

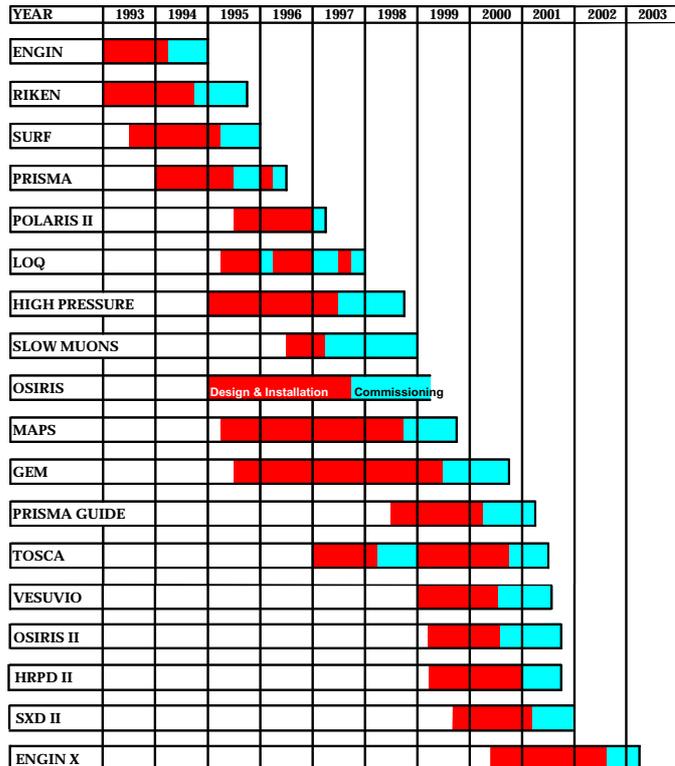
SCIENCE

Science at ISIS

ISIS is the world's most powerful spallation neutron source. It is designed primarily for the study of condensed matter, using neutrons as a scattering probe. The nuclear spallation process induced in a tantalum target by an 800 MeV proton beam is highly efficient, releasing 30 MeV per neutron compared with 190 MeV per neutron for fission, and hence the target dissipates a modest 160 kW from a 200 μ A proton beam at a repetition rate of 50 Hz. The fast neutrons produced in the target are slowed down by a range of hydrogenous moderators to feed currently 20 different neutron scattering instruments. Three different moderators, 20K liquid hydrogen, 100K liquid methane and ambient water, provide different spectral characteristics for a wide range of applications. The target/moderator assembly is 'decoupled'; that is, the neutrons are under-moderated, and retain a sharp pulse structure. Hence the present target station emphasises the thermal / epithermal region of the spectrum, and the 20 millisecond time frame limits band width for cold neutron applications and for instruments requiring long flight paths.

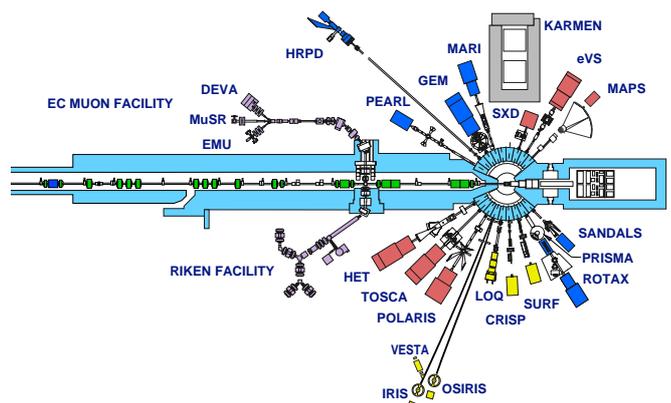
The Present Instrument suite

A suite of instruments for techniques which include inelastic scattering, diffraction, spectroscopy, small angle neutron scattering (SANS) and neutron reflectometry (NR), is used for a broad range of investigations in Condensed Matter Physics, Materials Science, Chemistry, Biology, Earth Science, and Engineering (see instrument summary opposite). The instrument suite has developed substantially over the past 10-15 years, and new instrumentation and instrument concepts



The ISIS instrument development programme over a 10-year period.

have emerged: reflectometry, high resolution powder diffraction and high energy magnetic inelastic scattering, for example. More recently, advances in detector technology, neutron optics, polarisation, data acquisition and computing have given added impetus to the development of improved instrumentation, and a second generation of instruments (SURF, MAPS, GEM, OSIRIS, and TOSCA) has been developed and introduced (see above). These have been funded predominantly through Collaborative Research Grants in the UK, and through collaborations with overseas international partners.



The Present ISIS Instrument Suite

HRPD

High Resolution Powder
Diffraction

POLARIS

High Intensity
Powder Diffraction

SXD

Single Crystal Diffraction

PEARL

Engineering and
High Pressure
Instrument

GEM

General Purpose Diffraction,
Liquids and Amorphous
Structures

SANDALS

Small Angle Liquids &
Amorphous Diffraction

CRISP, SURF

Neutron Reflectometry

LOQ

Small Angle Scattering

HET

Excitations at Low
Momentum Transfer

MARI

$S(Q, \omega)$ Vibrational
& Magnetic
Spectroscopy

PRISMA

Coherent
Excitations and
Critical Scattering

ROTAX

Multiple Purpose
Diffractometer

MAPS

Single Crystal Excitations

IRIS

Low Energy Spectroscopy
Long d-spacing Diffraction

TOSCA

Molecular Spectroscopy
and Crystal Fields



Setting up the CRISP reflectometer for studies of water penetration in float glass surfaces.

eVS

Electron Volt Spectroscopy

OSIRIS

Polarisation Analysis Spectroscopy
and Diffraction

MuSR

Transverse and Longitudinal Field
Implanted Muon Spectroscopy

EMU

Implanted Muon Spectroscopy
optimised for Longitudinal Field

DEVA

Muon Development Beam

RIKEN

Surface and Decay Line Muon
Facility

KARMEN

Neutrino Facility

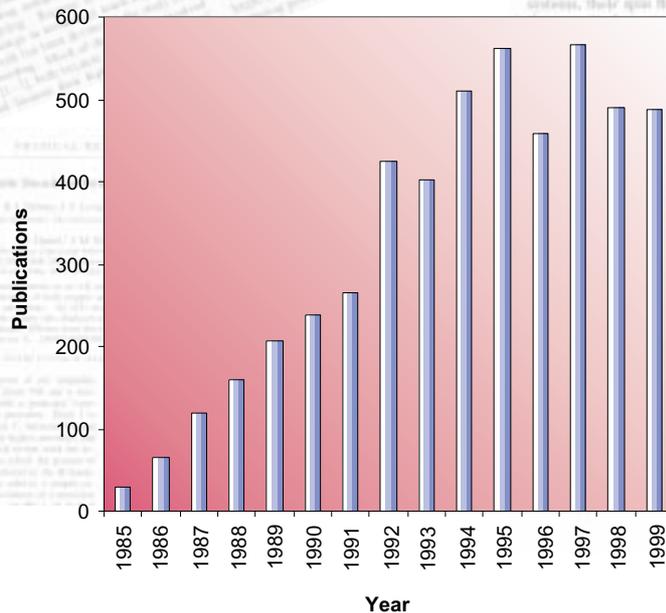
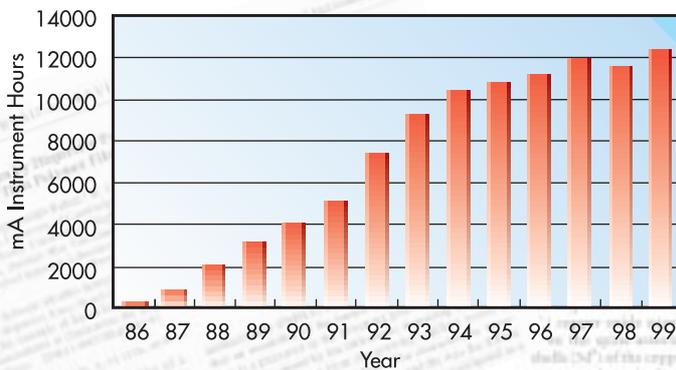


The ISIS synchrotron.



ISIS Performance

The facility delivers beam for the experimental programme for ~ 170 days per year. Academic users from the UK and 10 other countries with major programmes at ISIS make up the ~1200 scientists who visit annually to perform some 600 experiments. The majority of the instruments are substantially over-subscribed by more than a factor of 2. This international and interdisciplinary research programme has resulted in some 4,000 publications over the past decade - by any measure a vibrant and highly successful programme.



This broad research programme covers a variety of topics at the forefront of Physics, Chemistry and Materials Science, and, more recently, Geology, Biology and Engineering. Notable examples include the determination of the high resolution structures of high T_c superconductors, fullerenes, GMR materials, lithium battery electrodes and negative thermal expansion materials; magnetic excitations in high T_c superconductors and heavy fermions, and excitations in quantum fluids; the behaviour of complex fluids (surfactants, polymers, colloids, proteins) at interfaces and in bulk solution; high pressure studies, both of crystalline materials and super-critical fluids; and determination of the structures of metallic glasses and ceramics. Highlights of this diverse programme are presented in the remainder of this section.

Soft Condensed Matter

Soft condensed matter encompasses a wide range of molecular materials, such as polymers, surfactants and colloids. The physical and chemical properties of these systems are of increasing technological importance, and this is an area often driven by the commercial significance of products which are highly complex mixtures and structures. Although a variety of experimental techniques is used to investigate both bulk and surface properties, the specific advantages of neutron scattering (principally ‘contrast’, and the ‘weak interaction’ - see table on page 8) makes the neutron a particularly powerful probe in this area. As a result, soft condensed matter studies using neutrons have grown enormously in recent years. Some recent examples from ISIS involving the structure of polymer films, surfactant adsorption, polymer intermolecular interactions and aggregation (self-assembly) in complex extreme environments are presented.

Polymer-polymer inter-diffusion

Polymer-polymer interfaces are important as they play a dominant role in the nature of polymer blends and in surface wetting, as well as applications such as adhesion, welding and mechanical strength. To understand polymer behaviour in such applications, the interface must be characterised at a microscopic level. In combination with deuterium labelling, neutron reflectivity provides unprecedented detail on interfacial shape and width at molecular resolution. This has been exploited in the study of the interface between a range of immiscible and partially miscible polymers, such as polystyrene-poly(methyl methacrylate). Industrially important polymers, such as polypropylene and polyethylene, are semi-crystalline, and a specially constructed ‘hot cell’ has been developed to study interfaces involving such polymers, at temperatures above their melting point (figure 1).

The interfacial widths measured by neutron reflectivity are greater than that predicted by theory, due to broadening by thermally induced capillary waves. Capillary waves produce a measured interfacial width which varies logarithmically with film thickness. The cut-off for observing short wave vector waves is determined by the in-plane coherence of the neutron beam for thick polymer films, and by dispersion forces across the film in thin films. This logarithmic dependence has been verified for measurements of the polystyrene – poly(methyl methacrylate) interface, for different polystyrene film thicknesses.

In-situ real time measurements provide the opportunity to measure the early stages of inter-diffusion at a polymer-polymer interface, and open up the potential for studying oligomer and solvent ingress (role of plasticisers). Using a development of the ‘hot cell’ described earlier, measurement

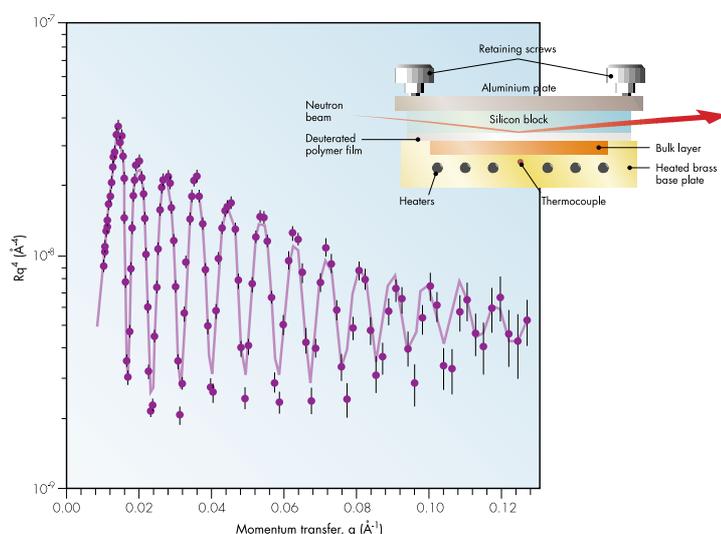


Figure 1. Neutron reflectivity data from the interface of deuterated polystyrene and polyethylene. Inset: schematic of the cell used for investigation of polymer interfaces in the melt.

times of <60 s have been achieved. The white beam time-of-flight method on a pulsed source makes such an approach possible, in that the entire reflectivity profile can be obtained simultaneously. The geometry is chosen to match the region most sensitive to the interfacial width, and the resolution relaxed to match the length scales in the bilayer. The variation in interfacial width and position of the interface for oligomeric styrene diffusing into high molecular weight polystyrene was measured. At early times the interface moved into the thicker high molecular weight film due to the styrene diffusion, and at later stages the interface broadened.

Surfactant adsorption (complex mixtures at interfaces)

The combination of neutron reflectivity and H / D isotopic substitution has been shown to be a powerful tool for the study of surface-active molecules at interfaces. Through deuterium labelling it is possible to highlight or isolate the contribution from particular components or fragments at the interface. This enables adsorbed amounts to be determined over a wide range of solution concentrations, measurements not possible by other techniques. This is especially important in the study of the interfacial behaviour of complex mixtures.

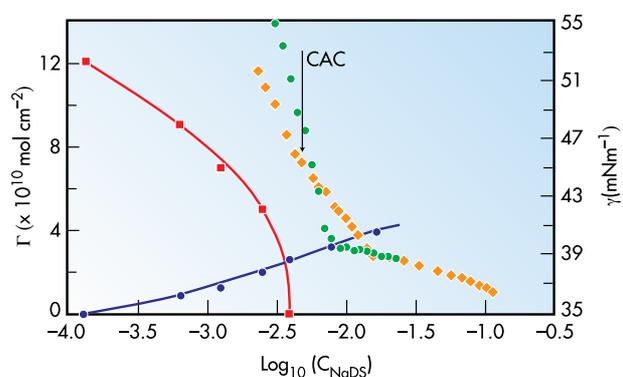


Figure 2. Adsorption isotherm (from neutron reflectivity) and surface tension behaviour for poly(ethylene oxide)/sodium dodecyl sulphate (PEO/SDS) at 35 °C. Red/blue: SDS/PEO adsorption. Green/orange: SDS/PEO surface tension.

The widespread technological, industrial, and domestic applications of surfactants invariably use mixtures, and neutron reflectivity is now providing a unique insight into the surface behaviour of such complex samples. In many formulations, such as shower gels and hair shampoos, polymers are also frequently incorporated, as viscosity modifiers, stabilisers or deposition aids. Such polymers often interact strongly with surfactants in aqueous solution, giving rise to a rich pattern of behaviour in properties such as surface tension. However, without additional information about chemical activities, only techniques such as neutron reflectivity can unravel what is happening at the interface (see figure 2), and often this is very different from the bulk behaviour.

More powerfully, detailed structural information on the surface layer can be obtained, and such studies have provided a new insight into the monolayer structure, revealing ‘surface layering’ at higher solution concentrations, and the onset of ‘surface micellisation’ in amphiphilic block co-polymers. More detailed labelling schemes enable the mean conformation of a surfactant molecule at the interface to be determined, and to identify contributions of capillary waves to the structure. For surfactant mixtures at the interface, detailed labelling schemes have provided a detailed description of the surface structure of such mixed monolayers (see figure 3).

Complex fluids under shear

The behaviour of complex fluids under shear flow (figure 4) is important in the context of product processing and delivery. Understanding the microscopic origins of the complex rheological behaviour that exists in these fluids requires techniques such as SANS.

Measurements on LOQ of the lamellar phase of the non-ionic surfactant $C_{16}E_6$ in a

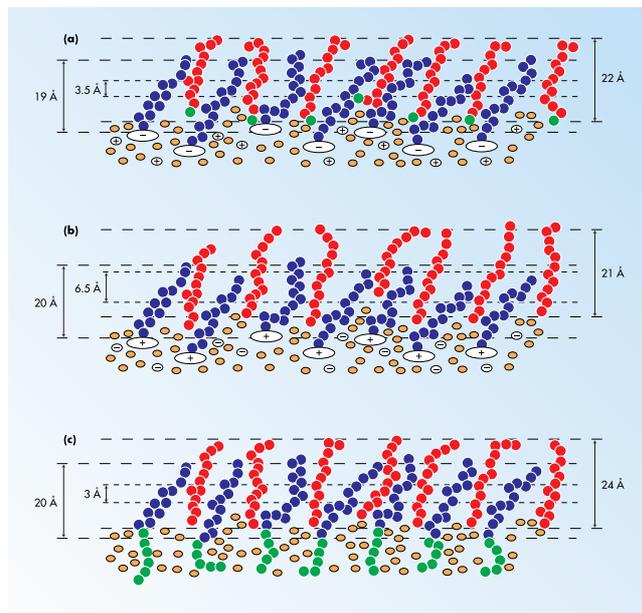


Figure 3. $C_{12}EO_5$ surfactant monolayer with adsorbed dodecane (top) compared with SDS/dodecane and $C_{12}TAB$ /dodecane (bottom).

well defined Couette flow show a complex behaviour. At low shear rates the lamellae are aligned parallel to the flow-vorticity plane, whereas at higher rates they are aligned in the shear gradient-flow plane. At intermediate rates a complex interplay between the two extremes of behaviour exists.

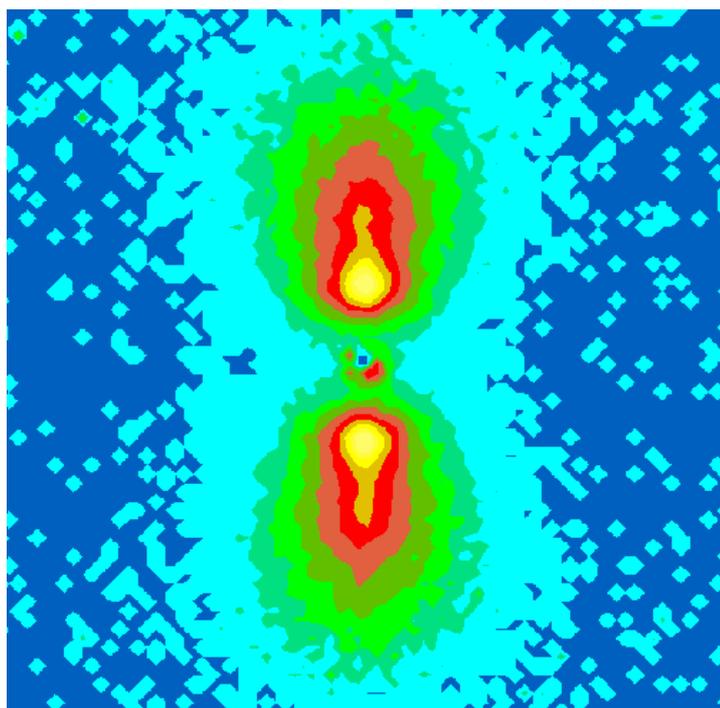


Figure 4. LOQ data from mixed surfactants under shear: 3% $C_{16}E_6 + C_{16}TAB$.

For the di-chain cationic surfactant, 2HT, under shear flow, a different type of behaviour is seen. At very low shear a highly aligned lamellar phase is observed, ordered in the flow-vorticity plane. At a critical shear rate, which is dependent upon concentration and increases with increasing concentration, the scattering becomes isotropic, consistent with the formation of multi-lamellar vesicles. In the ordered lamellar region, measurements at different scattering geometries with respect to the flow and gradient axes show an inconsistency which is reconciled by a distribution of orientational order across the Couette cell gap.

Aggregation in super-critical fluids (complex environments)

Liquid or super-critical carbon dioxide is a non-toxic, chemically inert, non-flammable fluid. As such it provides a safe alternative to potentially hazardous petrochemical solvents, and is being exploited commercially in processes involving flavour extraction (e.g. hops), decaffeination of coffee beans and dry cleaning. The high compressibility of CO_2 near the critical point enables a wide density variation which can be exploited to fine-tune solvent properties and enhance selectivity. A limiting factor in the solvent properties of CO_2 is the low solubility of 'polar molecules', which normally dissolve well in water. This problem has been approached by the addition of polar co-solvents, such as ethanol, to enhance solubilities, or by exploiting the nature of the C-F bond compared with C-H.

There is now growing interest in the formation of water-in- CO_2 micro-emulsions which are stable dispersions of nanometre-sized water droplets coated by a monolayer of surfactant (figure 5). Since the water droplets can solubilise polar molecules, micro-emulsions can provide a 'universal

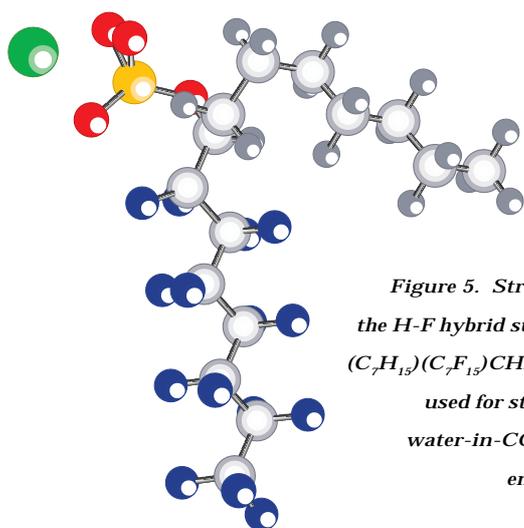


Figure 5. Structure of the H-F hybrid surfactant $(C_7H_{15})(C_7F_{15})CHSO_4Na^+$, used for stabilising water-in- CO_2 micro-emulsions.

solvent' for both polar and apolar molecules. SANS on LOQ has been used to investigate the structural features of these new systems to establish whether discrete micro-emulsion droplets are formed as opposed to simply a homogeneous solution of water in CO_2 . The penetrating power of neutrons makes the design of a pressure cell for such measurements straightforward, and SANS is a powerful technique for characterising aggregates such as micelles and micro-emulsions. Measurements have shown that the hybrid H-F di-chain surfactant does result in micro-emulsion formation in supercritical CO_2 above a certain critical pressure. The SANS measurements have provided structural information that has been vital to the design of new surfactants for the production of water-in- CO_2 micro-emulsions at optimal operating temperatures and pressures.

Bio-molecular Sciences

There is a modest but important user base in Bio-molecular Sciences at ISIS. The first example below is the determination of the structure of the antibody Immunoglobulin A in solution. This demonstrates how SANS is used to obtain low resolution (mesoscale) structural information of important macromolecular assemblies. It also

illustrates the frequently-used complementarity of neutrons and X-rays, leading to a model which provides an improved understanding of the functional properties of the antibody. The second example demonstrates the potential of an emerging area, the use of specular neutron reflection for the study of surfaces and interfaces of biological relevance.

Non-crystalline diffraction methods provide access to local solvent-solute, solvent-solvent correlations in such systems; for example, the effect of protein stabilisers or denaturants on the solvation shells of particular chemical groups on proteins.

High resolution single crystal and powder diffraction measurements are presently limited to smaller biologically-relevant molecules. Neutron diffraction provides accurate hydrogen positions and thermal ellipsoids. In conjunction with high-resolution X-ray data, this gives access to accurate electrostatic interaction parameters essential to understand, for example, drug-virus interactions.

Structure of Immunoglobulin A

Antibody or immunoglobulin molecules play a critical role in our body's immune defence against bacteria and viruses. Immunoglobulin A (IgA) is not only present in blood but is also the predominant antibody class found in mucosal surfaces of the lung and the gastrointestinal tracts, and so forms a critical first line of defence against

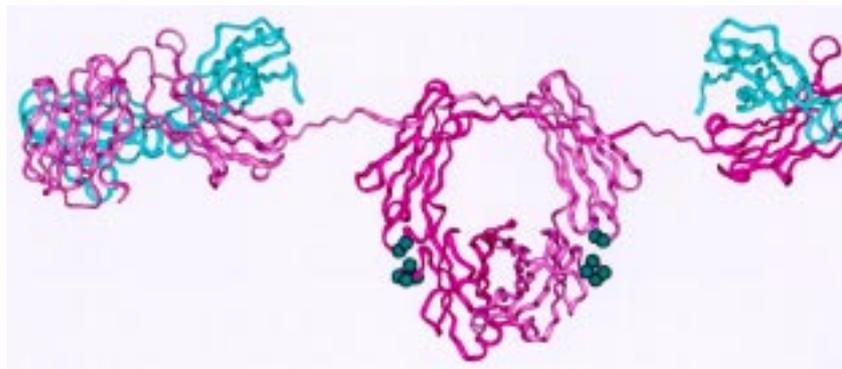


Figure 6. Ribbon diagram of the 3-D structure of immunoglobulin A1.

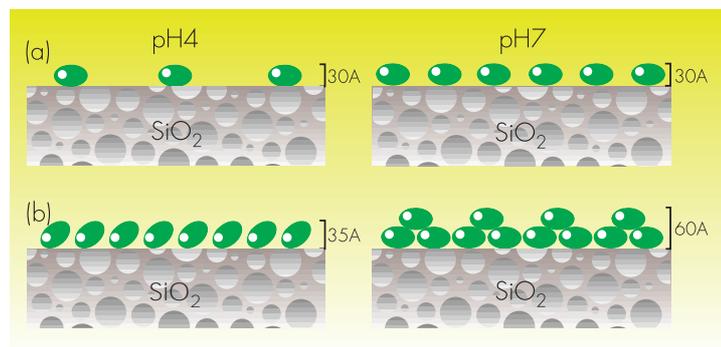


Figure 7. Schematic diagram of the surface coverage and orientation of lysozyme molecules adsorbed at the silica-water interface at different concentrations (a,b).

many invading pathogens. However, despite the abundance and importance of IgA, surprisingly little is known about its three-dimensional structure and how this relates to its role in immunity. A combination of small angle neutron and x-ray diffraction has been used to reveal the intermolecular arrangement, and in turn provide a better understanding of its functional properties.

Like other immunoglobulins, IgA has a basic monomeric structure composed of two heavy chains and two light chains, arranged into two identical side lobes and a central region, separated by a flexible hinge. The tips of the side lobes are responsible for recognising and binding to structures (antigens) on the surface of foreign cells or molecules. This region interacts with specific receptors on the surface of phagocytic immune cells to trigger mechanisms such as engulfment and cell killing to eradicate invaders.

Structure at medium resolution was determined using small angle diffraction, and from a refinement of complementary X-ray data and neutron data from samples in D_2O and H_2O . This medium resolution structure, to a resolution of about 10 \AA , was developed by a novel, highly-constrained technique, in which molecular-dynamics simulations of IgA1 (one of the sub classes of IgA) hinge peptides were used to create 12,000 randomised IgA1 molecules. Each one was built from homology models for the

central and side regions connected by the hinge peptides. After filtering to reject poorly-fitting models, the first averaged solution structure for serum IgA1 was obtained as a superposition of 104 best-fit models. A T-shaped structure was revealed in which the hinge of each heavy chain holds two side lobes apart with a very high side lobe centre-to-centre separation of 170 \AA (figure 6).

The model leads to an improved appreciation of the functional properties of IgA1. The two side lobe antigen sites are widely spaced apart at 230 \AA , and this enables them to access more widely spaced antibody targets on foreign particles compared with other antibodies, thus permitting a greater diversity of immune targeting in the blood.

Protein adsorption at interfaces

Protein adsorption is involved in a wide range of processes and applications. The deposition of blood proteins on to medical devices and implants, and the subsequent modification of their biological response, the bacterial fouling of ships hulls and the blockage of filtration membranes in bio-separation processes are examples of the unfavourable aspects of protein adsorption; the extensive use of proteins in food stabilisation and in the fabrication of bio-sensors are widespread applications.

Pioneering experiments on two common and well-characterised globular proteins, lysozyme and bovine serum albumin (BSA), have shown how neutron reflectivity can contribute to our understanding of protein adsorption at interfaces, and have opened the way to study more complex processes such as membrane-protein interactions (figure 7).

Adsorption at hydrophilic surfaces involves both the electrostatic interaction between the surface and the hydrophilic parts of the protein, and between protein



molecules at the interface. Further driving forces are the entropic changes associated with dehydration of the protein or with its structural rearrangement. Strong surface interactions may damage the native state of the protein, and lead to deformation or denaturation, the extent of which will depend upon the nature of the surface and the relative stability of the protein. Neutron reflectivity offers the opportunity of measuring not only adsorbed amounts, but the surface structure of adsorbed proteins to reveal the nature of those surface interactions.

Specular neutron reflectivity, combined with appropriate water contrast variation, was used to obtain a direct determination of the structural distribution of lysozyme and BSA at the air-water and liquid-solid interfaces. For lysozyme at the air-water interface the protein remains intact. At low concentrations the protein has its long axis parallel to the surface and is about 50% immersed in the solvent. At higher concentrations the long axis is vertical, and the protein is about 75% immersed in the solvent, consistent with some of the amino acid side chains being shifted out of the water. At the hydrophilic silica surface the adsorption of lysozyme was completely reproducible with respect to concentration, but irreversible. The structure normal to the surface was determined by varying the isotopic content of the water. The adsorption was completely reversible with pH, and the variation with pH implies that the surface excess is dominated by interactions between protein molecules rather than with the surface. Changes with pH and concentration indicate that the protein undergoes a transition from 'side on' to an 'end on' configuration, and that at higher concentrations layering occurs. The measurements also indicate that the lysozyme retains its tertiary structure at the hydrophilic interface. This is in marked contrast to adsorption at the hydrophobic

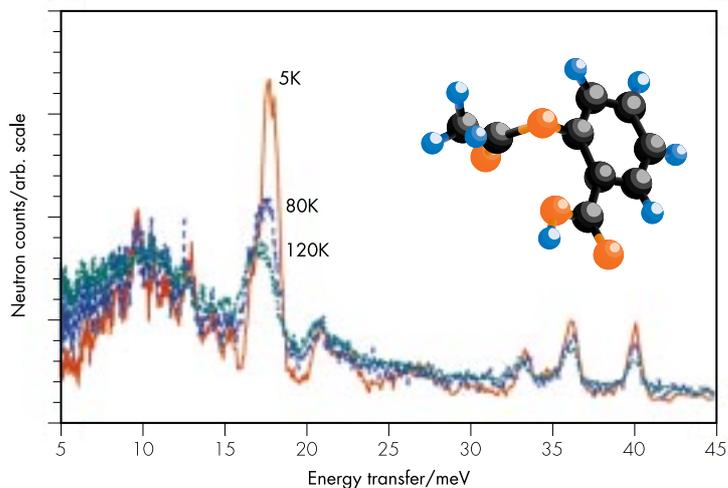


Figure 8. Inelastic scattering spectrum of aspirin. The strong feature is due to the fundamental transition of the methyl torsional motion.

interface, where denaturation does occur. Similar observations have been made for the protein BSA.

Dynamics of Molecules

The energies of thermal neutrons are similar to those of atomic motions. This enables molecular vibrations, lattice modes and diffusional motion to be probed (figure 8). The momentum transfer and energy transfer space (Q, ω) accessible by neutrons translates to a real time space of 0.1 – 1000 Å and 10^{-8} – 10^{-15} s. Vibrational spectroscopy is a frequently used method, and the neutron technique is complementary to the optical (infra-red and Raman) methods, often leading to a better understanding due to the absence of 'selection rules' and the simplicity of the interaction. Measurements over a broad (Q, ω) range also give spatial information on the vibrational wavefunction. This is a particularly powerful method for hydrogen-containing systems, and, as illustrated in the example below, provides the sensitivity to study catalytic surfaces. The broad (Q, ω) range also provides access to a variety of other processes such as quantum excitations, the

rotational tunneling of small molecules, diffusional motion of small molecules through solids such as zeolites and crystal field effects.

Catalyst poisoning by methyl groups

Catalysts are an integral feature of everyday life, from catalytic converters on vehicles to the refining of crude oil to petrol. Most commodity chemicals can only be produced economically by the use of catalysts. Vibrational spectroscopy is extensively used to characterise species on catalyst surfaces, and inelastic neutron scattering (INS) performed on TFXA (now replaced by the TOSCA instrument) has helped to reveal why an industrial catalyst became deactivated in-process.

A palladium catalyst that had been used for a process involving the hydrogenation of C-O groups to C-OH groups of functionalised aromatic and polyaromatic systems, but which had become deactivated, did not show evidence of coke formation

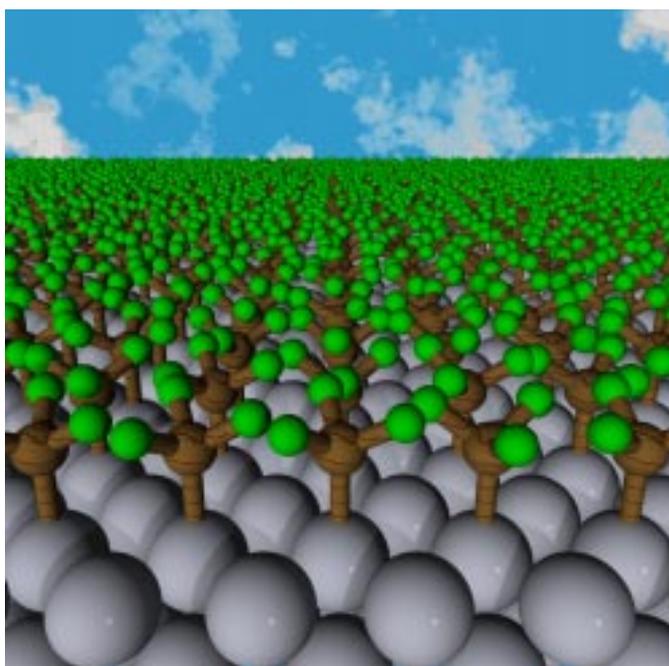


Figure 9. Idealised view of the palladium catalyst surface covered by methyl groups.

(the most common cause of deactivation) although some carbon was present. Palladium is the catalyst of choice because it readily dissociates hydrogen; however, measurements of the surface area and hydrogen capacity were normal. Investigation by a range of analytical techniques did not show any clue as to the cause of the loss of activity. Raman spectroscopy, using either visible or near-infrared excitation, and infrared spectroscopy were both unable to resolve the problem.

The INS spectra, from TFXA, of a deactivated catalyst showed a series of sharp peaks which were completely absent on an active catalyst. The most striking feature of the spectrum was its simplicity - there were remarkably few bands. This implied either a highly symmetric structure with many degenerate modes, or a small molecule. The intense 302 cm^{-1} feature suggested a methyl torsion, and a detailed analysis showed that the spectrum was consistent with a layer of methyl groups in an on-top site configuration on the surface.

The sharpness of the peaks suggest that the methyl groups are bound to the top-most atomic layer of the catalyst, and the intensities suggest that most of the non-extractable carbon was present as methyl groups. The relative intensities, when normalised to the amount of sample in the beam, showed an excellent correlation with the degree of deactivation of the given catalyst sample. The large quantity of bound methyl groups presumably lowered the catalyst performance by a surface blocking effect (figure 9).

Structure of crystalline materials

Understanding the exploitable properties of new materials requires a detailed

knowledge of their structure. Neutron scattering has played a principal role in developing this understanding in almost every area of modern structural Chemistry and Physics.

High resolution allows phase transitions, subtle structural effects and complex structures to be studied. High flux at medium resolution enables rapid data collection in complex environments and for in-situ processes. The time-of-flight Laue technique provides access to structural and disorder information in single crystals. The following examples cover this broad range of diffraction applications.

Solid State Chemistry

The broad range of d-spacings accessible with good resolution using the white beam time of flight method has enabled powder diffraction at ISIS to make a real impact in the area of structure-property relationships for a range of technologically important materials.

■ The ability of neutron diffraction to probe the location of light atoms in the presence of heavier ones is particularly important in the study of lithium batteries, where the synthesis of new cathode materials is an important aspect of the development of high power density, light-weight cells for applications such as laptop computers and mobile phones. A detailed knowledge of the crystal structure is required to understand the dynamics of the Li^+ intercalation mechanism, including the effects of repeated charging/ discharging, to determine those factors which limit the ultimate lifetime of the battery (figure 10).

The recent ab-initio structure determination of the polymer electrolyte poly-(ethylene oxide)₆: LiAsF_6 is a notable example of the complex structures that can be determined from powder diffraction on a pulsed neutron source. Polymer

electrolytes consist of salts dissolved in solid, high molecular weight polymers, and represent a unique class of solid coordination compounds. Their importance lies in their potential for the development of truly all-solid-state rechargeable batteries. The structure of the 6:1 complex is particularly important, as it is a region where the conductivity increases markedly and is distinct from all known crystal structures of PEO : salt complexes. The Li^+ cations are arranged in rows, with each row located inside a cylindrical surface formed by two PEO chains, with the PEO chains adopting a previously unobserved conformation. Furthermore the anions are located outside the PEO cylinders and are not co-ordinated with the cations.

■ Neutrons uniquely are able to probe the nature of the magnetic ordering within crystalline solids. In recent years this has been illustrated by the considerable interest in the so-called Giant Magneto-Resistance (GMR) materials, which exhibit significant changes in their electrical resistance under applied magnetic fields and thus have potential applications as, for example, magnetic storage media.

■ The absence of a form-factor for neutron scattering allows diffraction data to be collected to significantly lower d-spacings than its X-ray counterpart. This, coupled

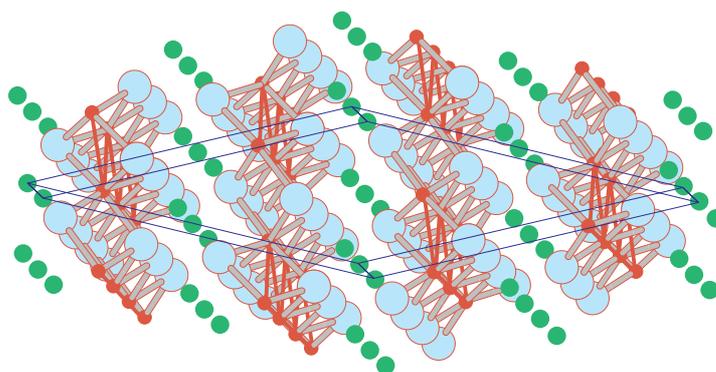


Figure 10. The structure of LiMoO_2 , a potential cathode material for advanced Li batteries.

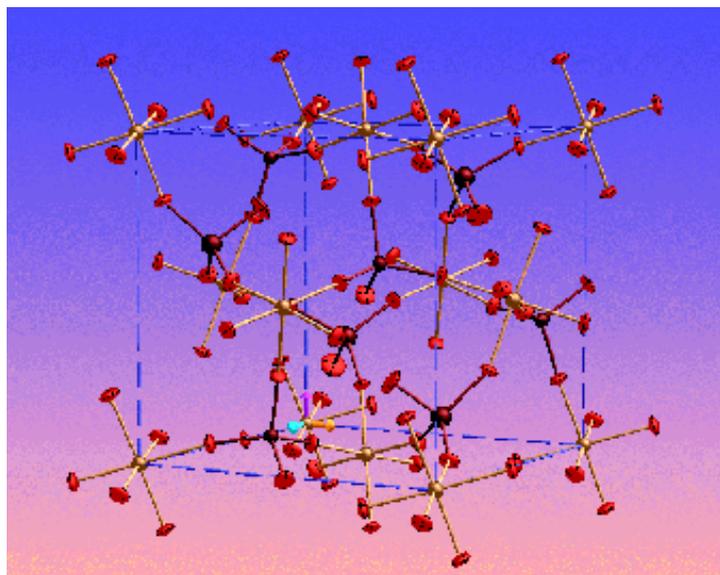


Figure 11. Structure of the negative thermal expansion material ZrW_2O_8 .

with the high flux of epithermal neutrons produced by the ISIS source, allows the chemical occupancies of partially filled sites within the crystal structure to be accurately determined. Such crystallographic information is important for the design of optimised materials using selective chemical doping, such as increasing the superconducting temperature in high T_c materials or maximising the mechanical strength of engineering ceramics.

■ The HRPD instrument at ISIS collects diffraction data with an extremely high resolution of $\Delta d/d \sim 4 \times 10^{-4}$ which is essentially independent of d-spacing. This unique facility has found many applications, including the study of subtle phase transitions and small structural distortions. Such a high intrinsic resolution allows the variation of crystal structure parameters to be determined accurately as a function of temperature, pressure and chemical composition. In a recent study neutron powder diffraction was able to provide a unique insight into the mechanisms of the negative thermal expansion material zirconium tungstate, which contracts on heating over its entire temperature range as a solid (0-1050K) (figure 11).

Structure of solids under very high pressures

The study of materials under extreme pressures has long been an important topic in condensed matter research (figure 12). Pressure and temperature are complementary thermodynamic variables. Temperature allows the effects of entropy to be studied, whereas pressure monitors changes associated with enthalpy. The application of hydrostatic pressure is a very effective means of changing the distances between atoms in a solid. The general 'rule-of-thumb' states that cooling to absolute zero brings about a reduction in sample volume comparable to the application of a pressure of ~ 1 GPa, which is straightforward to achieve experimentally. As a consequence, experimental data describing the evolution of the crystal structures of the elements and simple (i.e. binary) compounds under compression is routinely used to test the reliability of potentials derived ab-initio.

The most effective means of subjecting samples to extreme pressures (greater than, say, 5 GPa) is to use relatively small samples (typically less than 1 mm^3). Neutron diffraction studies of samples under these conditions are desirable to locate light atoms

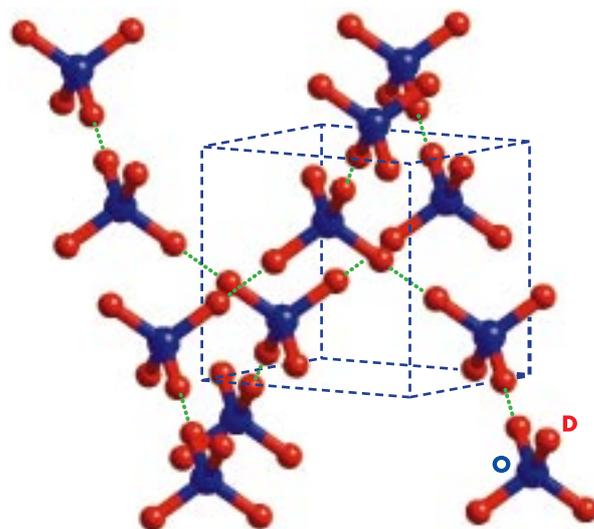


Figure 12. The structure of cubic ice VII, formed at pressures above 2GPa.

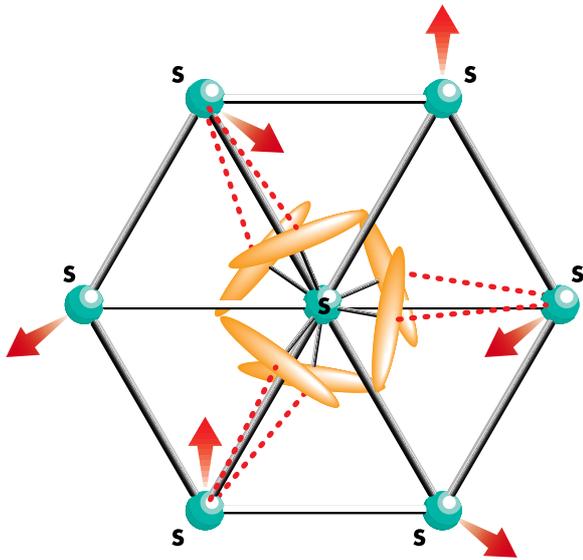


Figure 13. Part of the D_2S high pressure phase I' structure showing a central sulphur atom, the six associated deuterium sites (ellipsoids) and the six nearest neighbour sulphur atoms.

in the presence of heavier ones and to study magnetic ordering. However, the requirement to use small samples suggests intuitively that neutron diffraction will be at a distinct disadvantage compared to its X-ray counterpart for such studies. The flux of X-ray photons produced by a third generation synchrotron source is many orders of magnitude higher than the flux of neutrons at ISIS, even though it is the world's most intense pulsed neutron source. However, over the last decade a collaborative project at ISIS involving the Universities of Edinburgh and Paris has shown that this is not the case. In particular, novel design of the pressure cell allows sample volumes of $\sim 100 \text{ mm}^3$ to be routinely pressurised to greater than 10 GPa. Moreover, optimised design of both the cell and the diffractometer to exploit the inherent characteristics of the ISIS pulsed source allows high-quality diffraction data to be collected in relatively modest counting times (typically a few hours). Specifically, the diffraction experiments at a pulsed source such as ISIS are performed at fixed scattering geometry. The pressure cell then only requires narrow apertures for the incident

and scattered beams, because the detector is not scanned as it would be if the experiment were performed at a monochromatic (reactor-based) diffractometer. Using scattering angles close to 90° and suitable collimation of the incident and scattered beam apertures, it is possible to define an effective scattering volume which lies entirely within the sample volume. This enables the collection of a diffraction pattern from the sample (under its extremely non-ambient conditions) without contamination by spurious peaks from the surrounding pressure cell components.

Earth Sciences

In the Earth Sciences, the application of neutron techniques benefits from the same advantages (see table on page 8) as in many areas of materials research. In spite of this, the Earth and Environmental Sciences have until recently remained relatively uncharted territory for neutrons, perhaps because earth materials are considerably more complex structurally, and frequently they are composed of a number of different phases and compositions. Also, the conditions under which they must be studied push the experimental techniques for attaining high temperatures and pressures to their limits.

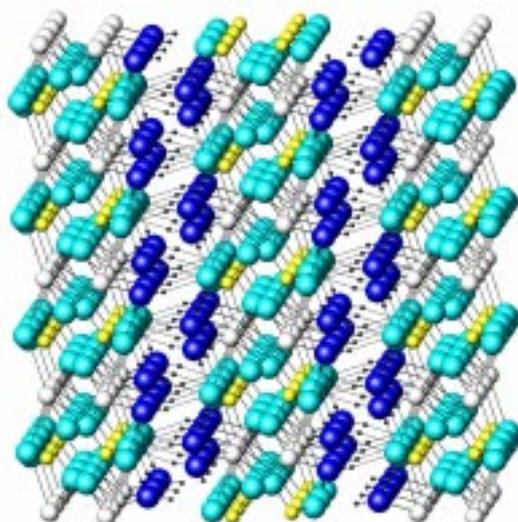


Figure 14. The structure of gypsum.

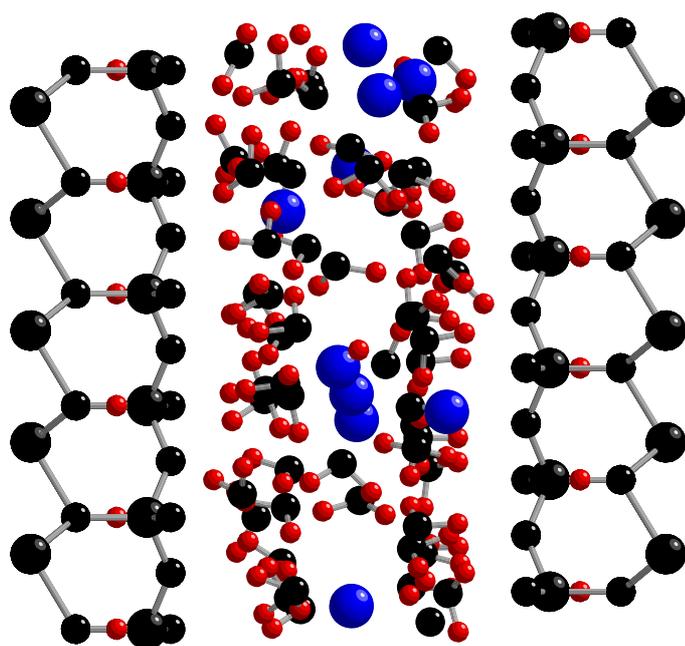


Figure 15. Molecular graphics snap-shot of water within a swelling clay.

However, there has recently been a dramatic expansion of the use of ISIS in this area, and the available instrumentation and analysis techniques have enabled these challenging problems to be tackled.

A notable recent example is the work on cation-ordering in olivines (figure 16), which illustrates how neutron single crystal and powder diffraction can be used to elucidate features of mineral structures and their geophysical relevance. Olivine is a major constituent of the Earth's mantle and it has long been appreciated that the ordering of the cations onto distinct sites in olivine structures is strongly dependent on temperature - this provides clues as to the conditions under which olivine-containing rock was formed. However, attempts to quantify this have long foundered on the requirement for studying quenched samples using, for example, X-ray diffraction techniques. Quenching methods are based on the assumption that rapidly changing a thermodynamic variable (temperature, pressure) can lead to the retention of the phase of interest but under conditions which are more amenable to study. There are many cases where this method can be applied, but in the case of olivine the re-ordering

processes are now accepted to be faster than the accessible quench rates and such studies can be highly misleading - the cation ordering does indeed alter on quenching and the samples studied do not accurately represent the pre-quench conditions. With the possibilities offered by neutron diffraction of performing routine, in-situ studies, the veil has now been lifted on some of the mysteries of this important system. A further advantage of neutron diffraction is the high contrast available between cations close in atomic number, for example Fe and Mn, which are all but indistinguishable using X-rays.

ISIS has been used in both single crystal studies of natural olivines of meteoric origin, and in neutron powder diffraction studies of synthetic olivine samples. In the first case, Italian and ISIS scientists studied a Mg-Fe sample of an olivine from Southern Ireland and discovered that not only was there a gradual preferential ordering of the cations up to ~ 900 °C, but beyond this temperature the preference was reversed, a hitherto unsuspected and unobserved feature which has challenged thermodynamic models of this system. The powder diffraction measurements confirmed these observations in synthetic Fe-Mn samples. The improved quantification of the precise temperature dependence of the effect in the latter case led to the concept of 'Geospeedometry' by which the cation ordering found in olivine

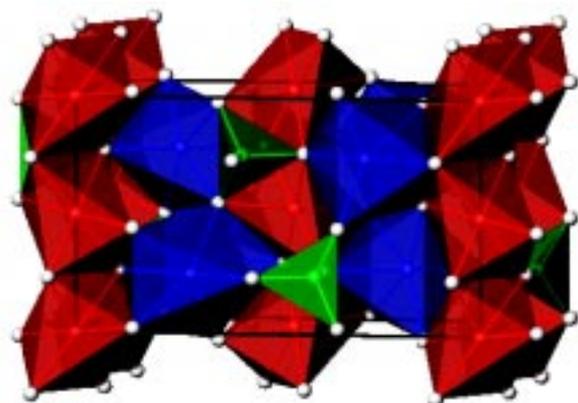


Figure 16. Olivine structure.

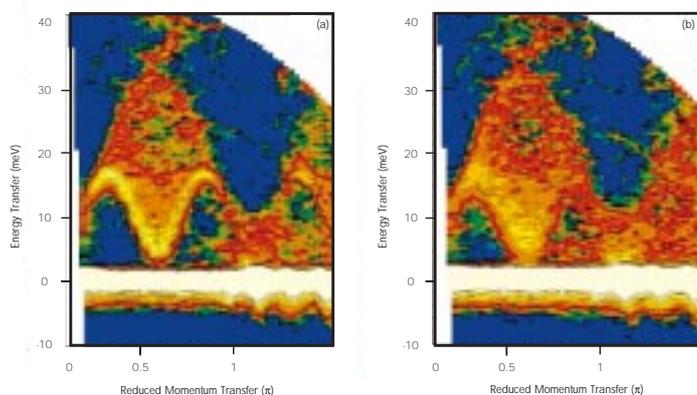


Figure 17. The excitation spectrum of the spin-Peierls system CuGeO_3 at 10K and 20K.

samples can be used to gauge the rate of cooling upon formation of the rocks in which they are found.

Hard Condensed Matter

The impact of neutron scattering in Condensed Matter Physics, which includes magnetism, superconductivity, quantum systems, lattice dynamics and phase transitions, has been of outstanding importance. Neutron scattering often provides the basic atomic and magnetic structural and dynamical information for new materials, such as heavy fermion systems and high-temperature superconductors, and is often concerned with the solution of basic questions in quantum and statistical mechanics in the solid state. One of the highlights of the ISIS scientific programme over the past fifteen years has been the correct determination of the structure of the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. Neutron scattering is the only method for the determination of magnetic structures.

Inelastic neutron scattering experiments also provide rich information on fundamental magnetic interactions that cannot be obtained by other probes and which can be compared to detailed theoretical models. The ISIS spectrometers

have made a major impact in this field, in areas like CMR and high temperature superconductivity. The ability to collect large data sets allows the simultaneous measurement of entire dispersion relations, for example the data collected from the spin-Peierls compound CuGeO_3 (figure 17). Chopper spectrometers allow access to energy transfer ranges that cannot be reached at other neutron sources; consequently the ISIS instruments have been used to study materials such as one-

dimensional chains and spin ladders that cannot be investigated anywhere else in the world. Two examples - the impact of inelastic scattering in the understanding of High- T_c superconductors and CMR materials - are described here in more detail.

High- T_c Superconductors

The parent compounds of high- T_c superconductors, such as La_2CuO_4 (figure 18) or $\text{YBa}_2\text{Cu}_3\text{O}_6$, are insulating

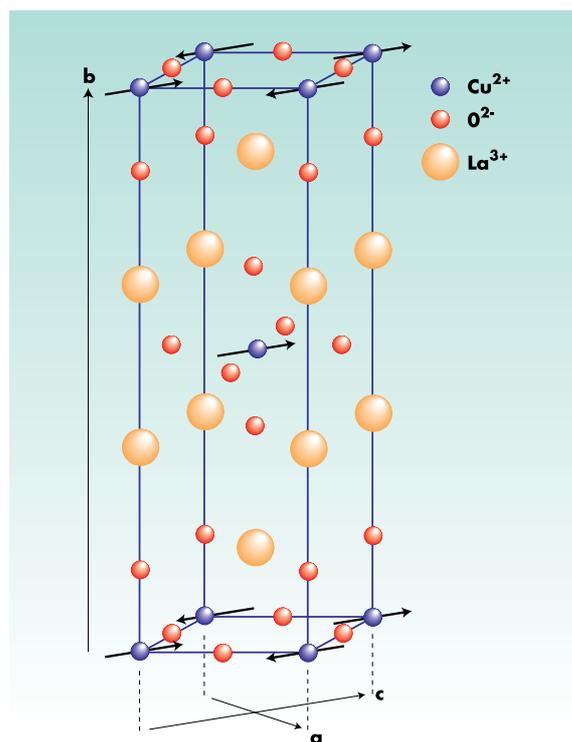


Figure 18. Structure of the antiferromagnetic insulator La_2CuO_4 .

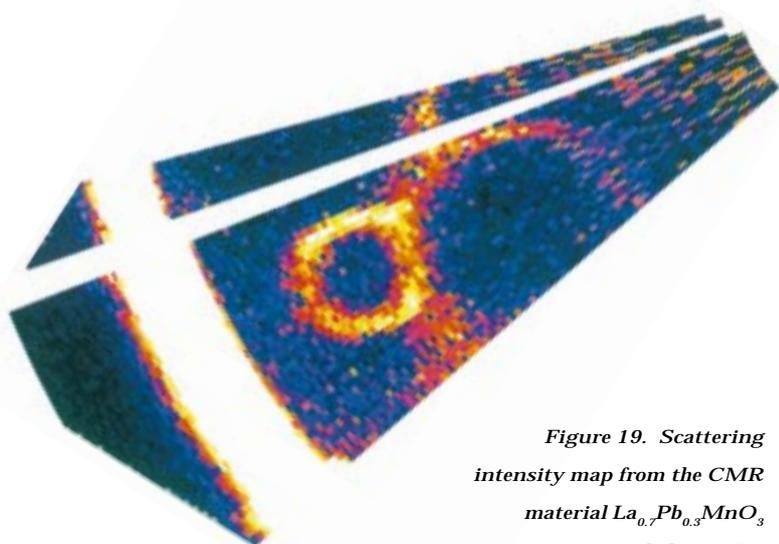


Figure 19. Scattering intensity map from the CMR material $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ recorded on HET.

antiferromagnets, which, when chemically doped with Sr or O to remove electrons from the Cu-O planes in the crystal structure, become metallic and superconducting. While the superconducting compositions no longer show long-range magnetic ordering, strong antiferromagnetic correlations between the fluctuating magnetic moments remain. It is widely believed that these magnetic fluctuations are responsible for the bonding between pairs of electrons responsible for superconductivity. However, the nature, energy spectrum and precise role of the fluctuations in the superconductivity still remain incompletely resolved. Until recently, the spectrum of magnetic fluctuations in the two most widely studied examples, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{CuO}_{6+x}$, appeared to be very different at the energy scale of the bonding between the two electrons in the superconducting pairs. Use of the recently installed position sensitive detectors on the HET spectrometer at ISIS allowed images of the fluctuations to be recorded in the Cu-O planes of $\text{YBa}_2\text{CuO}_{6+x}$. The data show a 4-peaked pattern with the same intensity, orientation and peak separation as in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, revealing a unifying feature in the magnetic fluctuations and suggesting a common explanation for the origin of high T_c superconductivity.

Colossal magnetoresistance

In recent years there has been a huge revival of interest in manganese oxides with the perovskite structure $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$, where RE is a rare earth, for example La, Pr or Nd, and A is a Group-II metal such as Ca, Ba, Sr, Pb. This is because of the massive change in electrical resistance they can display when placed in a magnetic field – over two orders of magnitude in a few Tesla. The interest is not just because of the fundamental physics of metal-to-insulator transitions, but because of the potential technological applications. As with the high temperature superconductors, the undoped parent materials (i.e. $x=0$) are antiferromagnetic insulators, but with sufficient doping, $x=0.2-0.4$, the materials are ferromagnetic metals which become insulating above the Curie temperature. The colossal magnetoresistance (CMR) is displayed at temperatures near T_c , typically 200-400K. Knowledge of the magnetic fluctuations is vital to test models of the interactions between the current-carrying electrons and the magnetic moments of the Mn ions, which lie at the heart of the CMR phenomenon. Several groups from around the world are using the spectrometers at ISIS to investigate these materials. One question is the extent to which a model for the interactions dating from the 1950's is a good starting point to understand the ferromagnetic state. Data taken on HET (figure 19) for $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ show good agreement with the predictions of the model, with a realistic value for the metallic band-width.

Magnetic thin films

Polarised neutron reflection, PNR, is a sensitive probe for the study of both structural and magnetic properties of magnetic thin films and multi-layers. The neutron spin-dependent reflectivities provide an absolute and sensitive measurement of magnetic moments,

distribution and orientation in thin films. It has now also been demonstrated that ‘off-specular’ scattering provides direct information about domain sizes and orientation.

The power of PNR as an absolute layer-sensitive vector magnetometer has been impressively demonstrated in the recent work on the Cu/FeNi/Cu/Co/Cu/FeNi/Cu cobalt / permalloy spin valve structure. At high values of an external field the moments are ferromagnetically aligned. The spin dependent reflectivity data at low fields (50 G), after reverse-saturation, show that the Co layer rotates by 35° from the anti-aligned case. Further 90° rotations of the sample do not reveal the expected four fold symmetry, suggesting that a small but significant uniaxial anisotropy exists. This shows how sensitive measurements are essential for understanding the behaviour in such devices and their extensive applications as sensors, random access memory and disk read-write heads.

Disordered Materials

Disordered materials, which include liquids, glasses and disordered crystalline materials are common in our environment.

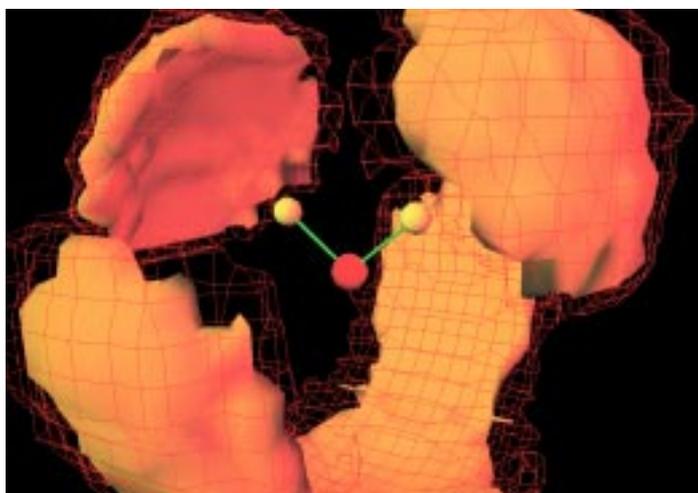


Figure 20. Distribution of molecules in water.

The control of many modern materials’ properties is through disorder and defects. Neutron scattering provides a unique probe of local order and dynamics in such substances, and increasingly it is being applied to more complex samples related to real applications.

The exploitation of isotopic substitution in such neutron diffraction measurements provides a powerful advantage over other scattering probes in determining local structure. The examples described here use the optimisation of the non-crystalline diffraction instruments at ISIS for H/D isotopic substitution measurements.

Structure of high and low density water

The local structure of water (figure 20) has attracted a revival of theoretical interest in recent years. These new approaches all predict an anomaly in the thermodynamics at 220K and 1 kbar, indicative of a structural phase transition.

From measurements on SANDALS using H/D isotopic substitution, the O-O partial structure factors were obtained at three different densities. The changes seen in these partial structure factors have all the hallmarks of a structural phase transition

occurring within the liquid as the density of the liquid increases. The principal finding is that, whereas the inner near-neighbour shell of water molecules is almost unchanged with the application of pressure, the second and subsequent shells collapse inwards by about 1 Å for the higher density form of water compared to the low density form. It is therefore clear that whatever may happen at lower temperatures near the postulated anomaly, where the liquid is only metastable or may not exist at all, some form of structural

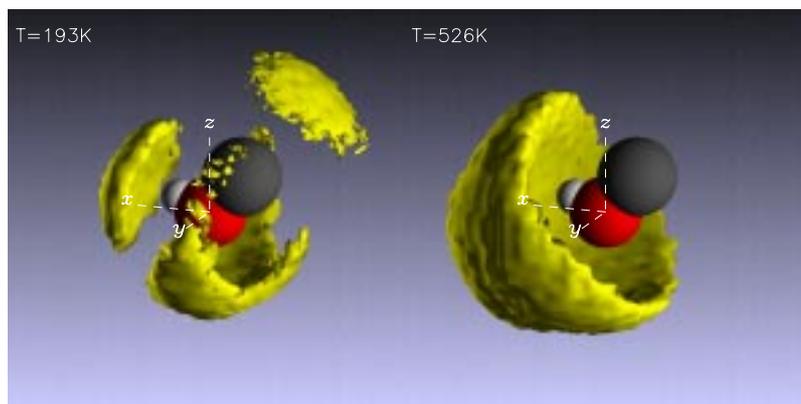


Figure 21. Spatial density of methanol molecules around a central molecule.

transition does occur even in stable water with increased pressure. Other recent diffraction evidence indicates that the equilibrium between the two structures is easily affected by adding ions and other solutes to the water. It is very likely that the structural balance between the two forms of water plays a pivotal role in determining the degree to which solutes will phase separate, associate or dissolve when mixed with water.

Structure of water around ions and molecules in solution

Non-crystalline diffraction and H/D isotope substitution allows specific ionic or

molecular sites to be identified, and the structure of water around those sites to be explored.

Around positive ions such as sodium, water molecules tend to line up with their dipole moment vectors pointing away from the central ion. There is, however, a distinct distribution of orientations, and it is found that while the most probable orientation is along the ion-water molecule axis, significant fluctuations about this direction occur, with the water molecule rotating about an axis parallel to its own plane, making the average orientation closer to 20°. For negative ions such as chlorine on the other hand, the hydrogen bonding nature of water molecules prevails, with one of the OH bonds on the water molecule pointing directly towards the ion, albeit again with a significant distribution of orientations, primarily this time about an axis perpendicular to the plane of the water molecule.

For hydrophobic species such as methane, the observed orientations are exactly out of phase with those seen for ions. In this case, for orientations which derive from rotations about the axis parallel to the water molecule plane, the dipole moment

tends to point more towards the solute, while for orientations derived from rotations about the perpendicular axis, the dipole moment vector tends to point away from the solute. Thus in either case no hydrogen bonds form with the central methane. Quantification of these orientations from neutron diffraction data presents a powerful constraint on possible models of the aqueous systems under consideration.

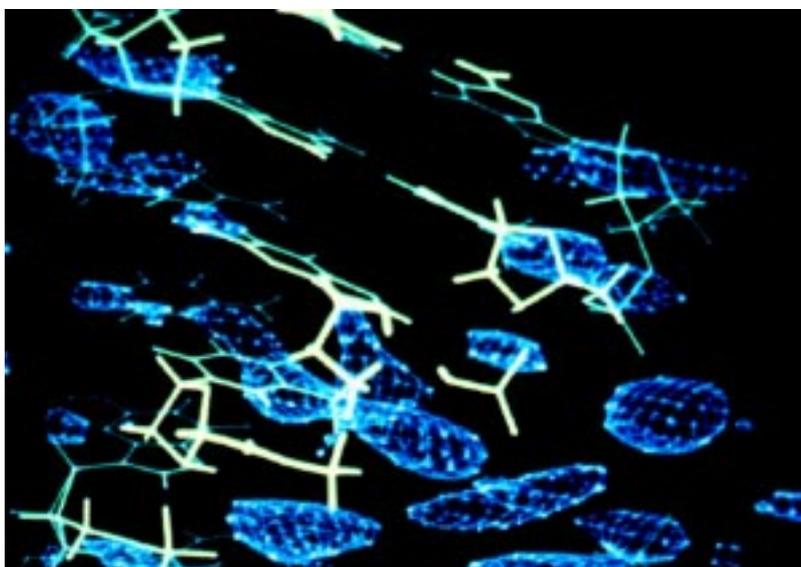


Figure 22. Structure of water around DNA.