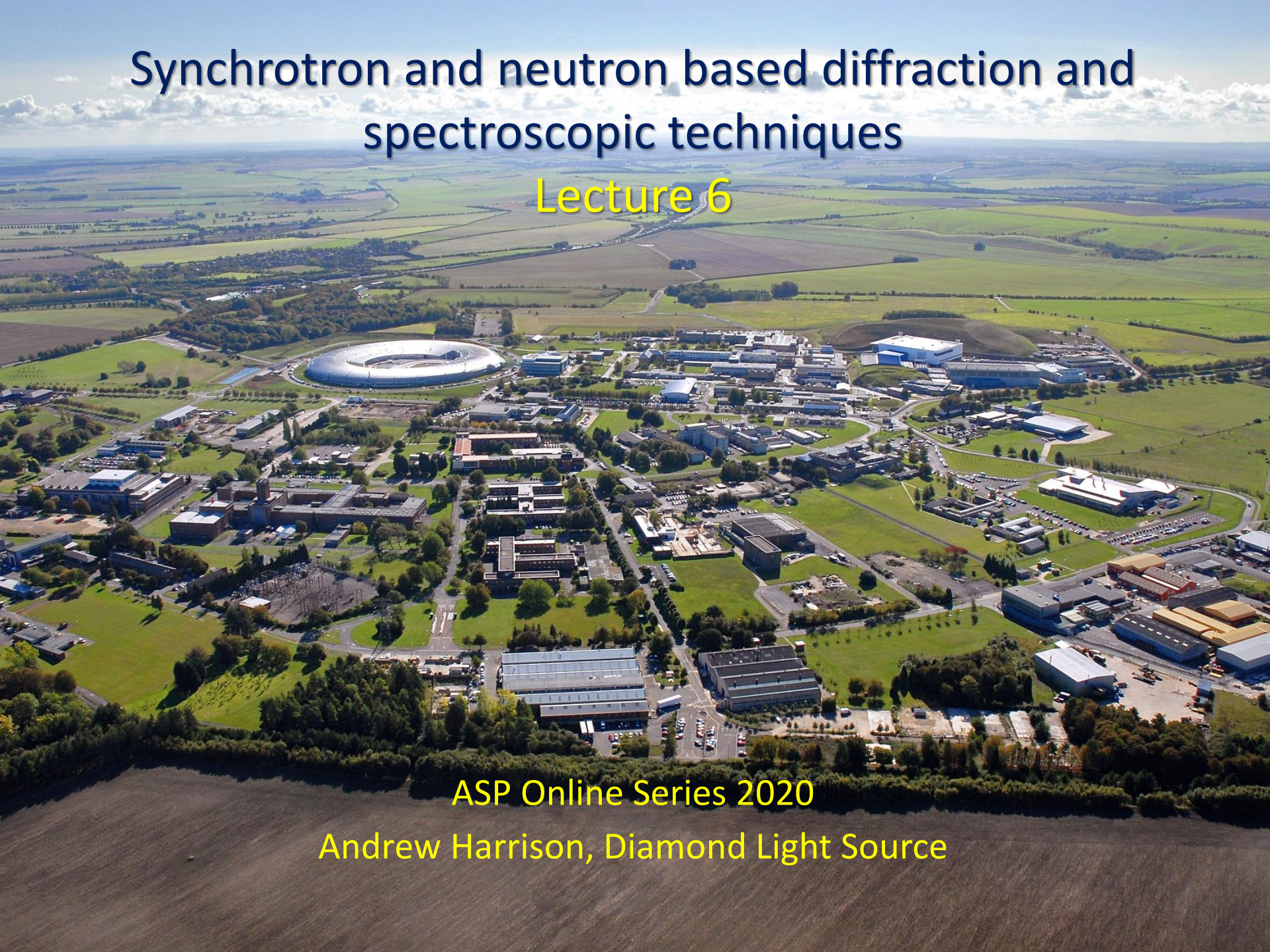
Synchrotron and neutron based diffraction and spectroscopic techniques

Lecture 6

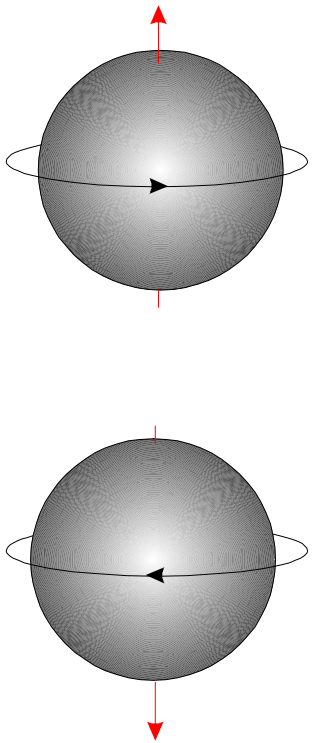


ASP Online Series 2020

Andrew Harrison, Diamond Light Source

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.

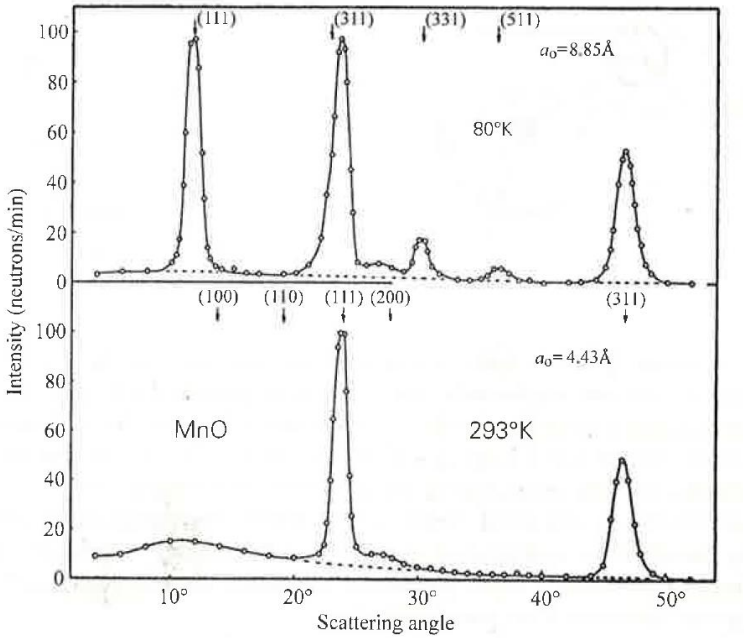


PHYSICAL REVIEW VOLUME 76, NUMBER 8 OCTOBER 15, 1949

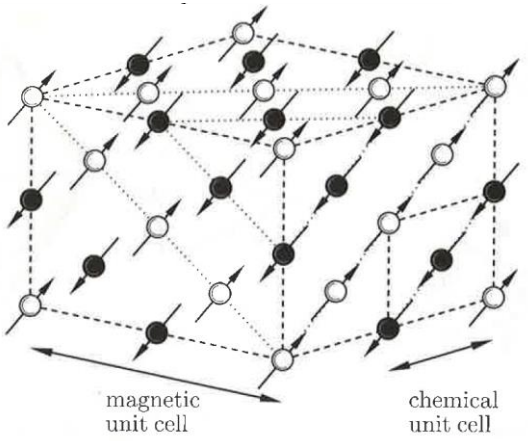
Letters to the Editor

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

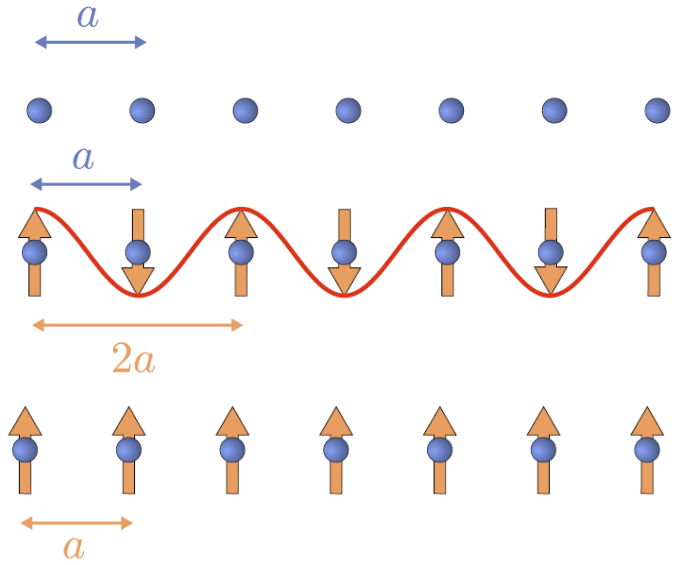


Mn^{2+} ($3d^5$) in O_h environment
S = 5/2 –
large moment



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)



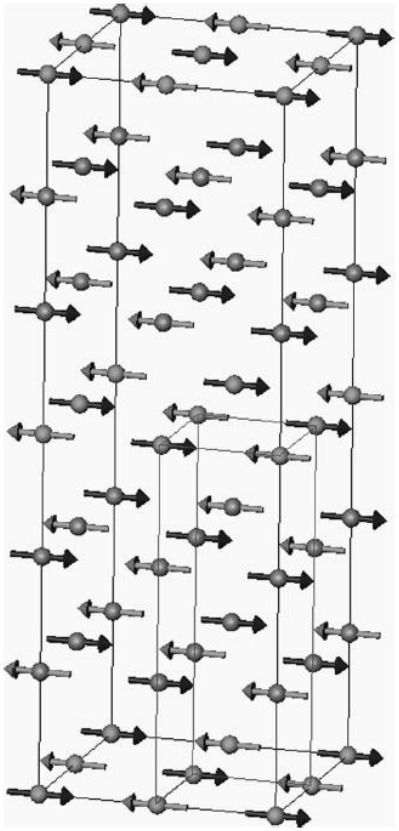
Nuclear structure, reflections at (h 0 0)

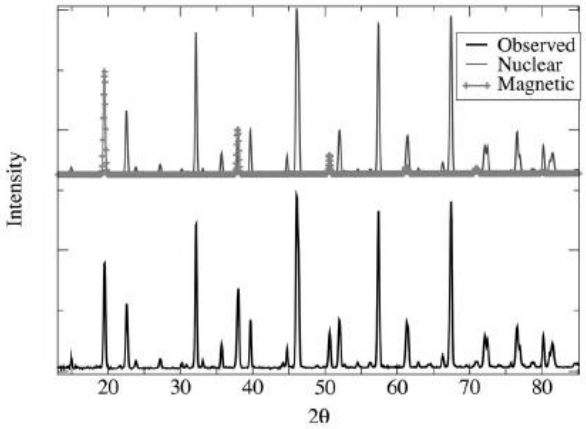
AFM structure, reflections at (h/2 0 0)

FM structure, reflections at (h 0 0)

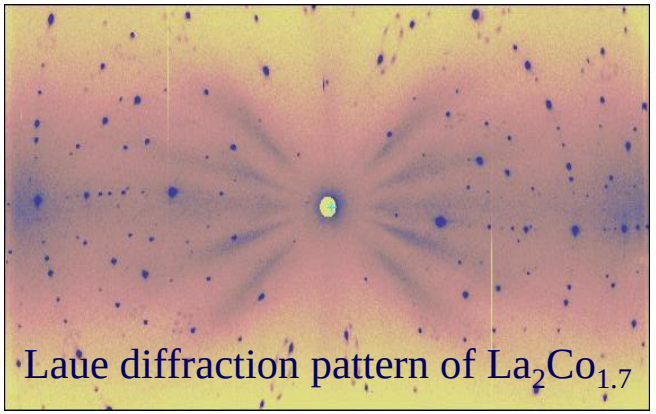
Magnetic scattering

- 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





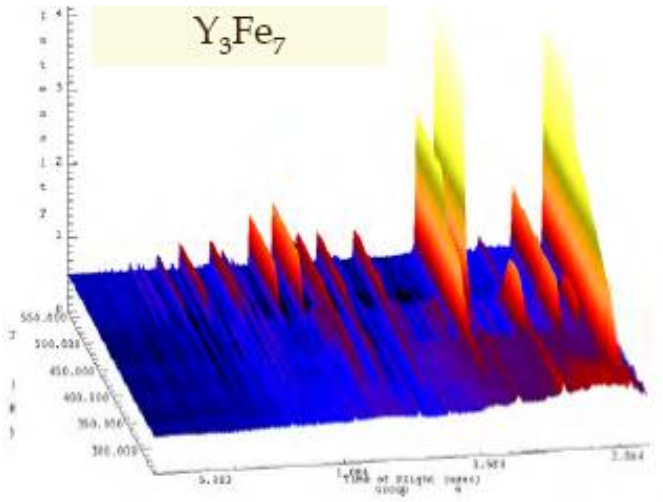
$YBa_2Fe_3O_8$ – antiferromagnetic order gives additional Bragg peaks corresponding to doubling of unit cell along each edge
Observed pattern (lower) contains specific peaks that are modelled separately from nuclear peaks (upper)

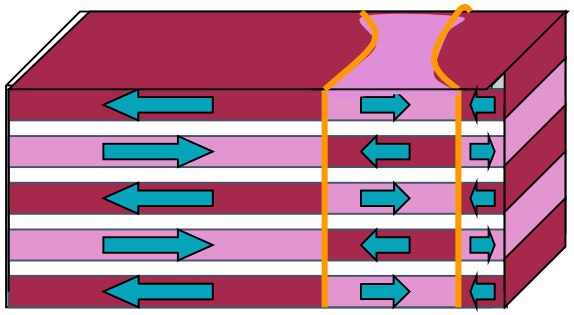


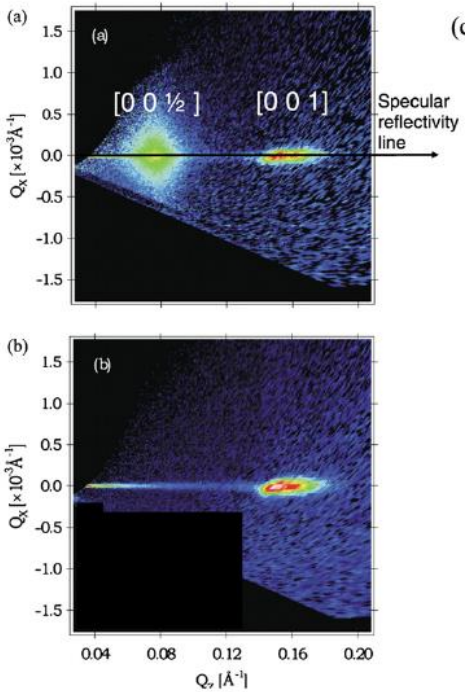
Single crystal diffraction refined in a similar fashion to X-ray pattern with different atomic scattering cross section, and rapid fall off in magnetic intensity with 2θ (form factor)

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

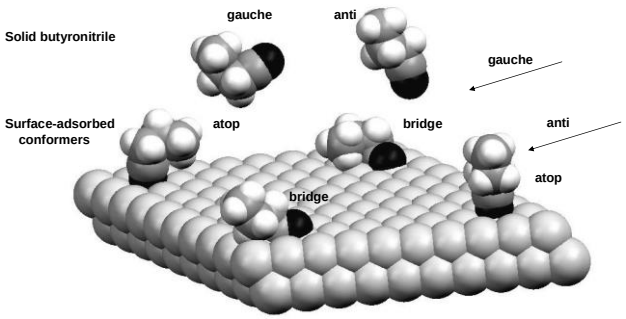


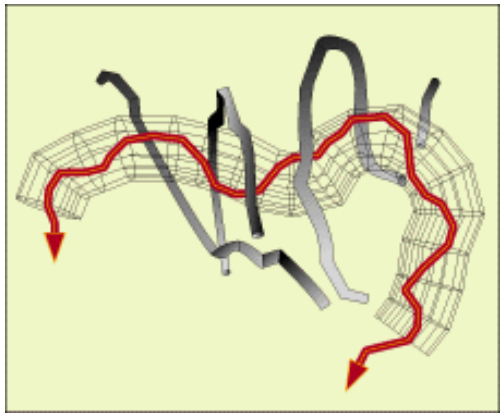


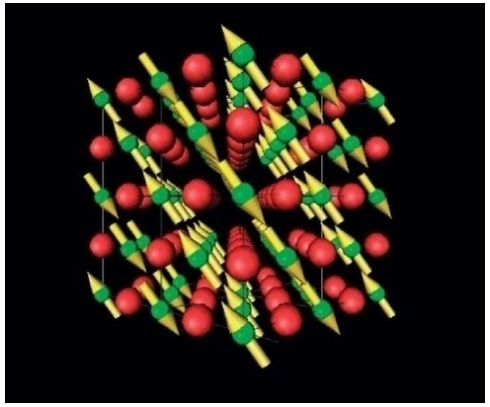


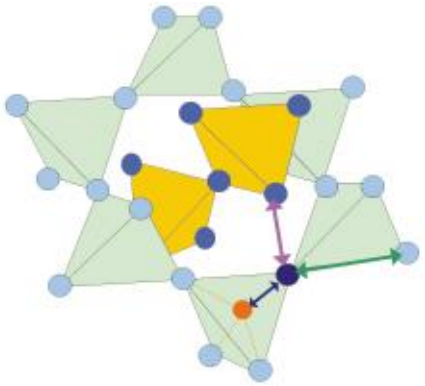
Atomic and molecular motion in materials

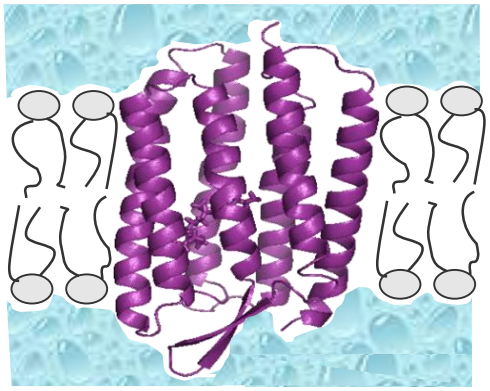
- Atomic and molecular vibrations, rotations and translations are essential to key processes in materials e.g. thermal conductivity and expansion, polymer processing and properties, biochemical processes, magnetic storage media, superconductors

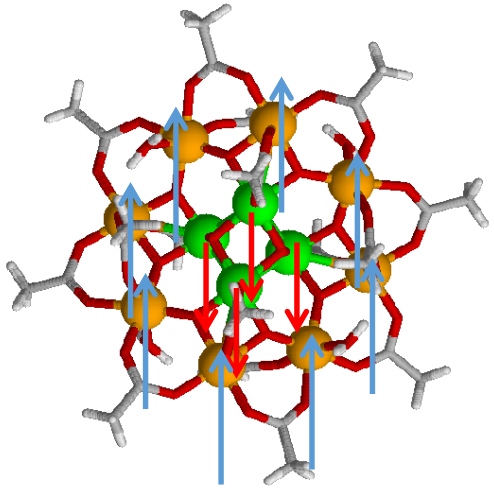






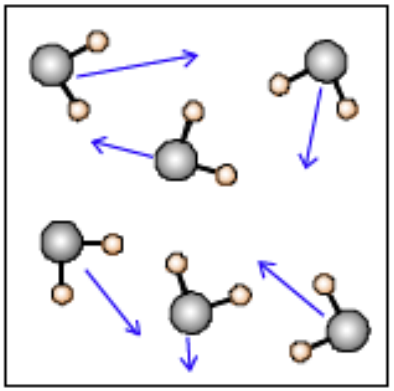




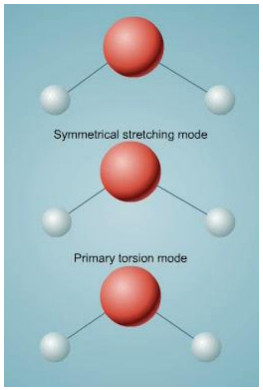


Atomic and molecular motion in materials

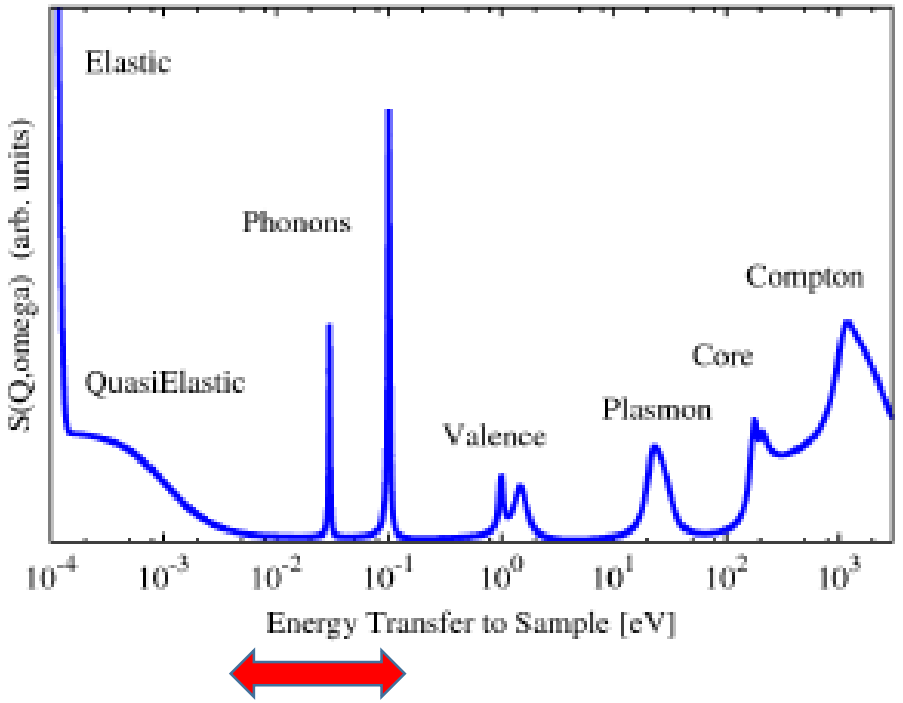
- Diffusion, rotation and vibrations span a wide range of energies and timescales (s-fs) and are commonly studied by NMR, microwave, IR and Raman spectroscopy, as well as computational techniques (MD)



Molecular diffusion or rotation



Molecular vibration

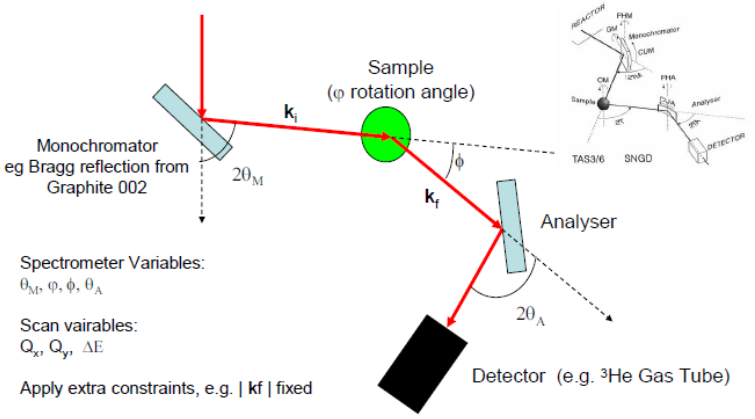


Typical energy range of ‘cold’ to ‘hot’ neutrons

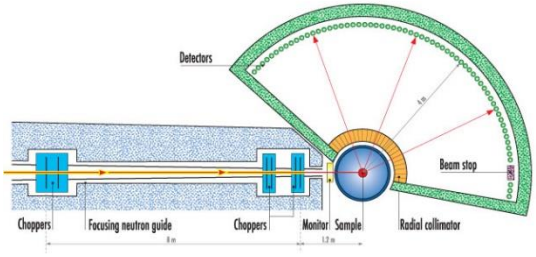
Neutron-matter interactions (3) - excitations

- 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)



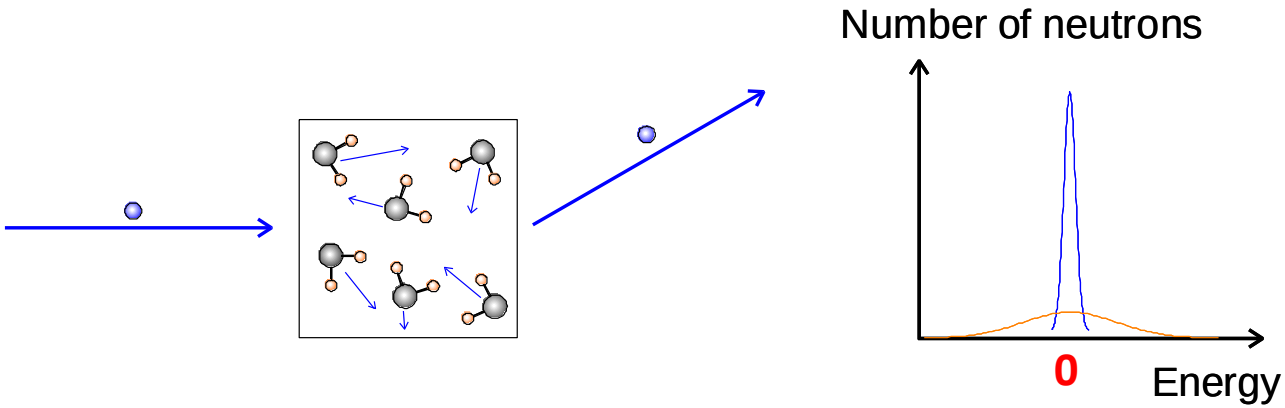
Time of flight spectrometer – based on timing of neutron pulses and velocity measurements – at reactor (choppers) or spallation source (proton pulse arrival sets t = 0)



$hv = E_f - E_i$ $\quad$ $k\ (\text{excitation}) = k_f - k_i$

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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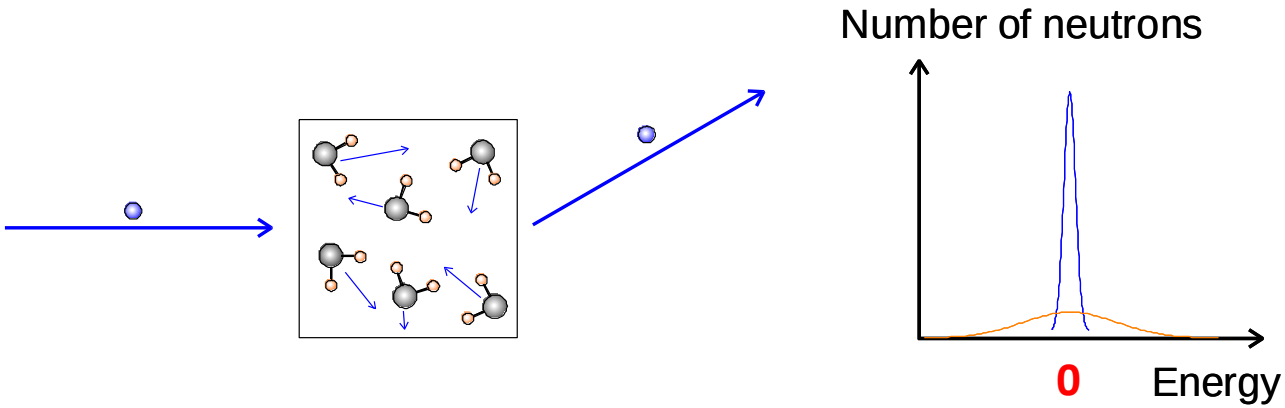
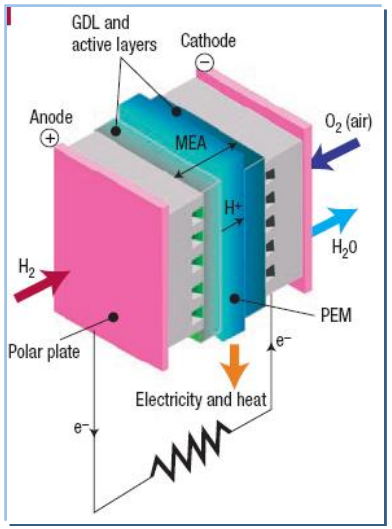
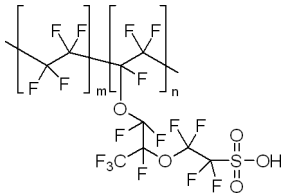
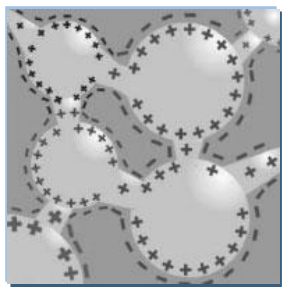
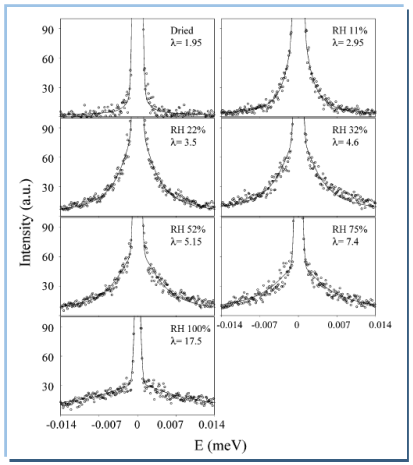


e.g. diffusion of Li ions in cells, H^+ or H_2O in fuel cells, or optimising the motion of H^+ in polymers such as Nafion









Inelastic neutron scattering

- Match spectrometers to different energy regimes (use hotter or colder neutron – shorter or longer wavelength) with different resolution specs.
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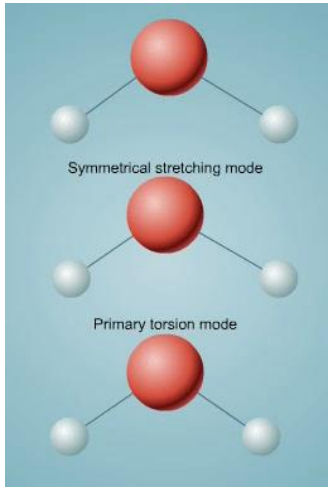

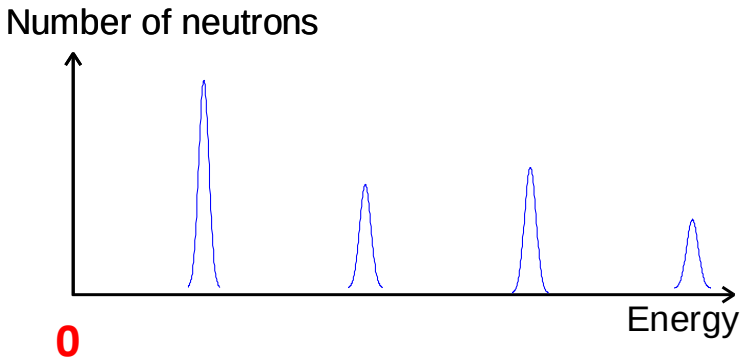

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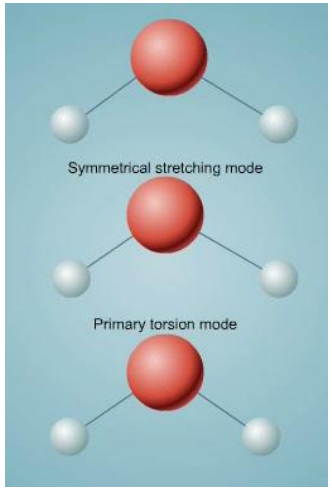
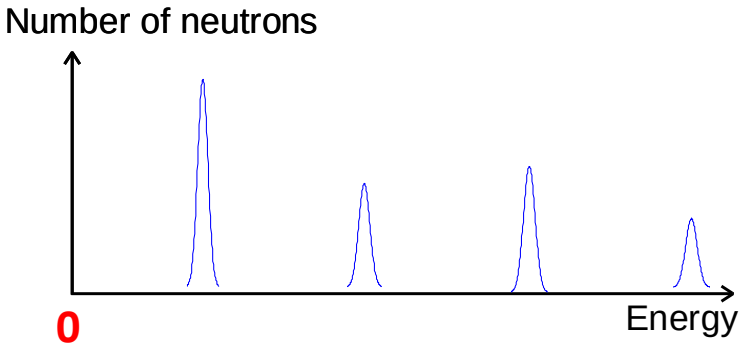
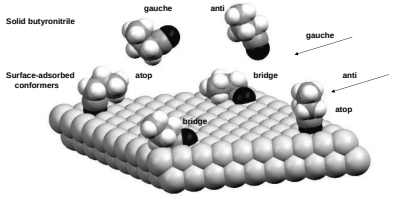
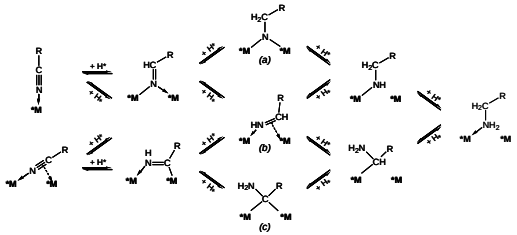
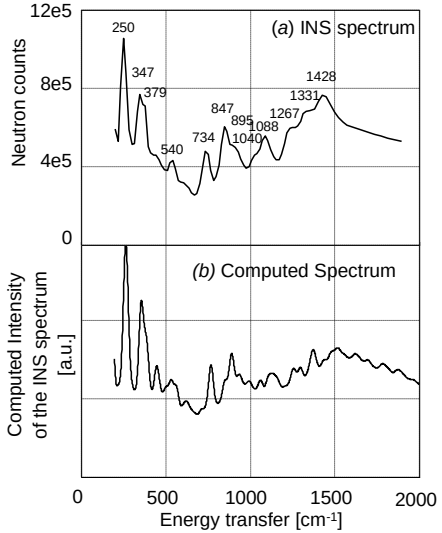




e.g. characterization of molecular species on a catalysis in systems opaque to IR and Raman methods and more sensitive to low amplitude vibrations (opposite of IR, Raman)

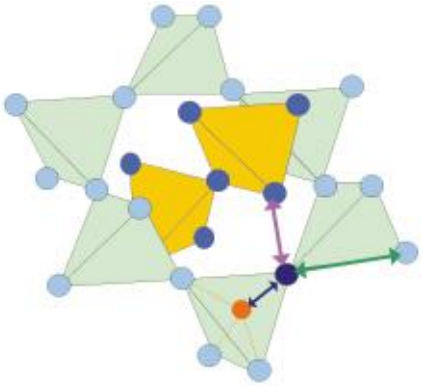


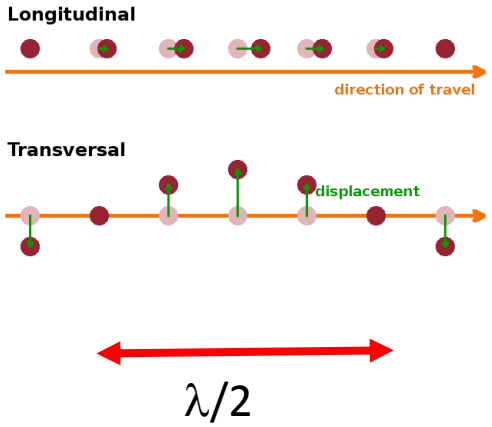


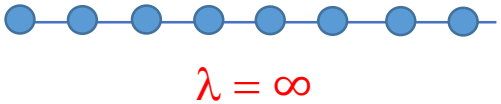


Excitations in solids

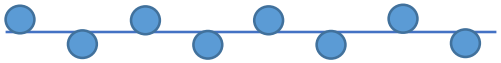
- In solids we see structural excitations of the lattice in the form of waves (phonons) characterised by the relationship between energy and wavelength – conventionally expressed as plot of E vs k ($2\pi/\lambda$).
- The full range of excitations runs from the undisturbed lattice ($\lambda=\infty$) to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







$\lambda = \infty$



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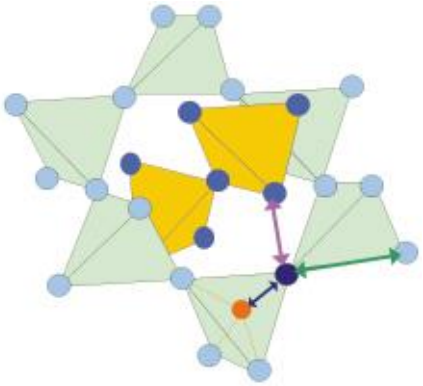
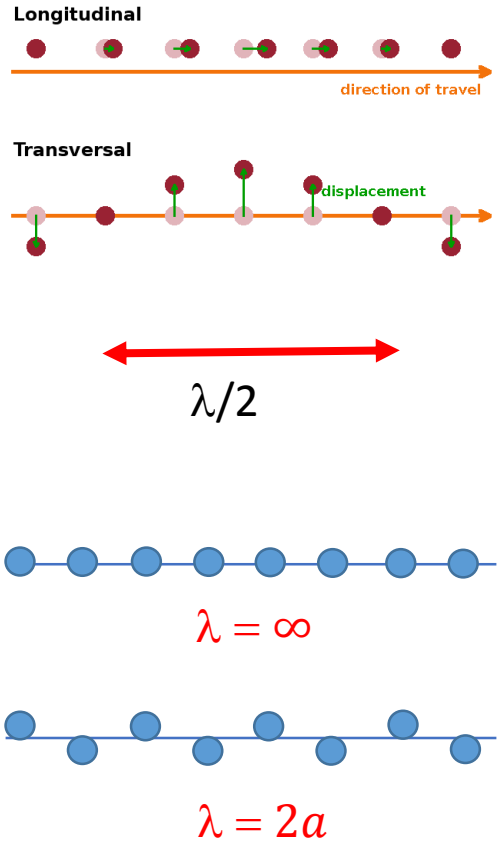
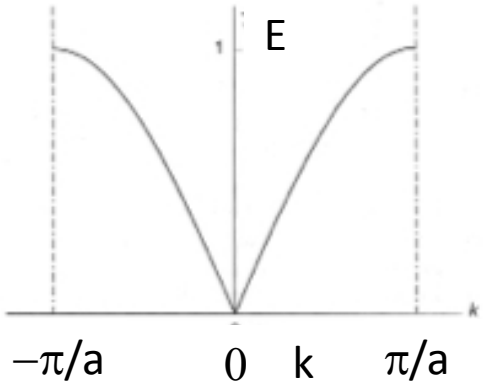


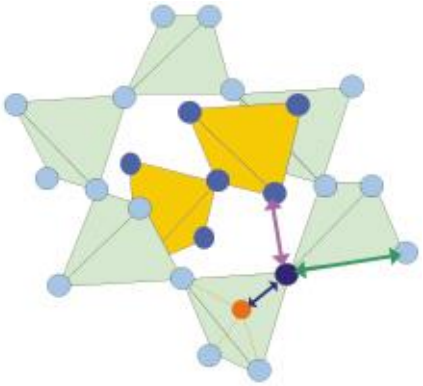


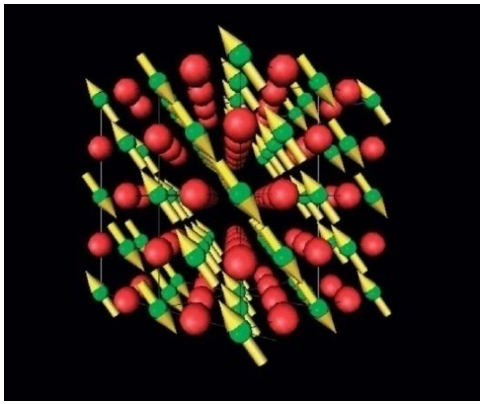


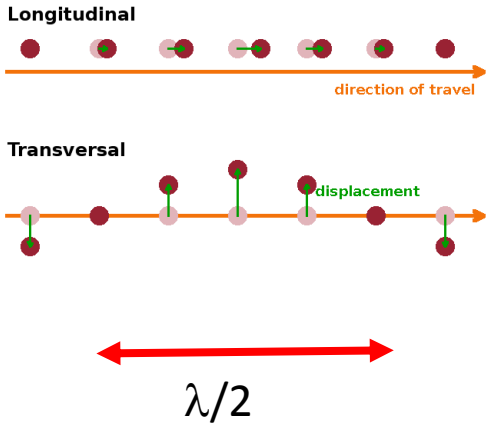
Summarise phonon properties in dispersion curve: E vs k ($2\pi/\lambda$) covers range in $\lambda = \infty \rightarrow 2a$

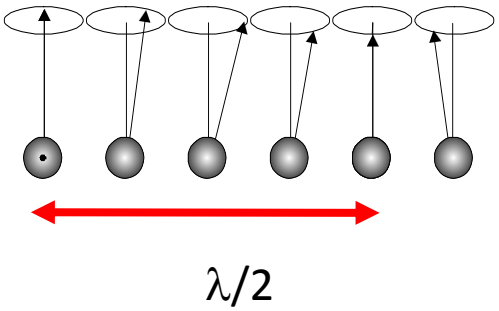
Excitations in solids

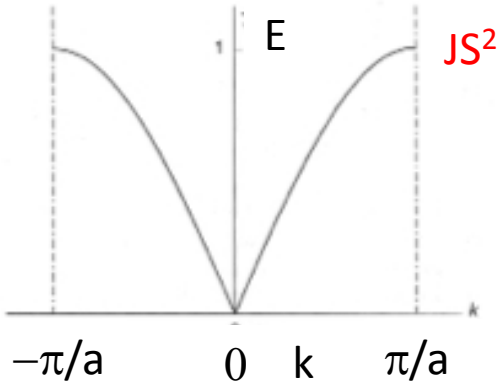
- In solids we see structural excitations of the lattice in the form of waves (phonons) characterised by the relationship between energy and wavelength – conventionally expressed as plot of E vs k ($2\pi/\lambda$).
- Analogous phenomena are observed in ordered magnets where we see 'spin waves' or magnons'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







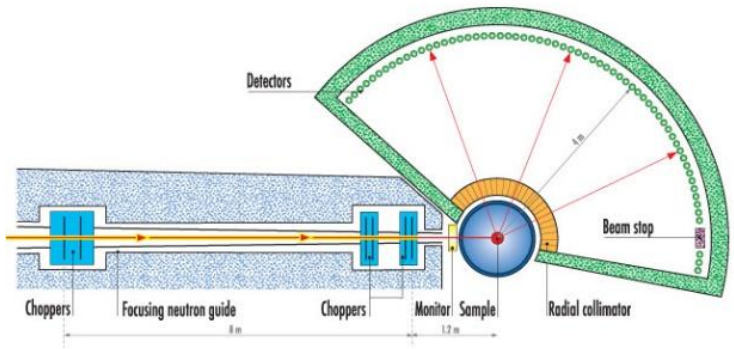


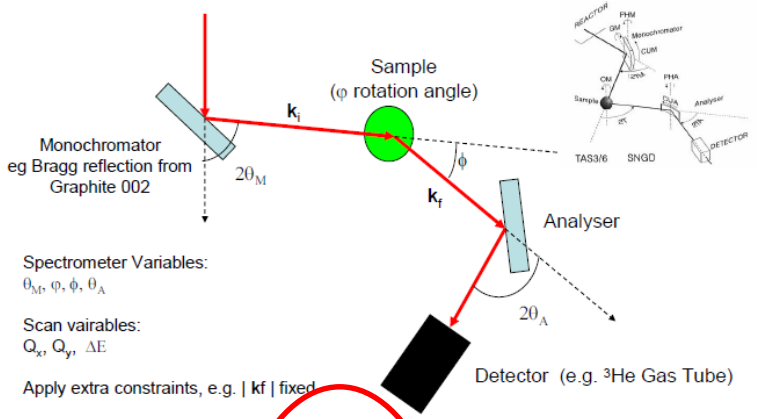


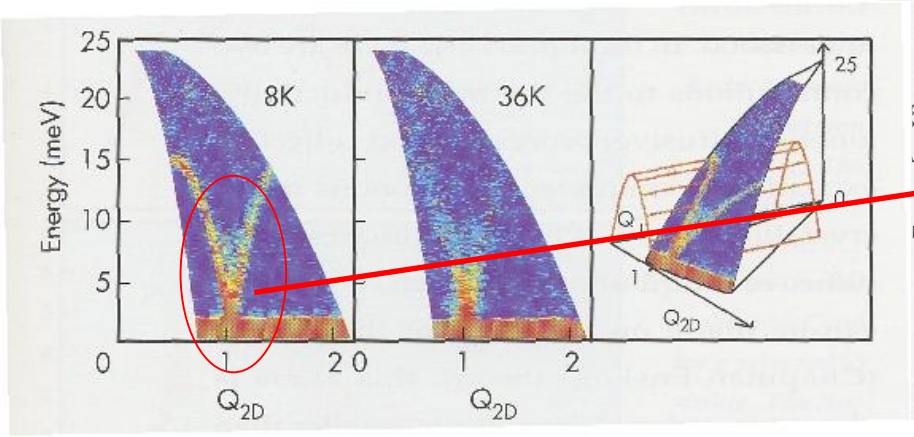
Summarise phonon/magnon properties in dispersion curve: E vs k ($2\pi/\lambda$)
covers range in $\lambda = \infty \rightarrow 2a$

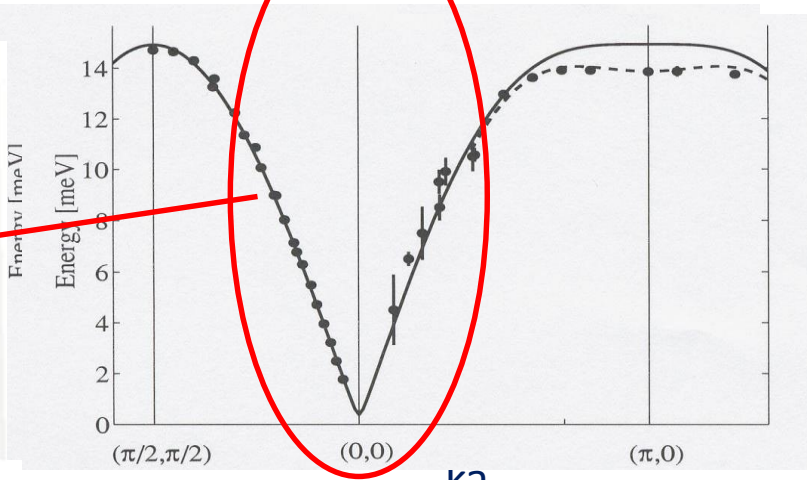
Mapping excitations in solids

- 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)



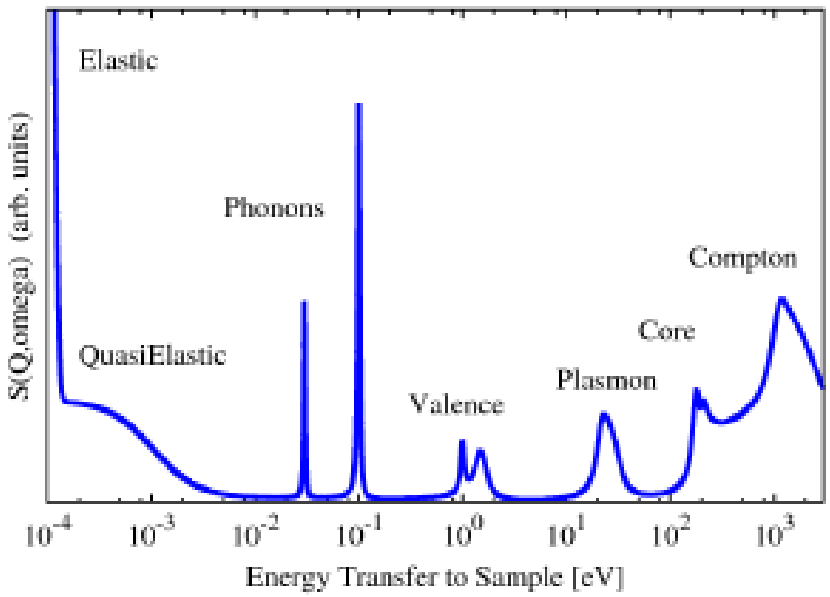


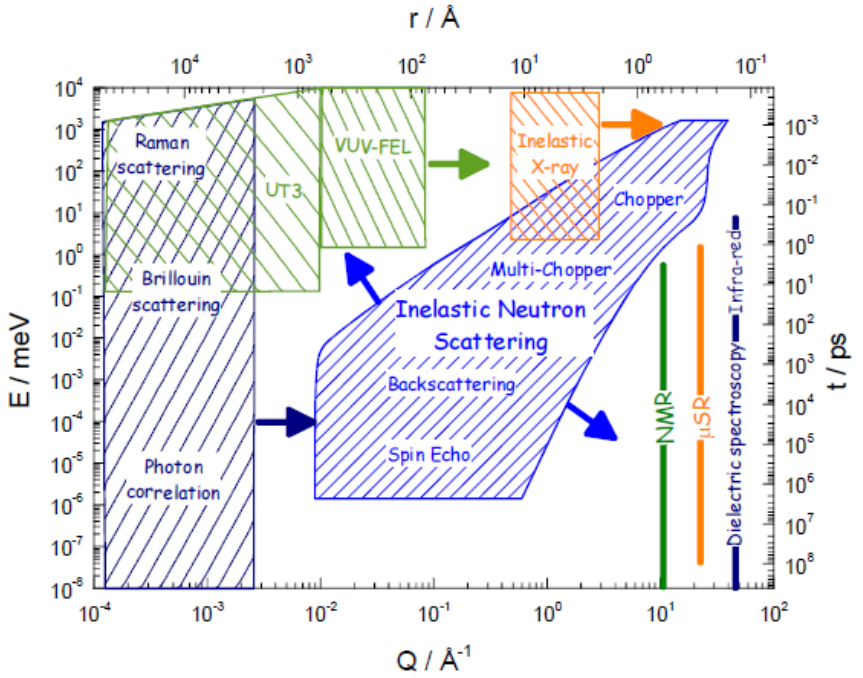




Inelastic neutron scattering

- 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.

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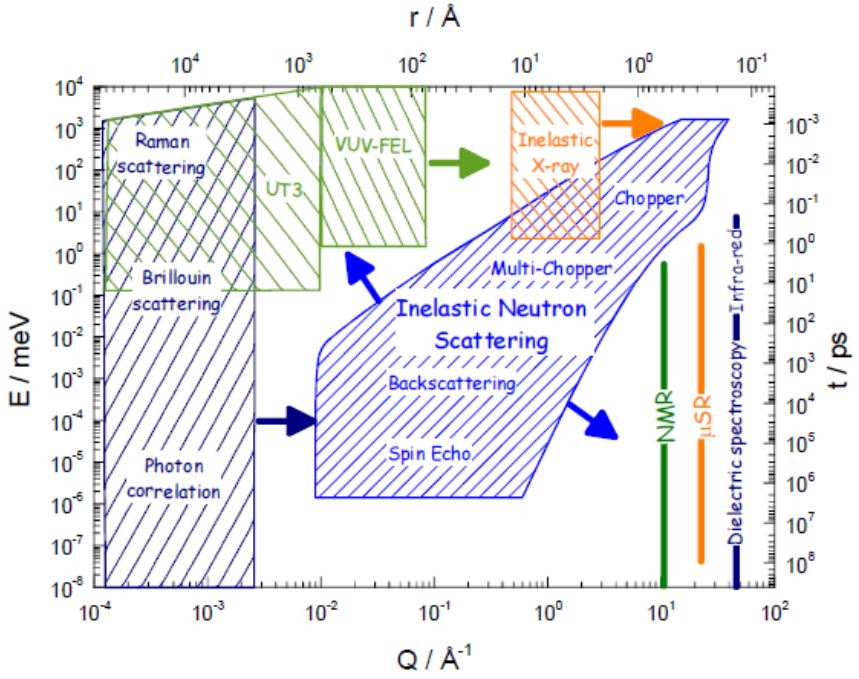
- Typically wish to measure vibrations and magnetic excitations in the range 1-100 meV as a function of k ($1/\lambda$) so the wavelength of the neutrons or X-rays should typically be of the order of 1-2 Å (0.1-0.2 nm)
- 1 Å corresponds to 12.4 keV for X-rays and 81.8 meV for neutrons so instrumental resolution is ***much*** more challenging for X-rays (10 meV: $\Delta E/E \cong 10^{-6}$ 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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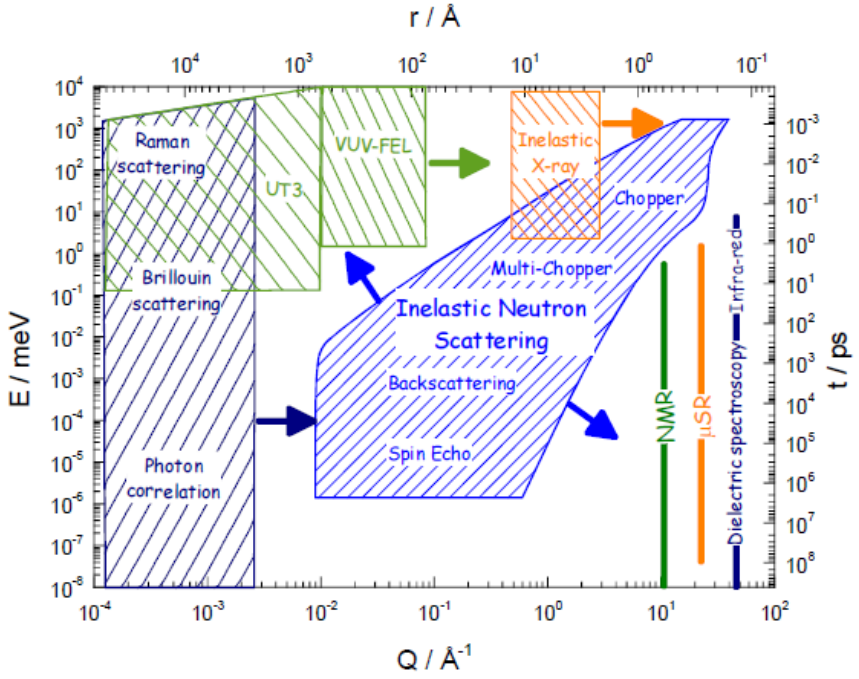
Why bother ? X-rays can work with much smaller samples – films a few atoms thick or sub-micron regions of devices and if done resonantly (RIXS) can tune to specific orbitals to look at how they are implicated in excitation

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