An holistic approach to science

NEUTRONS FOR SCIENCE

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10th Oxford School on Neutron Scattering
4 - 14 September 2007
University of Oxford

Edinburgh University (just out of shot)

ILL and its environs

Overview

- What are neutrons good for?
- What are neutrons not so good for?
- Case studies
  - Pure and applied magnetism, from bulk materials to nanoparticles
  - Mesostructures, surfaces and catalysis
  - Soft solids and biology

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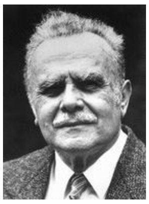
What are neutrons good for?

- 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



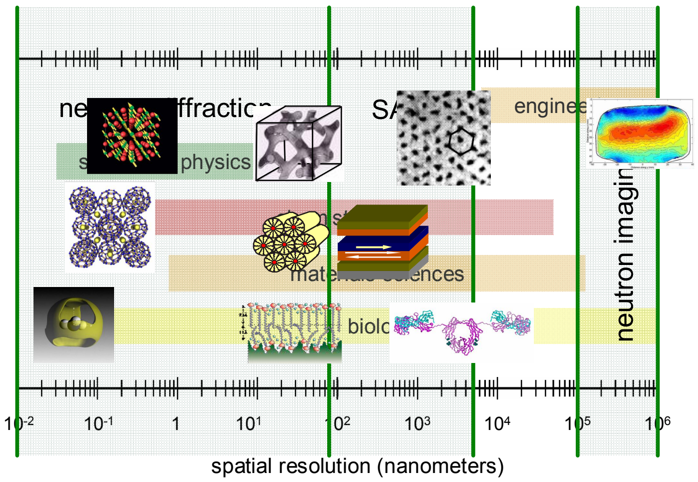
Bert Brockhouse

Cliff Shull

  - Wavelength
  - Energy
  - Scattering by the nucleus
  - Magnetic moment and polarisation
  - Ability to penetrate hard matter

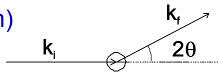
Lengthscales

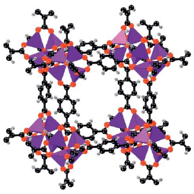
- Wavelength comparable to key distances in condensed matter
  - typically 0.1 – 1 nm (often use Å = 0.1 nm)

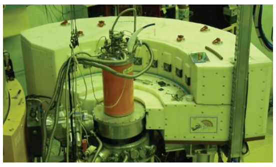


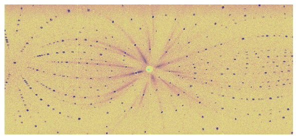
Lengthscales, from less than a bond length…

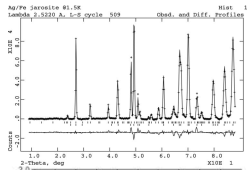
- Wavelength comparable to key distances in condensed matter
  - typically 0.1 – 1 nm (often use Å as units too – 1 Å = 0.1 nm)
  - $n\lambda = 2d\sin\theta$ - probe smallest distances at widest angles

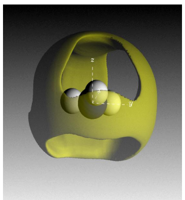


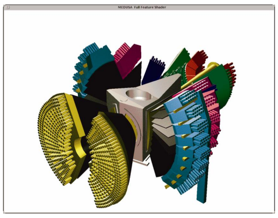


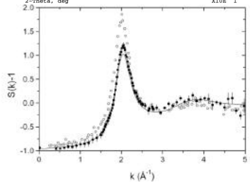






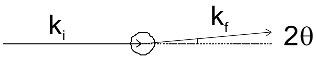


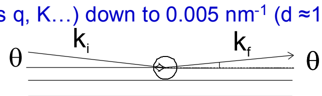


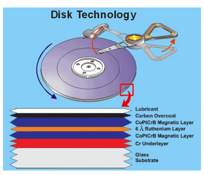


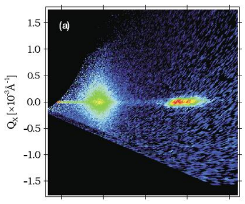
…to nanostructures, and beyond

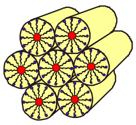
- Wavelength comparable to key distances in condensed matter
  - $n\lambda = 2d\sin\theta$ - larger objects at fixed $\lambda \rightarrow$ smaller θ (larger $Q = 2\pi/d$)
    - SANS, reflectometry – Q (sometimes q, K…) down to 0.005 nm^{-1} (d ≈1000 nm)

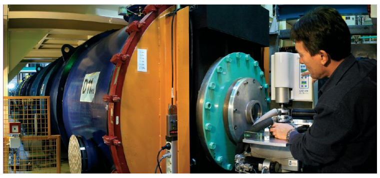


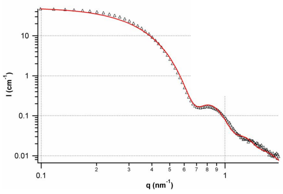






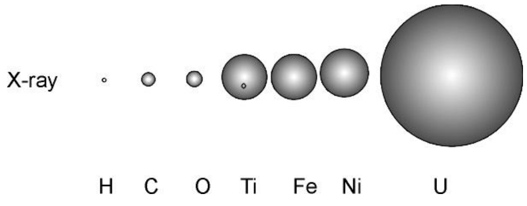






Contrast between atoms and objects

- Wavelength comparable to key distances in condensed matter
- Scattered by nuclei (as opposed to electrons – *c.f.* X-rays)
  - Location of light atoms in presence of heavy atoms
  - Discrimination between isotopes



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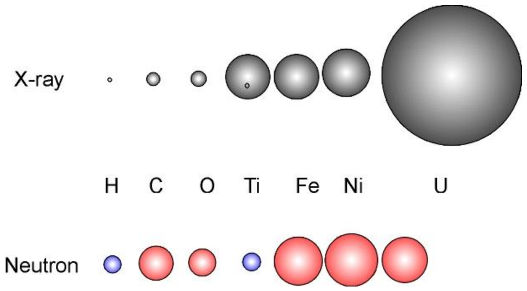

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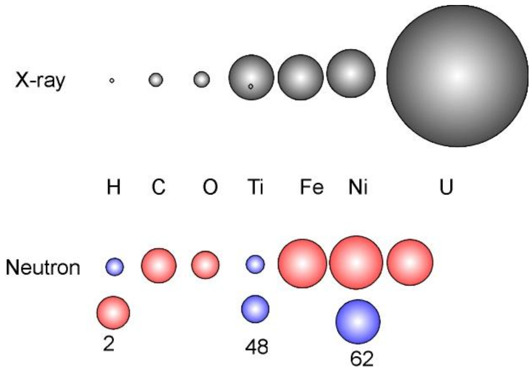

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Contrast between atoms and objects

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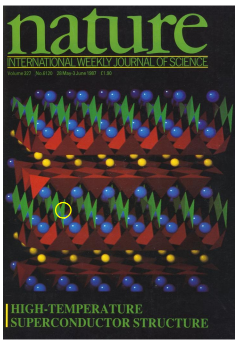
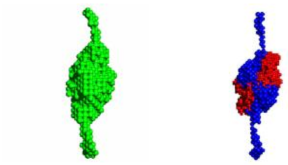
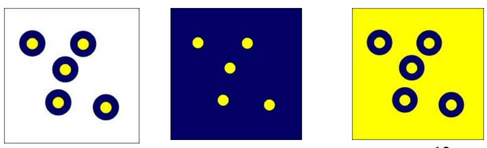
  - Location of light atoms in presence of heavy atoms
    - E.g. first full structure of high-T_c material $YBa_2Cu_3O_{7-x}$ - location of all O
  - Discrimination between isotopes
    - Contrast variation in solvents of variable scattering length (H/D ratio)







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Contrast between objects and media

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- Scattered by nuclei (as opposed to electrons – *c.f.* X-rays)
  - Location of light atoms in presence of heavy atoms
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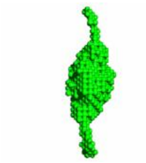
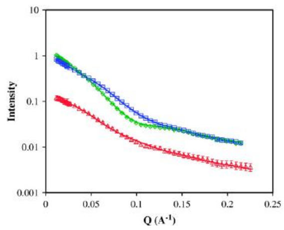
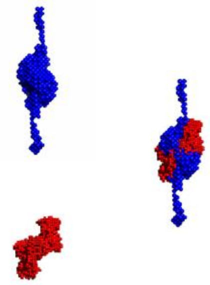


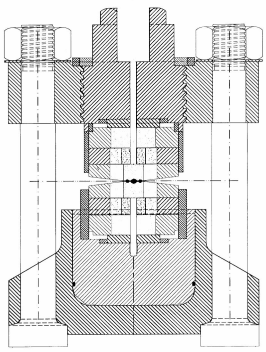


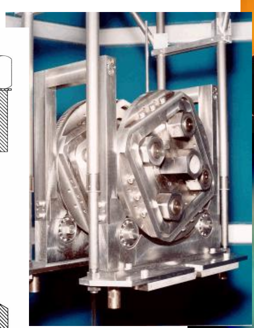


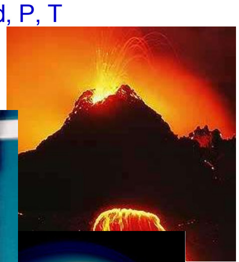
Enzyme contains two subunits M, S
All hydrogenated in D_2O (green)
D-M and H-S in D_2O (blue)
D-M and H-S in 40% D2O (red)
Callow *et al, J.Mol.Biol.* (2007)

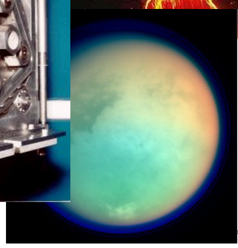
Looking deep inside materials

- Wavelength comparable to key distances in condensed matter
- Scattered by nuclei (as opposed to electrons – *c.f.* X-rays)
- Uncharged particles – highly penetrating
  - Complex sample environments – *e.g.* high magnetic field, P, T
  - Probe deep inside materials without damage -









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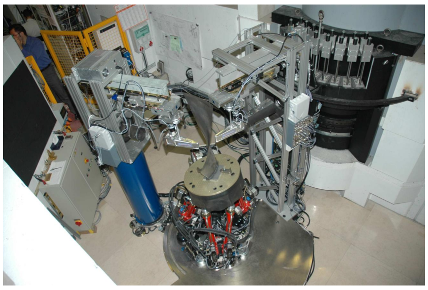

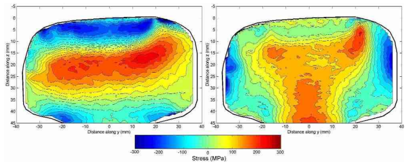

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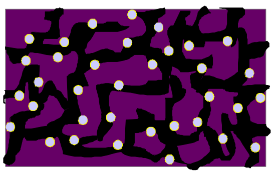
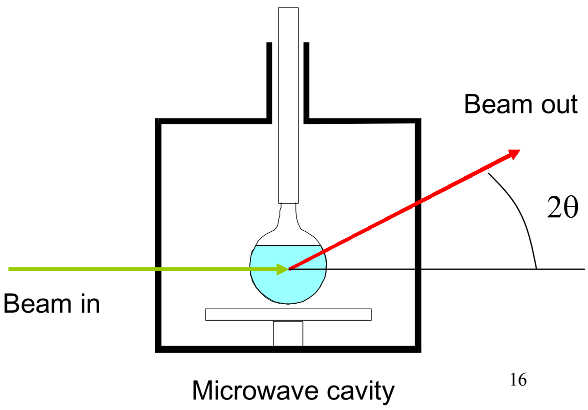
Microwave chemistry in real time

- Microwaves are being used increasingly to drive chemistry
  - Very fast transfer of energy to susceptible objects e.g. metal powders
  - Circumstantial evidence that metal catalysts are activated through superheating
  - Perform diffraction experiment during irradiation to determine cell size, hence T





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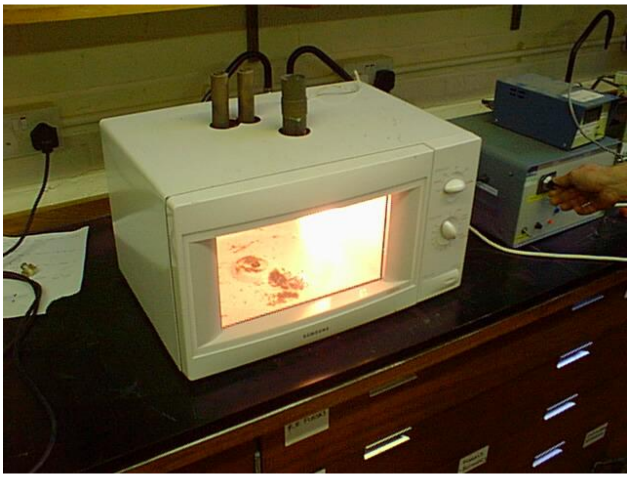
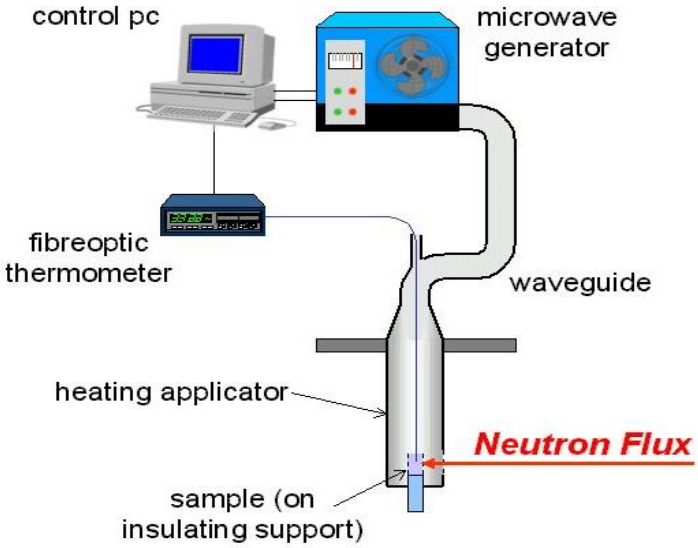
(don't try this at home)

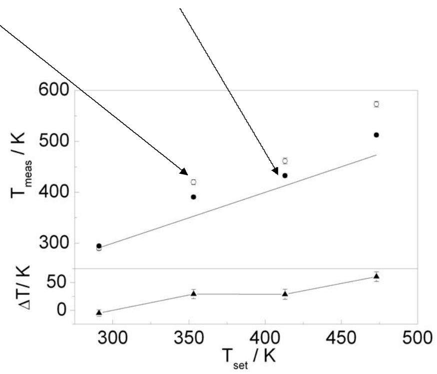


Tailored microwave oven



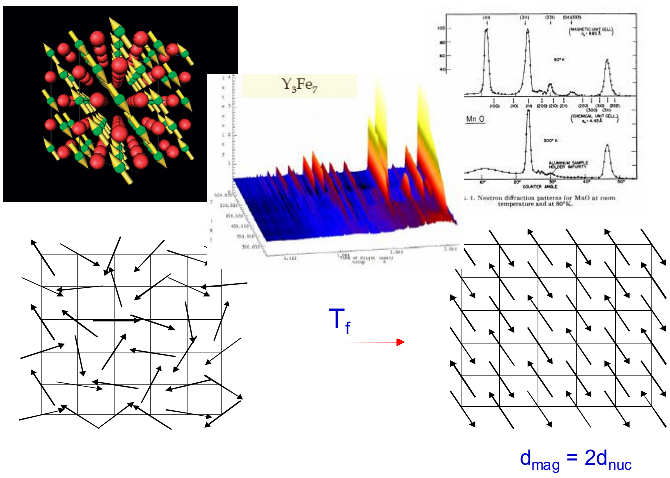
Phase-selective nanoscale thermometry

- Take high-resolution powder diffraction pattern of MoS_2 on Al_2O_3
  - Measure unit cell size as function of temperature with conventional heating
  - Obtain calibration curve (V *vs* T)
  - Repeat with μwave heating so that average T measured with ext. probe is same
  - MoS_2 cell is proportionally larger at same set T than Al_2O_3 with μwave heating
    - MoS_2 heated more than Al_2O_3 with μwaves



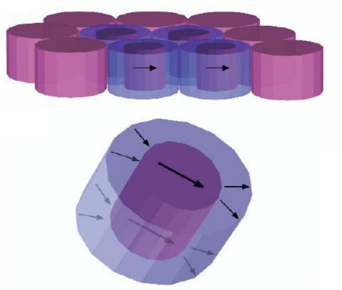
Unravelling spins

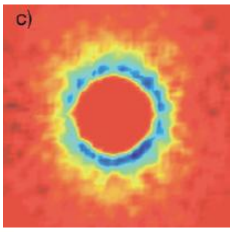
- Magnetic moments (‘spins’ – on account of their origin)
  - Direct, unambiguous probe of magnetic structure at atomic scale
  - $n\lambda = 2d\sin\theta$ - expansion of d leads to new features at smaller θ



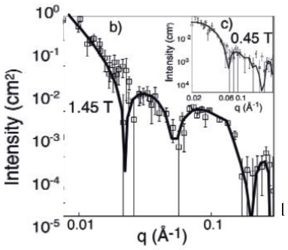
Mapping domains

- Magnetic moments
  - Direct, unambiguous probe of magnetic structure at atomic scale
  - Magnetic domains or order in nanostructures – SANS and reflectometry



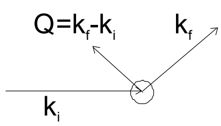


Grains ≈ 11nm (110 Å) → Q ≈ 0.05 $Å^{-1}$
(see smaller features – magnetic core smaller)



Probing excitations and motion

- Energy/timescale comparable to that of key processes in condensed matter
  - Typical thermal neutron energy ≈ 0.1 meV (1 meV ≈ 0.24 THz ≈ 8.07 cm^{-1} ≈ 11.6 K)
  - A range of spectroscopy techniques provide energy range 10^{-5} – 100 meV
  - Note – we can also get information about Q at the same time

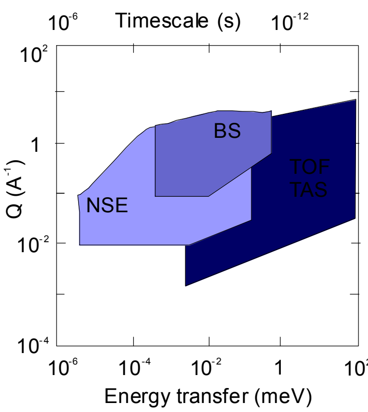


$$E = \hbar^2 k^2 / 2m$$

$$\Delta E = (\hbar^2 / 2m)(k_f^2 - k_i^2)$$

$$\lambda = h^2 k^2 / (2mE)^{0.5} = 9.04 E^{-0.5}$$

(λ *in* A, E in meV)



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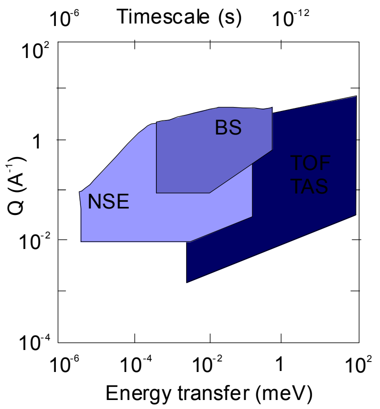
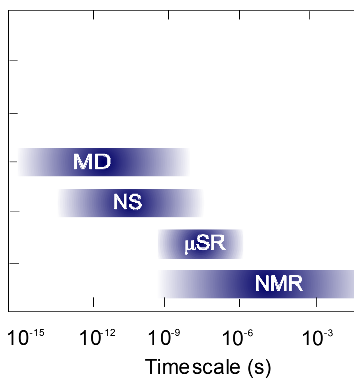
  - Note – we can also get information about Q at the same time
  - Probe motion in the time window 10^{-8} – 10^{-13} s





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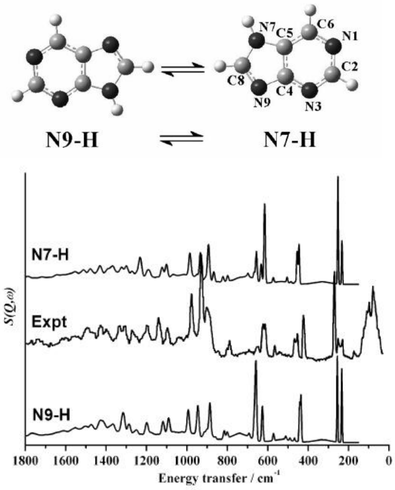
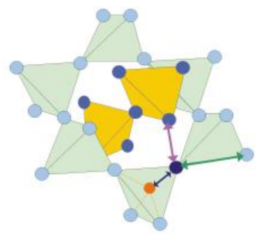
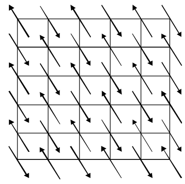
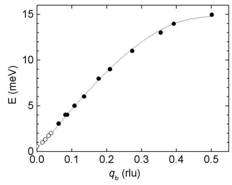


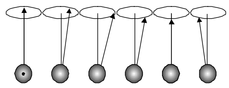


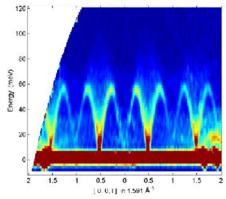
Probing excitations and motion

- Energy/timescale comparable to that of key processes in condensed matter
  - At higher energies (0.1 – 100 meV) – probe vibrations (phonons) and spin-waves (magnons)









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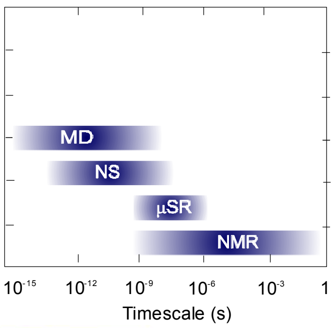
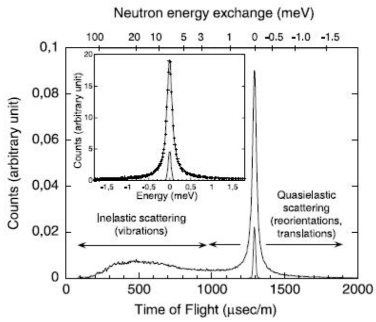
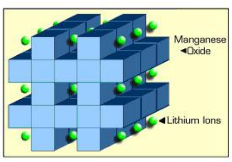
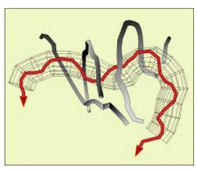
Probing excitations and motion

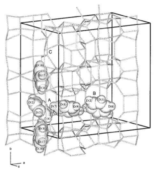
- Energy/timescale comparable to that of key processes in condensed matter
  - At lower energies probe lower-energy motion + diffusive processes – typically ns - ps











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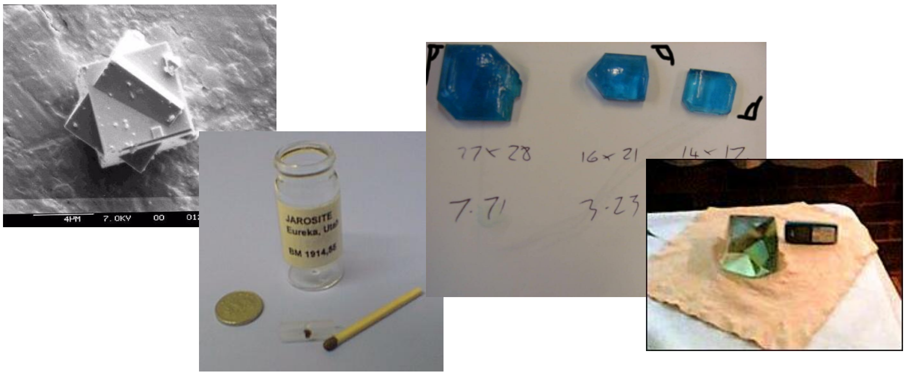
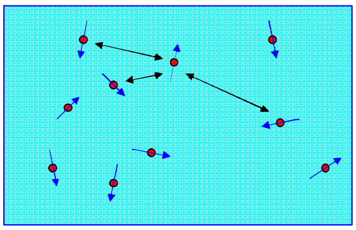
Things that neutrons are not so good for

- Flux weak relative to some other techniques (e.g. X-rays)
  - need large samples and/or longer times
- Usually need to exchange H for D in coherent scattering
- Hard to study magnetic systems with small moments
- Relatively expensive – often characterise first by other techniques
- Usually provides an average picture, rather than of specific region



Case study – frustrated magnets

- Spin-glasses
  - Dilute moments in metallic matrix – *e.g.* *Cu*Mn - interact *via* conduction electrons
    - Long range
    - Sign may change with separation
  - Interactions may be random



  - On cooling, array freezes with random orientations – a *spin glass*
  - Not all bonds can be satisfied all the time – they're *frustrated*

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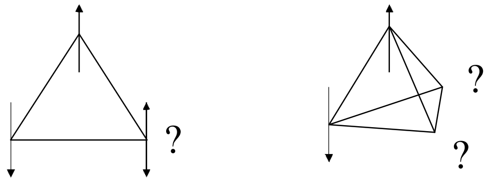
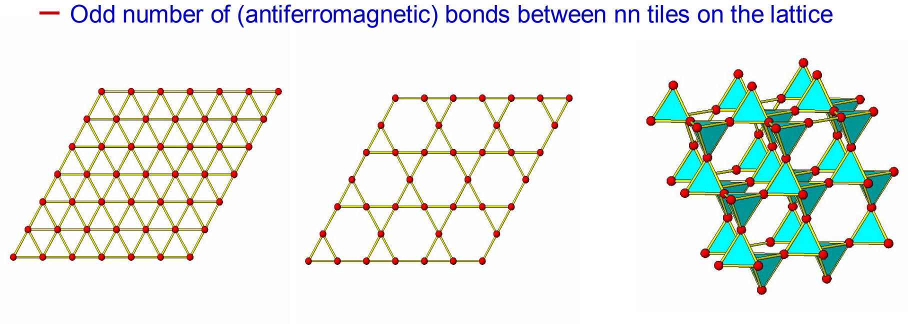
Frustration in regular lattices

- Frustration can also occur without any disorder in the exchange pathways

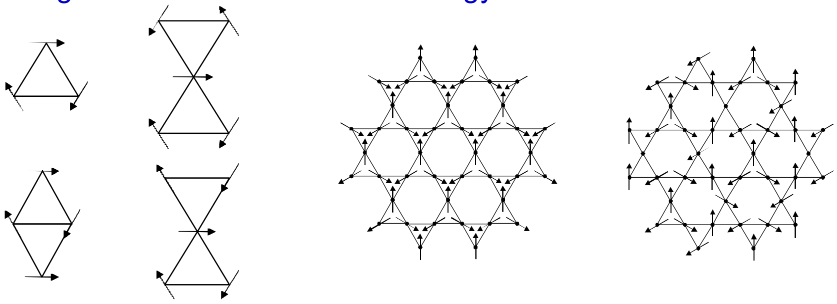


- General case for geometrically frustrated magnet (GFM)
  - Odd number of (antiferromagnetic) bonds between nn tiles on the lattice



So what?

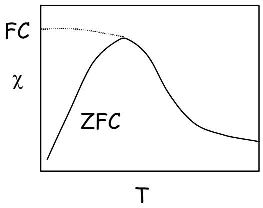
- Macroscopic lattice may have macroscopic degeneracy – many possible ground states of the same energy

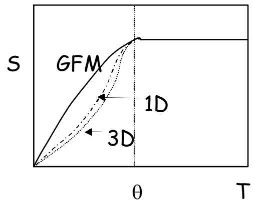


- This could lead to glassy or liquid-like magnetic behaviour
  - Key problems in fundamental physics – glasses, disordered systems, soft solids
  - If magnetic fluctuations coupled to other types of behaviour – *e.g.* conduction – might lead to new types of charge transport…

Studying frustrated systems: thermodynamics

- DC magnetic susceptibility - χ
  - Cool sample in zero field (zfc) – broad peak in χ in region of T_f
  - Cool in applied field (fc) – spin polarisation freezes in be low Tf : $\chi_{fc} > \chi_{zfc}$





- Heat capacity
  - Provides a measure of the entropy of the system (and can also locate T_N)
  - Frustrated systems may maintain significant disorder (entropy) to low T/ θ

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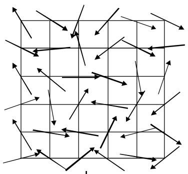
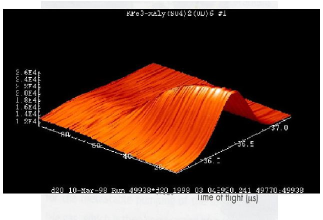
Studying frustrated systems: neutron scattering

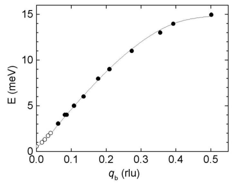
Paramagnet

T_f

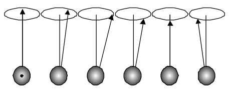
Ordered array
Supports spin waves

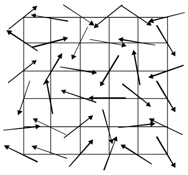


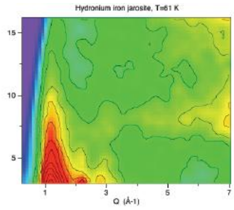


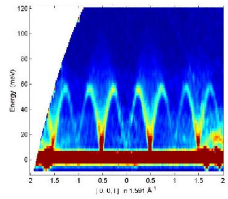


T_f









Glass

Diffusive motion

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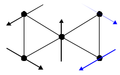
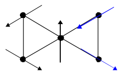
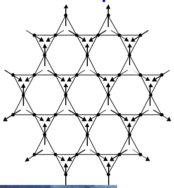
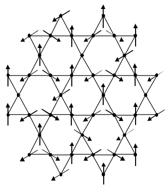
‘simple’ system - kagome antiferromagnet

- Many possible degenerate ground states - vertex-sharing does not convey spin information uniquely
- Thermal fluctuations select coplanar states by ‘order through disorder’
- But what is the ‘order’: spin nematic, conventional LRO?

‘q = 0’

‘ √3 x √3 ‘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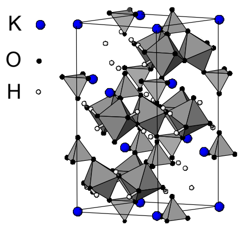
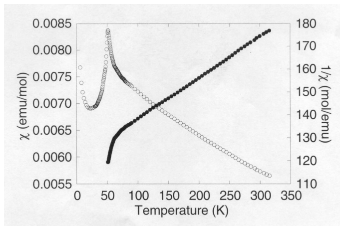
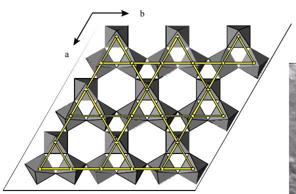
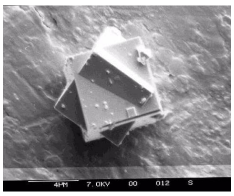
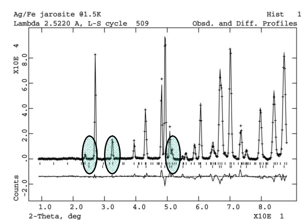
Kagome lattices: the real thing

- Jarosites - family of minerals: $AFe_3(SO_4)_2(OH)_6$ (A = Na, K, H_3O…)
- S=5/2 (Fe^{3+}) showing LRO (q=0) at $T_N \sim 60K$ (except A = H_3O)

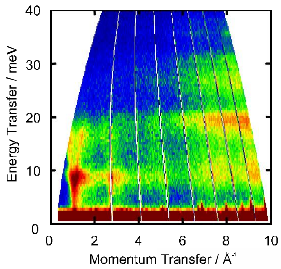


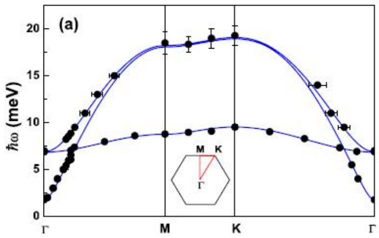



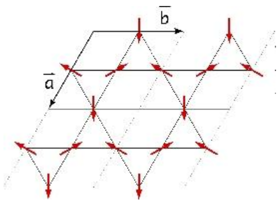




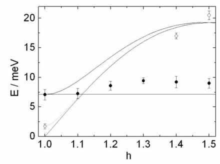
Ironing out the wrinkles

- To really pin down what is happening, need precise magnetic structure and spin-waves to determine additional interactions
  - Natural single crystal allows precise structural determination (coplanar to 1º)
  - Inelastic scattering much weaker – eliminate D in synthetic powders
  - Coup de grace – deuterated synthetic crystals ; ideally use single crystals



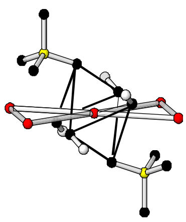


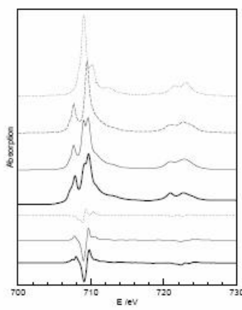


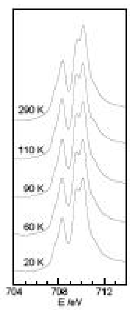


Shining light on Fe^{3+} magnetism with X-rays

- Fe^{3+} is nominally S = 5/2 with no orbital component – so why does it have ligand-field terms?
  - XAS on this material probed Fe $2p^63d^5$-$2p^53d^6$ transition, providing estimate of LF parameters – significant Fe^{2+} character
  - Ligand field parameters compatible with INS data
  - Central fig:calculated LF multiplet XAS for various models (top); LD spectra (bottom); RHS fig. corresponding XAS data taken at L_3 edge of natural crystal

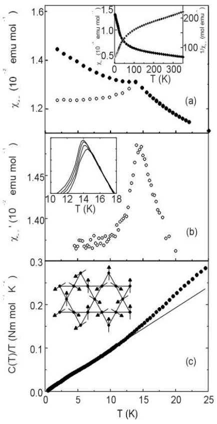


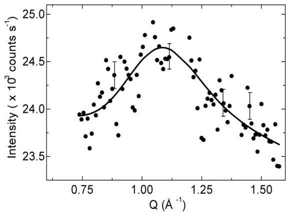




The exception (there's always one)

- The deuteronium salt $(D_3O)Fe_3(SO_4)_2(OD)_6$ shows no magnetic lro
- Observe spin-glass like transition at $T_f \approx 15$ K in susceptibility
- Only diffuse (magnetic) scattering of neutrons at low T (ξ across star)





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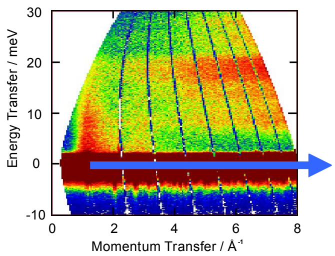
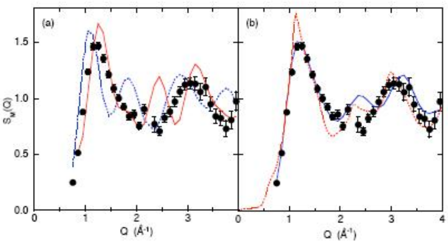
Probing magnetic correlations

- Map $S(Q,\omega)$ for $(D_3O)Fe_3(SO_4)_2(OD)_6$ on spectrometer MARI at ISIS
  - Pull out elastic scattering (S(Q)) below T_f and model with glass shell model $\langle S_0.S_1\rangle=-0.29(8)$; $\langle S_0.S_2\rangle=-0.46(11)$)





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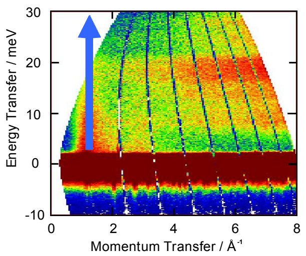
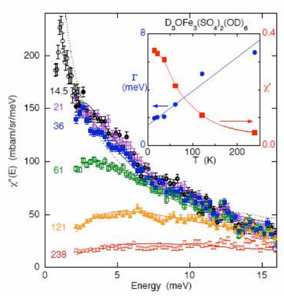
Probing magnetic correlations

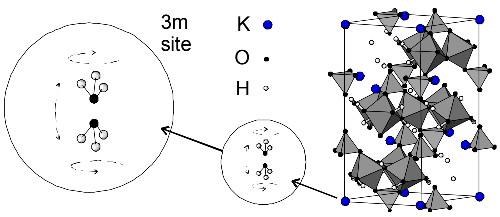
- Map $S(Q,\omega)$ for $(D_3O)Fe_3(SO_4)_2(OD)_6$ on spectrometer MARI at ISIS
  - Pull out elastic scattering (S(Q)) below T_f and model with glass shell model $\langle S_0.S_1\rangle$=-0.29(8); $\langle S_0.S_2\rangle$=-0.46(11))
  - Inelastic scattering allows us to characterise dynamics – slows down as $T \rightarrow T_f$, with range of timescales – glassy dynamics





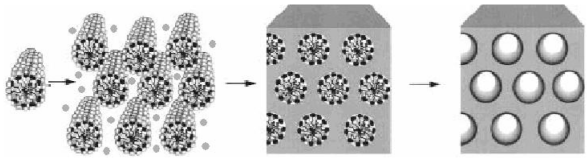
Origin of spin-liquid behaviour

- Origin of glassy behaviour: why is the deuteronium salt different?
  - Spin-glasses generally require some disorder
  - Neutron diffraction shows some structural disorder of D_3O^+ group
  - However, most likely to be be exchange of D from interlayer D_3O^+ to intralayer Fe-OD-Fe - altering exchange locally (IR, nmr studies)
    - (Grohol and Nocera, Chem. Mat. 19 (2007) 3061)



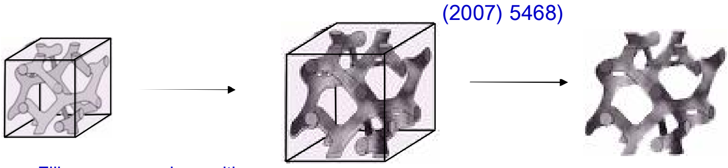
From bulk to mesostructured materials

- What happens when we alter the state of division of materials?
  - E.g. fine particles, films, mesostructured solids
- Mesostructure provided by preparation in mesostructured medium
  - Huge range of architecture provided through liquid-crystals/surfactants



SBA-15 host (Impéror-Clerk *et al*, Chem. Comm. (2007) 834

KIT-6 host (Jiao *et al.* JACS 128 (2007) 5468)



Fill aqueous regions with material precursor

Calcine (burn) to remove surfactant and leave hard material (without collapsing!)

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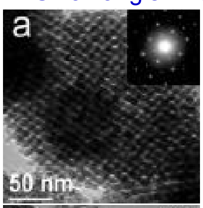
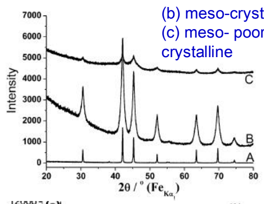
Characterisation - structure

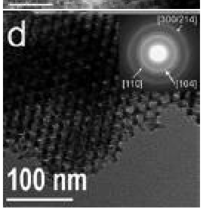
- Would like to know structure (at various length-scales) and properties
  - ‘Direct’ imaging with transmission electron microscopy
  - Area-selected electron diffraction
  - Wide-angle X-ray diffraction for ‘average’ atomic-scale structure
  - Small-angle X-ray diffraction for ‘average’ mesostructure



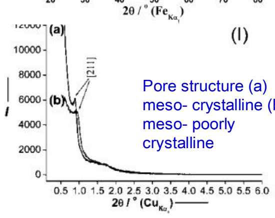
Crystalline



Pore structure (a) bulk (b) meso-crystalline (c) meso- poorly crystalline



Poorly crystalline

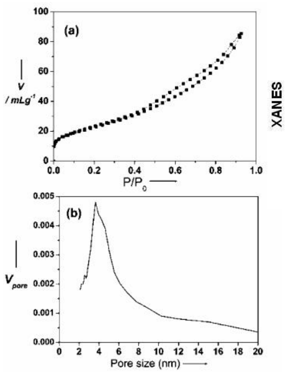


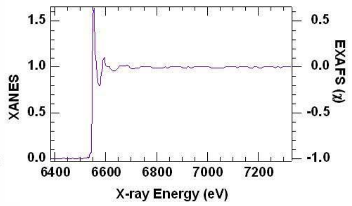
Pore structure (a) meso- crystalline (b) meso- poorly crystalline

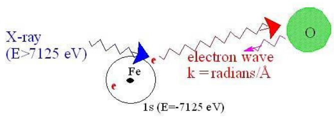
KIT-6 host + α-Fe_2O_3 (hematite) (Jiao,Harrison, Jumas, Chadwick, Kockelmann, Bruce, JACS 128 (2007) 5468)

Characterisation - structure

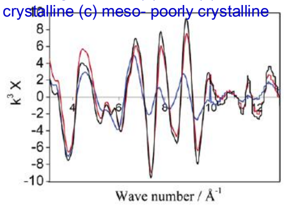
- Would like to know structure (at various length-scales) and properties
  - Pore size probed through gas (N_2) adsorption – tie up with SAXS data
  - Correlations in non-crystalline materials probed through EXAFS (Extended X-ray Absorption Fine Structure) – a probe of average local atomic environment



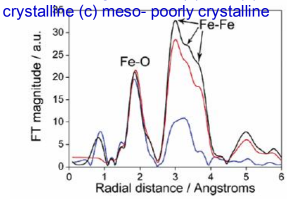




Fe K-edge EXAFS (a) bulk (b) meso-crystalline (c) meso- poorly crystalline



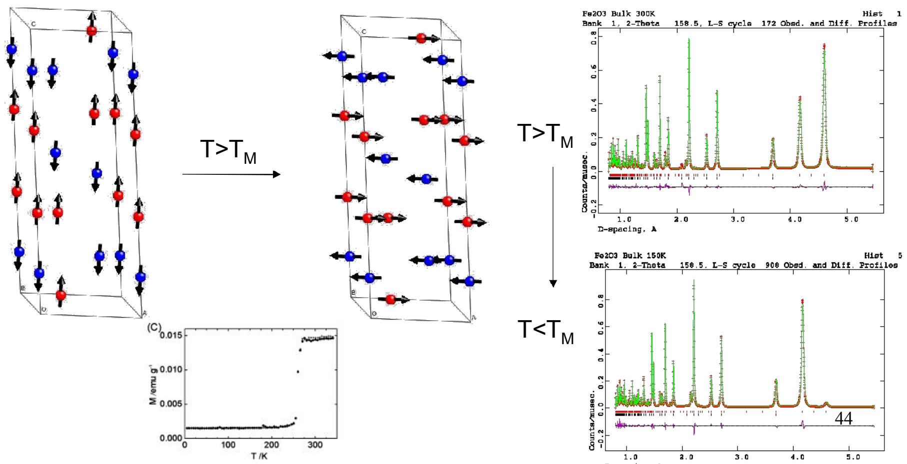
FT of Fe K-edge EXAFS (a) bulk (b) meso-crystalline (c) meso- poorly crystalline



KIT-6 host + α-Fe_2O_3 (Jiao, Harrison, Jumas, Chadwick, Kockelmann, Bruce, JACS 128 (2006) 5468)

Characterisation - magnetism

- Bulk hematite undergoes transition (Morin) at T_M = 260 K
  - Canted moment above T_M; no net magnetisation below T_M
  - Arises from competition between magnetic coupling and ligand/crystal field
  - Clear signature in χ and neutron scattering



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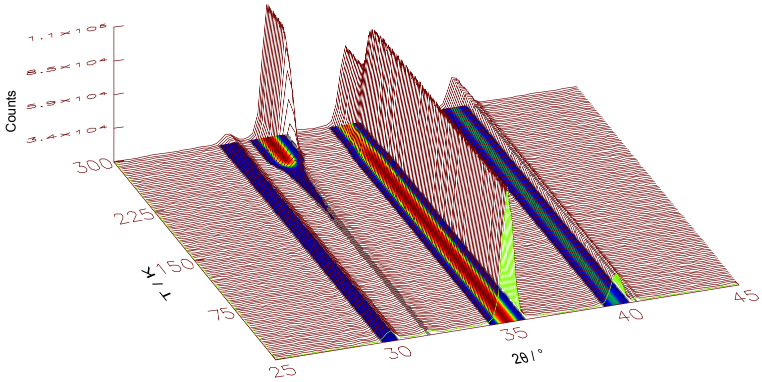

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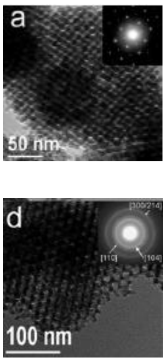
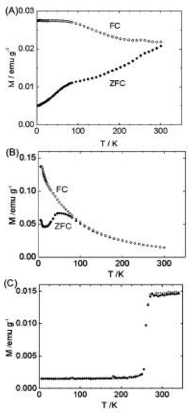
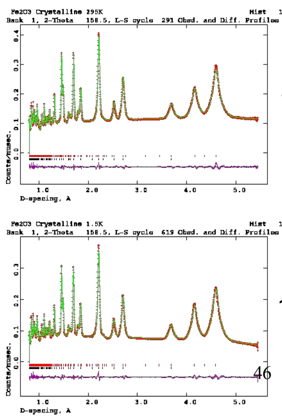
Mesostructure controlling magnetism

- Mesostructured crystalline hematite stays weakly ferromagnetic to 1.5K
  - Neutron diffraction reveals high-T stucture down to 1.5 K
  - Similar suppression of Morin transition in nanoparticles
  - More atoms at surface influencing balance of forces? But how?







295 K

1.5 K

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Mesostructure controlling magnetism

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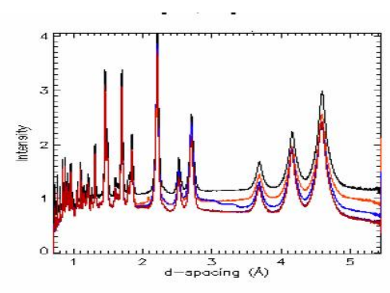
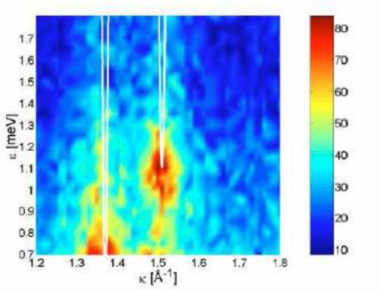
  - Neutron diffraction reveals high-T stucture down to 1.5 K
  - Similar suppression of Morin transition in nanoparticles
  - More atoms at surface influencing balance of forces? But how?
  - Need to measure *energies* of excitations – allows determination of forces on spins





16nm hematite nanoparticles -
S.N. Clausen et al, PRB 70 (2006) 214411

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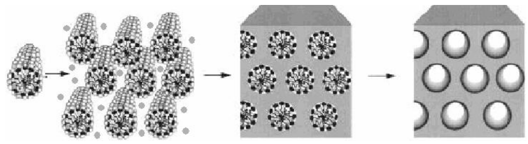
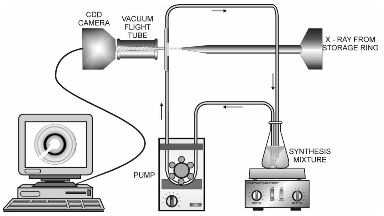
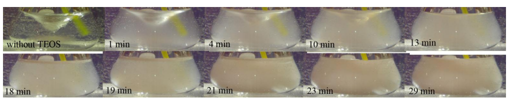
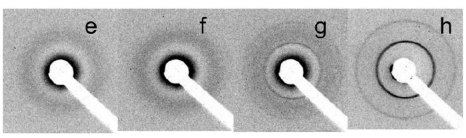
Mesostructure synthesis

- How can we study the growth process (and perhaps learn to control it)
  - *post mortem* – study quenched system (TEM, diffraction, NMR)
  - *in vivo* (*in situ*) – SAXS and SANS
- Real-time picture of evolution of structure of silicate + surfactant
  - Initial stages studied by SAXS (fast) – silicate precursor (TEOS) +PEG polymer







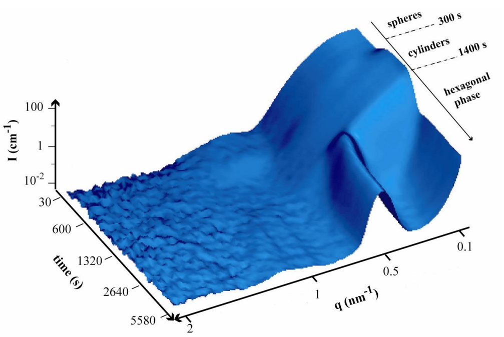


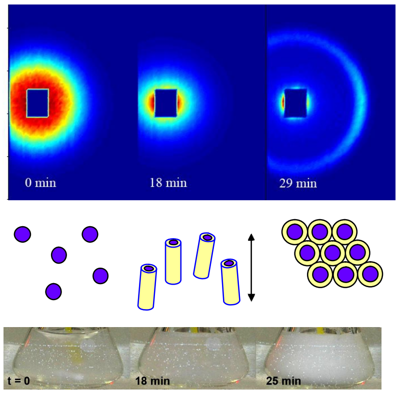
SBA-15 host (Khodakov *et al*, *J. Phys. Chem. B* **109** (2005) 22780

SAXS data 15, 20 ,25 , 30 mins after TEOS addition

Mesostructure synthesis

- Complementary SANS data
  - better contrast between surfactant structures (micelles) and solvent
  - Three steps seen in process
    - First 5 mins – not much change in scattering – monodisperse micelles; unlinked silica
    - 5-23 mins – spread of micelle size increases as spheres transform into cylinders
    - > 23 minutes – cylinders pack together and precipitation starts



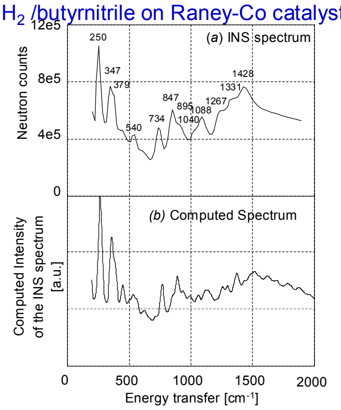


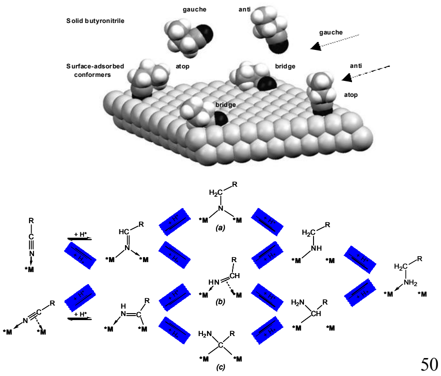
SBA-15 host (Impéror-Clerk *et al*, Chem. Comm. (2007) 834

Catalysis + complementary surface probes

- Key questions in heterogeneous catalysis:
  - What is on the surface of a catalyst (substrate and reacting species)
  - How do they change throughout a reaction?
  - Response to conditions, ideally in realistic (dirty, complex…) conditions with materials that may be unsuitable for optical spectroscopy
  - Particularly sensitive to H (high incoherent cross-section)

H_2 /butyrnitrile on Raney-Co catalysts





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Chojecki *et al*, *Catalysis Lett*. 97 (2004) 155

Complementary surface probes + catalysis

- Key questions in heterogeneous catalysis:
  - What is on the surface of a catalyst (substrate and reacting species)
  - How do they change throughout a reaction?
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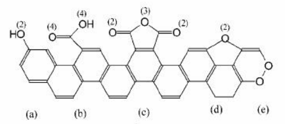
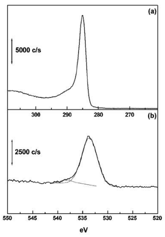
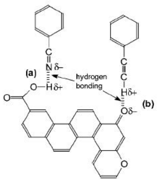
Surface chemistry of activated carbon (v. tricky by optical methods)



Surface oxygen funtionalities associated with activated carbons: (a) phenolic hydroxyl group; (b) carboxylic group; (c) carboxylic acid anhydride group; (d) ether group; (e) cyclic peroxide group



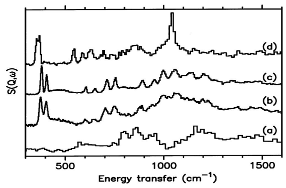
activated carbon XPES: (a) C(1s) and (b) O(1s) spectra – broad, indicating O bound in various ways to carbon surface



Proposed bonding configuration of polar adsorption of substituted aromatics on the carbon surface: (a) benzonitrile on the acidic carbon surface and (b) phenylacetylene on the basic carbon surface.

Lennon *et al*, *Langmuir* 8 (2002) 4667

INS spectra for (a) activated carbon (x30) , (b) adsorbed pyridine difference spectrum (c) pyridine, and (d) pyridinium chloride.



Complementary surface probes + catalysis

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  - What is on the surface of a catalyst (substrate and reacting species)
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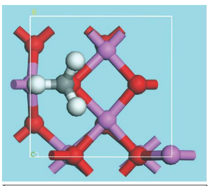
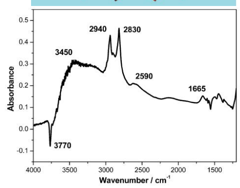
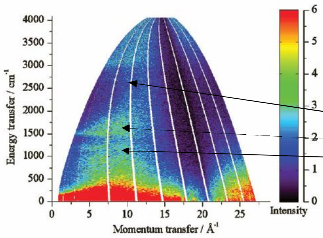
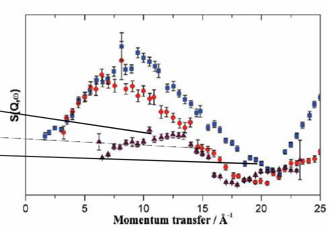
Methanol on η-alumina – INS complementing IR to show nature of adsorbed species

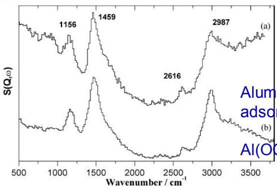




Transmission IR 293 K – feature near 2600 cm^{-1}?







Alumina + adsorbed MeOH

$Al(OCH_3)_3$

Dependence of intensity on Q related to spatial character of vibration – new mode not seen by optical methods

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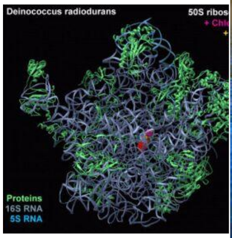
McInroy *et al*, *PCCP* 7 (2005) 3093

Joined-up science

Joined-up science

More than simply neutrons

- Opportunities for new users: bring more facilities and science to ILL
  - Deuteration laboratory (EPSRC)



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More than simply neutrons

- Opportunities for new users: bring more facilities and science to ILL
  - Deuteration laboratory
  - Partnership for structural biology – with ESRF, EMBL, UJF, IBS

Carl-Ivar Branden Building – opened January 13th 2006