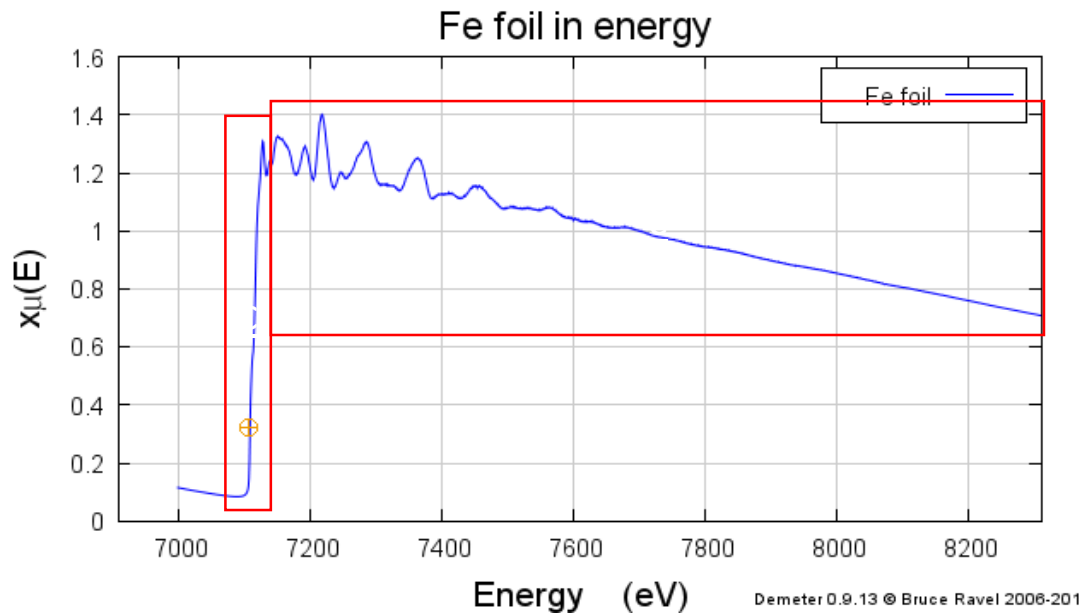
e.g. Eleanor J. Schofield, Ritimukta Sarangi, Apurva Mehtab, Mark Jones, Fred J. W. Mosselmanns, and Alan V. Chadwick,* *Materials Today*, 14 (2011) 354

The sulfur problem - solved



EXAFS

- Extended X-Ray Absorption Fine Structure – arises from the interference between the wave of a photoelectron and the waves backscattered from neighbouring atoms, giving constructive and destructive interference – so we need to know the wavelength λ_e of these waves (destructive interference when d is odd multiple $\lambda_e/2$)



EXAFS

- Extended X-Ray Absorption Fine Structure – arises from the interference between the wave of a photoelectron and the waves backscattered from neighbouring atoms, giving constructive and destructive interference – so we need to know the wavelength λ_e of these waves (destructive interference when d is odd multiple $\lambda_e/2$)

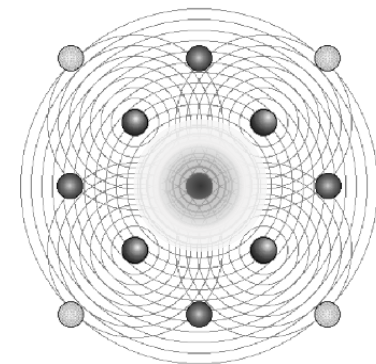
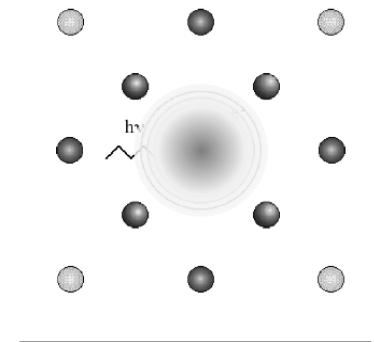
By de Broglie: $p = h/\lambda_e$ and $E_e = \frac{p^2}{2m_e} = \frac{h^2}{2\lambda_e^2 m_e}$

Also $E_e = h\nu - E_B$ where E_B is electron binding energy

Therefore $\lambda_e = h[2m_e(h\nu - E_B)]^{-1/2}$

So the condition for minima in the EXAFS spectra arises when $2d = n\lambda_e$ with $n = 1, 3, 5$

So $h\nu = \frac{1}{2m_e} \left(\frac{nh}{2d}\right)^2 + E_B$ with $n = 1, 3, 5$

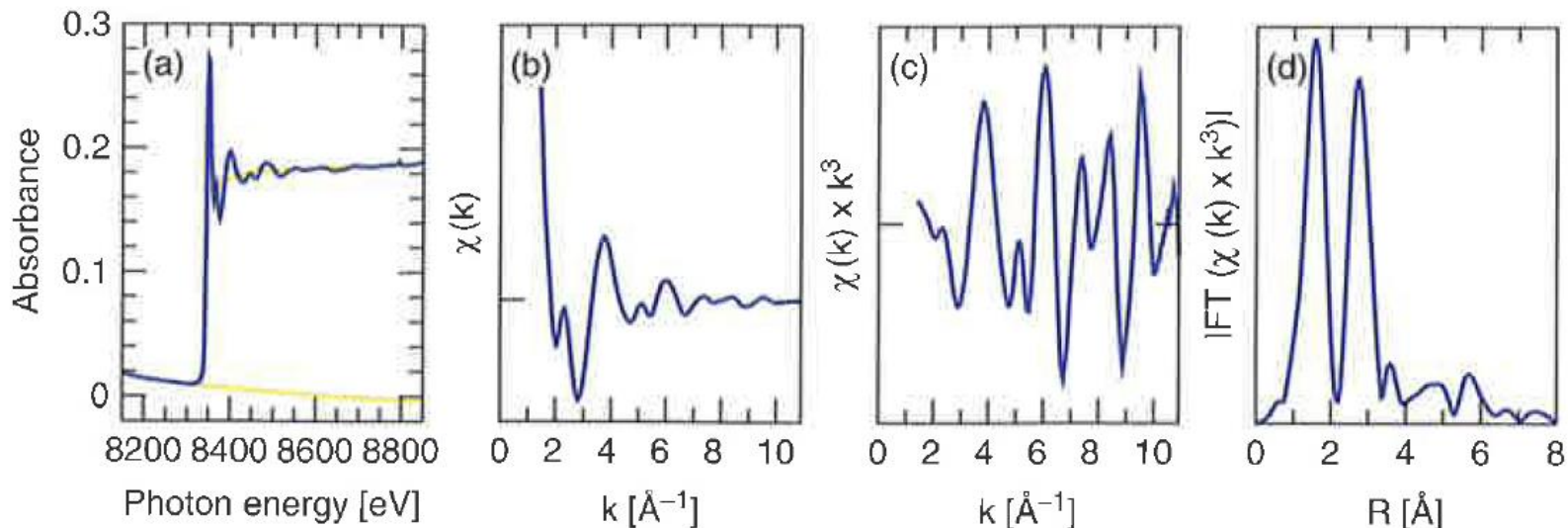


EXAFS

- In practice we convert the EXAFS spectrum (i.e. absorbance μ vs E) into units proportional to the momentum of the photoelectron, i.e. as function of wavevector $k = 2\pi/\lambda_e (=2\pi p/h)$ once it has been corrected for the absorption of the free atom, $\mu_0(k)$.

This is called the EXAFS function, $\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$

The oscillations fall off rapidly with k so they are often multiplied by k^2 or k^3 to enhance them then Fourier transformed to real space to reveal the atom-atom distribution *e.g.* below Ni K-edge for Ni adsorbates in the mineral montmorillonite



EXAFS

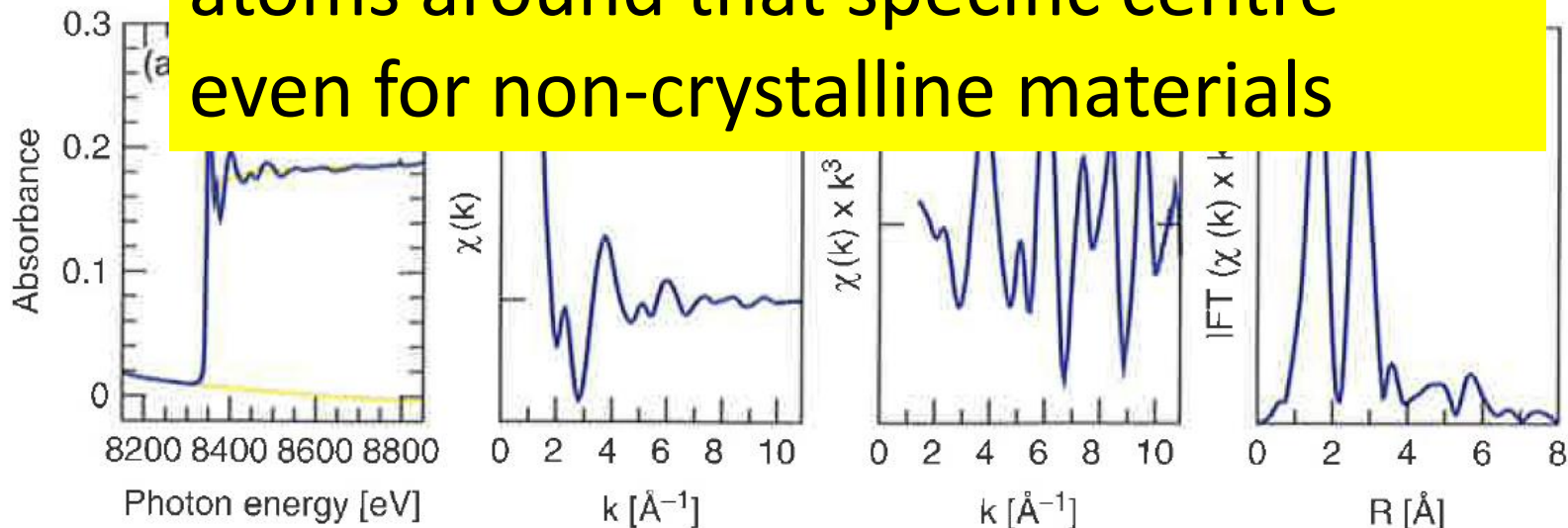
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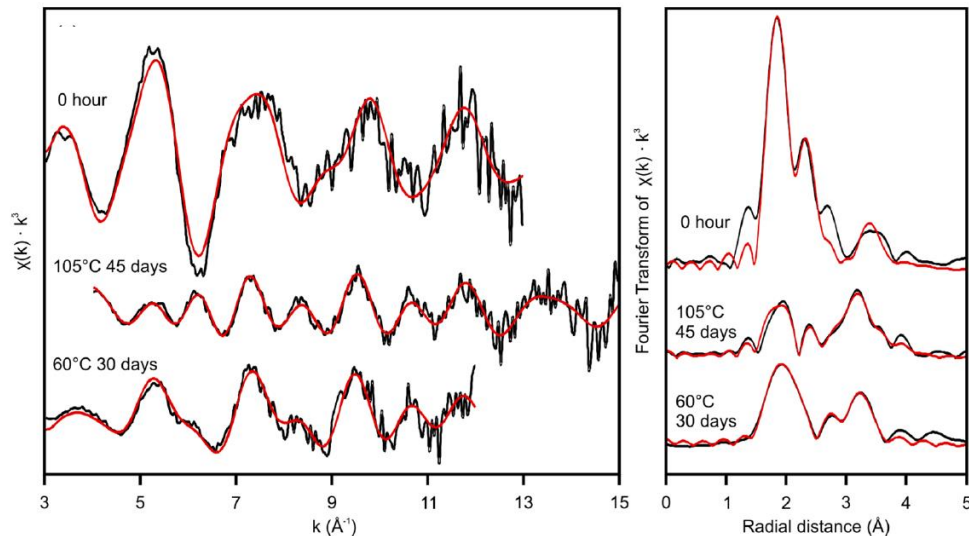
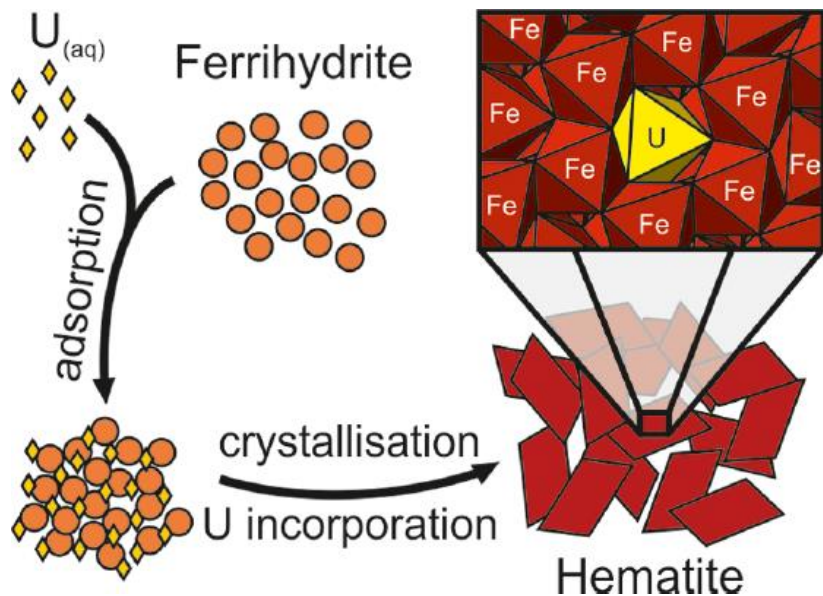
The oscillations are often multiplied by k^2 or k^3 to reveal the distribution of the adsorbate

EXAFS provides an element specific probe of the distribution of other atoms around that specific centre – even for non-crystalline materials

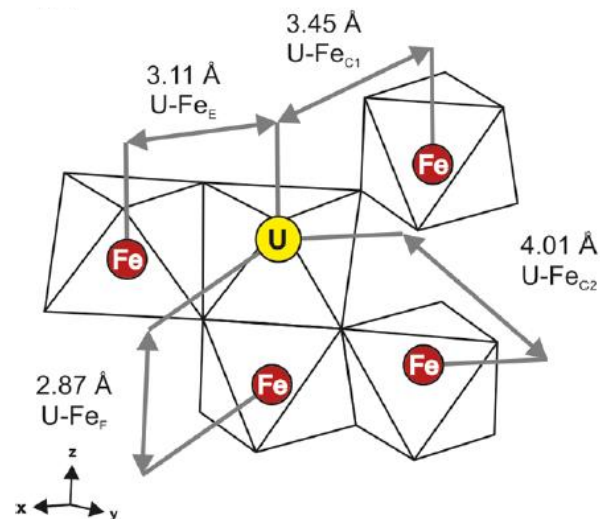
is determined by the distribution of the adsorbate



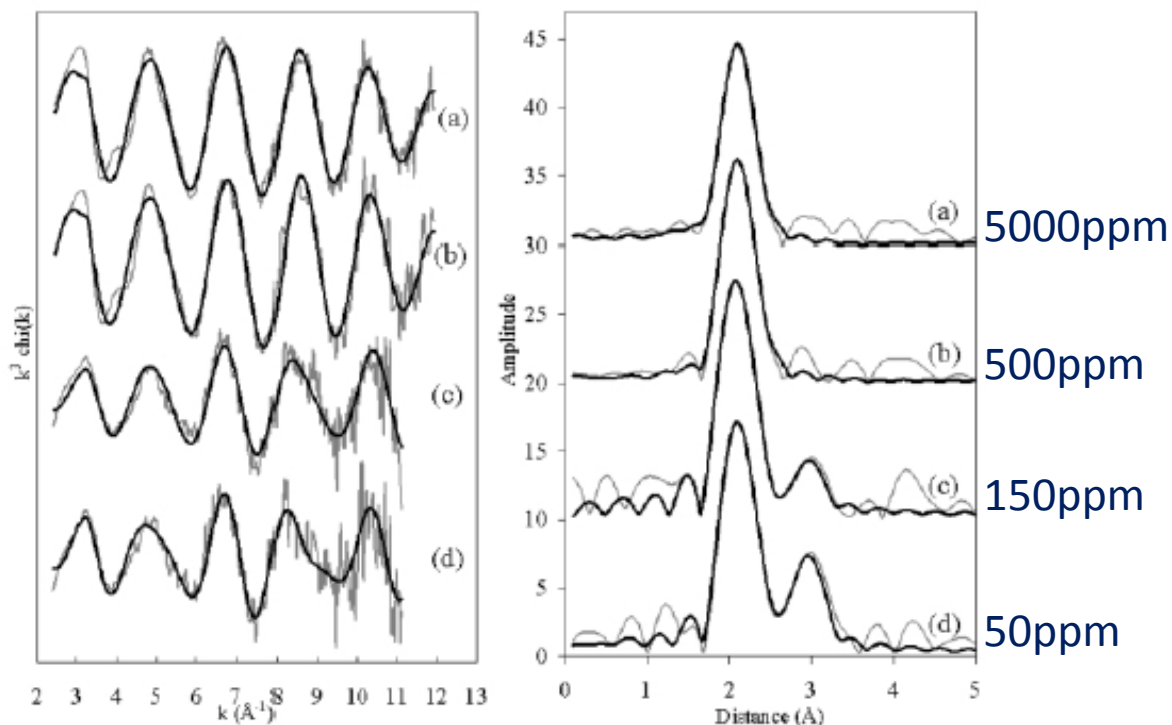
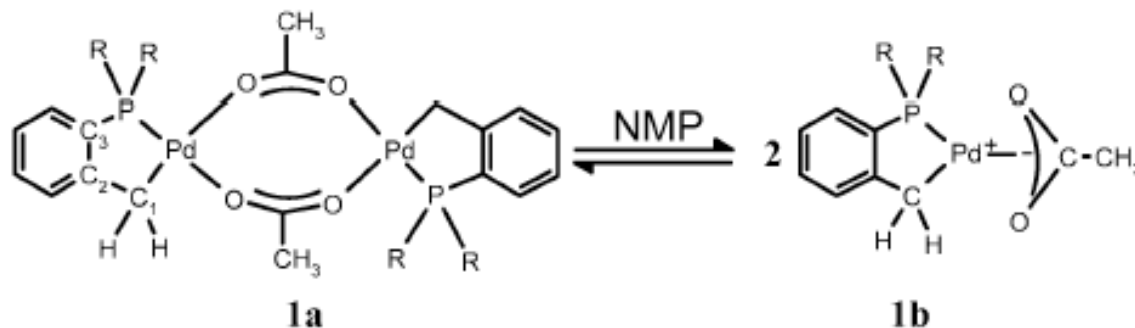
Looking for U



Follow incorporation of U compounds into iron oxides by EXAFS – confirms not only presence of element in particular oxidation state at 1000's of ppm but nature of binding



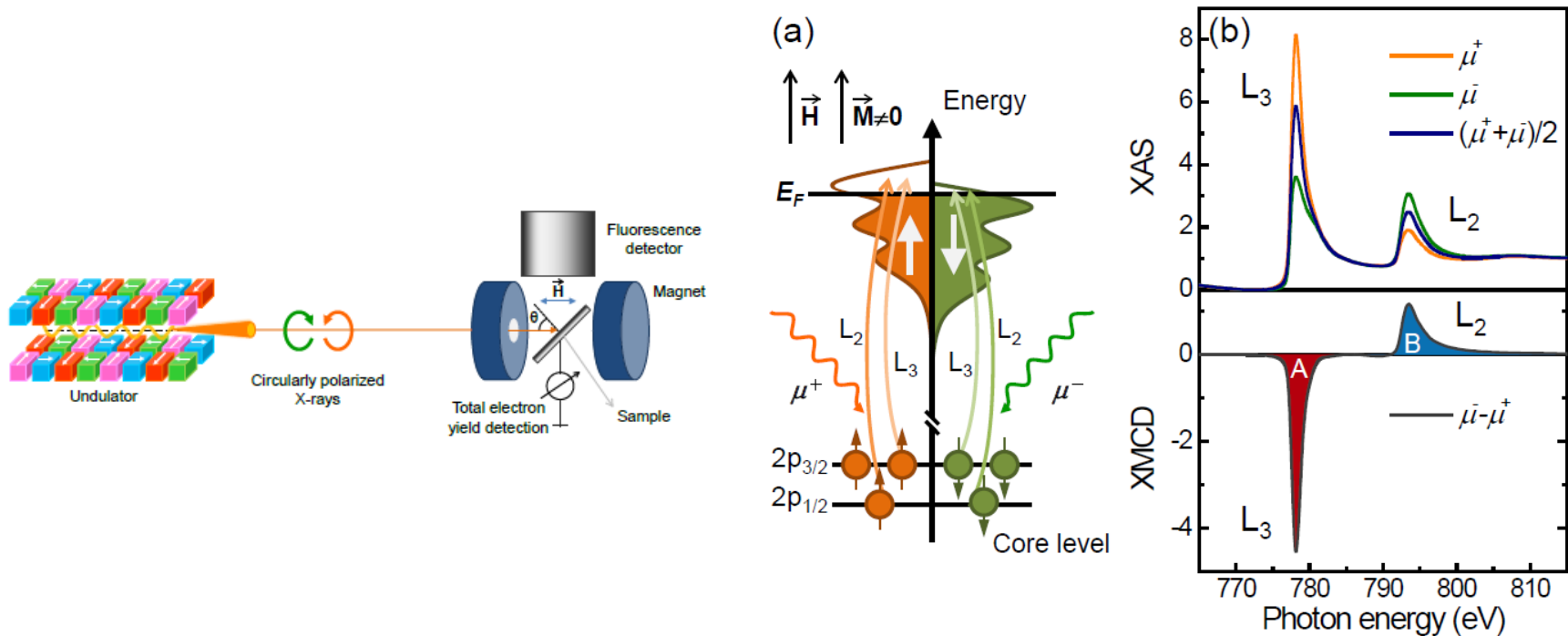
What the Heck ?



Future limits ?
I20 at Diamond will give
ppb of chemical species
- *much* more sensitive
chemical analysis
especially for env/earth
sciences

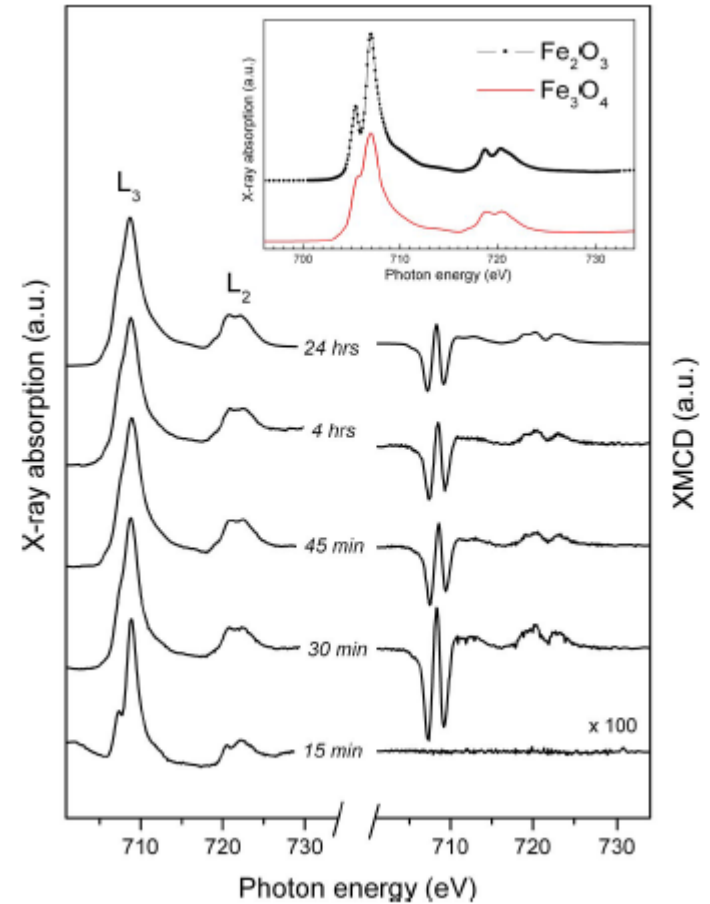
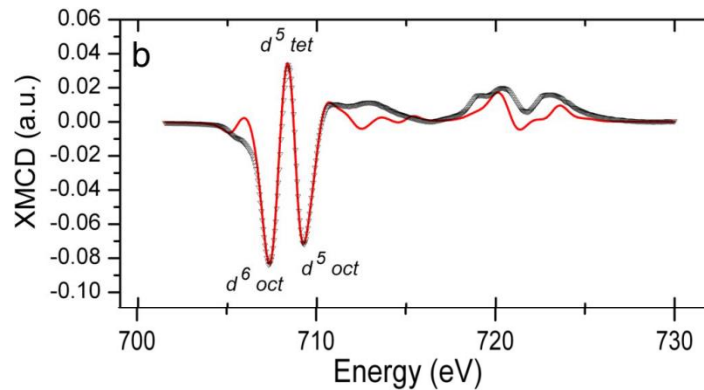
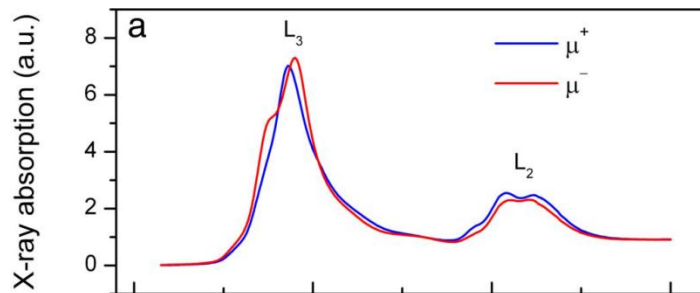
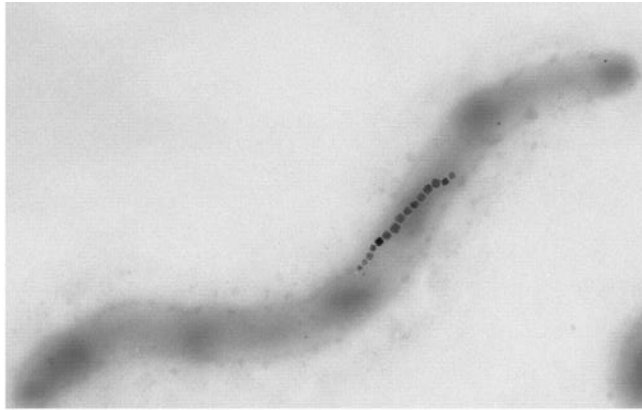
Mapping magnetism

- 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: $\Delta (\perp //) \sim \langle M^2 \rangle \rightarrow$ XMLCD

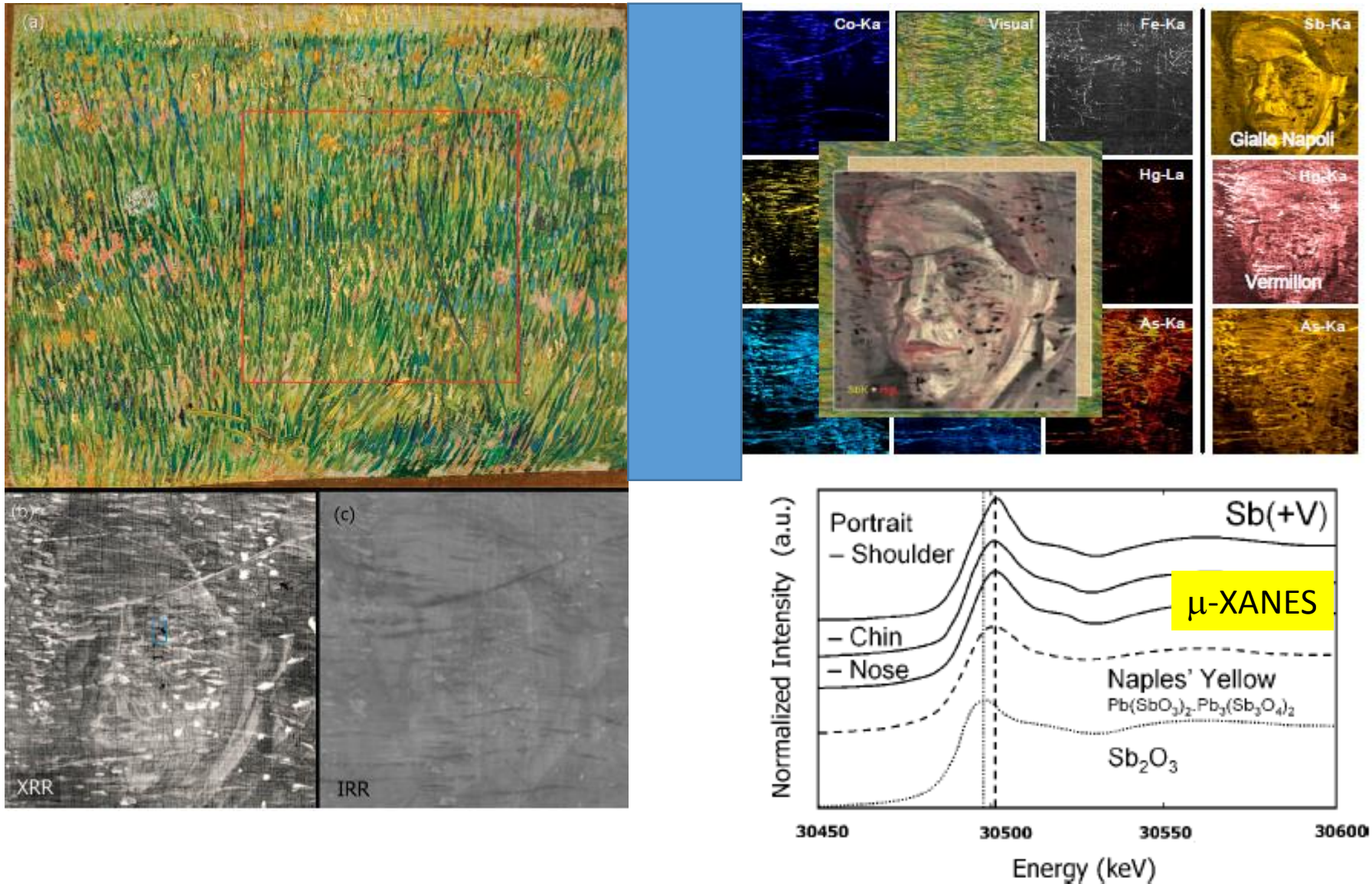
Magnetic bugs



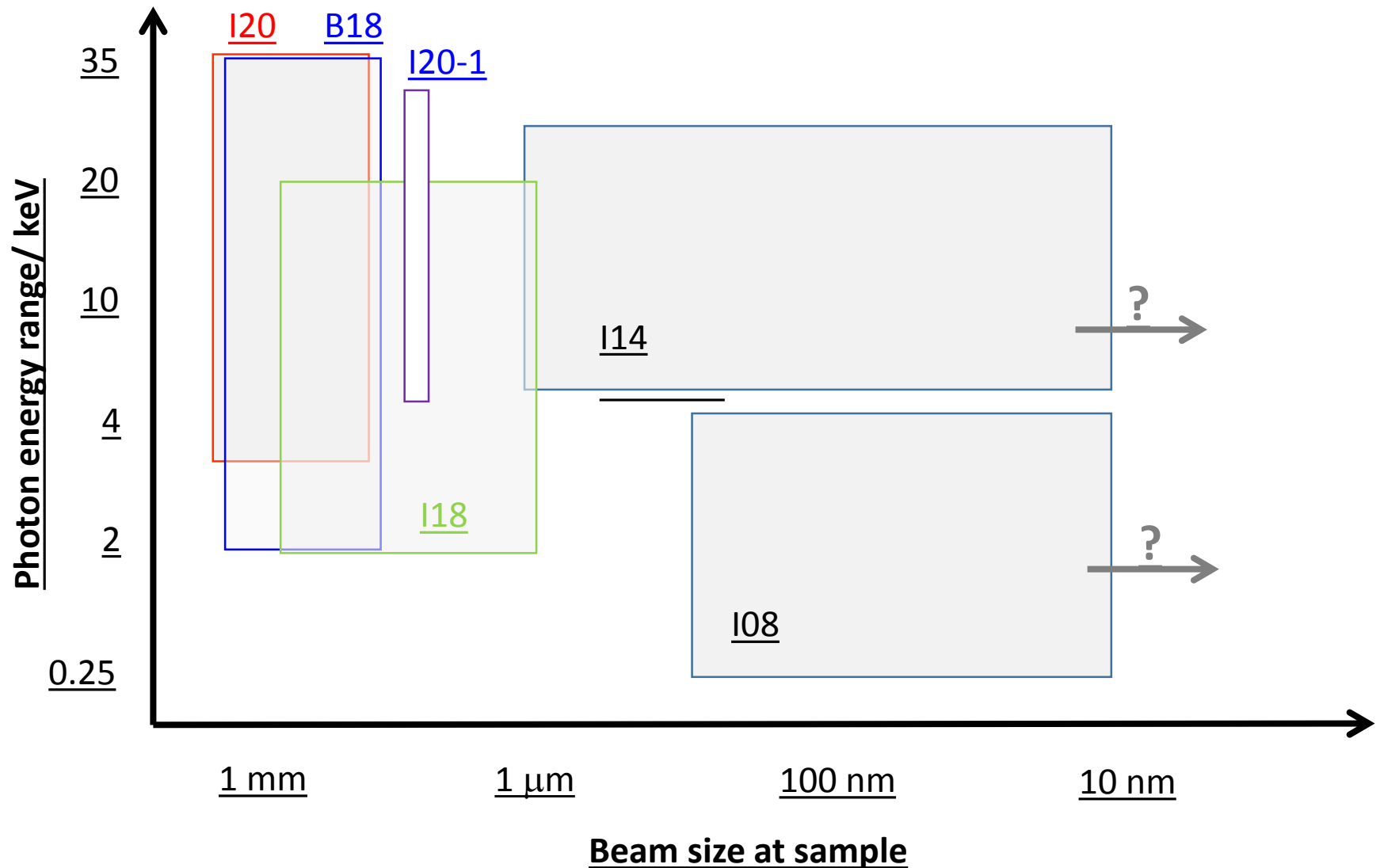
Follow growth of magnetic particles in situ by XMCD

XRF

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

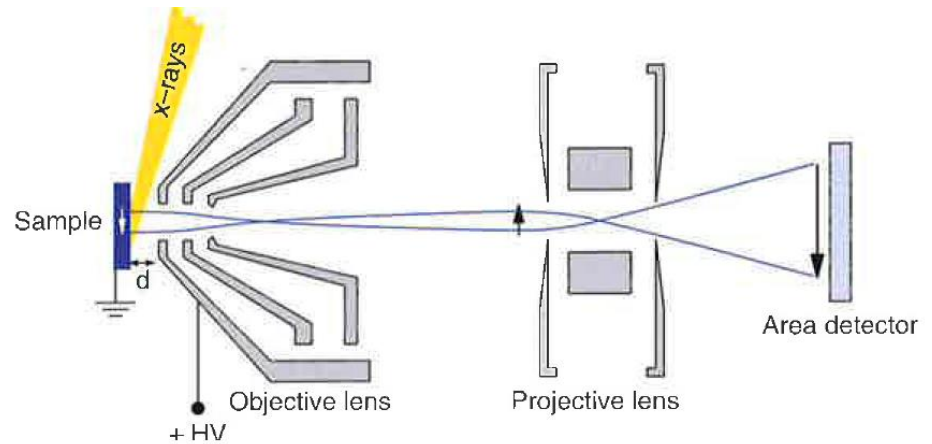
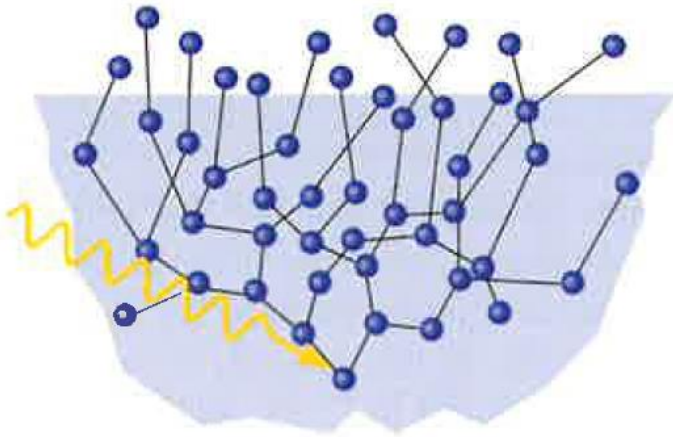


Micro- and nanoprobe suite



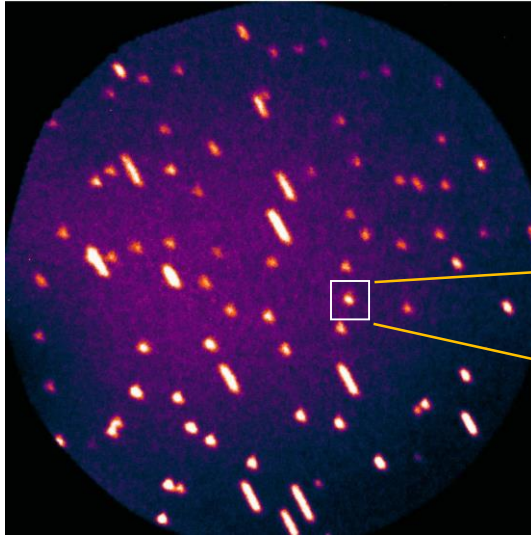
XAS Nanoprobes

- 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

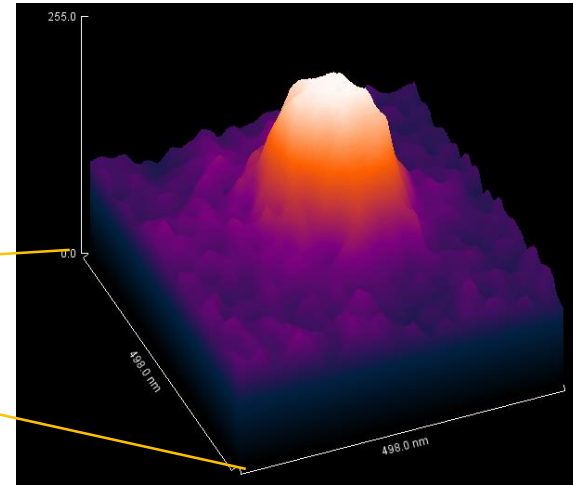


XAS Nanoprobes

- Exploit to make nanoscale maps of chemical character

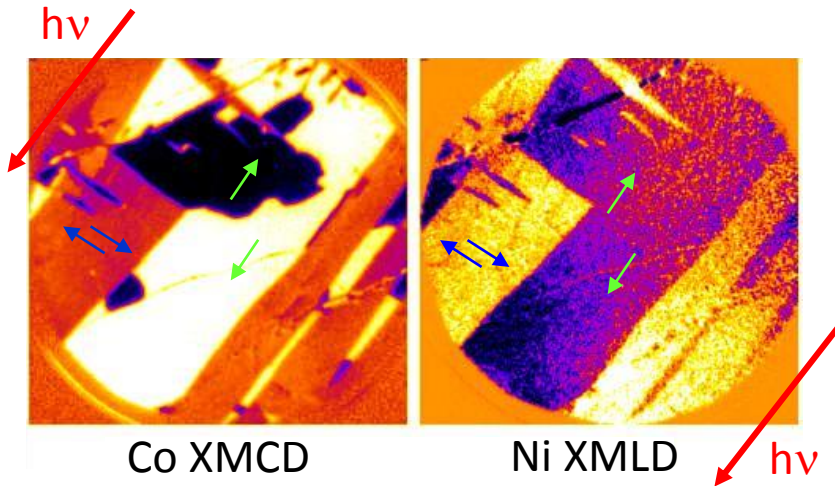


Thornton et al, UCL



Pd nanorods on TiO_2 recorded using $h\nu = 450\text{eV}$, FOV = $10\ \mu\text{m}$

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

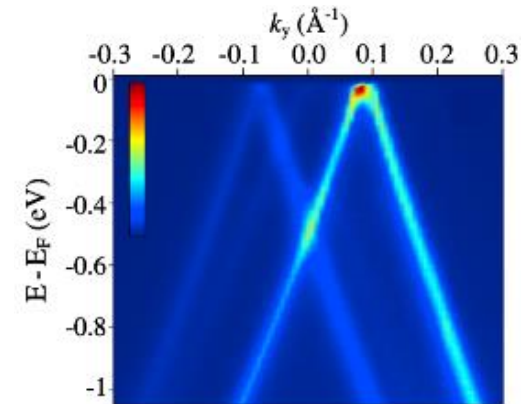
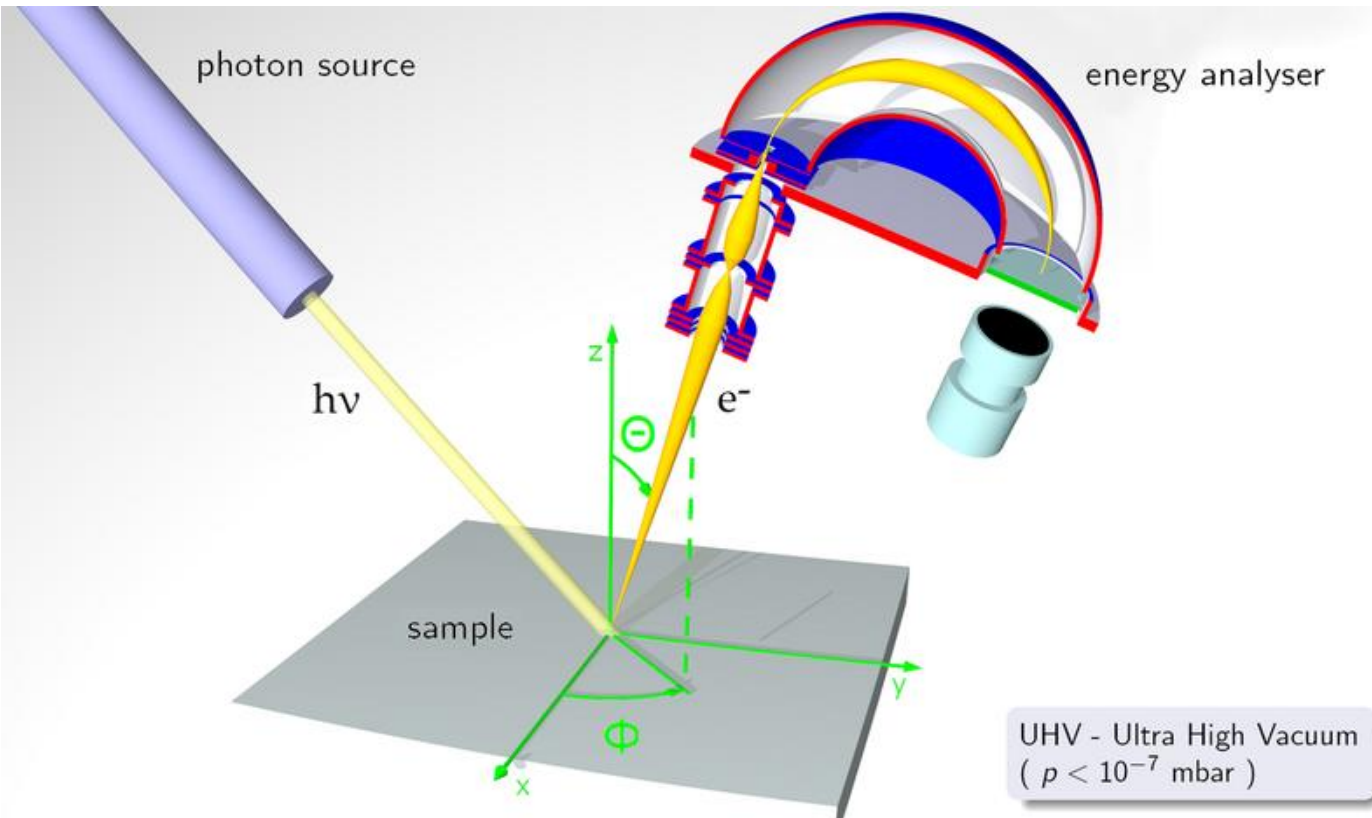


XMCD for (FM) Co L3 and XMLD for (AFM) Ni L2 shows orientation of the two types of moments at the interface is perpendicular – opposite of what was inferred from less precise measurements, crucial for device function

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



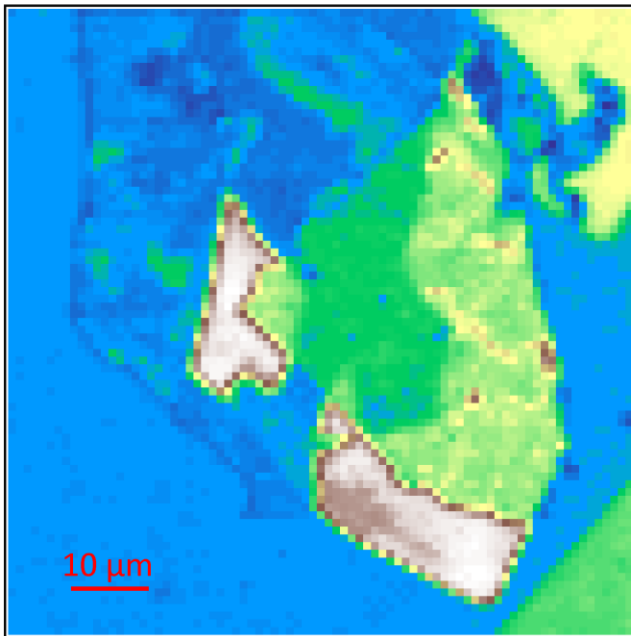
Graphene on SiC

ARPES and nano-ARPES

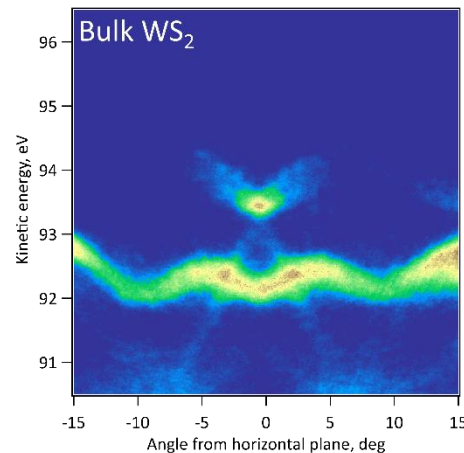
Synchrotrons enable ARPES to be measured with spatial resolution $< 1\mu\text{m}$

Map out electronic properties of heterogenous materials, devices....

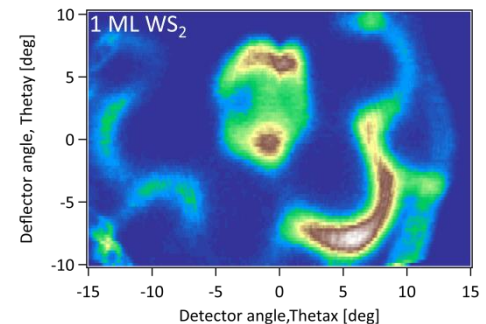
Spatially resolved ARPES image from first user experiment –
Graphene on 1 ML WS_2/BN , Wilson and Teutsch (Warwick)
(integrated over 30° angle and 7 eV energy band)



ARPES from image



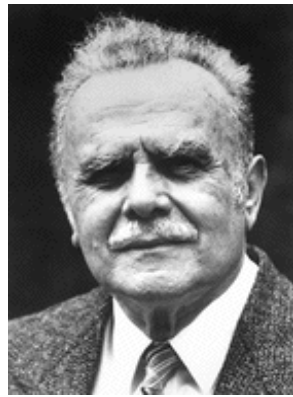
Energy cut of 3D ARPES scan
from micro-spot



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



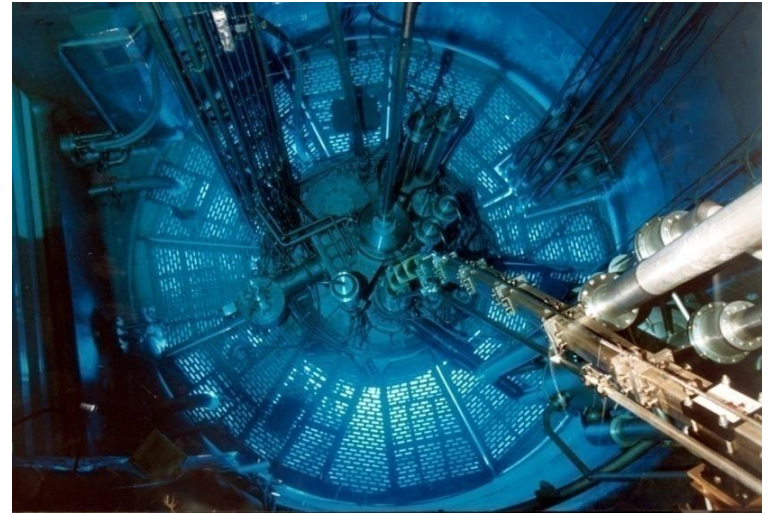
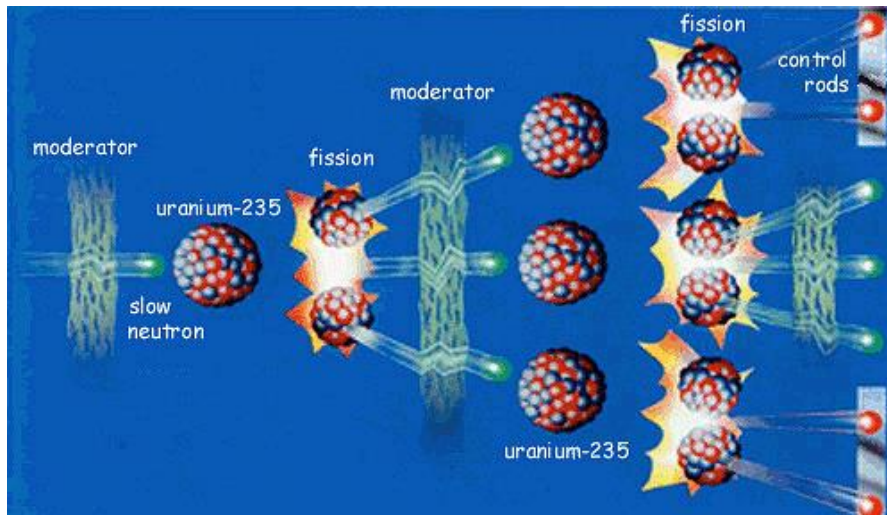
Cliff Shull

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. $^{235}\text{U} + ^1_0\text{n} = \text{fission fragments} + 2.4 ^1_0\text{n} + 192.9 \text{ MeV}$

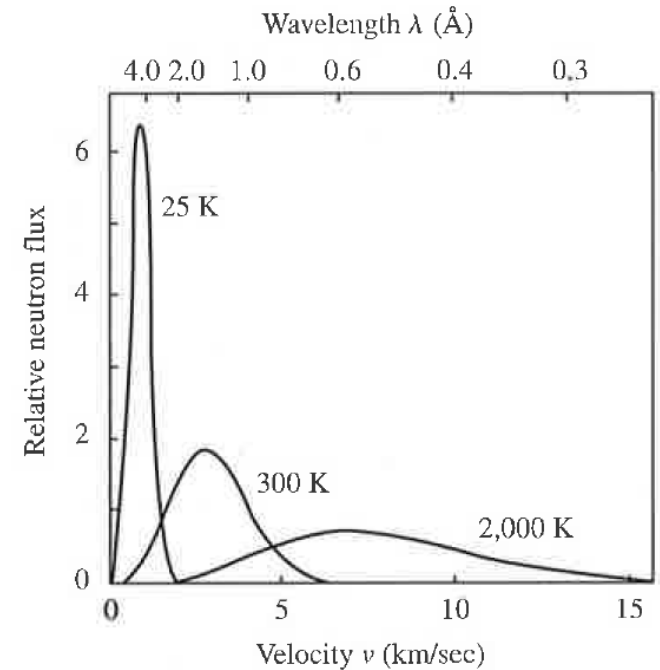
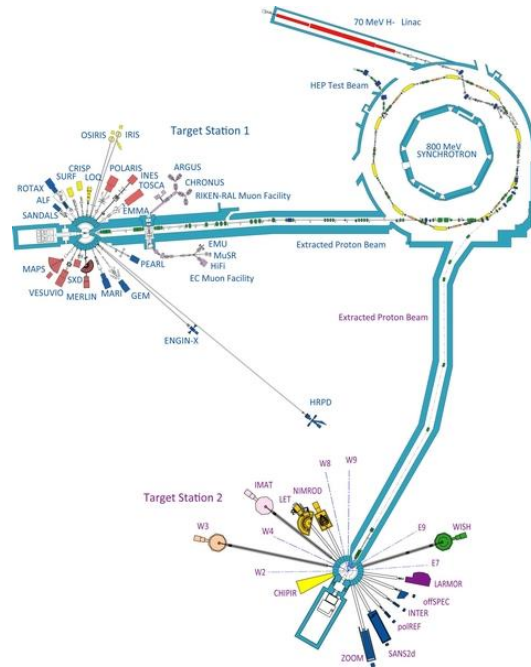
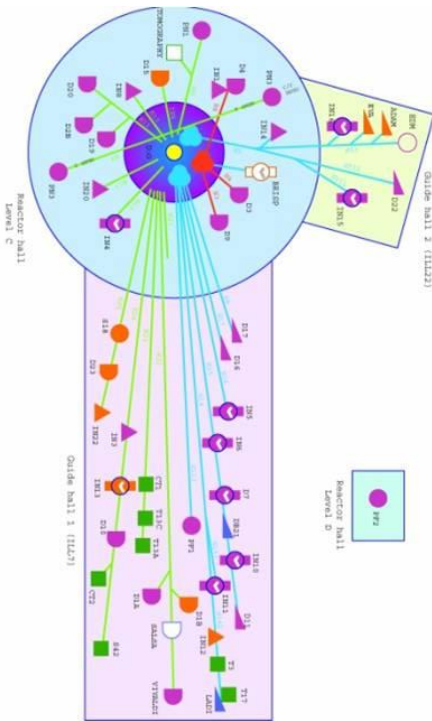
Spallation – high energy protons + heavy metal target (W, Hg) = high energy neutrons



- Wave-particle duality: $\lambda \cong 1.8 \text{ \AA}$ at room temp ($\sim 2 \text{ km/s}$) – diffraction
- Possesses a small magnetic moment equivalent to $s = \frac{1}{2}$ - magnetic probe

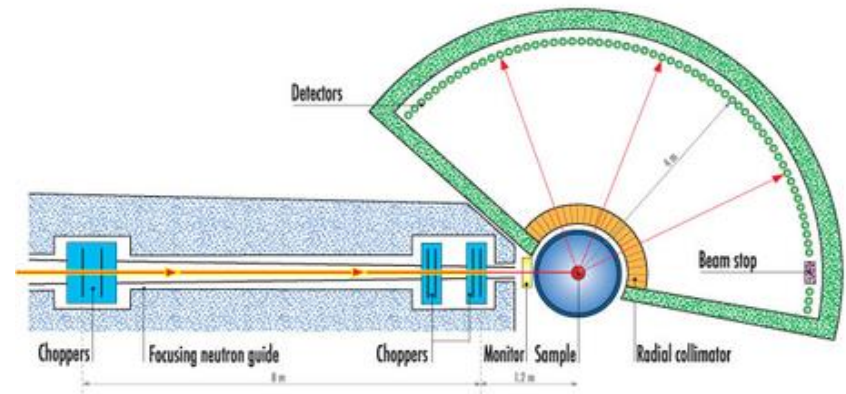
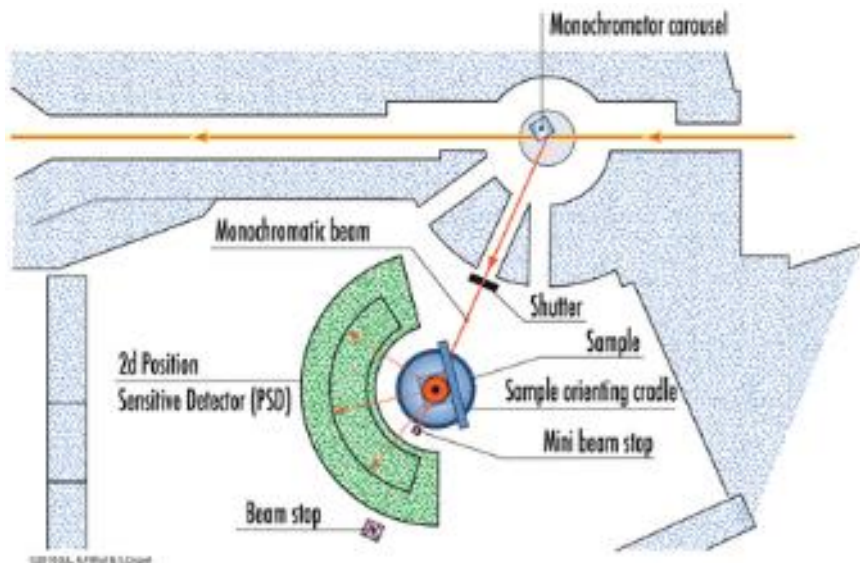
Harnessing neutrons in facilities

- 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 H₂, solid CH₄ 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

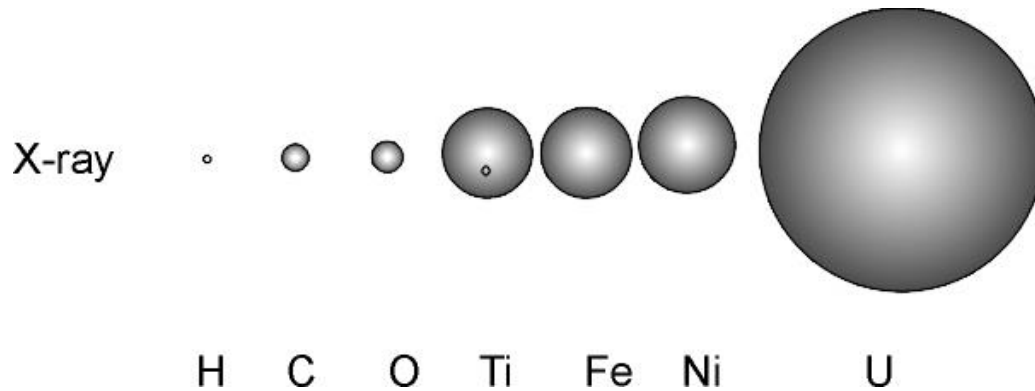
1 – Deeply penetrating and reveal position of light elements such as H or Li

2 – The magnetic structure of materials regardless of magnetic element

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

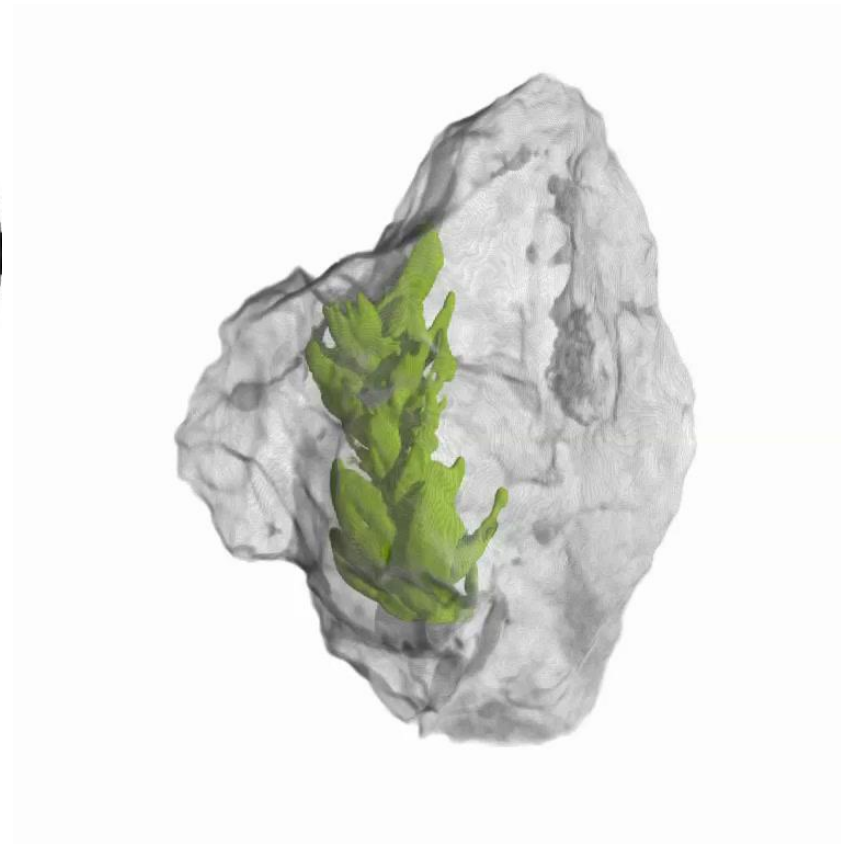
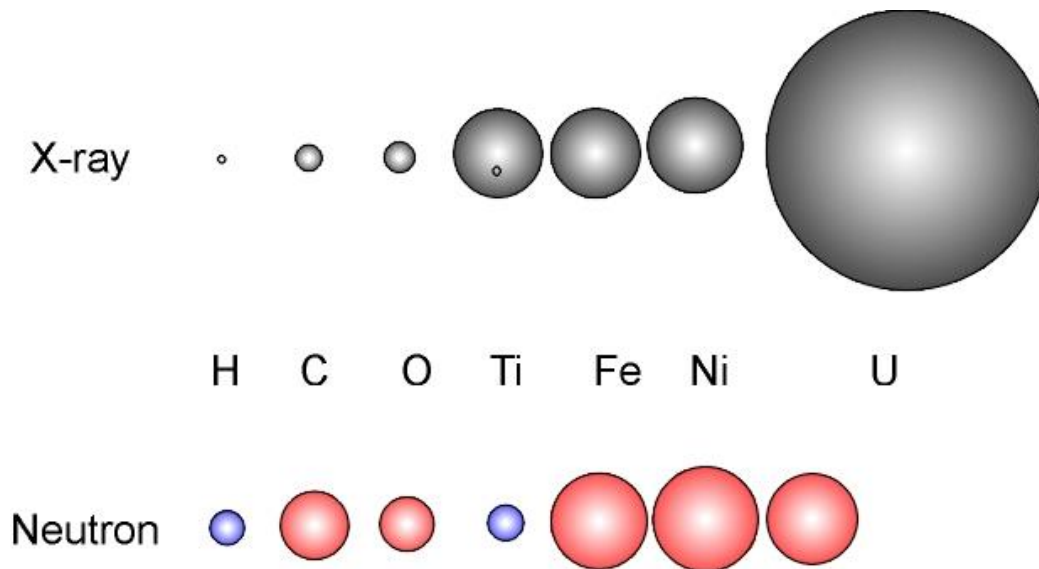
Neutron-matter interactions (1)

- 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.



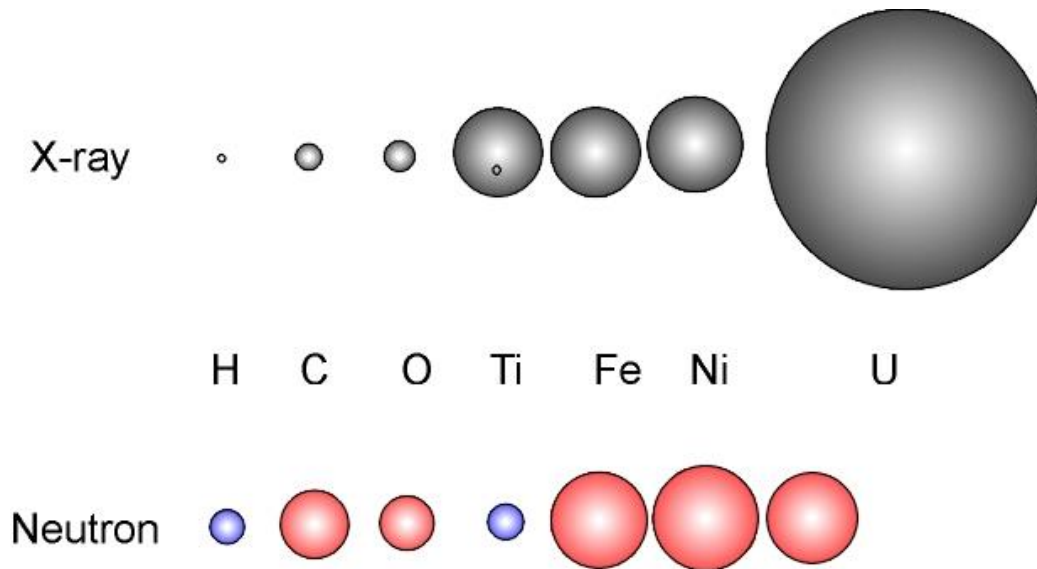
Dependence of scattering strength on Z

- 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

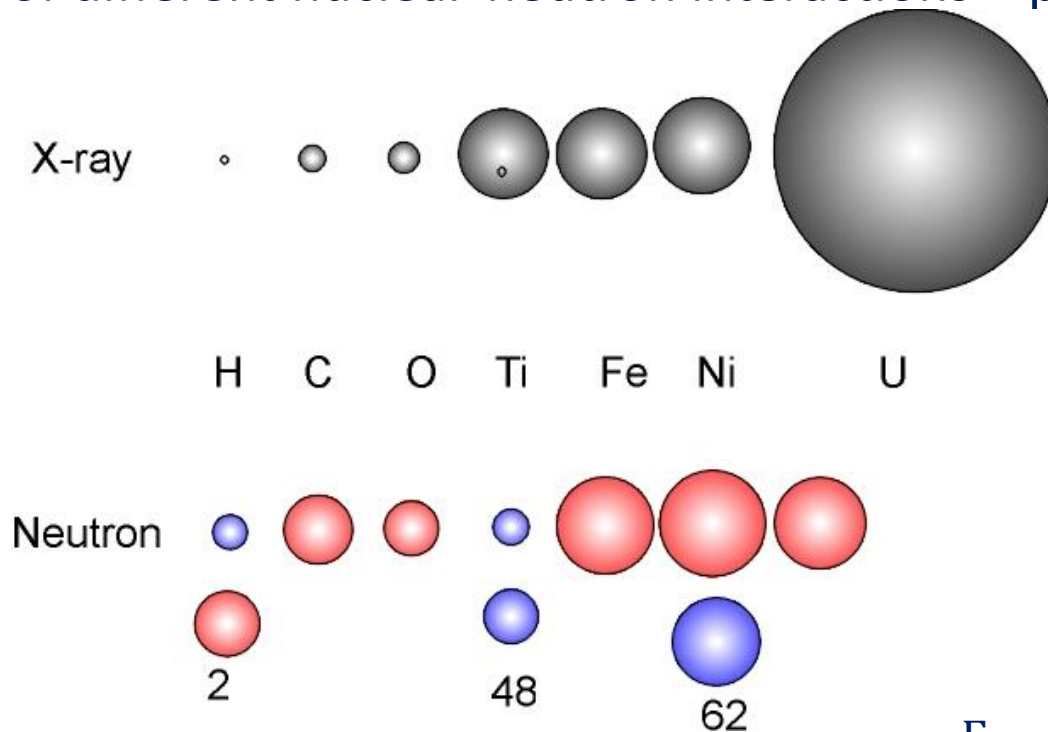
- Neutrons are scattered primarily by the nucleus of atoms, and the scattering length b (or cross-section, $\sigma = \pi b^2$) rises on average with Z much less steeply than for X-rays, as well as having some very distinct deviations from a smooth dependency
- Can look deeper inside dense engineering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

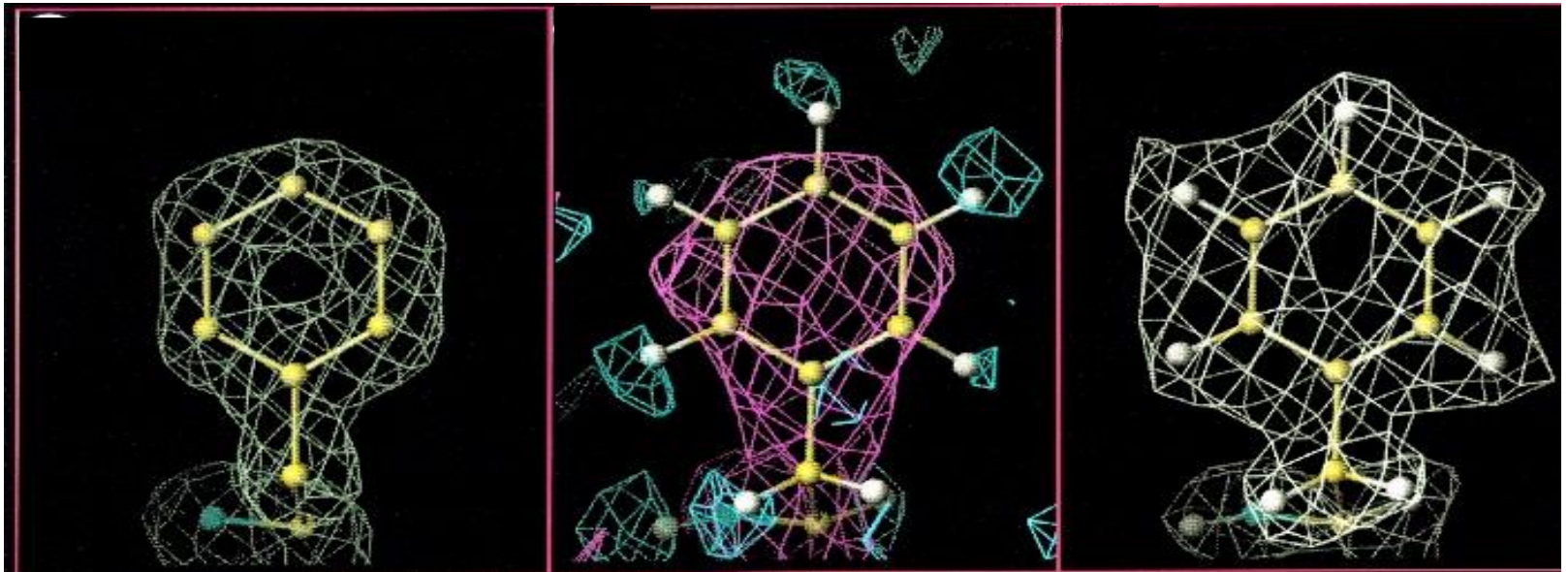


Different colours correspond to different signs for b : positive (red) and negative (blue)

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

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

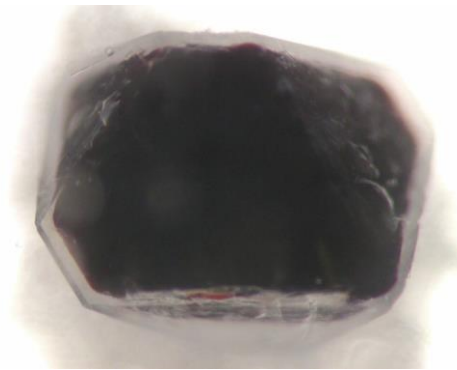
Neutron map (H)

Neutron map (D)

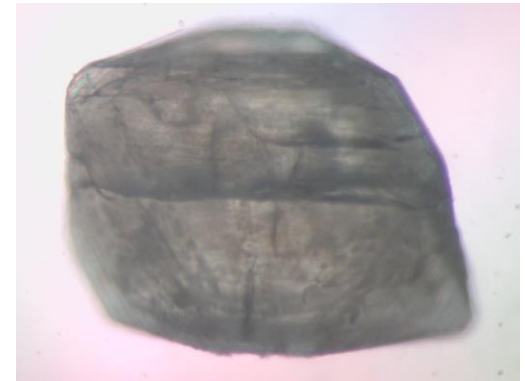
Though we could infer position of H's knowing where the other atoms are and using chemical intuition...

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



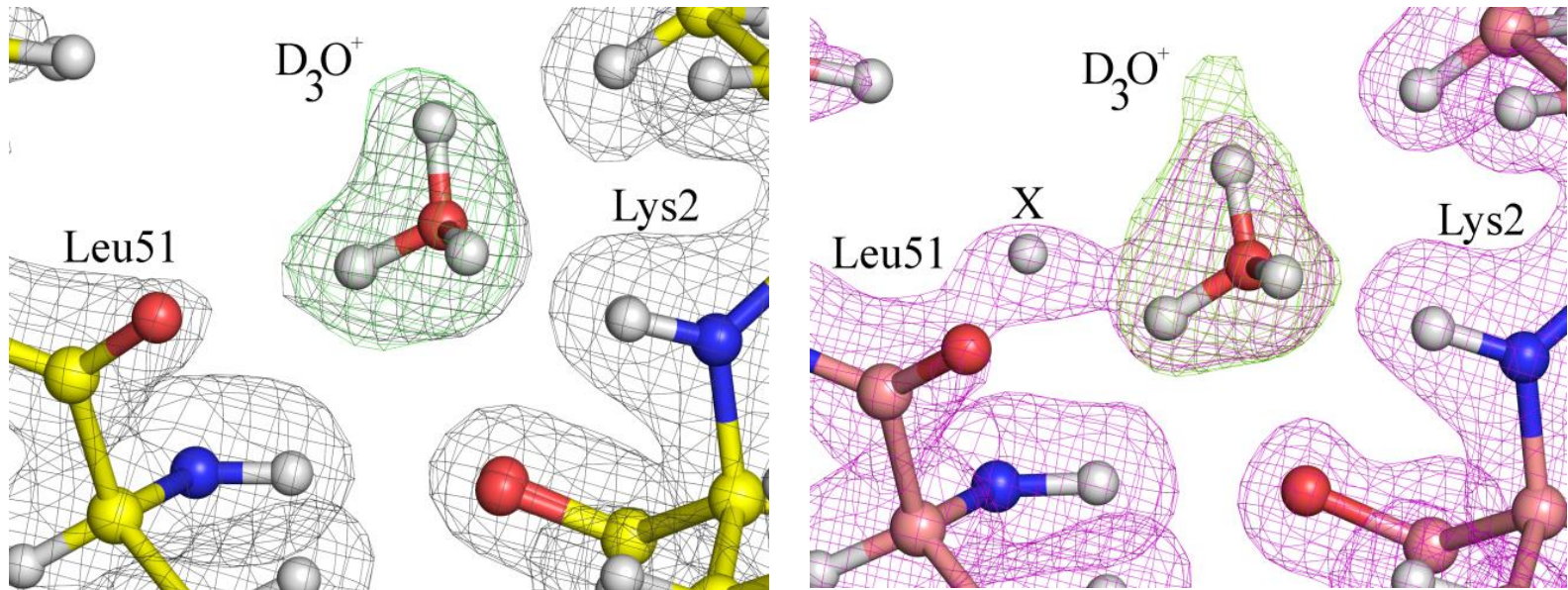
Fe^{3+}



Fe^{2+}

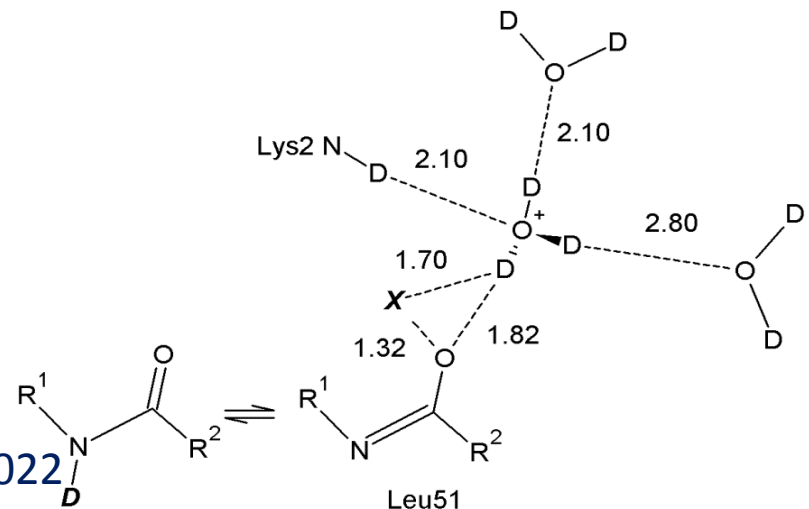
Pinning down light elements

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



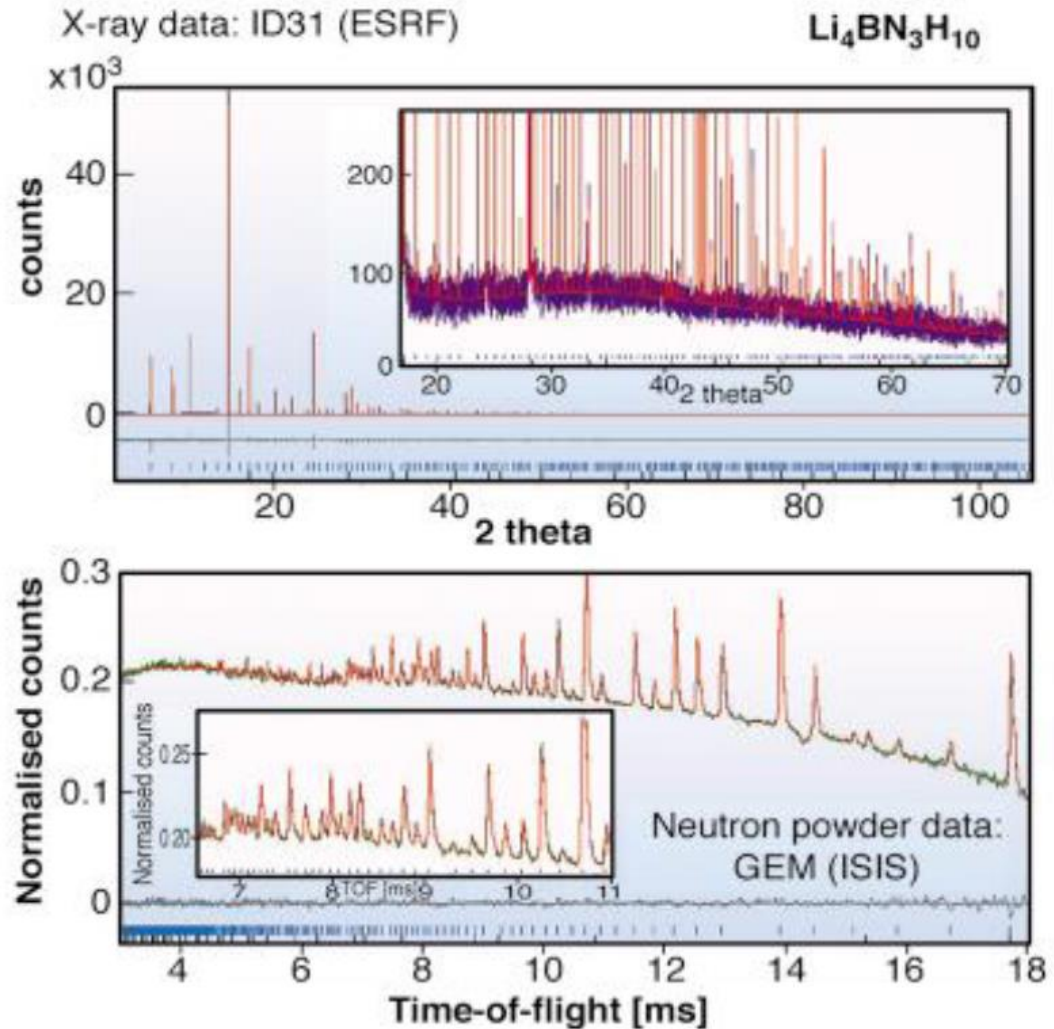
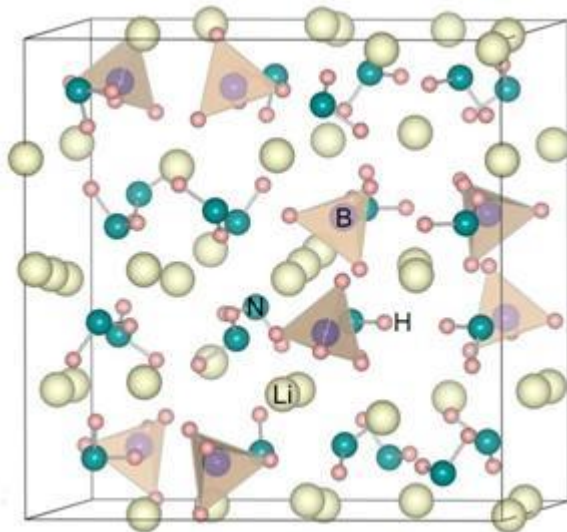
Observation of hydronium (D) ions and of tautomeric shifts following the change from the oxidised form to the reduced form

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



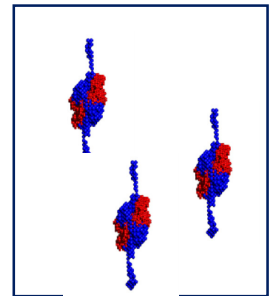
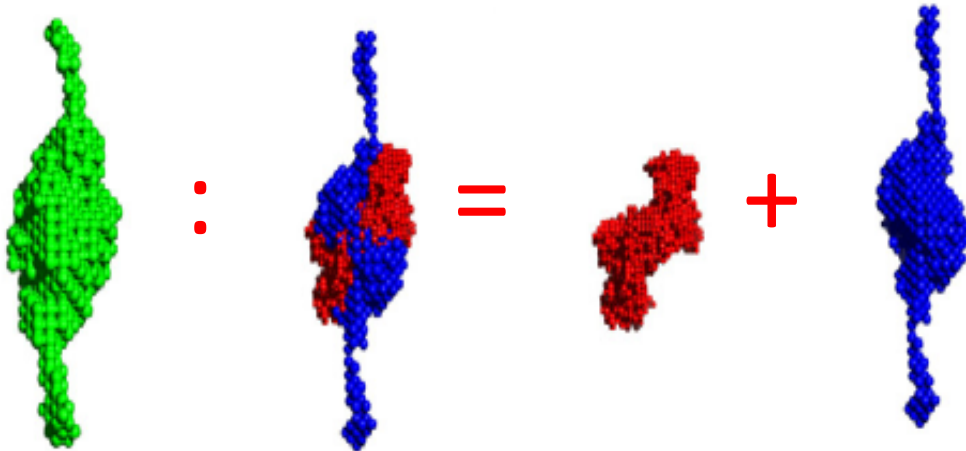
'Hard' materials

- 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....



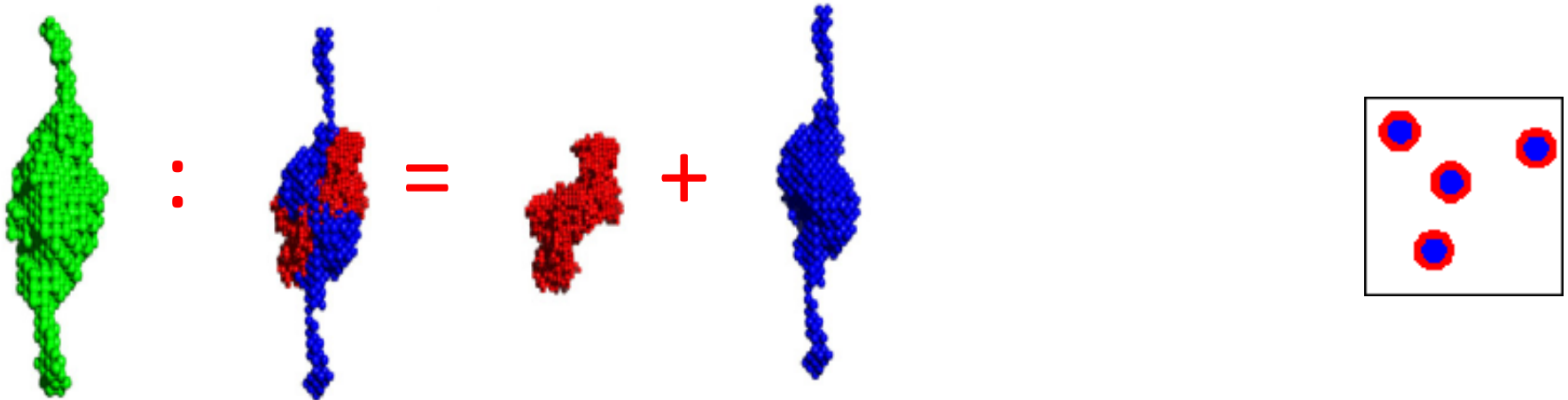
Contrast variation

- 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 ($\text{H}_2\text{O}/\text{D}_2\text{O}$)



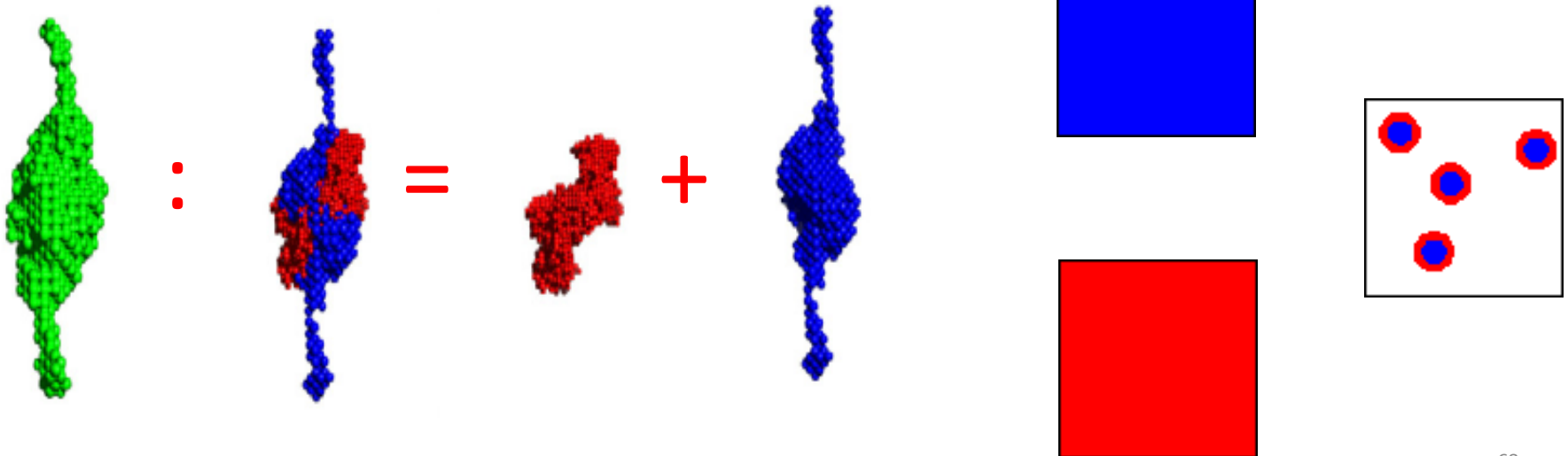
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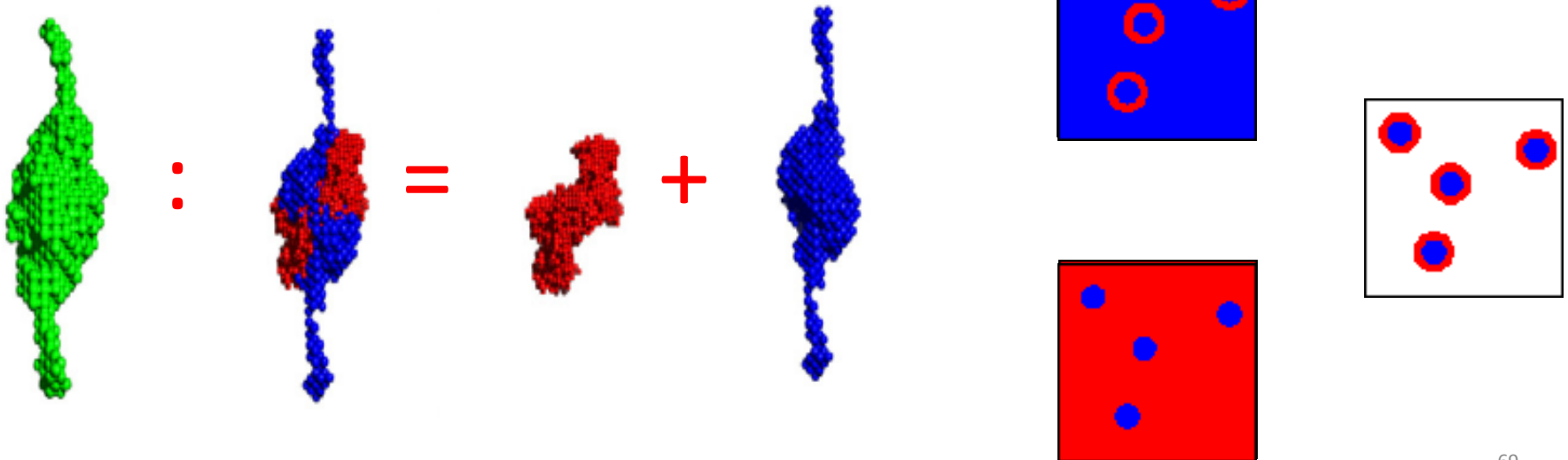
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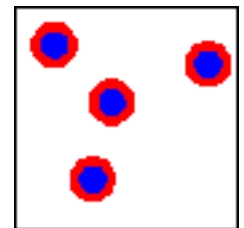
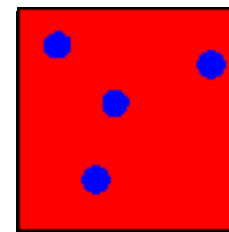
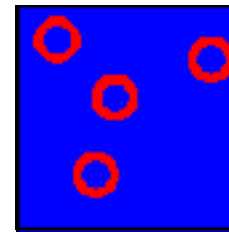
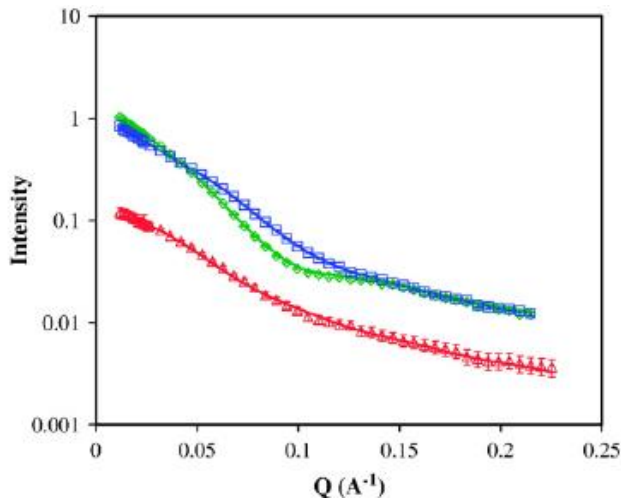
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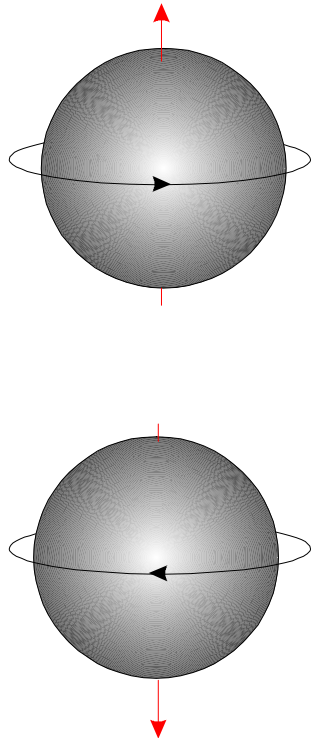
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Neutron-matter interactions (2)

- The small magnetic moment on the neutron means that it is sensitive to scattering from ordered magnetic moments in materials. In contrast with X-rays, the strength of this scattering is comparable to the nuclear scattering and the data relatively easy to interpret.



PHYSICAL REVIEW VOLUME 70, NUMBER 3 OCTOBER 15, 1949

Letters to the Editor

Detection of Antiferromagnetism by Neutron Diffraction*

C. G. SHULL

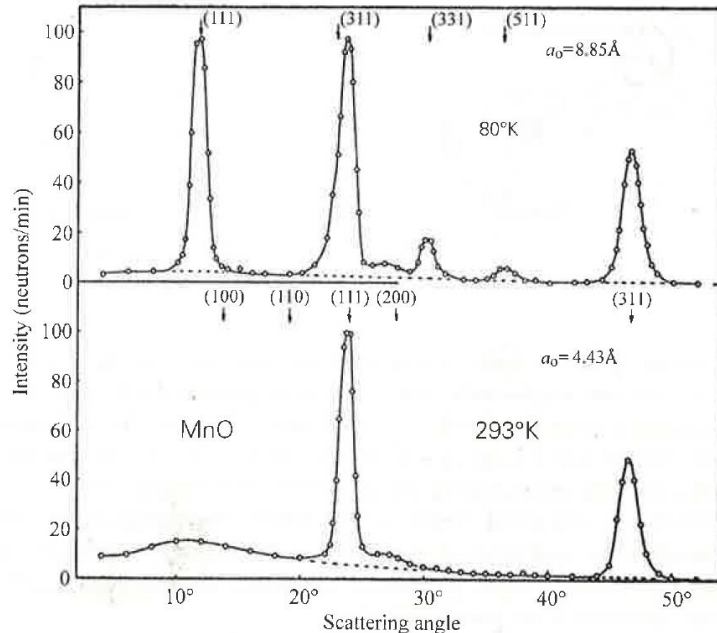
Oak Ridge National Laboratory, Oak Ridge, Tennessee

AND

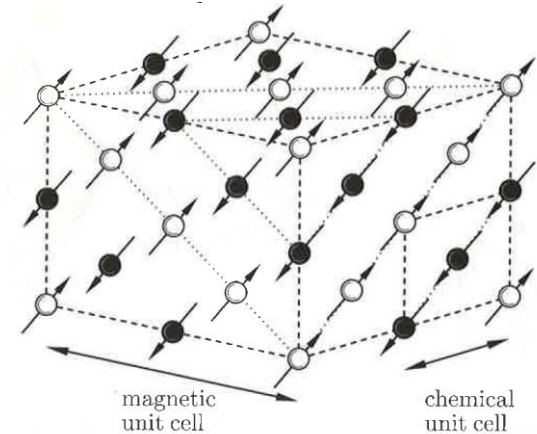
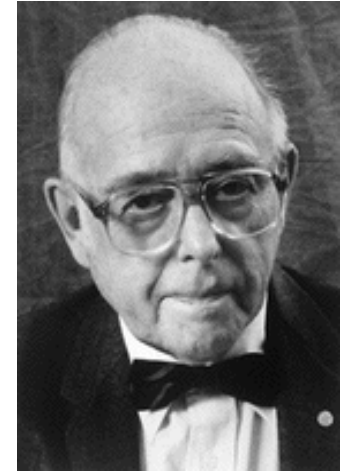
J. SAMUEL SMART

Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

August 29, 1949

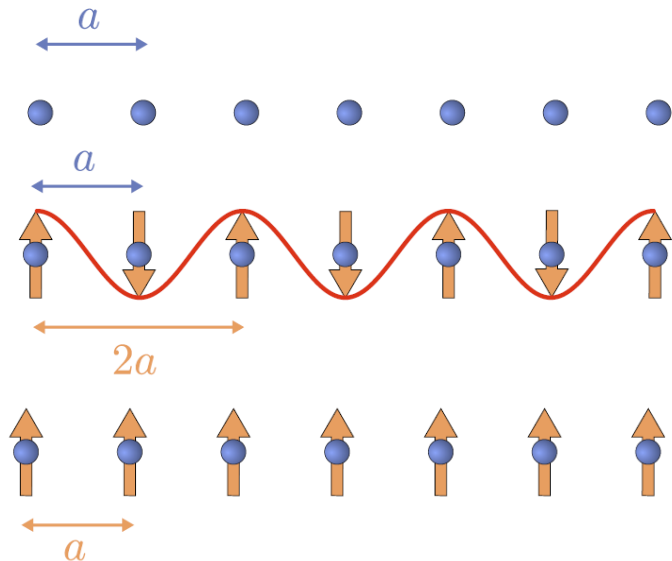


$\text{Mn}^{2+} (3d^5)$ in O_h environment
 $S = 5/2$ – large moment



Magnetic scattering

- The small magnetic moment on the neutron means that it is sensitive to scattering from ordered magnetic moments in materials. In contrast with X-rays, the strength of this scattering is comparable to the nuclear scattering and the data relatively easy to interpret.
- The majority of materials that show long-range magnetic ordering on cooling do so antiferromagnetically. This often leads to an expansion of the unit cell (for example a doubling of the cell edge, so that reflections at $(h\ 0\ 0)$ may now be accompanied by reflections at $(h/2\ 0\ 0)$)
- For the much less common case of a ferromagnet, the magnetic structure maps directly onto the nuclear structure with reflections at $(h\ 0\ 0)$



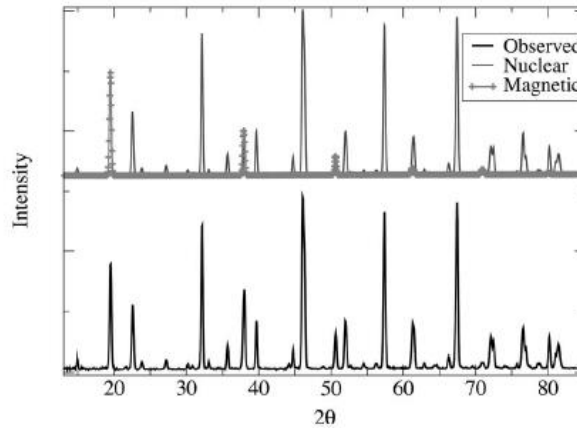
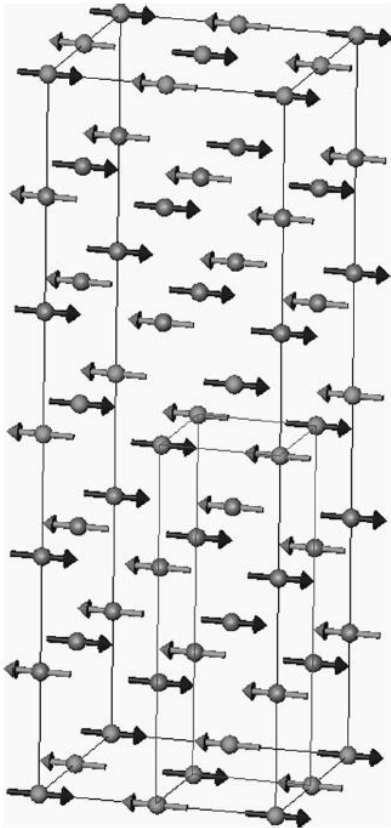
Nuclear structure, reflections at $(h\ 0\ 0)$

AFM structure, reflections at $(h/2\ 0\ 0)$

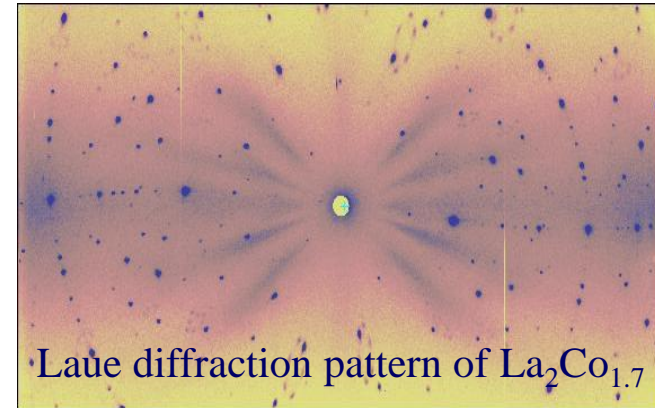
FM structure, reflections at $(h\ 0\ 0)$

Magnetic scattering

- Scattering from the ordered magnetic structure gives additional intensity relative to scattering just from the nuclear structure.
- This can be modelled or refined just as for the nuclear structure



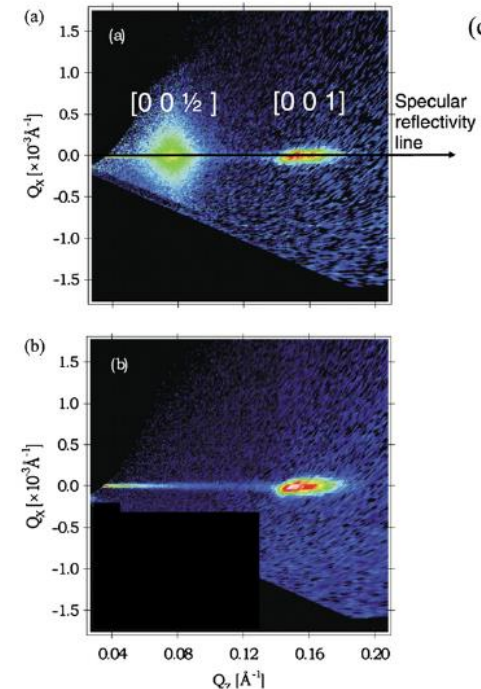
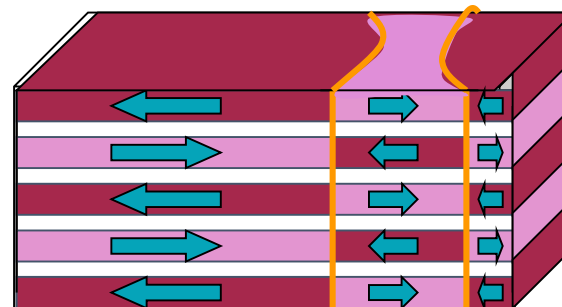
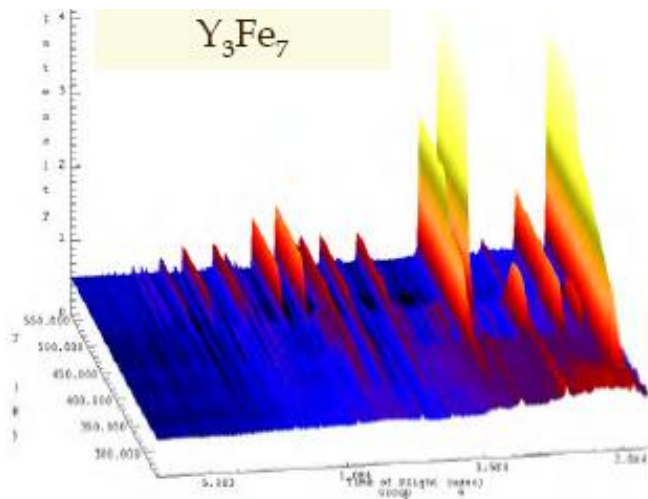
YBa₂Fe₃O₈ – antiferromagnetic order gives additional Bragg peaks corresponding to doubling of unit cell along each edge
Observed pattern (lower) contains specific peaks that are modelled separately from nuclear peaks (upper)



Single crystal diffraction refined in a similar fashion to X-ray pattern with different atomic scattering cross section, and rapid fall off in magnetic intensity with 2θ (form factor)

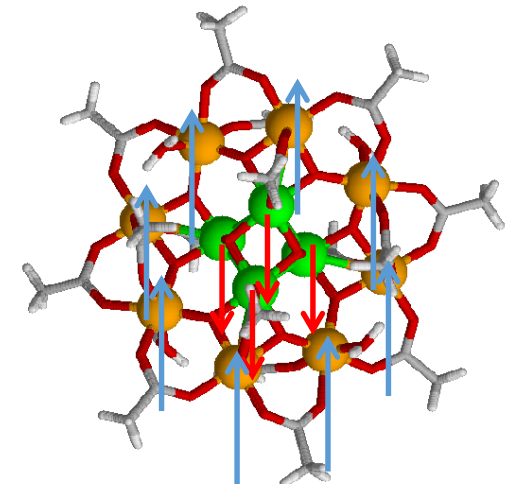
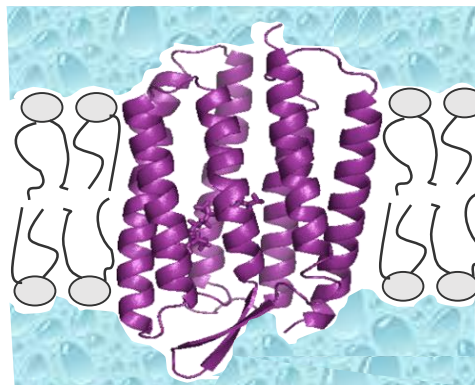
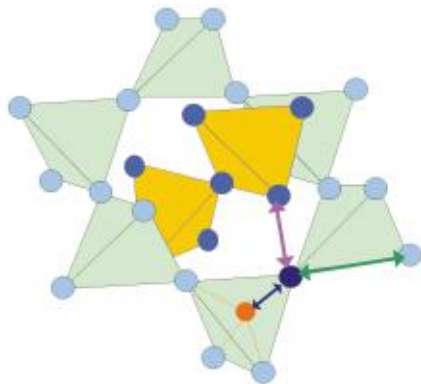
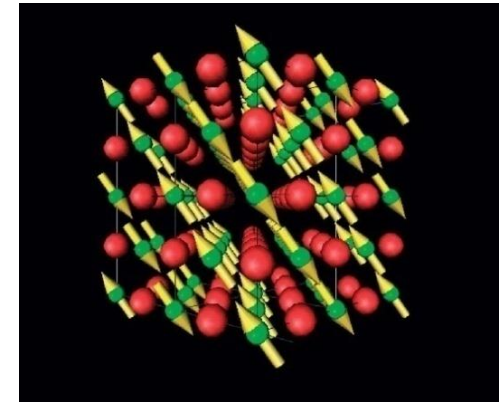
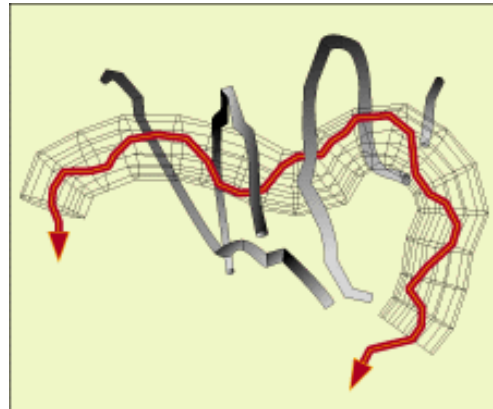
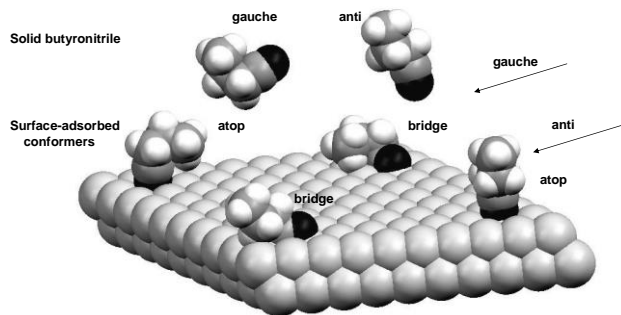
Magnetic transitions, structures and devices

- Variable-temperature powder diffraction reveals the onset of magnetic order; in principle one can also refine the structure from a starting model
- Neutron beams can be polarised (spin 'up' or 'down') and the polarisation dependence of the scattering from single crystals provides the most incisive probe of magnetic structure
- Magnetic reflectometry may also be performed to depth profile magnetic films and layered structures such as those used in magnetic storage media



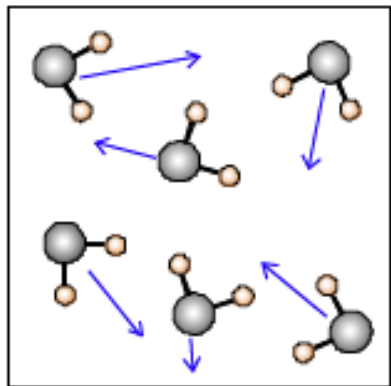
Atomic and molecular motion in materials

- Atomic and molecular vibrations, rotations and translations are essential to key processes in materials e.g. thermal conductivity and expansion, polymer processing and properties, biochemical processes, magnetic storage media, superconductors

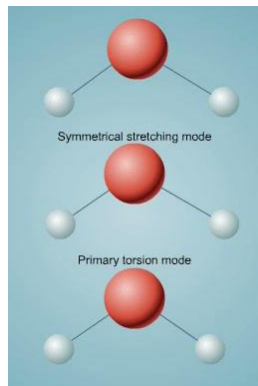


Atomic and molecular motion in materials

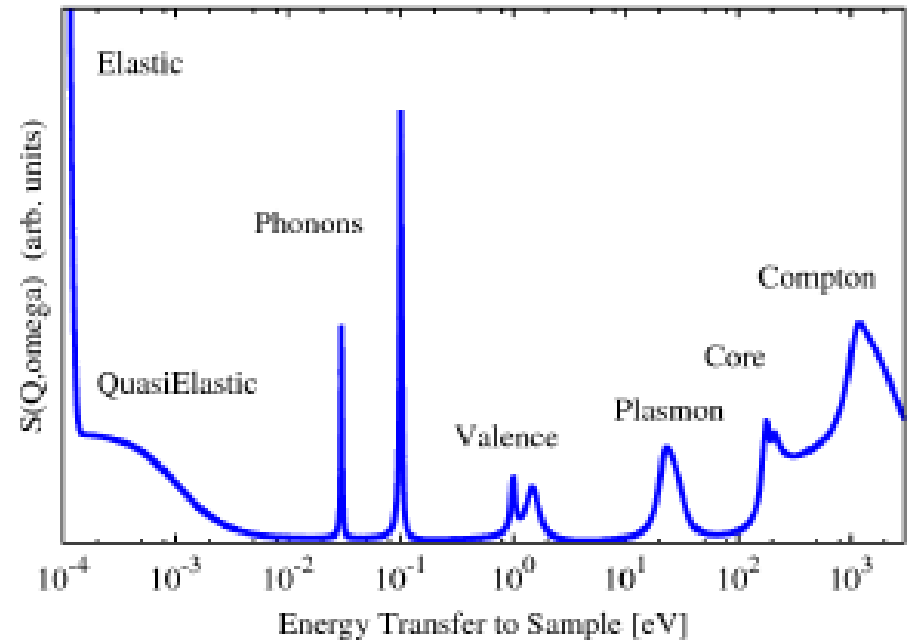
- Diffusion, rotation and vibrations span a wide range of energies and timescales (s-fs) and are commonly studied by NMR, microwave, IR and Raman spectroscopy, as well as computational techniques (MD)



Molecular diffusion
or rotation



Molecular
vibration

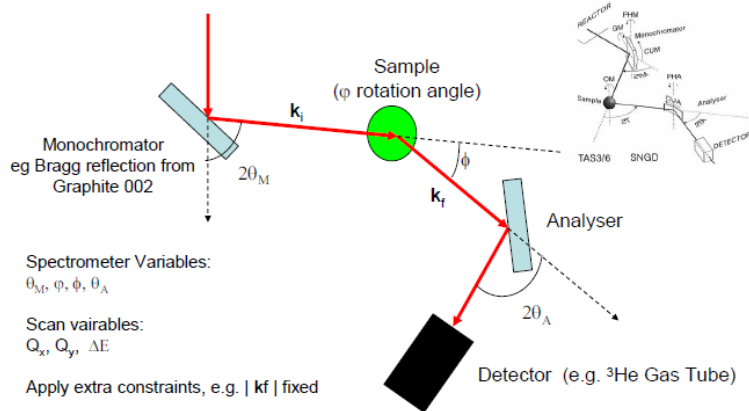


Typical energy range of 'cold' to 'hot' neutrons

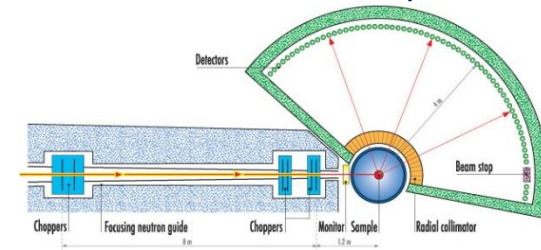
Neutron-matter interactions (3) - excitations

- Measure the energy (E) and the momentum of the neutron before and after scattering and determine the energy of the excitation and some measure of the amplitude (molecules) or the momentum (k, solids)
- Thermal neutrons typically have energies comparable to vibrations

Triple-axis spectrometer (M-S-A)



Time of flight spectrometer – based on timing of neutron pulses and velocity measurements – at reactor (choppers) or spallation source (proton pulse arrival sets $t = 0$)



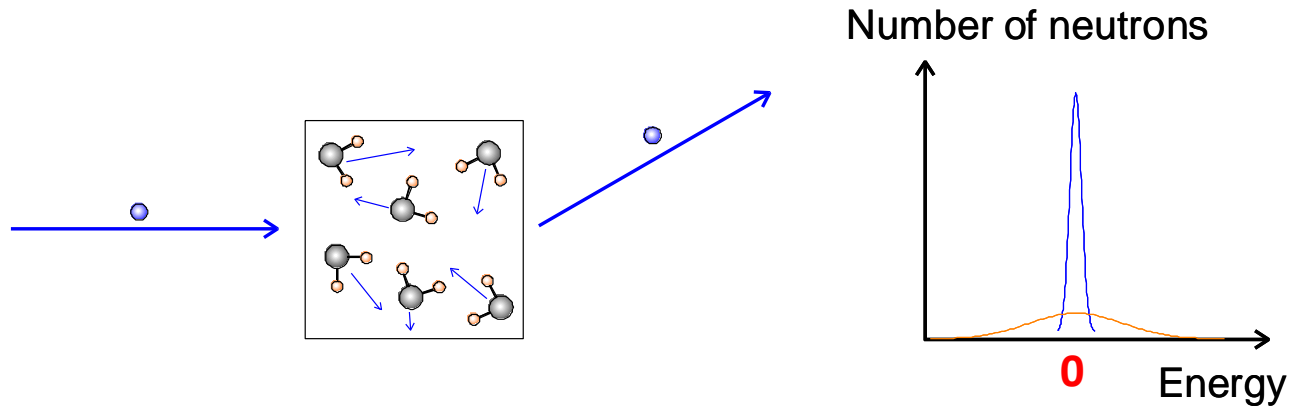
$$h\nu = E_f - E_i$$

$$k \text{ (excitation)} = k_f - k_i$$



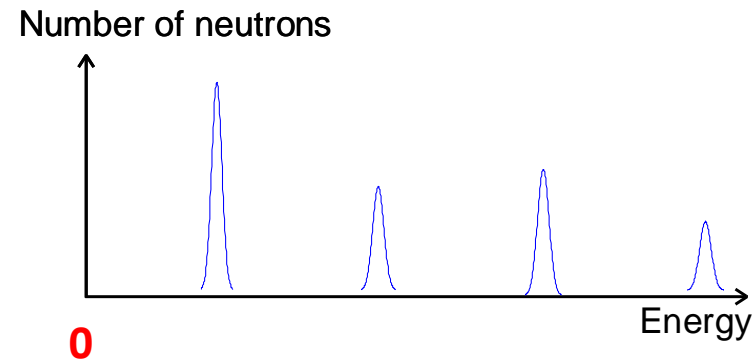
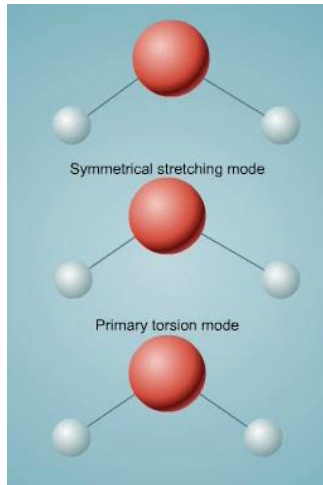
Inelastic neutron scattering

- Match spectrometers to different energy regimes (use hotter or colder neutron – shorter or longer wavelength) with different resolution specs.
- Look at change in energy on scattering to probe diffusion and rotation (quasielastic) – particularly with H (strong scatterer)



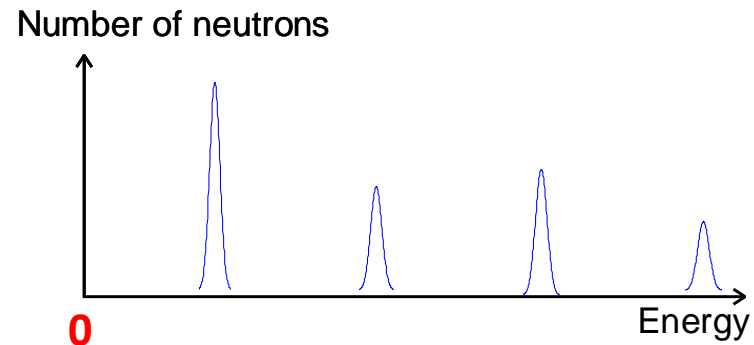
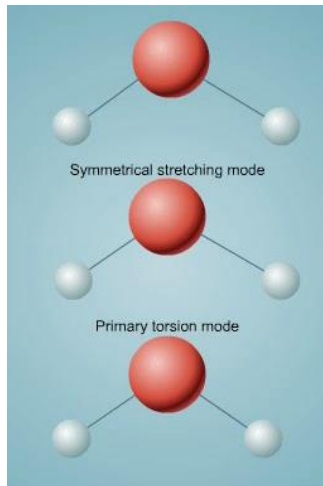
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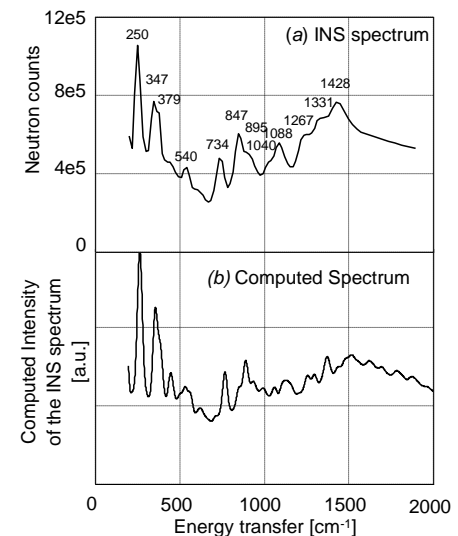
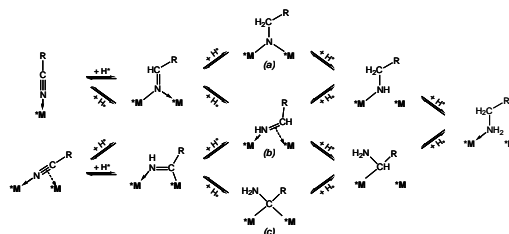
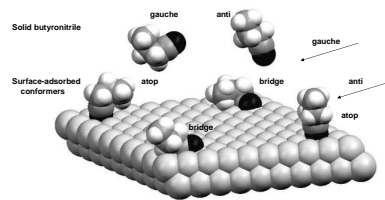


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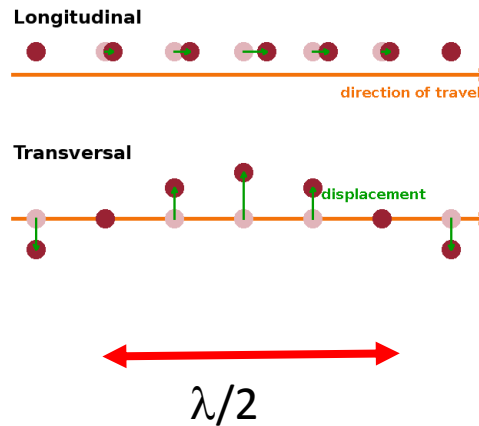
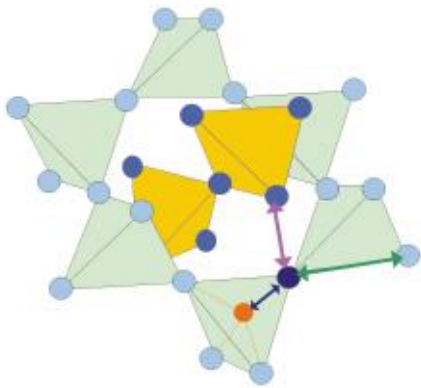


e.g. characterization of molecular species on a catalysis in systems opaque to IR and Raman methods



Excitations in solids

- In solids we see structural excitations of the lattice in the form of waves (phonons) characterised by the relationship between energy and wavelength – conventionally expressed as plot of E vs k ($2\pi/\lambda$).
- The full range of excitations runs from the undisturbed lattice ($\lambda=\infty$) to the maximum disturbance where a neighbouring atom is 180° out of phase ($\lambda=2a$)



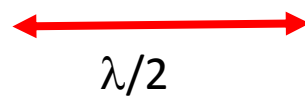
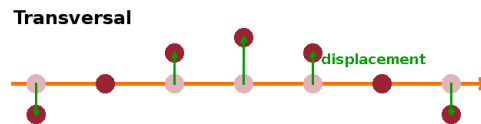
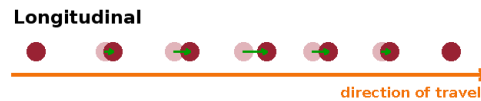
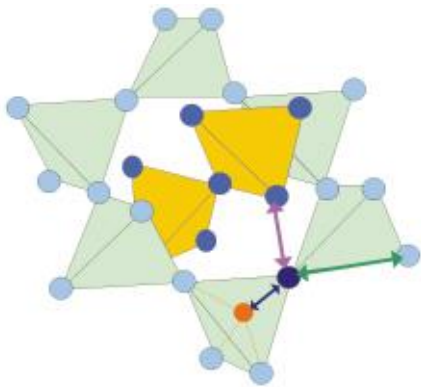
$$\lambda = \infty$$



$$\lambda = 2a$$

Excitations in solids

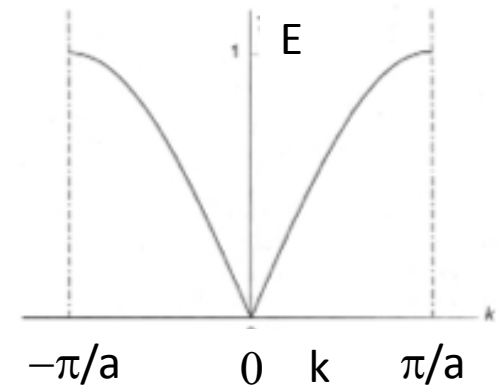
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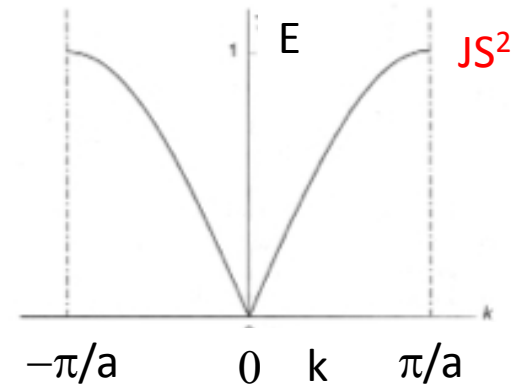
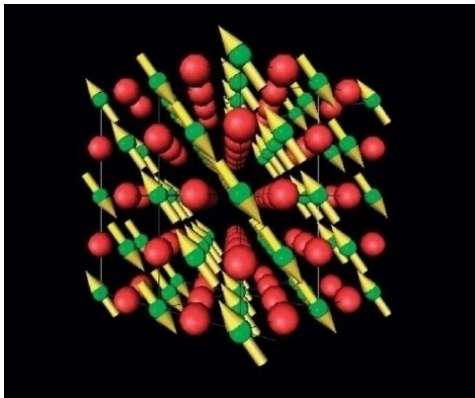
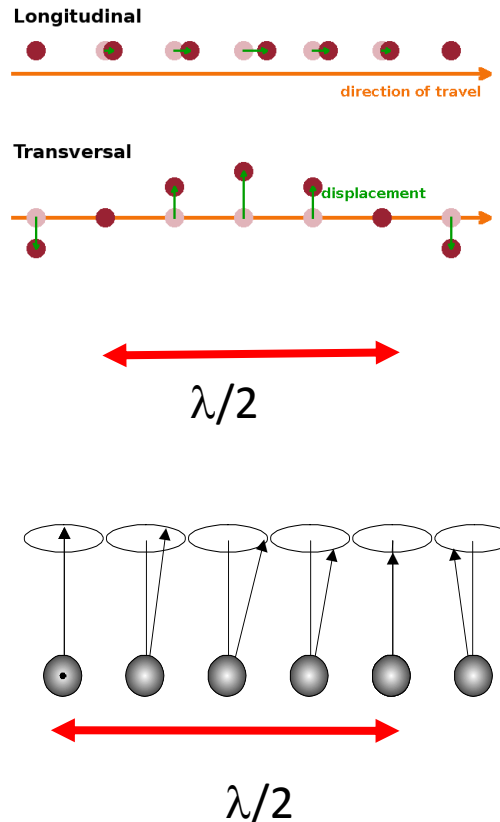
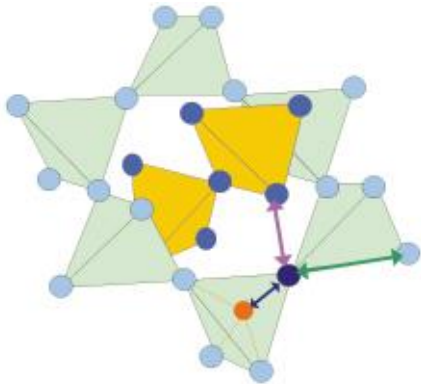
$$\lambda = 2a$$



Summarise phonon properties in dispersion curve: E vs k ($2\pi/\lambda$) covers range in $\lambda = \infty \rightarrow 2a$

Excitations in solids

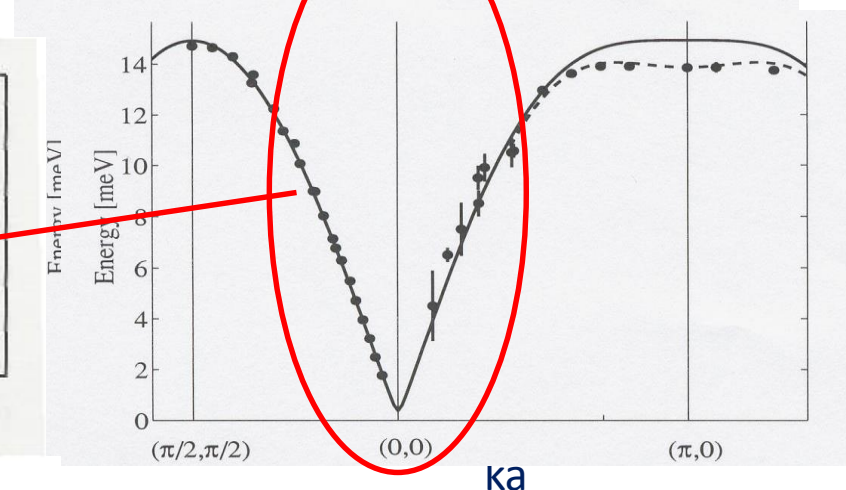
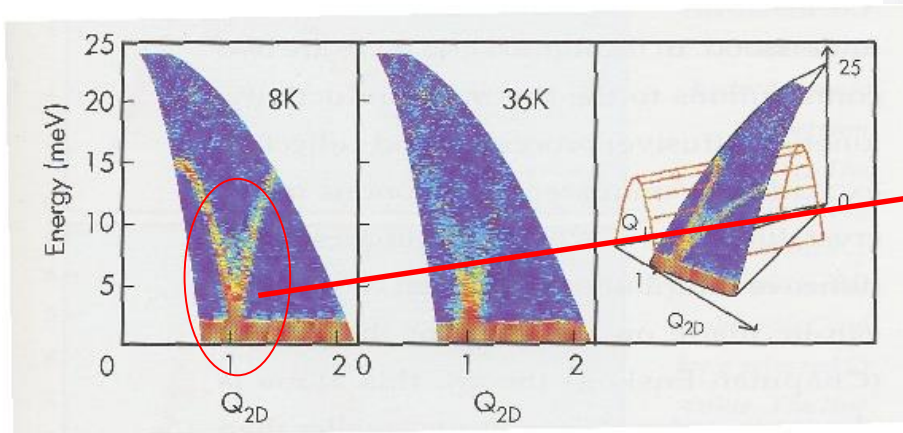
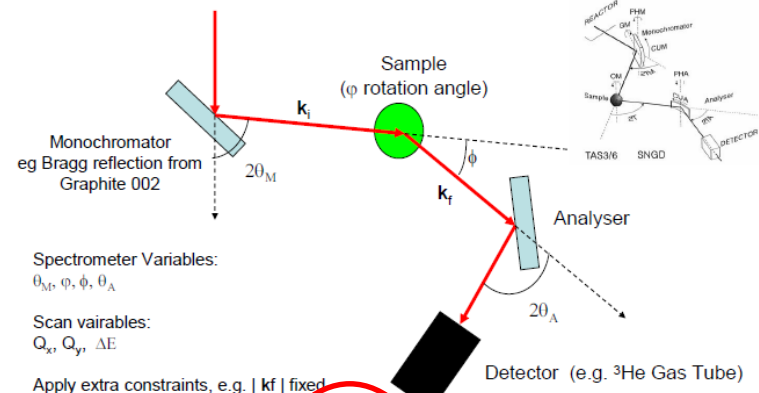
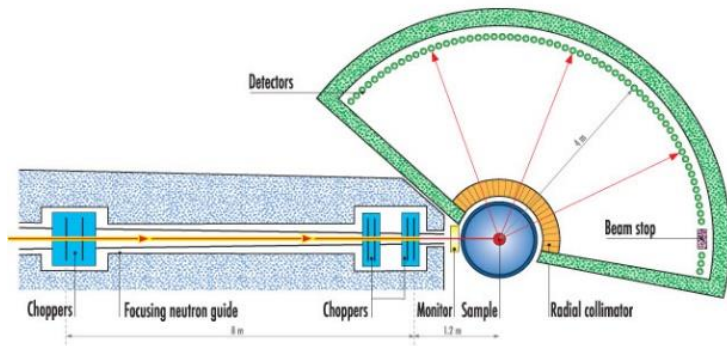
- In solids we see structural excitations of the lattice in the form of waves (phonons) characterised by the relationship between energy and wavelength – conventionally expressed as plot of E vs k ($2\pi/\lambda$).
- Analogous phenomena are observed in ordered magnets where we see ‘spin waves’ or magnons’ – maximum energy at JS^2 for spins S coupled through J



Summarise phonon/magnon properties in dispersion curve: E vs k ($2\pi/\lambda$) covers range in $\lambda = \infty \rightarrow 2a$

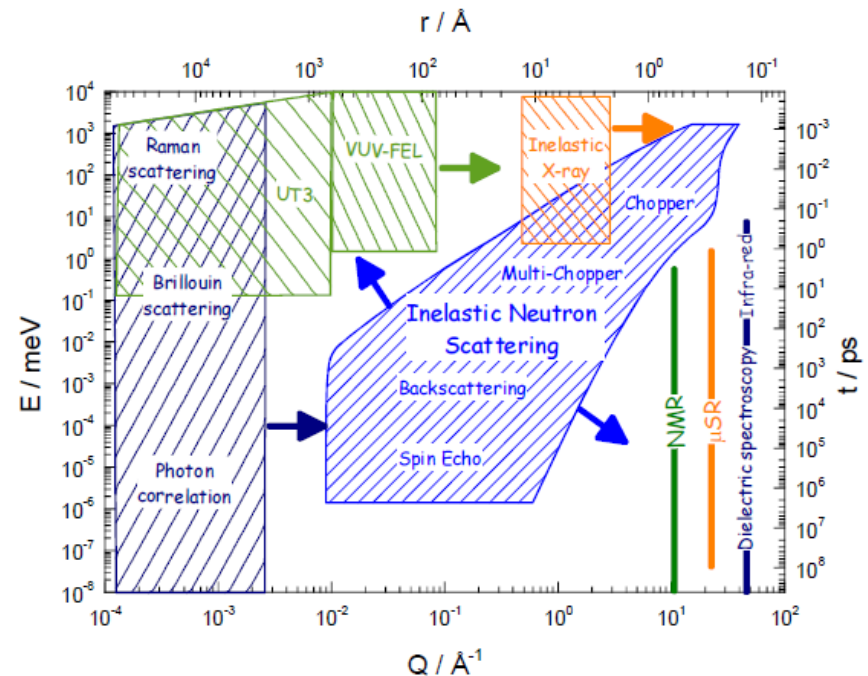
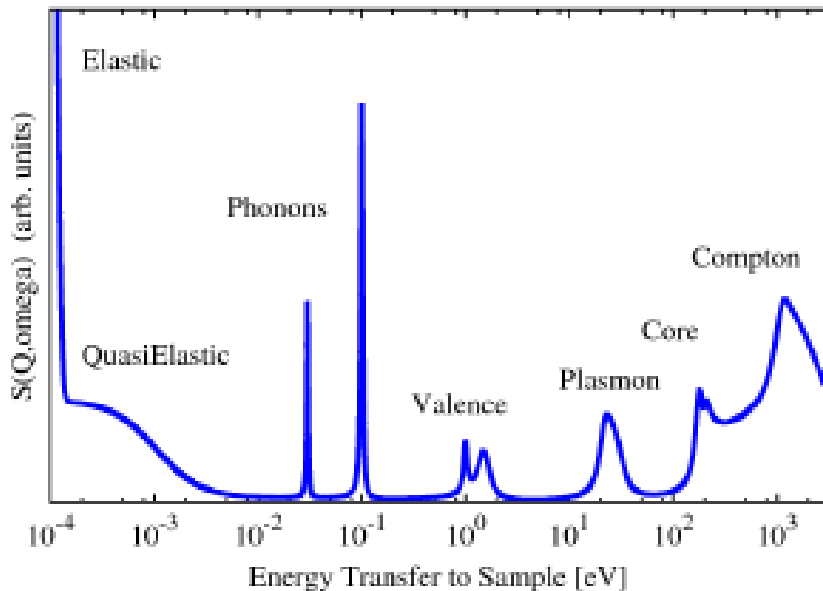
Mapping excitations in solids

- Neutrons allow us to map out E as a function of the momentum k of the excitation – either point-by-point with a TAS, or as whole slices of E - k space with ToF instruments (k, q, Q sometimes used interchangeably)



Inelastic neutron scattering

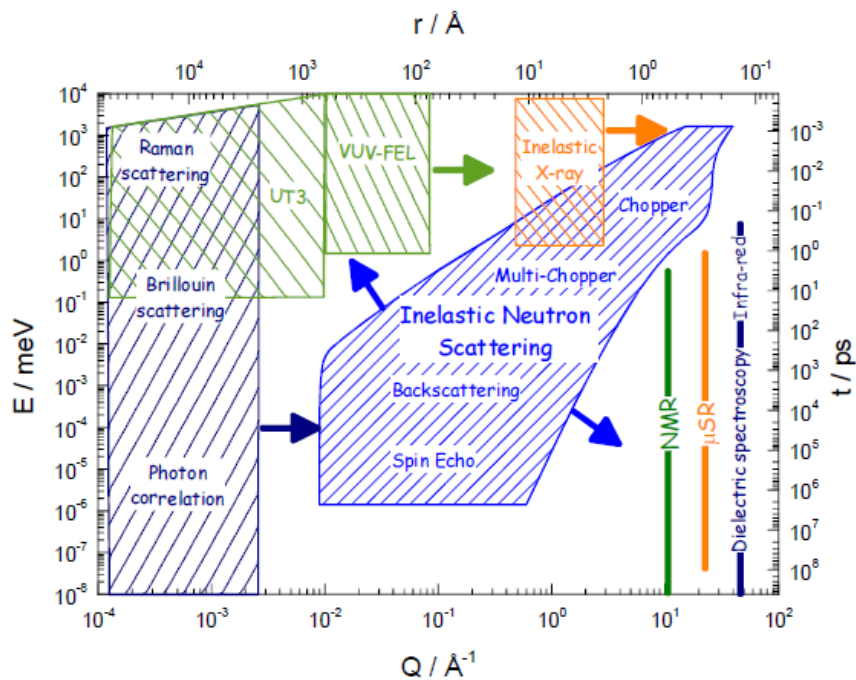
- Thermal neutron energies are particularly well matched to excitation energies (typically enabling probes from <1 meV to 100 meV)
- Provide a simultaneous measure of the energy of the excitation and its wavelength or amplitude
- No selection rules as for IR and Raman (and low amplitude easier to 'see')
- Highly penetrating – study deep inside materials
- Particularly sensitive to H



Inelastic X-ray Scattering

"When a crystal is irradiated with X-rays, the processes of photoelectric absorption and fluorescence are no doubt accompanied by absorption and emission of phonons. The energy changes involved are however so large compared with phonon energies that information about phonon spectrum of the crystal cannot be obtained in this way. The same is true for Compton scattering."¹ W.Cochran, 1966.

- Typically wish to measure vibrations and magnetic excitations in the range 1-100 meV as a function of k ($1/\lambda$) so the wavelength of the neutrons or X-rays should typically be of the order of 1-2 Å (0.1-0.2 nm)
- 1 Å corresponds to 12.4 keV for X-rays and 81.8 meV for neutrons so instrumental resolution is *much* more challenging for X-rays (10meV: $\Delta E/E \cong 10^{-6}$ vs 10^{-1} IXS vs INS) though modern IXS beamlines can approach $\Delta E/E \cong 10^{-5}$, enabling study of much smaller samples (neutrons typically down to 1 mm beam, X-rays of order of 1 μm)



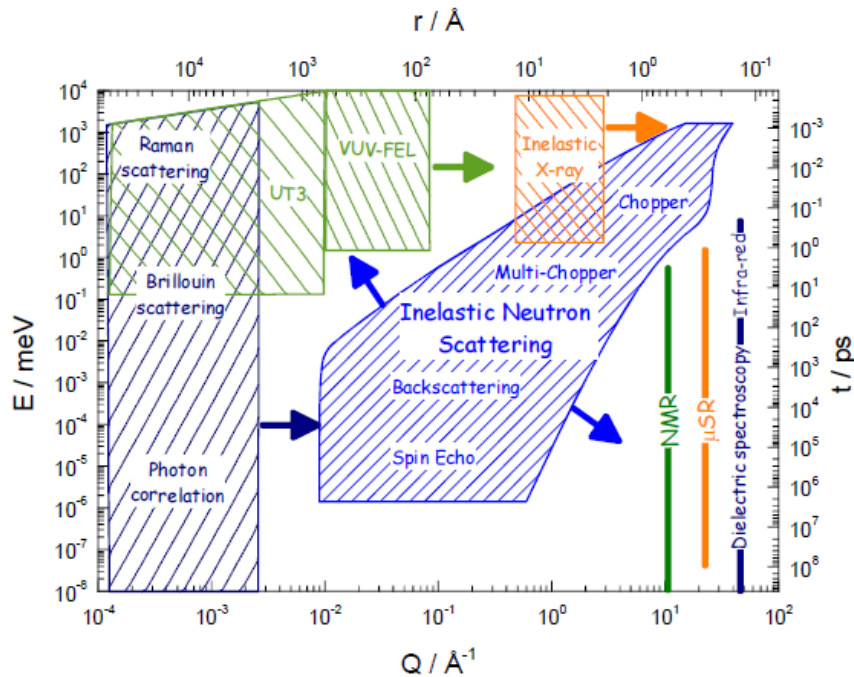
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Why bother ? X-rays can work with much smaller samples – films a few atoms thick or sub-micron regions of devices and if done resonantly (RIXS) can tune to specific orbitals to look at how they are implicated in excitation

Energy range 1-100 meV
Sample size would typically be

Instrumental resolution
(0.1-10⁻¹ IXS vs INS)
Spatial resolution (of much smaller size than
of 1 μm)





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