EXPLORING MATTER WITH NEUTRONS

highlights in research at the ILL

Institut Laue Langevin, Grenoble, France

EXPLORING MATTER WITH

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foreword

Left to right: ILL directors Dirk Dubbers, Christian Vettier and Colin Carlile

Progress in science increasingly depends on observing and measuring subtle effects in ever more sophisticated experiments. It is vital, therefore, that central facilities like ILL provide instrumentation and resources that match users requirements. With this in mind, we have now set in place an ambitious programme the Millennium Programme to upgrade ILL s instruments and infrastructure to new standards of excellence, and to attract new users. The programme will be implemented in two parts over the next 10 years, and aims at improving the overall instrument performance by a factor of 10. This will allow our user community to carry out new types of highly sensitive experiments not possible before. The programme is not yet finalised but we have already started the upgrade of a first group of instruments. We hope to continue with other instruments and to renew the neutron guides. These refurbishments will especially benefit those areas of research that are currently creating a great deal of excitement amongst the scientific community, either because they have tremendous commercial potential such as electronics, catalysis, pharmaceutical development, materials and engineering, or are at the frontiers of knowledge such as magnetism and particle physics.

The ILL has an exciting future ahead. However, we can also look back at the many successes over the past 30 years. In the pages that follow you will find a cross-section of recent results which illustrate the range of research carried out at ILL. I hope you enjoy reading about them.

Professor Dirk Dubbers Director

About the ILL

The Institut Laue Langevin (ILL) in Grenoble, France, is a major international facility for scientific research, operating the most intense continuous source of neutrons in the world. It possesses a wide range of instruments for carrying out simultaneously many different kinds of experiments to investigate the structure of matter at a microscopic level across the disciplines of biology, materials science, engineering, chemistry and physics.

About 1200 scientists visit the Grenoble site every year to work with our on-site scientists in carrying out cutting-edge research. Although much of the research is in fundamental science, a substantial amount is of direct industrial relevance. Neutron scattering experiments have made significant contributions to our understanding of the structure and behaviour of biological and soft condensed matter, to the design of new chemicals such as drugs and polymers, and to materials used in electronics and structural engineering. Neutron studies also offer unique insights into the nature of complex systems at the most fundamental level.

ILL was founded in 1967 as a bi-national enterprise between France and Germany with the UK joining later in 1973. As well as these three Associate Members, six Scientific Members now participate in ILL: Spain, Italy, Switzerland, Austria and Russia, and more recently the Czech Republic. The Institute has a German director (Dirk Dubbers) and two associate directors, one from France and one from the UK (Christian Vettier and Colin Carlile).

introduction to neutron scattering

Neutrons are excellent probes of all kinds of matter. They are more penetrating than X-rays and provide complementary information on structure and dynamics

Neutrons are subatomic particles found in the nuclei of atoms. They are emitted during certain nuclear processes including the fission of uranium-235 so can be obtained from a nuclear reactor. Like all subatomic particles neutrons obey the laws of quantum mechanics, which means they behave like waves as well as particles. The wavelength of neutrons (tens of nanometres) corresponds to the distances between atoms and molecules in solids and liquids. Consequently when they interact with matter for example, a regular array of atoms or molecules in a crystal lattice the neutron waves are reflected, or scattered. Waves reflected from similarly oriented planes of atoms in the crystal interfere and re-inforce each other periodically to produce a characteristic diffraction pattern (like water waves on a lake that meet after being reflected off two rocks). The pattern can be recorded as a series of peaks of the scattered neutron intensity, which provides information about the position of the atoms and the distance between them.

There are many variations of the scattering process which gives the technique its wide applicability to many different kinds of materials. For instance, the structure of larger molecular or atomic assemblies such as biological membranes, polymers, engineering structures and minerals, can be studied by measuring very small angles of scattering (the wider the distance between atoms the smaller the angle of reflection). This is called small angle neutron scattering (SANS) and requires a special, very long instrument to resolve the small angles.

Neutrons scatter off hydrogen atoms quite strongly (unlike X-rays) so are also used to establish their positions in biological materials, particularly those containing water (H_2O). What is more, hydrogen scatters very differently from its heavier isotope, deuterium. This means that selected components in a structure can be highlighted by substituting hydrogen with deuterium. The degree of isotopic substitution can also be controlled such that the scattering strength in one part of a structure is the same as in the surrounding medium, rendering it invisible so that another part of the structure stands out in contrast .

As well as determining structure, neutron scattering also reveals the motions of atoms and molecules via an exchange of energy between the neutrons and the sample (inelastic scattering). Very small changes in energy measured at low temperatures may also be used to measure subtle quantum processes in exotic materials.

Neutrons also have a spin, or magnetic moment, which can interact with the electron spins in magnetic materials. Beams of polarised neutrons (in which all the spins are aligned) offer a unique tool for characterising exotic materials with complex magnetic structures an area of growing interest.

Another area of increasing importance, is the study of thin films and multilayers. Many of the most important biological, chemical and electronic/magnetic phenomena occur at surfaces and interfaces. Under appropriate experimental conditions, neutrons can be reflected off surfaces and interfaces so that the depth of the layers and their structure and dynamics can be determined.

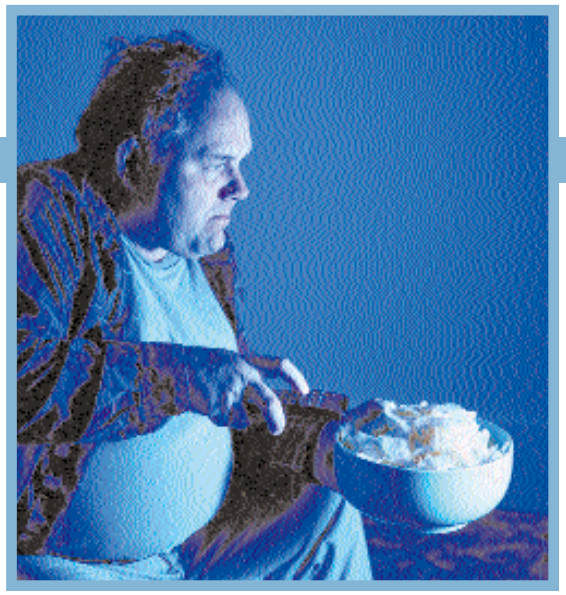
Finally, the neutron itself is used to investigate the laws of Nature. ILL has facilities to prepare beams of neutrons of very low energies (cold neutrons) for extremely precise experiments on gravity and on particle properties significant in developing a unified theory of the fundamental particles and forces of the Universe.

Neutrons help fight obesity

Studies revealing the shape and structure of a molecular complex involved in fat digestion could lead to new slimming drugs

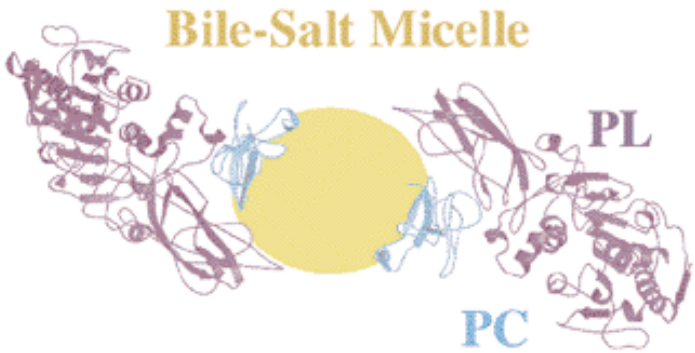
biology

DAVID PIGNOL & PETER TIMMINS



Mammals, including humans, digest food with secretions produced in several organs along the digestive tract – the salivary glands in the mouth, the stomach, the gall bladder, the pancreas and the intestine. The secretions contain enzymes which break down the complex food molecules – proteins, fats and carbohydrates into simpler molecules that can then be absorbed into the bloodstream.

We are particularly interested in the way fats are broken down. The reason is that the process is quite complicated. Ninety-five per cent of fats in the Western diet consist of molecules known as triglycerides which, because they do not dissolve in water, exist in the form of oily droplets. To be digested, an enzyme produced by the pancreas called pancreatic lipase (PL) must first attach itself to the oil globules. However, PL can't act alone. Its molecular shape is such that its so-called active site – the area in the enzyme structure where the triglyceride would interact and be broken up – is hidden away. Two other components are needed to unmask the site and help the enzyme adsorb onto the droplet surface. These are colipase, which forms a complex with PL, and bile salts which solubilise the fatty acids from the triglyceride breakdown to form minute spherical structures called micelles.



Calculated model of the active complex built with two lipase/colipase molecules per micelle corresponding to observed crystal structure

Analysing the active complex

We wanted to understand at a molecular level how these components come together to form an active complex. A technique called small angle neutron scattering, as described on page 3, is ideal for investigating large molecular structures such as this one. By using a method called contrast variation, we could visualise specific parts of the complex whilst other parts remain invisible. The principle behind this is the same as the familiar school laboratory experiment whereby sugar is slowly added to water in which is immersed a glass rod. At a certain sugar concentration the glass rod becomes invisible because it has the same refractive index as the sucrose solution. In other words, light is scattered equally by the glass and the solution. We say that there is no 'contrast' between the rod and the solution. In the case of neutron scattering, heavy water is added (water in which hydrogen is substituted by its heavier isotope deuterium, D_2O). So, for example, when the water contains 10 per cent heavy water to 90 per cent ordinary water, the lipase and colipase are visible and the bile salt invisible.

Using these techniques we have been able to show that the complex contains two molecules of colipase attached to each pancreatic lipase molecule and they are connected and stabilised by a micelle of the bile salts. The model of the complex is shown in the Figure.

This knowledge could enable us to design drugs that can prevent the complex from forming in the first place and thus limit the amounts of fat assimilated by the body. Our colleagues in Marseille are currently conducting preliminary clinical studies using rats. 1

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Highlighting the composition of cellulose

Cellulose is an extremely important composite material. Even after more tha 20 years of extensive research its structure is not well understood. Inelast neutron scattering may offer some of th missing clues

HELMUT SCHOBER, CHRISTOPH CZIHAK & MARTIN MULLER

The bio-material cellulose is found everywhere. All plants and certain marine animals and bacteria contain cellulose, as do the materials we use derived from plants, such as wood, paper and textiles. Despite being an important resource, we still have much to learn about its structure. Cellulose is a composite carbohydrate with a basic molecular structure consisting of a chain of 1000 to 20 000 linked glucose (sugar) molecules. In the native state, these polymer chains tend to align into compact needle-like crystals called microfibrils which are stabilised by weak hydrogen bonds and electrostatic forces and are about 0.01 micrometres across (see Figure 1). In between the microfibrils, are regions where the chains are arranged in a disorderly way. Cellulose fibres like the plant material flax consist of bundles of many microfibrils.

Microfibril structure

However, not only is the crystal structure of the microfibrils still controversial but also the exact way these microfibrils are held together. Are they glued together by a few disordered polymer chains lying on the surfaces of the crystals or by more extended regions of disordered cellulose polymers? This information is important because the mechanical properties of cellulose strongly depend on the arrangement of crystalline regions and disordered regions within the material.

A combination of the neutron inelastic scattering method and the contrast variation method, described on the previous page, offers an excellent probe. Inelastic scattering happens when some of the energy of the incoming neutrons is absorbed by the atoms in a material, as they oscillate during the scattering process, causing a change in the energies of the scattered neutrons. This change in energy reflects the characteristic vibrations of the atoms depending on how they are bonded to their immediate molecular environment. At the same time, by substituting certain hydrogen atoms with deuterium in chosen regions of the material we can render the disordered regions invisible and highlight the dynamic response the spectrum of atomic vibrations of just the crystalline microfibrils, and vice versa.

From these results we found that neutron inelastic spectra of the disordered parts of cellulose were distinctly different from those of the crystalline parts, closely resembling that of completely disordered artificial cellulose. These spectra therefore constitute true signatures of the respective parts of cellulose. The universal character of these signatures indicates that the disordered regions are similar in all types of this material and do not depend on its source. From the amount of hydrogen that can be substituted by deuterium we also concluded that the disordered regions are mainly formed by the surfaces of the crystallites.

These results will be useful in the industrial processing of cellulose and for understanding how cellulose is made in plants. 1

Figure 1 (left) Hierarchical organisation of cellulose. The polymer (top left in figure) aggregates to cellulose nano-crystallites, which are interconnected by disordered interface layers (bottom right). These crystallites are organised in microfibrils of diameter 2 to 20 nanometres (bottom left)

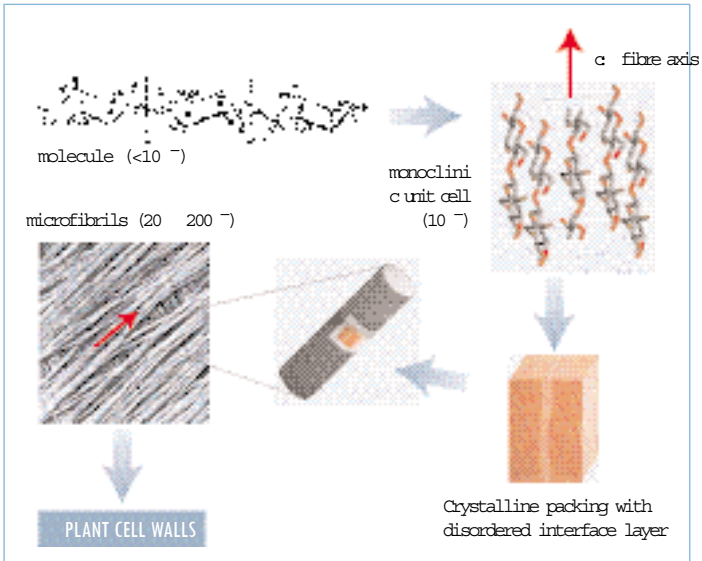
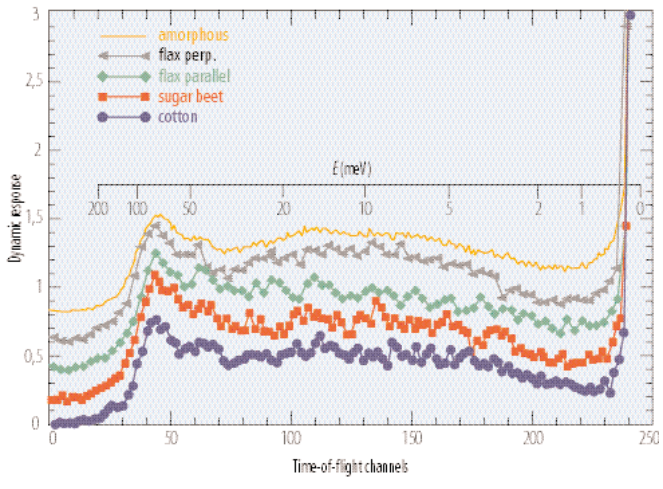


Figure 2 (below) The dynamic response of disordered regions of cellulose samples of different origin



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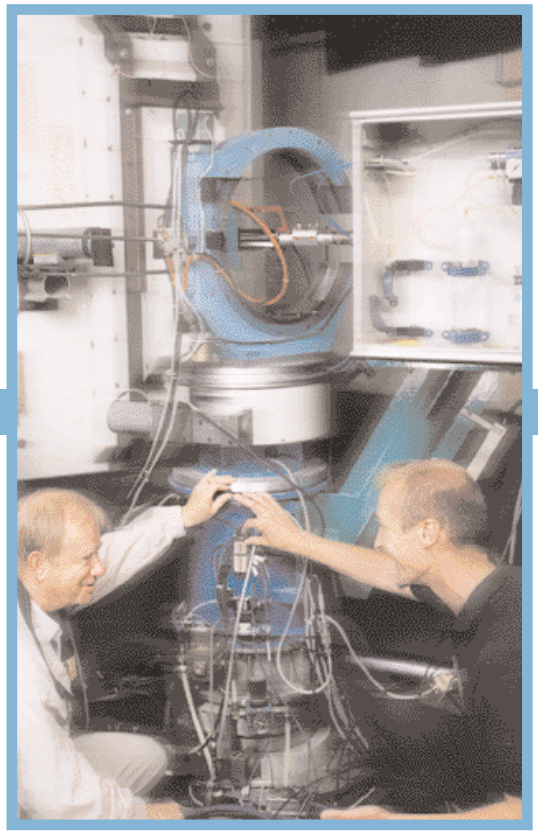
Neutron fibre diffraction offers an excellent way to study the intricate bonding in natural polymers like cellulose

biology

New insights into cellulose structure

HENRI CHANZY, PAUL LANGAN & YOSHIHARU NISHIYAMA



Instrument D19 at ILL

Cellulose is often said to be the most abundant polymer on Earth. It is certainly one of the most important structural elements in plants and other living systems. In Nature it occurs as slender rod-like crystalline microfibrils. One of the key features of cellulose is that each of the units making up the polymer bears three hydroxyl groups (OH). It is these hydroxyl groups and their ability to bond via weak hydrogen bonding that not only play a major role in directing how the crystal structure forms but also in governing important physical properties of cellulose materials.

Cellulose can occur in a number of different forms. Natural cellulose is known as cellulose I, but other forms such as cellulose II, cellulose III and cellulose IV have been described. We are involved in a long-term study at ILL to unravel the fine details of these different forms.

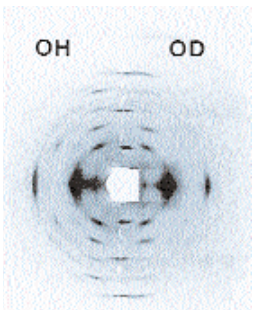


Figure 1 A comparison of the two diffraction patterns of cellulose from normal and deuterated cellulose

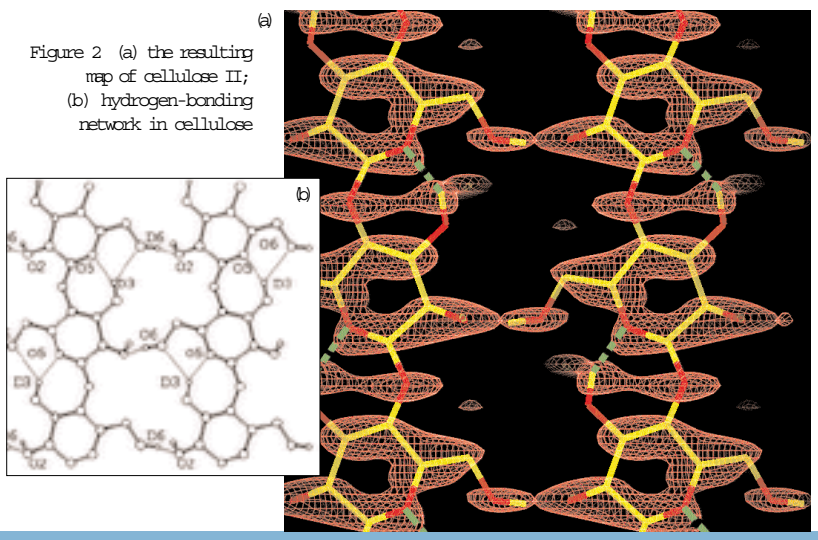


Figure 2 (a) the resulting map of cellulose II; (b) hydrogen-bonding network in cellulose

Importance of hydrogen bonding

Neutron diffraction provides the only method that can offer a detailed visualisation of the hydrogen bonding network in cellulose fibres. The experiments were carried out on an instrument called D19. This is the only instrument in the world that can carry out this sort of study (in the past it has also been used to carry out work on other biological molecules such as other polysaccharides, DNA, filamentous viruses).

The idea behind the experiment is simple. Neutrons are fired at the sample of cellulose and the pattern of neutrons scattered by the sample is recorded. This pattern can be used to determine the structure of the cellulose. Since hydrogen atoms cause significant scattering of neutrons their position in the cellulose can be determined as well. To be absolutely sure of the process, crystalline fibres were also prepared in which the hydrogen in all the OH groups were replaced by deuterium (deuterium scatters neutrons even more strongly than hydrogen does) and the same diffraction experiment repeated.

Recently we studied cellulose II fibres that result from the swelling of fibres in concentrated sodium hydroxide in this way. There were two suggested model structures. Studies using X-ray crystallography could not distinguish between the two models. Using our neutron diffraction data we were able to decide which of the models was correct.

Figure 1 shows the diffraction patterns recorded from cellulose II. The left half of the picture shows the diffraction pattern recorded from normal cellulose and the right half shows that from deuterated cellulose (each picture has been cut in half and they are shown side by side for comparison). The differences between these two patterns arise from the hydrogen/deuterium atoms alone. These patterns were used to calculate maps that show where the hydrogen atoms are located. Figure 2(a) shows the map, and Figure 2(b) shows the hydrogen bonding network in cellulose that was determined from it. This study is the first three-dimensional description of a hydrogen bonding system in a fibrous polysaccharide. [1]

Research team H. Chanzy (CERMAV-CNRS, Grenoble), Y. Nishiyama (Univ. Tokyo), P. Langan (Los Alamos National Laboratory), T. Forsyth (ILL)

A new model of a biological membrane


Giovanna Fragneto-Cusani (right) with colleagues, Laurence Perino and Isabelle Grillo

A new model for studying cell membranes is helping researchers to understand how these important structures work

biology

GIOVANNA FRAGNETO-CUSANI

All living cells have an outside wall, or membrane, formed mainly from lipids. These long-chain molecules consist of a head which likes water and a hydrocarbon tail that hates water. They align in a double layer, or bilayer, with the tails tucked away inside an internal impermeable core and the heads pointing outwards so as to form a protective barrier permeable only to certain very small molecules. The structure of the bilayer plays an important role in the activity of the cell and is very complicated. For example, the membrane also contains proteins which act as guardians regulating what goes in and out of the cell, and whose behaviour is influenced by changes in the lipid bilayers. Such systems are difficult to study at the molecular level.

To study membrane structure and behaviour more easily, researchers resort to simple models of bilayers, in particular those based on a class of lipids called phospholipids. We have succeeded in preparing a new, and we think improved, model system a phospholipid bilayer freely floating in water, which will enable us to study interactions between membrane bilayers and molecules like proteins.

A double bilayer on a surface

The model was created by assembling two bilayers (double bilayer) on a flat solid surface in contact with water. The first bilayer is strongly adsorbed on the surface and the second the free bilayer floats just above it. At a certain temperature depending on the composition, phospholipid bilayers change from a gel phase, where the lipid chains are rigid and well-ordered, to a fluid phase, where the chains are disordered. In cells, membranes are fluid and fluctuate in structure, but since it is more difficult to deposit fluid bilayers on solid substrates we formed the bilayer in the gel phase and then raised the temperature to get in the fluid phase.

We then used neutron reflectivity measurements to follow the evolution of the system. Neutrons are reflected off an interface just like light. Our experiment consisted in bouncing a neutron beam off the bilayers at the solid/water interface and collecting the reflected neutrons on a detector while rotating the sample. The signal from the reflected neutrons at the different angles was analysed to obtain the structure at the interface.

The reflectivity curves obtained at different temperatures, both in the gel, at the transition point and in the fluid phase, are shown in Figure 1. Those curves were interpreted by using mathematical models (continuous lines in Figure 1). This allowed us to determine the structure of the bilayers very precisely. Results are shown in Figure 2.

Around the transition point between the two phases we observed a giant swelling (a big increase of the thickness of the water layer between the two bilayers) and an increase in the unevenness of the free bilayer. Well above and below the phase transition the systems present a similar structure and in both phases they are stable. This means that the fluid phase of the free bilayer is suitable for investigating the interaction of lipids with proteins. Moreover, the giant swelling might be the first direct observation of a phenomenon theoretically predicted more than 20 years ago.

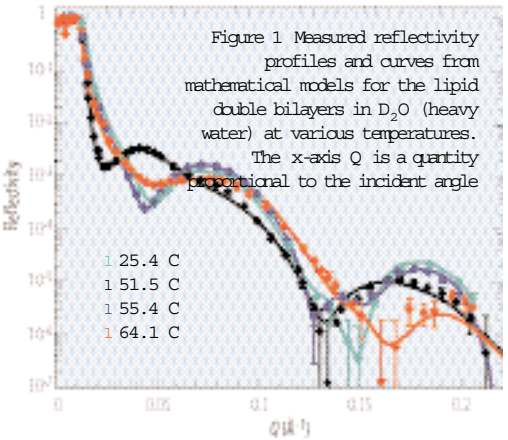


Figure 1 Measured reflectivity profiles and curves from mathematical models for the lipid double bilayers in D_2O (heavy water) at various temperatures. The x-axis Q is a quantity proportional to the incident angle

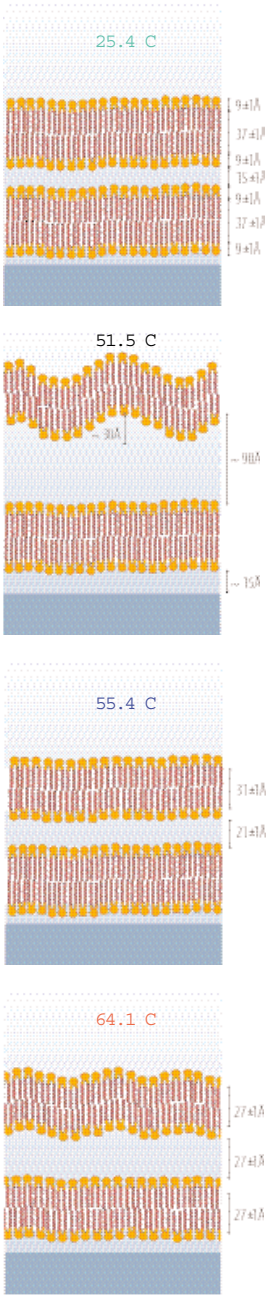


Figure 2 Possible interpretation of models that fit the data measured

Research team G. Fragneto and E. Bellet-Amalric (ILL), F. Graner and L. Perino-Gallice (UJF, Grenoble), T. Charitat (ICS, Strasbourg)

Neutron reflectivity reveals much more about the structure of multilayer lipid membranes than was previously thought possible

Mapping lipid membranes

biology

Christian Münster & Tim Salditt

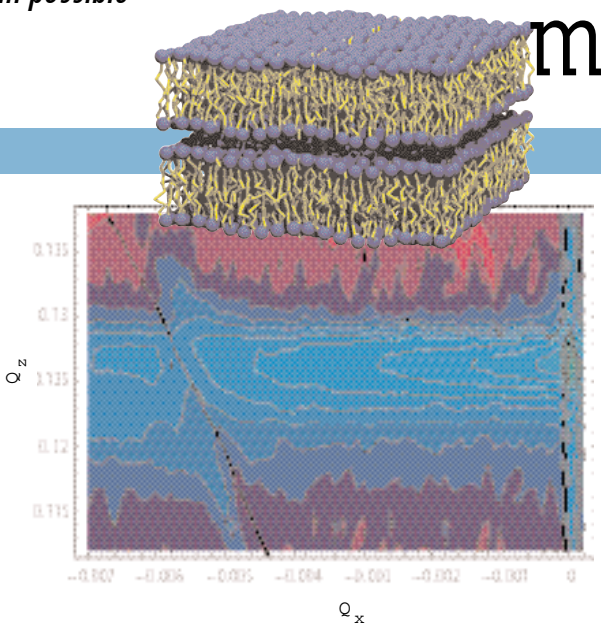


Figure 1 (a) Sketch of two lipid bilayer membranes; (b) scattering pattern of a stack of multilamellar phospholipid membranes

Lipid bilayers (see page 7) are the basic building blocks of biological membranes. Understanding their physical properties such as their elasticity, small dynamic fluctuations, and the intermolecular interactions that govern how they assemble is extremely important in various research areas, including engineering synthetic biomaterials and drug development.

In this last context, the interaction between lipid bilayers of cell walls and antimicrobial peptides (short-chain proteins) is of particular interest, since the latter show broad antibacterial, fungicidal and . However, the structural ing the interaction are nderstood. We are, therefore, al physical properties in model lipid systems with and without antimicrobial peptides such as Magainin derived from the skins and intestines of frogs.

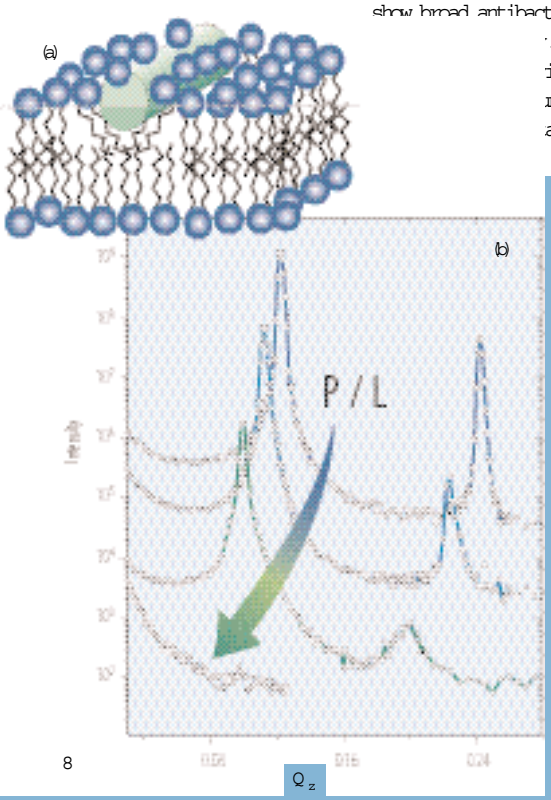


Figure 2 (a) A peptide P (green) adsorbed on the lipid bilayers L (blue); (b) reflectivity curves at increasing peptide concentration from top to bottom: pure lipid (P/L=0), P/L = 0.025, 0.05, 0.1. The peptides affect the multilamellar order

When combined with the contrast variation method described on page 4, neutron reflectivity offers unique possibilities for studying the structure of lipid membranes at the molecular level. Specular scattering, when the angle of reflection equals the angle of incidence, gives information on the vertical profile of lipid membranes the thickness of the layers, the roughness of the interfaces between the layers, and so on. But there is also the possibility of observing diffuse, nonspecular scattering which reflects properties along the surface or interface such as lateral fluctuations, elasticity, and density variations in the layers.

Using specular and nonspecular scattering

By preparing the sample on a transparent silicon substrate, with the neutron beam incident from either the air or substrate side, the diffuse scattering can be measured for a range of positive and negative angles of incidence and exit. This method gives previously inaccessible information on the lateral membrane structure, in particular, concerning thermal fluctuations.

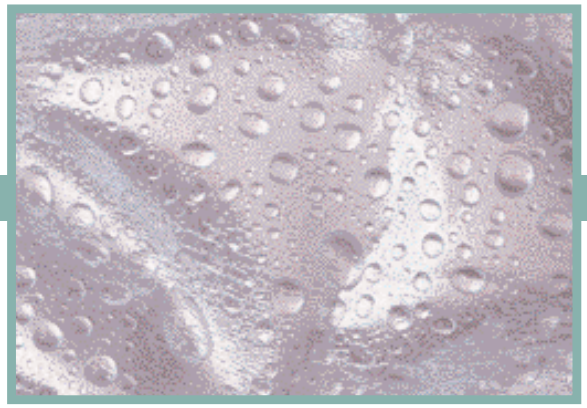
For the experiments, samples of stacks of several thousand bilayers had to be oriented perfectly on a silicon substrate. The samples were either partially hydrated (there is a water layer of 1 to 1.5 nanometres between membranes) and kept at constant temperature in a humidity cell or completely immersed in water.

The samples produced a tremendous amount of diffuse intensity reflecting the softness of the system. The data obtained (Figure 1) on the specular reflections showed that the average distance between the lipid bilayers is 4.98 nanometres corresponding to a water layer of about 1.4 nanometres between adjacent membranes. The nonspecular, diffuse scattering pattern reveals the range of fluctuations in the layers and how they correlate across several adjacent layers. These results can then be compared with those predicted from theoretical models.

When antibacterial peptides such as Magainin are inserted in the lipid layers we noted that there were drastic changes in the specular and nonspecular reflectivity as the ratio of peptide to lipid increased. This was a result of the distortion of the lipid membranes inflicted by the presence of the peptide. The data also provided information on the configuration of the peptides with respect to the lipid bilayer. We demonstrated that this technique can reveal lateral structures on length-scales from a nanometre up to several millimetres. In the future we hope to apply this same method to many interesting lipid membrane-based materials, including lipid/peptide, lipid/protein or lipid/DNA systems. l

Research team C. Münster, and T. Salditt (Univ. Munich), B. Bechinger (MPI Biochemie, Martinsried), R. Siebrecht and V. Leiner (ILL and Univ. Bochum)

A new tool to observe ultra-thin polymer films



Extremely thin polymer films are finding use in many high-tech areas. A new advanced neutron scattering technique can probe their structure and chemical composition

PETER MULLER-BUSCHBAUM

Polymer films are used in many applications such as coatings and increasingly in electronics. With miniaturisation becoming the major technical driver in most advanced technologies, ultra-thin polymer films will be increasingly in demand. However, as the thickness of the film is reduced to that close to the polymer s molecular dimensions, its properties change from those of the bulk material. To achieve an even thinner film, the polymer molecules must be confined or squeezed and thus their conformation the internal arrangement of atoms is changed. This so-called confinement is not only limited to single polymer films but also those fabricated from polymer mixtures.

To investigate such confined polymer films requires rather special experimental techniques. Atomic force microscopy (AFM) which relies on a microscopic probe to feel the polymer s topology at atomic resolution can be used but is limited to very small areas of the sample. Neutron scattering methods therefore have to be applied in order to obtain a statistically representative description of the film. Unfortunately, the thinness of the sample means that the diffraction signals obtained by passing the neutrons through the film are too weak to measure. The trick is instead to reflect the neutron beam off the polymer film at grazing angles of about 1 degree (see Figure 1). We have been developing this method (grazing incidence small angle neutron scattering, GISANS) to obtain scattering signals that reveal peaks at positions characteristic of the polymer film s structure.

Dewetting in polymer films

One experiment showing the potential of this technique was the investigation of the dewetting of confined polymer films. Dewetting is frequently observed in daily life, for example, when rain dewets on a car windscreen a once-continuous film breaks up into spherical drops. Using GISANS we could study a confined polymer film, measuring the average diameters of the droplets and the distance between them. The results gave similar values to those obtained with AFM (Figure 2). A simple theoretical model, describing the dewetting of thicker films also supported these results.

In samples of polymer blends GISANS can also be used to distinguish the chemical structures and geometrical arrangements of the different polymer phases using the contrast method described on page 4. Again hydrogen is substituted with deuterium in one polymer.

Naturally, the technique is not limited to polymer samples. It opens up new possibilities to probe the topology and chemical composition of any type of sample surface. 1

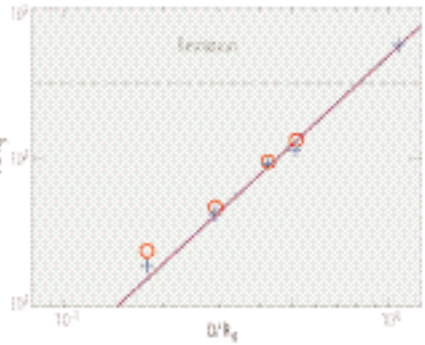
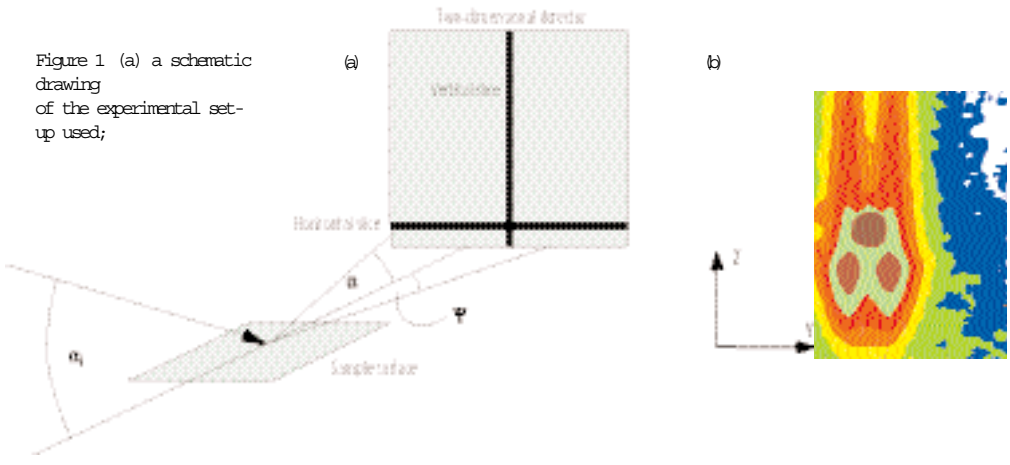


Figure 2 GISANS (circles) and AFM (crosses) give similar data which are described by a simple theoretical model (solid line)

Figure 1 (a) a schematic drawing of the experimental set-up used;



Research team P. M ller-Buschbaum and W. Petry (TU Munich), J. S. Gutmann, O. Wunnicke and M. Wolkenhauer (MPI Polymerforschung Mainz), R. Cubitt (ILL), M. Stamm (IPF Dresden)

Pouring tomato sauce or washing-up liquid out of a bottle involves complex changes at the molecular level, as neutron experiments are revealing

Detergents, foods and pastes understanding their flow

soft matter

SIMONA BARE AND ADRIAN RENNIE

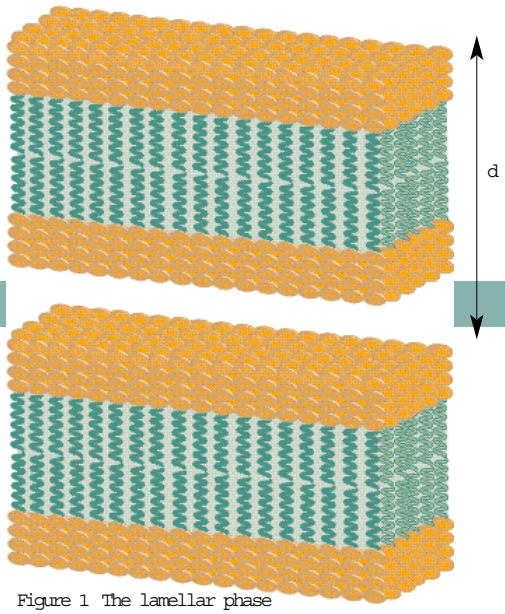


Figure 1 The lamellar phase structure of surfactants showing the inter-lamellar spacing d used to determine the orientation

Many familiar materials such as thixotropic paints, foods like tomato ketchup, the mineral and latex dispersions used to coat paper and detergents are colloids. These are dispersions of particles or aggregates of molecules suspended in a fluid. A common feature of most of these materials is that the viscosity changes with the rate of flow. The pressure required to maintain a flow decreases as the shear rate, or gradients in speed of flow, increases.

The industrial importance of these liquids has meant that scientists have made considerable effort to understand the behaviour of these materials in terms of the structure and interactions of the particles and the fluid. Neutron scattering provides many advantages in this work because it can probe the particles at the required dimensions in the range of 1 nanometre to a few micrometres. Exploiting the contrast obtained by substituting deuterium for hydrogen in molecules, as described in previous articles, allows particular structural regions to be located. A class of materials that we are particularly interested in, which also behaves rather like the particulate systems, are concentrated dispersions of surfactant (for example, soap) molecules in water. These are the sort of material used in detergents or shampoos. At high concentrations they form bilayers, like the lipids mentioned on the previous page, that pack into layered sheets, or lamellae (see Figure 1).

Experiments with detergents

We were interested to know how the lamellae were oriented to the direction of flow at different shear rates and at different concentrations. A full study of this problem clearly requires measurement of the orientation in all three spatial dimensions (see Figure 2). For this study a special cell that could maintain uniform shear flow was used that could be rotated in all directions in the neutron beam. The diffracted neutron intensity from the bilayer structure can then be used to monitor the alignment of the surfactant layers.

We carried out the experiments with a non-ionic surfactant called $C_{12}E_4$ in heavy water. When we measured the orientations of the lamellae we found that there was a large difference between samples with 40 per cent of surfactant by weight and those with 60 per cent. Surprisingly the 60-per-cent sample showed a maximum in the alignment at an angle of about 45 degrees to the flow direction as shown in Figure 3. This behaviour had not been seen in previous experiments on surfactants but does resemble that seen in dispersions of rigid, plate-like particles. 1

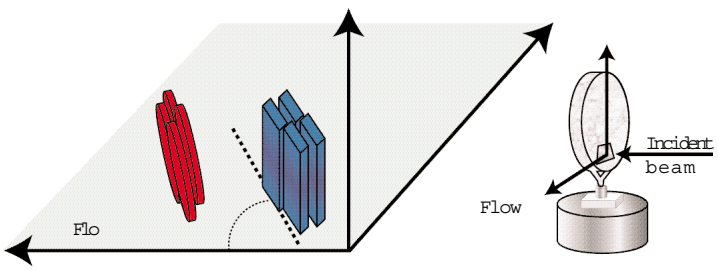


Figure 2 Orientation of particles or lamellae in a shear flow. The alignment with respect to the sample cell can be measured by rotating it in the beam

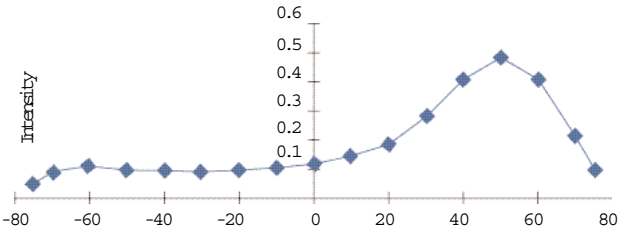
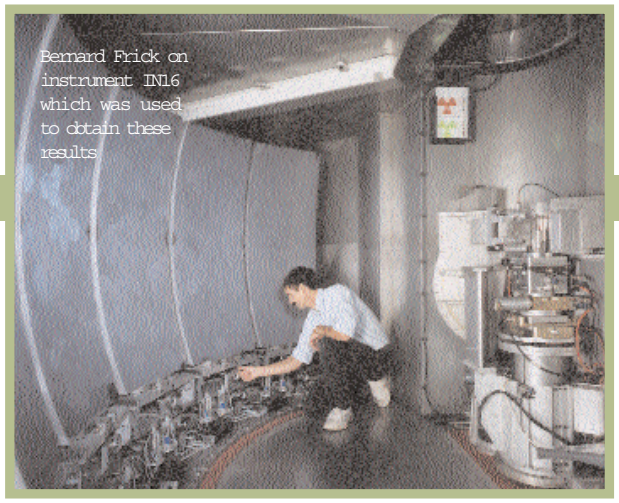


Figure 3 Plots of the normalised diffracted intensity against the angle for $C_{12}E_4$ at 60 per cent weight and a shear rate of 30 s^{-1}

Research team S. Bare and A. R. Rennie (Kings College London), E. Bellet-Amalric and G. Fragneto (ILL)

The glass transition made easy


Bernard Frick on instrument IN16 which was used to obtain these results

An international team has been carrying out experiments to test a conceptually simple model of how a supercooled liquid changes to a glass

F. JAVIER BERMEJO

As has been known since the days of the famous French chemist Joseph Louis Gay-Lussac (1778-1850), a pail of pure water left outside during winter may avoid freezing into an ice block if the temperature decreases fast enough through the freezing point. The state attained by the liquid under such conditions is referred to as metastable . This means that it takes just a small perturbation to push the liquid into the state that s the most stable under the ambient conditions, in other words, normal ice. For many substances, subsequent cooling of this metastable state usually referred to as a supercooled liquid leads to a transformation into a solid phase known as a glass, which shares some physical properties with many everyday materials such as window glass.

The details of how the atoms or molecules move within a supercooled liquid, as well as the mechanisms which drive the solidification of the liquid into the glass phase (glass transition), have mesmerised scientists for many decades, and the topic has been identified as one of the main challenges in the field of condensed matter. Very active research during the past few decades has led scientists to realise that the behaviour of glasses and supercooled liquids is also shared by a good number of objects, which span from disordered crystalline materials to cosmological black holes.

The hard-needle model

The characteristics of these disparate systems in particular, the way the motions of the particles composing the supercooled liquid come to a halt when approaching the glass-transition temperature can be described by a conceptually simple model (Figure 1). This is a system of hard, infinitely thin needles which sit on the nodes of a cubic crystalline lattice and may rotate freely.

To profit from this analogy and understand glass transitions better, our research group (a team of European and American physicists) decided to find a real material that behaved like the hard-needle model and then study what happens as it approaches the glass transition. Fortunately, a common material, pure ethanol, exists in two forms, or phases, that behave just like the hard-needle model above and below the glass transition (Figure 2). Both are crystalline with the molecules sitting at the nodes of a cubic lattice. However, in one phase the rotator phase the molecules can rotate like the needles. In the other phase, this orientational disorder has become frozen in. The fact that the glass transition from the first phase to the second involves molecular rotations only, while preserving the overall crystal structure, gives us an opportunity to describe this phenomenon just in terms of the possible molecular reorientations within a cubic crystal environment a much simpler situation than in a supercooled liquid in which the molecules are free to move around.

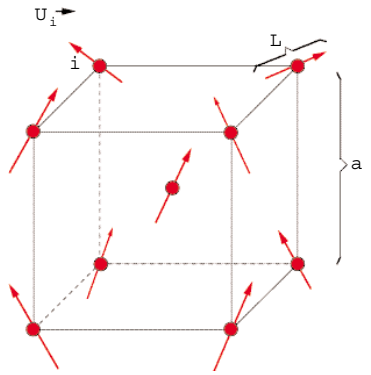


Figure 1 A system of hard-needles sitting on the nodes of a body-centred cubic lattice a simple model for particles approaching a glass transition

We used quasielastic neutron scattering which measures very small energy changes to study the change in dynamics through the rotational glass transition in the ethanol phases and compared the spectra obtained with those calculated for the hard-needle model. We found that rotational freezing within the real material is closely mimicked by that shown by the hard-needle model. The implications of such a finding are far-reaching since it shows that this glass transition can be understood in terms of a purely dynamic phenomenon. l

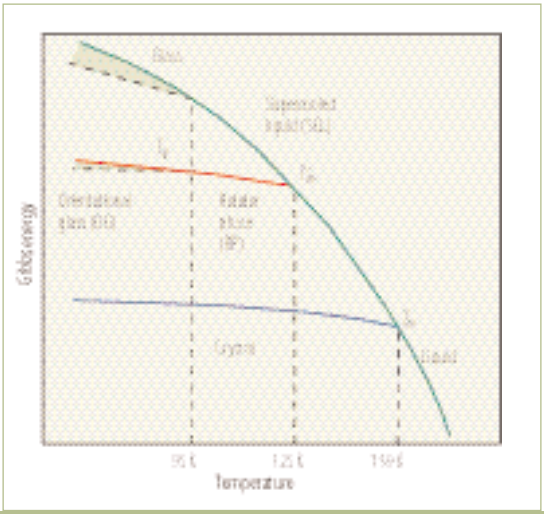


Figure 2 The Gibbs free-energy of the different phases of condensed ethanol

Research team M. Jim Ønez-Ruiz, A. Criado, F.J. Bermejo and C. Cabrillo (CSIC Madrid), F.R. Trouw and R. Fern Ández-Perea (Argonne National Laboratory), H. L wen (Univ. D sseldorf), H.E. Fischer (Orsay), G.J. Cuello (ILL)

A team of German and Italian scientists has been investigating sound propagation in water, which should help shed light on its complex physical and biological behaviour

The sound of water

CATERINA PETRILLO

Water is certainly the most common substance in our everyday world but, most importantly, it is vital to the existence of life. Because of the basic role that water plays in living systems, it is one of the most studied liquids. And because of its complex and unique characteristics it is also one of the most fascinating. One of the properties of water that deserves detailed investigation is its dynamic behaviour – how the constituent molecules vibrate – which is known to affect biological systems. For example, the functions of biological molecules are driven by the interplay of the vibrational and diffusional motions of the surrounding water molecules. A weak type of bonding called hydrogen bonding links these water molecules together into complex networks. It also links water to biological molecules such as proteins. Many of the complex dynamic characteristics of water are thought to be related to hydrogen bonding.

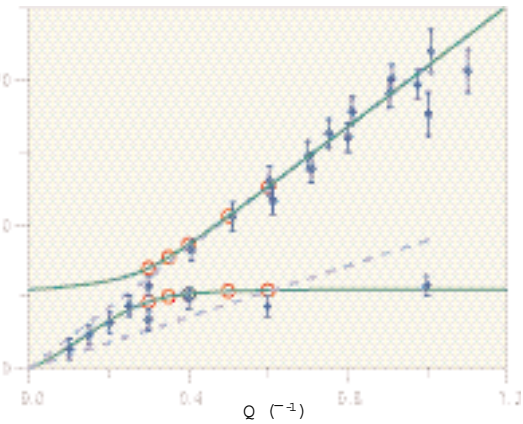


Figure 1 The energy of the different vibrations in water. The lines are deduced from the neutron scattering experiment; the dots are the results of the previous X-ray experiment. The dashed lines represent the expected behaviour of the sound waves when the velocity is assumed to be about 3000 metres per second or 1500 metres per second

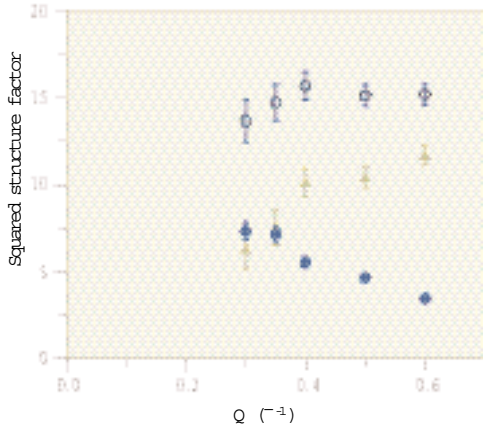


Figure 2 The intensity of the different vibrations in water. The dots represent the intensities of the low-frequency vibrations, the triangles those of the high-frequency vibrations, and the open symbols the sum of both

Strange acoustic vibrations

It turns out that at low frequency the molecular vibrations correspond to the normal sound, which can be heard by humans. These vibrations often extend up to frequencies as high as 1 terahertz (one million million vibrations a second) and are responsible for many properties of liquids. In the case of water, however, researchers have observed that the velocity of these high-frequency sound waves is much greater (about 3000 metres per second) than that of normal sound (about 1500 metres per second). Scientists consider this effect quite anomalous and they had not yet been able to offer a simple explanation.

Inelastic neutron scattering is often used to study the vibrations of atoms, as mentioned on page 5, and it is this technique that we used at the ILL to investigate the vibrations in water. We employed heavy water because deuterium atoms are much stronger scatterers than hydrogen, and are comparable to oxygen in this respect, thus giving us a strong neutron spectrum for analysis. Analysing the results of the neutron scattering experiment, we have been able to give a good account for the strange behaviour of the high-frequency molecular vibrations in water. We have identified two different vibrations, that reflect the presence in water of small groups of molecules tightly bound together. There are the vibrations inside each group of molecules (these are optical vibrations, so-called because they diffuse optical light) and the high frequency sound which allows the vibrations of one group to propagate to another group of molecules (acoustic vibrations).

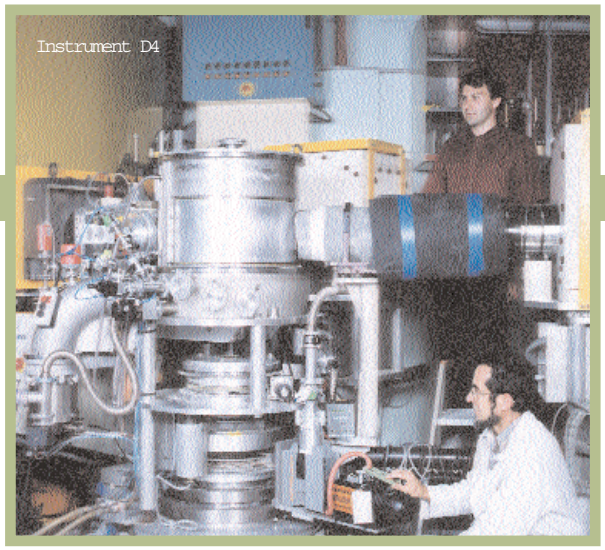
We have been able to compare the energies of the different vibrations (Figure 1) with previous data obtained from the companion technique of X-ray scattering, an experiment performed at the nearby European Synchrotron Radiation Source in Grenoble. It has been particularly satisfying to see that the neutron scattering results give a more complete account of the X-ray data. The neutron scattering experiment also enabled the measurement of the intensity of the two vibrations at different wavelengths, as shown in Figure 2.

Research team C. Petrillo and F. Sacchetti (INFM, Perugia), B. Dorner (ILL), J. B. Suck (TU Chemnitz)

Super cool water!

Water is a surprisingly complex substance forming many structural variations in different physical environments. Under certain conditions, it can even remain liquid at 40 degrees below its normal freezing point!

JOHN DORE



The properties of water and ice are familiar to everyone and the simple chemical composition, H_2O, is the first (and in some cases the only!) formula that anyone learns at school. Yet, the behaviour of water is still not well understood. Its structure at a molecular level is remarkably complex as the result of interactions between the water molecules called hydrogen bonding. These weak forces are, for example, responsible for the arrangement of molecules in the normal crystalline form of water, hexagonal ice. Each molecule has only four nearest neighbours leading to an unusually low density, which is why ice floats on water.

Hydrogen bonding also influences the structural properties of liquid water, as neutron or X-ray scattering studies reveal. The pattern for most liquids changes very little with temperature over the whole of the liquid range. Water, however, is different. It is much more sensitive to temperature which affects the hydrogen bonding and thus the relative positions and orientations of neighbouring molecules.

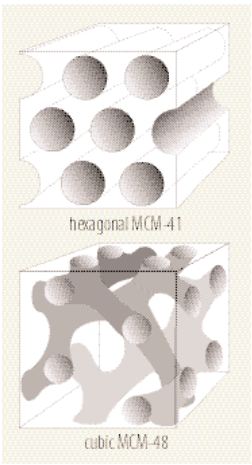
One interesting feature is that liquid water can be cooled well below its normal freezing point. Various studies have shown that the degree of hydrogen bonding increases in this metastable regime, leading to a more random network structure characteristic of a low-density glassy ice formed when water is condensed onto a cold plate at temperatures lower than 140K. The properties of bulk super-cooled water in this region are more like a gel than a liquid.

Water in a solid matrix

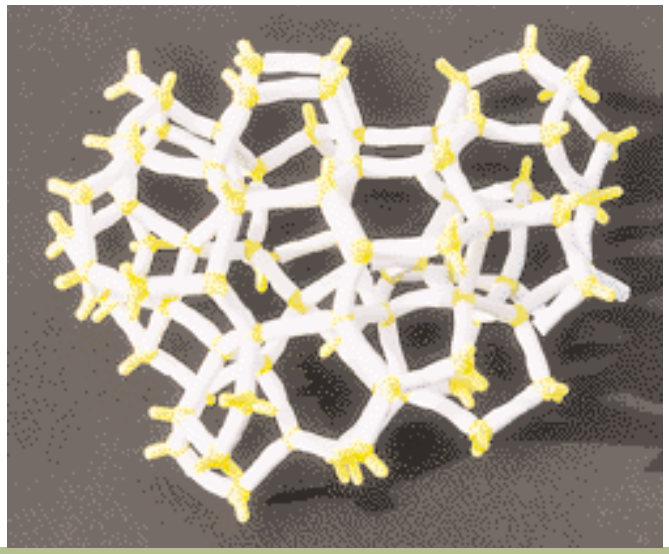
We have found that a similar effect occurs, quite naturally, when water is confined in the pores of a solid matrix, such as a mesoporous silica with a pore size of about 10 nanometres. Furthermore, the water remains in the liquid state below its normal freezing point, eventually forming a defective version of cubic ice instead of hexagonal ice. The formation of cubic ice was unexpected as it is metastable in the bulk state, converting to hexagonal ice above 200K.

The depression of the freezing point is greater in the smaller-sized pores, and recently we found that we could super-cool water even further by confining it in a new type of ordered mesoporous silica (see right) with pores between 2.5 to 3.5 nanometres across.

Neutron diffraction studies with heavy water performed on ILL instrument D4 over a range of temperatures revealed that the water remains liquid down to 235K and then undergoes a reversible transformation to cubic ice. This low-temperature state of water offers the possibility of investigating water properties in a very unusual condition. The enhanced network connectivity due to the hydrogen bonds means that the properties are very different from those of normal water. However, the water structure remains delicate in the sense that it is easily modified by environmental influences. It is therefore conceivable that these features are significant in defining the behaviour of confined or interfacial water in biological systems. Water does seem to have some perplexing characteristics but there is no doubting the important influence that it has over our lives! 1



The geometry of mesoporous MCM silicas; a) hexagonal, b) cubic



A schematic model of low-temperature water based on the structure of low-density amorphous ice

Research team J. Dore (Univ. of Kent, Canterbury), C. Haggenmüller (Univ. München), P. Behrens (Univ. Hannover), H. Fischer (Orsay)

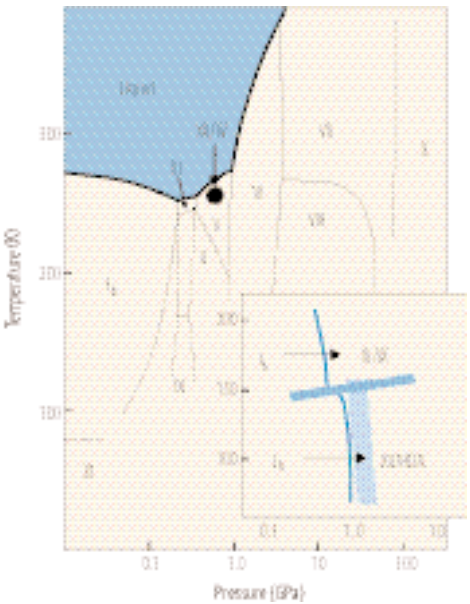
Water exists in an extraordinary number of forms, some of them discovered only recently. Neutron scattering experiments are helping researchers to understand the subtle forces that govern the transitions from one form to another

The many phases of water

chemistry & structure

MICHAEL KOZA & HELMUT SCHOBER

Although, water has been the object of extensive experimental and theoretical investigation it still rewards us with new and unexpected properties. Because of its hydrogen-bonded molecular network (as mentioned in the previous article) the structure of crystalline water (ice) is strongly influenced by pressure and temperature. To date, not less than 12 different ice phases (structural forms) are known. The stability of these phases over a range of temperatures and pressures can be shown on a so-called phase diagram (see right). The hexagonal form is the stable one at ambient pressure. Several ice phases are metastable in their region of existence on the phase diagram, transforming into more stable forms of ice if we wait long enough.



The phase diagram of water; 1represents the region in which ice XII has been observed (temperature: 260K; pressure 0.55: gigapascals). Note that this region is fully surrounded by ice V

Transition of ice XII towards hexagonal ice upon heating. The top photograph (a) shows ice XII as recovered from the pressure cell at low temperature. In contrast to high-density amorphous ice it has a milky appearance. The following photographs show the flocking of ice XII as it transforms to the lower density forms cubic ice and hexagonal ice (b and c)

(a)

(b)

(c)

Melting ice at -200 C

Researchers discovered so far two distinctly different non-crystalline (amorphous) forms of ice containing random networks of water molecules, and only recently also the twelfth crystalline ice phase. Called ice XII, it was produced at about half a gigapascal pressure (equivalent to a load of 5 tonnes per square centimetre!) and a temperature of -13 C. XII is built up from seven and eight-membered rings of water molecules leading to an incredibly dense structure. The two amorphous phases were found at much lower temperatures. High density amorphous ice (HDA) is produced by compressing hexagonal ice by applying a pressure of at least 1 gigapascal at temperatures of about -200 C. On heating to -150 C HDA transforms into a low-density amorphous phase (LDA). One interesting question here is whether the collapse of hexagonal ice to HDA is analogous to melting at normal pressures and temperatures where a slight pressure applied to the delicate open structure of hexagonal ice at just below 0 C causes it to liquefy (the molecular mobility involved, though, in this melting is orders of magnitude slower). Can we therefore think of HDA as a type of frozen liquid water but existing at -200 C?

There is another intriguing aspect of the new phases. Having been observed in totally different regions of water s phase diagram, the amorphous phases and ice XII were originally thought to be unconnected. However, HDA was found to be contaminated with an unidentified crystalline phase. Using ILL instruments we have since shown that the phase is in fact ice XII! This implies that from an stability poin of view the formation of HDA competes with that of ice XII. B altering the compression rate it is possible to favour the production of either ice XII or HDA. Under rapid compression the formation of ice XII dominates.

Ice XII, therefore, is more common in water s phase diagram than originally thought, existing in at least two separate regions. The study of the conversion of hexagonal ice to ice XII contributes valuable clues to the understanding of the formation of amorphous and crystalline phases under pressure. Crystallisation implies a reorganisation of water s hydrogen-bond network. This requires a high molecular mobility as can be provided by transient melting. More experiments are certainly necessary to determine definitely the lowest temperature at which such melting can occur. 1

Research team M. M. Koza, A. T lle and F. Fujara (Univ. Dortmund), H. Schober and T. Hansen (ILL)

Oil generation in fractal rocks

A view of the detector tube of the 80-metre small angle scattering instrument D11

Neutrons can penetrate porous rocks, revealing their 'fractal' nature and how trapped organic matter is transformed into oil which then seeps out of the rock. These findings help companies prospecting for oil

materials

ANDRZEJ RADLINSKI & PETER LINDNER

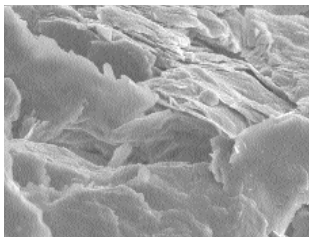
Sedimentary rocks are dirty systems. They are formed from a mixture of organic and inorganic debris deposited in an aqueous environment of lakes or marine incursions, in other words, from mud. The mud gets buried and compacted at elevated temperatures over geological periods of time. The resulting sedimentary rock develops a pore system through a long and complex redistribution of matter between its solid and liquid components. In the end, many types of sedimentary rocks have a fractal structure, which means that on average their pore structure looks the same at any magnification. This has been long recognised by traditional geology, where various objects are used to define the scale of rocks shown in photographs.

On the microscale, cold (low energy) neutrons are much better than the direct imaging techniques (like optical or electron microscopy) to detect fractal microstructure in rocks. The imaging techniques reveal an overwhelming wealth of detail on every scale, and time-consuming statistical analysis of many images needs to be done to determine the general characteristics of the averaged rock micro-structure. In contrast, neutrons penetrating rocks are naturally sorted according to the internal microstructure averaged over the volume of the entire sample (typically 1 centimetre square and 0.1 centimetre thick).

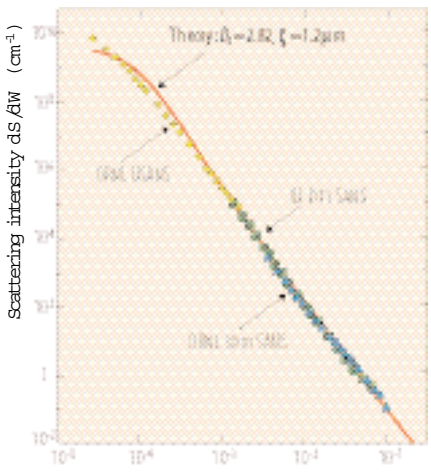
Rock micro-architecture

We have used small angle neutron scattering (SANS), see page 3, at ILL and at the Oak Ridge National Laboratory (ORNL) in Tennessee to determine the major properties of rock micro-architecture the internal surface area of the pores and their fractal scaling. When applied to petroleum geology, the SANS technique can detect the deformation of the pore space caused by the internal pressure due to the thermally-driven decomposition of large organic molecules into hydrocarbons, as well as observe the consequent transport of these hydrocarbons through the increasingly larger pores. We observed these phenomena in both the natural and laboratory-prepared series of rocks, and used them to predict the extent of oil generation in recently-drilled oil wells. The figure below illustrates how extensive the fractal properties of a sedimentary rocks can be. The figure shows a combination of SANS data taken on three different ILL and ORNL instruments. It may be seen that all three data sets overlap smoothly with no adjustable parameters. To our knowledge, these data represent the largest range to date over which fractal behaviour has been observed in a natural system. Such an extent of fractal microstructure in a rock is remarkable, when compared with the limited size range over which the fractal properties are usually observed typically 1.3 orders of magnitude.

This study extends the widest fractal length range previously observed in sedimentary rocks, which covered two decades (orders of magnitude) in length scale and 7.5 decades in intensity, and shows that sedimentary rocks are in fact one of the most extensive fractal systems found in Nature. As observed in Physical Review Focus: the constancy of the fractal dimension over so many scales is astounding, considering what a messy, heterogeneous material sedimentary rock appears to be ... this study will enhance the idea that you can describe rock with simple concepts ... There will be certain bona fide uses of fractal concepts, and one of them will be in the geological sciences. 1



Scanning electron micrograph of an oil-bearing sedimentary rock



SANS data from sedimentary rock showing that the pore-rock interface is a surface fractal over three orders of magnitude in length-scale and 10 orders of magnitude in cross-section (intensity)

Research team A. P. Radlinski (Australian Geological Survey Organisation, Canberra), E. Z. Radlinska (The Australian National University, Canberra), M. Agamalian and G. D. Wignall (Oak Ridge National Laboratory), P. Lindner and O. G. Randl (ILL)

Experiments at ILL using newly developed equipment are following the microstructural changes in nickel-base alloys at high temperatures. The work will help to optimise industrially important materials

Probing the hidden strength of alloys

GERNOT KOSTORZ

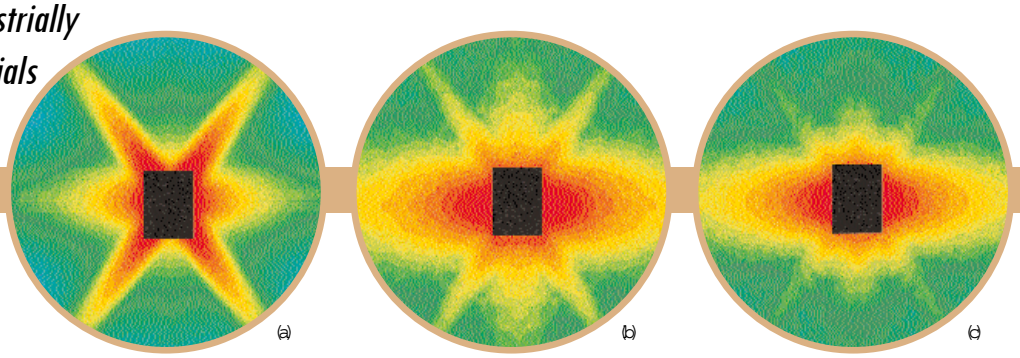


Figure 2 Small-angle scattering of nickel-rich nickel-titanium single crystals homogenised at 1440K and aged in situ for (a) 46 minutes at 1240K, (b) 10 minutes at 1220K, (c) 43 minutes at 1200K. One cuboidal main axis is the horizontal direction. The inclined streaks are perpendicular to the close-packed planes of the face-centred cubic structure of the matrix

Nowadays, nickel-rich alloys are widely used in structural components which are exposed to very high temperatures. The so called nickel-base superalloys have a particularly high mechanical strength and are very resistant to corrosive environments. They are used, for example, to make turbine blades or chemical-reaction vessels. The high-temperature strength of these alloys is primarily due to very strong, often microscopically small crystalline particles, or precipitates, which are embedded in large numbers in the nickel-rich matrix.

The technological development of superalloys is quite advanced, but there is still a broad need for reliable experiments to understand better the basic physical processes underlying the changes that the precipitates might undergo during use – changes in size, shape and population. The longevity of structural components depends on the stability of an optimised microstructure under various environmental changes.

Because the precipitates are a nanometre to a micrometre across, small angle neutron scattering is extremely useful to study their structure and behaviour (see page 3). Recently, our research team at the ETH Zürich, together with researchers at ILL and the Hahn Meitner Institut in Berlin, have developed a new device – a high-temperature cell in which samples of alloy can be studied with neutrons while being subjected to conditions similar to those in real processing. For example, we can follow what happens as the precipitates form during heat treatment by monitoring the small-angle scattering patterns over time.

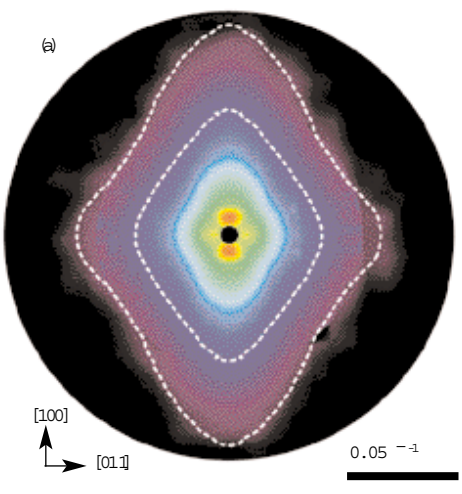


Figure 1 (a) Small-angle scattering pattern measured on D11 for a nickel-rich nickel-aluminium-molybdenum single crystal aged for 3 hours at 1073K. The dotted lines represent lines of equal intensity as calculated for a cuboidal precipitate; (b) outline of the best-fitting cuboidal shape. The size is about 20 nanometres

Microstructure of superalloys

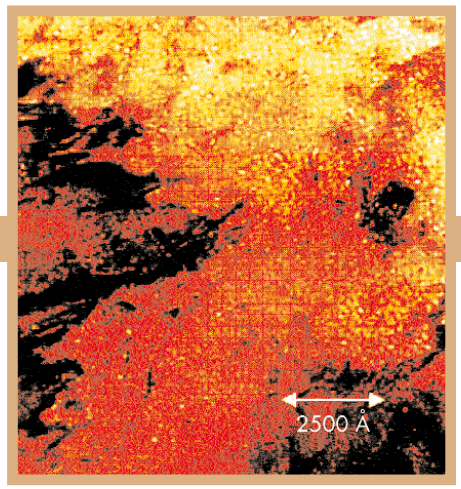
Our recent experiments have focused on investigating the microstructure of alloys of nickel with aluminium and molybdenum. The strength of these alloys is influenced by how well the dimensions of the crystal lattices of the ordered precipitates and the surrounding matrix match. The molybdenum serves to modify any mismatch between precipitates and matrix. A large mismatch introduces strain into the material and affects the rate at which the precipitates grow. We know from electron micrographs that when the mismatch is small, precipitates are almost spherical, but they become cuboidal (with rounded corners and edges) with increasing misfit. We followed the evolution of the size and shape of the precipitates with small angle scattering at various temperatures. Figure 1 shows the results for one particular situation.

Titanium is another element often incorporated in nickel alloys. Like those with nickel and aluminium, nickel-titanium alloys also form ordered precipitates. The precipitation sequence is, however, more complex. While in the case of aluminium the cuboidal precipitates are the final precipitate phase, with titanium they are only an intermediate stage, and an ordered hexagonal phase develops after sufficient ageing. Again, small-angle scattering experiments offer insight into the development of the microstructure. The small-angle scattering patterns of single crystals reveal the different symmetries of the scattering from the cuboidal and the hexagonal, plate-like precipitates. Figure 2 shows examples taken at three different temperatures. They indicate various stages of transition from the cuboidal phase forming initially, to the plate-like phase.

These data along with results from electron microscopy and large-angle X-ray diffraction serve as a basis for modelling and simulating the behaviour of alloys under real processing and service conditions, in the interest of improving the properties of these materials. ⎕

Research team J. Hecht, M. Kompatscher, G. Kostorz, J.-M. Schneider and B. Schönfeld (ETH Zürich), B. Demé (ILL)

Helium bubbles in steel



Neutrons probe the growth of helium bubbles in a type of steel developed for future fusion reactors

GIOVANNA CICOGNANI & ROLAND MAY

Scientists hope that our future energy needs will be met by electricity produced from fusion reactors. The idea is to reproduce the nuclear reactions that take place in stars, where a mixture (called plasma) of electrically-charged light elements (such as hydrogen) is burnt to heavier ones (such as helium) producing vast amounts of energy in the form of radiation.The reaction conditions extremely high temperatures and pressures and powerful magnetic fields are extremely difficult to realise in a man-made device. One of the problems to be solved is the choice of suitable materials for the reactor. The thermal stresses and very high radiation will induce dramatic changes in both the mechanical properties and the microstructure of the reactor walls, especially in the first wall the structural element closest to the plasma.

Radiation damage

The fusion process induces radiation damage such that helium accumulates in the first wall. Helium is not soluble in solids and it forms gaseous bubbles, whose growth at higher temperatures causes the swelling and consequent embrittlement of the wall components. These phenomena are key factors determining the life-time and the reliability of the steels that would be used as structural materials for fusion reactors. In order to understand better how these helium bubbles grow, we investigated the influence of temperature on their formation, evolution, and change in size.

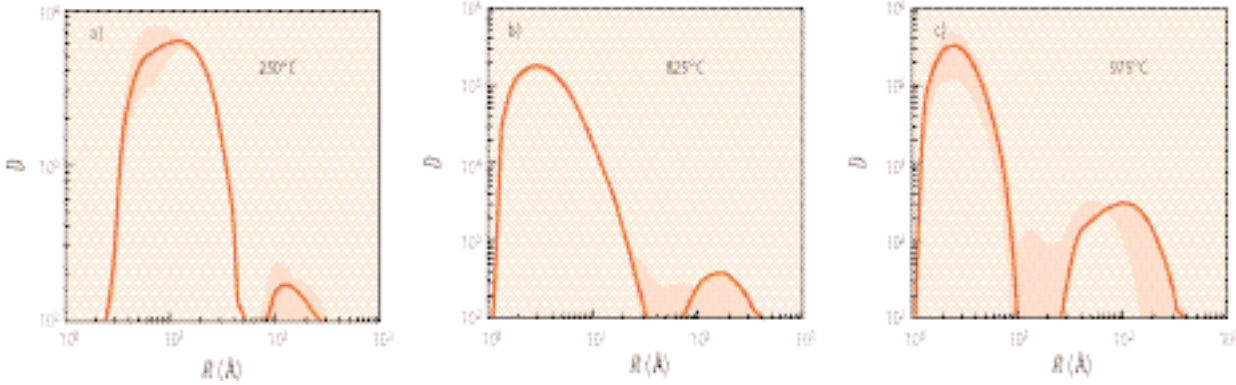
These effects can be simulated by bombarding samples of steels with charged helium atoms (alpha particles) in particle accelerators. It is difficult to observe the helium bubbles with an electron microscope because they are so small (see left). Small angle neutron scattering, on the other hand, is a particularly appropriate technique for this study, for several reasons: the neutrons have a wavelength of similar size to these particles; they penetrate relatively thick samples easily (up to several millimetres); and finally, because neutrons in a magnetic field can sense the magnetisation of the steel, this property can be used to enhance the visibility of the non-magnetic helium bubbles.

We investigated samples of a particular steel F82H, which were bombarded with helium particles at the cyclotron facility at the Karlsruhe Research Centre. They were then heat-treated at 525 C, 825 C and 975 C for two hours under high vacuum. These implantation conditions are representative of the effect of helium in fusion reactors.

The neutron scattering measurements were then carried out at ILL. From the scattering data we calculated the relative numbers of helium bubbles of different sizes (in terms of the total volume of bubbles of a given radius) for three different annealing temperatures. From the results shown in the figure below we concluded that the thermal treatment and coalescence of the initially implanted helium atoms is responsible for the growth of larger bubbles at the expense of the smallest ones. Neutrons thus have turned out to be an essential tool for characterising the bubble-growth mechanism in these steels in a quantitative way. 1

A transmission electron micrograph (left) of helium bubbles in F82H steel after implantation of helium at a temperature of 250 C

The distribution of helium bubbles according to size (in angstroms) obtained from the neutron scattering data at a) 250 C, b) 825 C and c) 975 C. The shaded areas represent the 80% confidence band. At the lower temperatures (a and b) we observe one well-defined peak centred around 1.5 nanometres corresponding to a dense population of small bubbles. At 975 C (c), a second distribution of bubbles, 10 times larger, appears. The density of both bubble populations is almost one order of magnitude larger than at 825 C. There is an increase of a factor of five in the relative value of the bubble volume fraction from 250 C to 825 C and of about 50 per cent from 825 C to 975 C

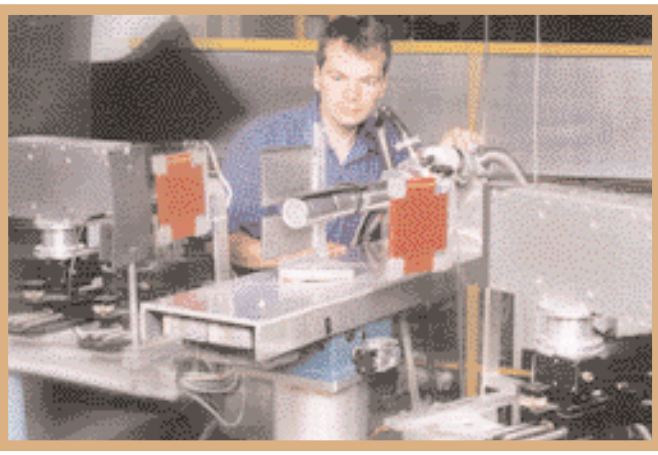


Research team R. Coppola (ENEA-Casaccia), G. Cicognani, R.P. May (ILL), M. Magnani (ENEA, Bologna), A. Moeslang (FZ Karlsruhe)

Glasses with tiny metal clusters embedded in them could lead to a new generation of information storage and fast-switching devices

Reflections on novel glasses for faster electronics

materials



Ralf Siebrecht with instrument ADAM used to obtain these results

CLAUDIA MONDELLI & RALF SIEBRECHT

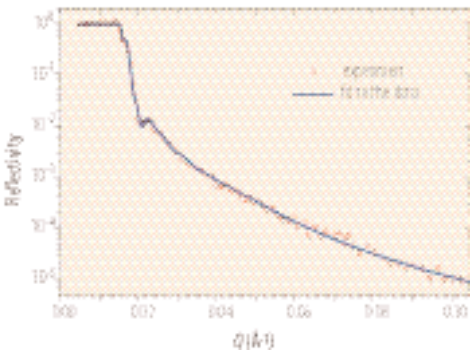


Figure 1 Reflectivity measurements (open circles) taken at ILL; the solid line is put in to fit to the data

A favoured method of making the complex materials required, for example, by the electronics industry is ion implantation, whereby a material is bombarded with highly accelerated ions (charged atoms or molecules) so that they become embedded just below the surface. Of particular interest are glasses implanted with metal ions, which form tiny clusters of atoms, only nanometres across, in a thin surface layer.

These metal nanocluster composite glasses, or MNCGs, show so-called nonlinear optical properties which are useful in optoelectronics using light rather than electricity to transfer information. In particular the refractive index of the MNCGs varies depending on the intensity of the light (optical Kerr effect). This feature could be exploited in high speed optical switching devices which would operate at rates of only a few thousand billionths of a second.

Futhermore, MNCGs obtained by implanting ions of metals like iron, nickel or chromium are important for their magnetic properties. When the size of magnetic particles inside a non-magnetic matrix is in the nanometre range, surface effects are dominant which significantly influences the magnetic properties. Such composite materials offer new technological possibilities. For example, electronic information is often stored as tiny magnetised areas on a disk or tape, and MNCGs offer the possibility for high-density information storage. Used in new ultra-fast switching devices, MNCGs could also replace classical electronic devices based on semiconductors.

Polarised neutron reflectivity

To tailor MNCGs with specific properties, researchers need to know how the clusters are distributed down through the surface layer, the range of sizes of cluster and how they interact with each other. Therefore, a non-destructive method is needed to analyse the sample s structure and especially the magnetic properties. A promising method of choice is polarised neutron reflectivity

As explained in the Introduction, polarised neutrons (their magnetic moments aligned) provide an indispensable tool for studying magnetic behaviour. Reflecting the polarised beam from a sample at angles just grazing the surface should help unravel the magnetic properties of the implanted magnetic particles.

First of all, we performed reflectivity experiments with unpolarised neutrons on a nickel-implanted MNCG to determine the range of sizes of the nickel clusters at various depths. The glass was bombarded with two beams of nickel ions of different energies and intensities. Figure 1 shows the reflectivity curve (open circles) we obtained. We then compared the result with that obtained from another method called Rutherford backscattering spectroscopy (RBS). Even though both techniques give the same overall chemical structure, RBS cannot reveal the sample s magnetic properties related to the nickel-cluster distribution.

This unpolarised reflectivity experiment is the first step to set a more general approach to MNCGs using neutron-based techniques, to study their magnetic properties. Recently, we went on to perform reflectivity experiments with polarised neutrons. We obtained new promising looking data which is currently being analysed. Soon, we hope to shed some light on the physical nature of magnetic MNCGs.

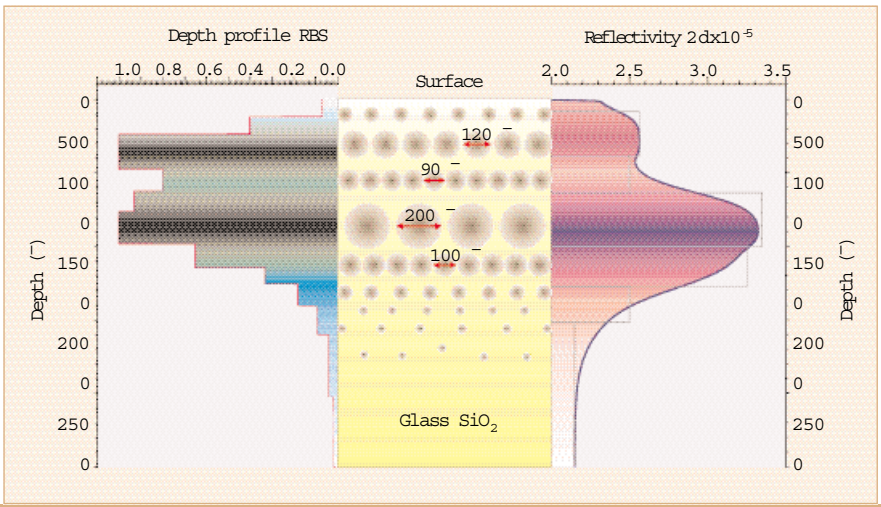


Figure 2 The experimental in-depth nickel distribution measured with Rutherford backscattering spectroscopy (RBS), left, and reflectivity, right

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Magnetic spirals

in very thin films

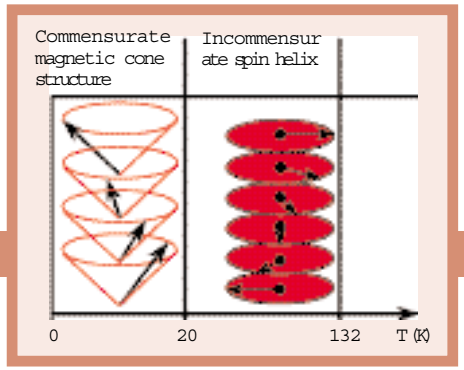

Figure 1 Phase diagram of bulk holmium

Investigating very thin layers of complex magnetic materials only a dozen or so atoms thick is difficult. Neutron scattering, however, rises to the challenge, offering unique insights

thin films

VINCENT LEINER & HARTMUT ZABEL

Today it is possible to grow ultra-thin magnetic films of very high quality. This allows us to raise the question of how magnetic properties of the bulk material are modified in thin films either because of the effect of reducing interactions to just two dimensions or because of interactions with adjacent layers of other materials. Information on such films is important not only in understanding complex magnetic behaviour at a fundamental level but also in the design of novel magnetic nanostructures integrated in new electronic devices. The most complete information on such ultra-thin structures comes from polarised neutron scattering, especially when the magnetic ordering is complex. In this context, we have been studying the magnetic behaviour in single ultra-thin films of holmium. This rare-earth metal is an excellent model system for such studies since its strong magnetic moment and long-range magnetic order result in intense magnetic scattering patterns.

Holmium s helical magnetic structure

Holmium is also interesting because in the bulk, the magnetic moments order helically below a transition temperature of about 132K. The spins order ferromagnetically in the basal plane that is, within a monolayer of atoms in the crystal. Then from one layer to the next, their orientation turns a certain angle, setting up a magnetic spiral perpendicular to the planes. However, the periodicity of the helix does not coincide with that of the crystal planes, in other words, the spin helix is incommensurate . At the transition temperature, the turn angle is 50 but decreases continuously to about 30 at 20K. Below 20K the magnetic moments tilt upwards out of the basal plane locking into a commensurate helical magnetic-cone structure with a turn angle of 30 (Figure 1).

We were interested in investigating the changes in magnetic ordering of very thin holmium films only 4.6 nanometres thick. The film was grown on a sapphire substrate sandwiched between two layers of niobium and yttrium. This prevented the holmium from oxidising and ensured that both surfaces of the film were symmetrical structurally and magnetically.

The magnetic scattering data gave us some unexpected results. Our results agreed with previous studies on holmium films as concerns the ordering of the magnetic structure as a function of temperature. However, the transition temperature from disorder to magnetic ordering was only 105K, considerably less than in the bulk, and the turn angle was bigger at 20K (46). Below 20K, the helical magnetic ordering remained incommensurate. However, we had expected much more dramatic changes in a holmium film which is only slightly thicker than the distance required to achieve one complete turn in the spin helix. Assuming a turn angle of 30 as in the bulk at 20K, 12 lattice planes, or single atomic layers, are required for a complete turn, which amounts to a film thickness of 3.4 nanometres. Theorists had suggested that the turn angle of the spin helix should get smaller as the numbers of layers of holmium atoms is reduced, and that below a film thickness of 10 nanometres the helical arrangement of spins should collapse to a more conventional ferromagnetic state.

Instead we found that the fewer the number of layers the larger the turn angle, thus shortening the pitch of the helix. This indicated that the spin-helix structure is rather robust. In future we hope to investigate what happens in even thinner films which are less than the dimension of a complete helical turn. We clearly still have a lot to learn about spin-helical magnetism. 1

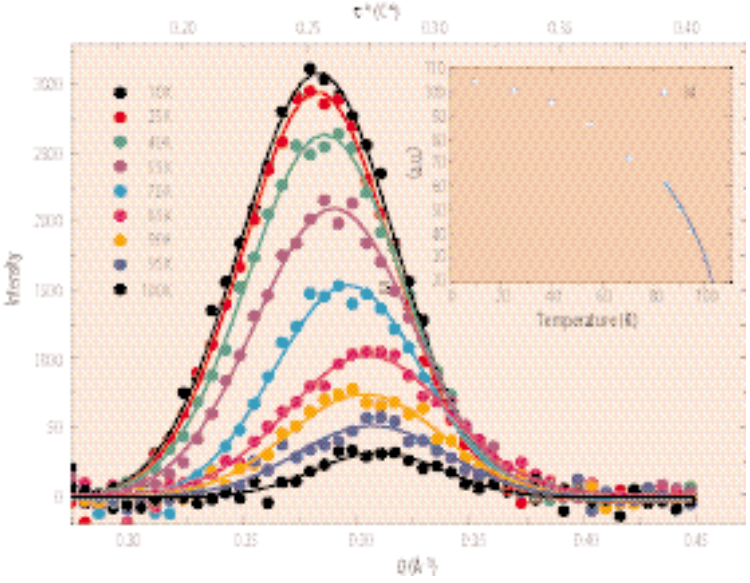

Figure 2 Radial neutron scans of the magnetic peak for the 4.6 nanometre-thick single epitaxial holmium film for different temperatures. The peak shifts to higher scattering vectors due to an increasing turn angle of the holmium spin helix with increasing temperature. Simultaneously the intensity decreases due to a loss of long-range magnetic order with increasing temperature. In the inset, the magnetic order parameter is plotted as a function of temperature

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Explaining giant magnetoresistance

Polarised neutron reflection experiments are revealing that the GMR effect used in the latest magnetic storage devices may be more complicated than at first thought

thin films

VALERIA LAUTER-PASYUK, HANS LAUTER & BORIS TOPERVERG

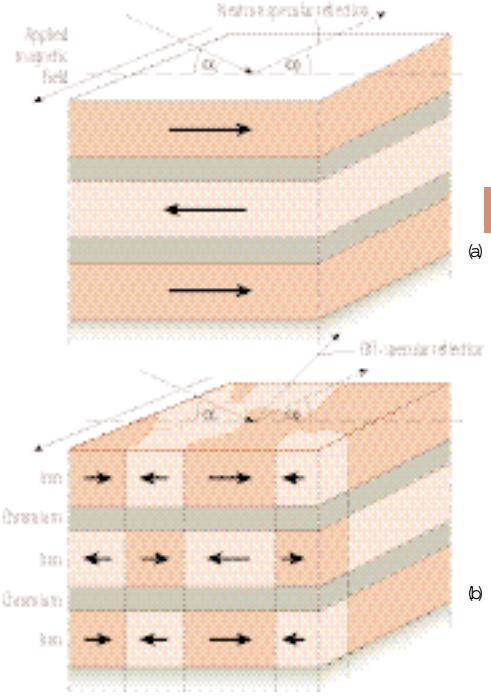


Figure 1 (a) an iron-chromium multilayer with scattering geometry for specular reflection. The arrows inside the multilayer indicate the idealised antiferromagnetic magnetisation direction in the iron layers; (b) the same multilayer with magnetic domains creating off-specular scattering seen in the scattering geometry. The spin configuration of the iron-layer magnetisation is idealised antiferromagnetic order, but the spins are turning somewhat into the external field direction

A few years ago, French and German scientists discovered a remarkable phenomenon called giant magnetoresistance (GMR) which is revolutionising the storage of computer data. Data are stored on hard disks as minute magnetised areas whose fields are detected as changes in electrical resistance in a read head – an effect called magnetoresistance. GMR is 200 times more powerful than ordinary magnetoresistance.

GMR arises in ultra-thin multilayers of magnetic materials. The simplest arrangement consists of two magnetic layers with a nonmagnetic layer in between. The conventional explanation of GMR is as follows. When a current passes through the layers, the electrons oriented in the same direction as the electron spins in a magnetic layer go through while those oriented in the opposite direction are scattered (leading to electrical resistance). If the sets of spins in the two magnetic layers are oppositely aligned then many electrons will be scattered and the resistance will be high. If the orientation of one of the magnetic layers is then switched by a magnetic field fewer electrons will be scattered and the resistance will fall dramatically.

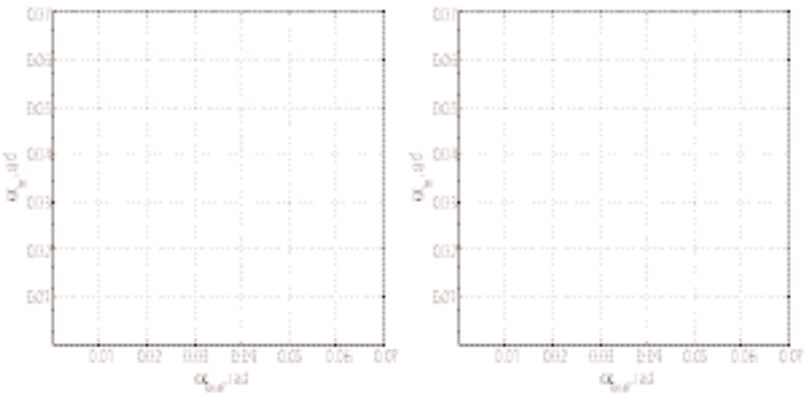
A more complex spin arrangement

In fact, the actual arrangement of spins in these multilayers turns out to be quite complicated, and we have been studying just how the electron scattering leading to GMR arises. The multilayer structure we studied is shown in Figure 1a. It consists of alternating layers of iron and chromium, 6.8 and 0.98 nanometres thick respectively. In each iron layer the spins are all aligned, but the magnetisation of each iron layer also interacts with that of the neighbouring iron layers through the chromium layers. For a certain thickness of the chromium layer the iron layers are antiferromagnetically ordered, in other words, the spin orientation of neighbouring iron layers is in the opposite direction. This arrangement shows a typical GMR effect.

Polarised neutron reflectivity is a very good technique for exploring the spin arrangements in these materials. Reflecting polarised neutrons off the surface and interfaces of the magnetic layers reveals not only information about the layer structure but also the layers' magnetisation. We measured two components of scattering: the specular reflections (where the angle of reflection a_f equals the angle of incidence a_i) which gives a vertical profile of the layers including thickness (Figure 1a); and off-specular reflections which reveals variations horizontally along the layers (Figure 1b).

Figure 2 shows the experimental data for specular scattering. The intensity variation along the diagonal ridge reflects the periodic composition of the multilayer. But there are also intensity 'wings' on the specular line due to off specular magnetic scattering and this reflects the lateral magnetic structure of the layers. Theoretical calculations suggest that what this shows is that there are tiny domains in each layer, about 200-300 nanometres in diameter and extending column-like across all the multi-layer. They are antiferromagnetically coupled (Figure 1b). We are still analysing the results but we think that these magnetic domains play an essential role in the electron scattering process responsible for the GMR effect. We believe they offer a more exact description than the simple explanation usually given in terms of stacks of homogeneously-ordered antiferromagnetic layers. 1

Figure 2 (a) An intensity map of specular scattered and off specular scattered neutrons from the iron-chromium multilayer as a function of the incident and outgoing scattering angle. The colours reflect the scattered intensity on a log-scale. The horizontal colour lines crossing the pictures are background effects; (b) a model calculation to simulate the experimental results



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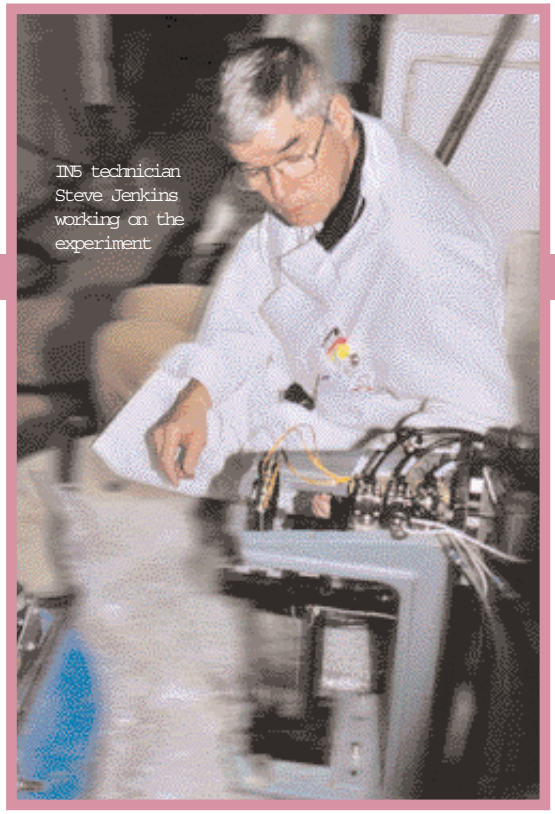
Quantum tunnelling
in molecular magnets

A European team has been studying the quantum 'peculiarities' in a large molecule that behaves as a mini-magnet

ISABELLE MIREBEAU



IN5 technician Steve Jenkins working on the experiment

Small clusters of atoms that behave as tiny magnets are currently of great practical interest as potential information storage devices. They are also of theoretical importance because their behaviour lies on the border between classical and quantum physics. Among them, molecular clusters are very attractive because of their behaviour simplicity: they are all identical objects, arranged over regular arrays, and weakly interacting with each other.

These large molecules contain typically a dozen similar metal ions whose magnetic spins (arising from the unpaired electrons) combine into one giant spin. These molecules are fascinating because even though they are quite large, they still behave as quantum objects. A molecule containing 12 manganese ions linked with acetate groups (Mn_{12}-ac) is the best studied of these spins clusters. The direction of the giant spin (S) is along an axis perpendicular to the plate-like shape of the molecule. According to quantum rules, the total spin S could have 2S+1 possible projections along this axis, yielding 2S+1 energy levels for the molecule. In Mn_{12}-ac, the arrangement of the manganese spins inside the cluster yields a total spin S = 10, that is, there are 21 magnetic energy levels (M) from -10, -9, to +9, +10.

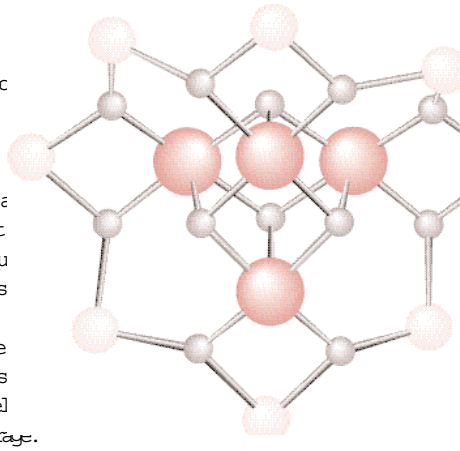
Magnetic transitions

We are interested to know how the giant spin flips from one energy level to another. This is a challenging question for theoreticians. Roughly speaking, two mechanisms could be considered. The energy barrier between the levels can be overcome by supplying heat (this is a classical process), but it is also pc to tunnel through the barrier. Tunnelling is a curious quantum process which is a result of the statistical nature of the quantum mechanics that there is always a small probability that the molecule can exist alternative state. Solving this fascinating qu may have important practical consequences since magnetic molecules could be used in future memories for new generations of computers and the study of their magnetic reversal hel determine the size-limit for information storage.

We used inelastic neutron scattering at very low temperatures to investigate the transitions. The neutron can exchange energy with the cluster, when the cluster passes from one energy state to another. It is not possible to see the tunnelling effect directly because it is too low in energy. However, we hoped to see it indirectly by a broadening of some energy levels. This broadening modifies the inten-sity and energy of the thermal transitions.

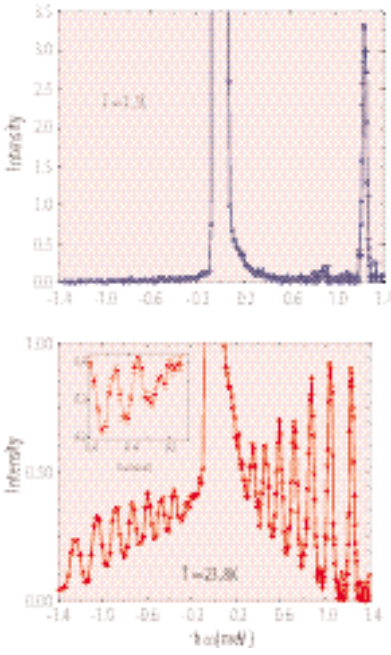
We found that we could see the transi-tions between these energy sublevels very clearly (see right). At 1.5K the spectrum revealed a well-defined transition from the lowest energy level (M = 10) to the first excited one (M = 9). At higher temperatures, the other levels start to be populated. At 23.8K all levels are popu-lated. The giant spin then starts to break up. At 23.8K, we could see observe how the transitions near the central peak are influenced by tunnelling. We were able to ascribe the observed effects to a term related to tunnelling in the equation describing the energy of the system.

Thanks to the neutron probe, the energy term responsible for the tunnelling was determined very precisely. Although extremely small, it could explain the main tunnelling transitions. More work needs to be done in understanding the whole tunnelling effect. 1



View of the core of the Mn_{12}-ac cluster, in which only the metal atoms and the bridging oxygens (small spheres) are shown. The total spin S=10 is built by an antiparallel arrangement of four Mn^{4+} ions (large spheres), and eight Mn^{3+} ions (medium spheres)

Energy spectra of the Mn_{12}-ac spin cluster at two temperatures



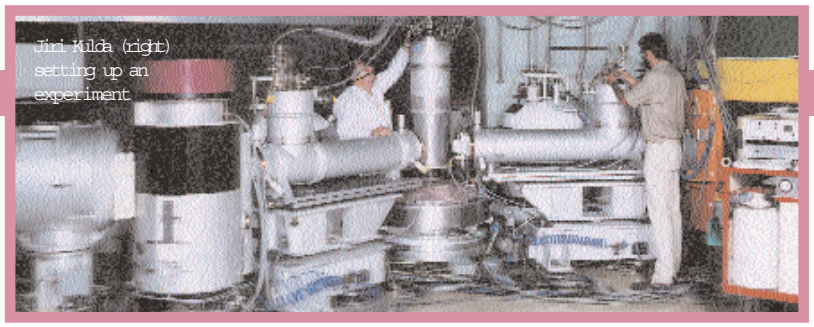
Research team I. Mirebeau and M. Hennion (LLB), H. Casalta (ILL), H. Andres and H. U. G del (Univ. Bern), V. Irodova (Inst. Kurchatov Moscow), A. Caneschi (Univ. Florence)

New class of magnetic phase transitions discovered

A mixed metal bromide ($CsMnBr_3$) has an unusual type of 'handed' magnetic order. Neutron experiments have confirmed that it represents a new kind of magnetic behaviour

magnetism

JIRI KULDA

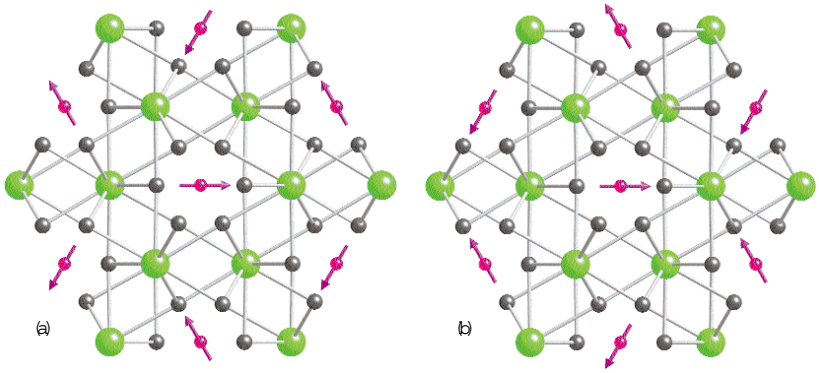


Jiri Kulda (right) setting up an experiment

There is currently a great interest in materials with exotic magnetic properties, for example, compounds containing magnetic atoms in which the direction of their electron spins are ordered in an unusual way. One such material is caesium manganese tribromide ($CsMnBr_3$). The manganese ions are arranged on a triangular lattice, in flat layers. This prevents their magnetic moments from lining up in an orderly antiparallel (antiferromagnetic) way as might be expected for a similar material, say, with a cubic crystal lattice. Instead, the magnetic moments of neighbouring manganese ions lie at angles of 120 to each other. This effect is called frustration and $CsMnBr_3$ is a well-known example of a frustrated two-dimensional triangular lattice antiferromagnet.

While frustration in such triangular antiferromagnets has been established for a long time, the collective behaviour of the spins is controversial. Two alternative spin configurations can exist, as shown below: passing along a line in the crystal lattice from one magnetic atom to the next you can see that the spins can either turn systematically to the left or to the right. The two spin patterns cannot be mapped onto each other by a simple translation or by rotating all the spins, and are said to be chiral , or handed . As with conventional magnetism, where there is a phase transition at a certain temperature from a state where magnetic moments point in any direction to an ordered magnetic state, this chiral ordering is also expected to set in below a certain transition temperature. Such phase transitions can be classified according to quantities called critical exponents. These describe how typical bulk properties like magnetisation, specific heat or magnetic susceptibility change with temperature as the phase transition temperature is approached either from above or below. The critical exponents reflect the structural symmetry of the material and its dimensionality whether the ordering is in one, two or three dimensions. According to S. Kawamura, the chiral ordering should have its own characteristic set of chiral critical exponents and would represent a new universality class of magnetic phase transitions.

The clockwise (a) and counter-clockwise (b) chiral domains in the magnetic structure of $CsMnBr_3$



Measuring chiral critical exponents

No one had, however, determined these critical exponents experimentally, so my colleagues Sergey Maleyev and Vladimir Plakhty from St Petersburg in Russia devised a strategy to measure them making use of fundamental rules relating the spin rotation and energy transfer in the scattering of polarised neutrons. At first we investigated their scattering by $CsMnBr_3$ at various temperatures above the transition, looking for traces of chiral ordering in the crystal which would fluctuate over time and location. The dynamics of this process would be revealed by small changes in the energies of the scattered neutrons correlated with their initial spin orientation. By successively orienting the spins of incident neutrons parallel and anti-parallel to an applied magnetic field and measuring the difference in the probability of the positive and negative energy transfers we have obtained information about the dynamic chirality. Ultimately, the temperature-dependence of this probability difference is described by the critical exponent associated with the chiral ordering.

We also looked at the ordered state, below the transition temperature of 8.22K, and found that unequal populations of left and right-handed domains were frozen in. Again we were able to use the neutron data to calculate another of the chiral critical exponents related to the spin ordering. Combining the two measured critical exponents, we could determine a third critical exponent. We found they were all in excellent agreement with the predicted values for this new class of magnetic materials. 1

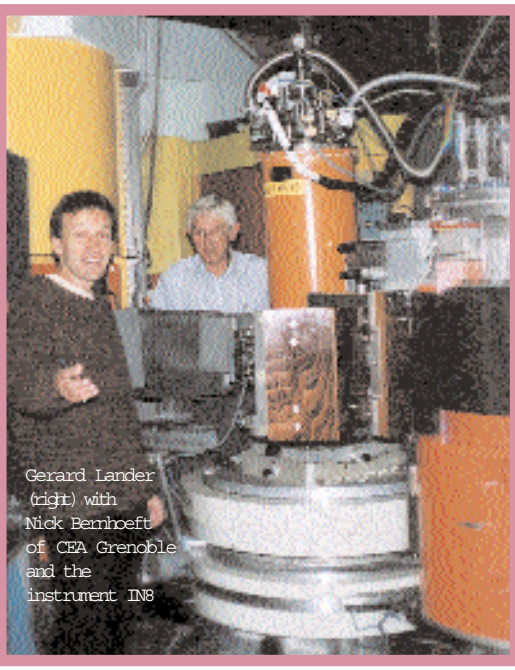
Research team V.P. Plakhty and E.Moskvin (PNPI Gatchina St. Petersburg), J. Kulda (ILL Grenoble), D. Visser (Univ. Warwick Coventry), J. Wosnitza (Physik. Inst. Univ. Karlsruhe), R.K. Kremer (MPI Stuttgart)

Inside modern magnets

Ingenious neutron scattering experiments combined with X-ray studies are for the first time revealing the complex electronic structures of modern permanent magnets

magnetism

GERARD LANDER



Gerard Lander (right) with Nick Bernhoeft of CEA Grenoble and the instrument IN8

A material is magnetic when its constituent atoms or molecules have a magnetic moment (due to the spin of single, unpaired electrons) which are aligned, or ordered in some way. The most familiar material is iron but today many practical magnetic devices are made from a combination of magnetic elements – so-called transition metals such as iron or cobalt, and rare-earth elements such as samarium or neodymium. Powerful permanent magnets made of samarium and cobalt ($SmCo_5$) or neodymium/iron/boron (Nd-Fe-B) compounds are in wide commercial use. The magnetic moments of the different types of atoms in these materials interact in complex ways and we still do not understand them. To find out more about their magnetic structure, and thus improve their performance, we need to look at model systems and measure the fundamental interactions.

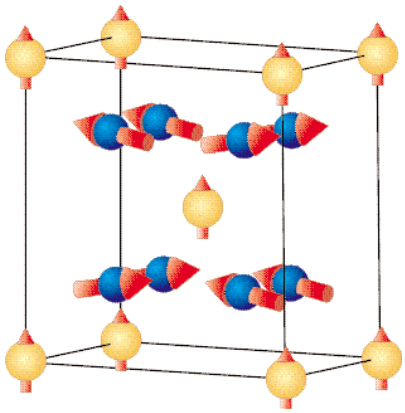
One such magnetic material is a compound containing iron, aluminium, and a rare earth M such as dysprosium or holmium, or an actinide uranium (MFe_4Al_8, where M = Dy, Ho, U). The electrons responsible for iron's magnetism sit in the so-called 3d electronic shell in the atom, while in dysprosium or holmium, which are heavier elements with more electrons, they sit in the 4f shell. In uranium, the heaviest element, they sit in an outer 5f shell.

Combining neutron and X-ray studies

We have been studying in considerable detail how the various electronic shells (3d, 4f and 5f) develop their ordered magnetic moments as the temperature is lowered. This has been the subject of considerable controversy in the past. Taking advantage of a new polarimeter at ILL, which supplies polarised neutrons in any chosen orientation and then measures changes in orientation of the outgoing neutrons, we could obtain information about the orientation of magnetic moments. From these results, coupled with certain magnetic X-ray measurements made at the ESRF, emerges a unified picture of the magnetic ordering process.

As we expected, the magnetic ordering is dominated by the 3d electrons of iron, although the type of ordering is influenced by the M atom. Surprisingly, in the rare-earth based materials the initial magnetic ordering occurs only in the array of iron atoms, whereas the rare-earth magnetic moments remain disordered. In contrast, in the uranium compound, the iron 3d and uranium 5f electron shells interact so that the two sets of atoms order at the same temperature.

The X-ray studies show that ordering in the 4f electrons is more complicated and involves the information being transmitted to the 4f shells via the intermediary 5d electrons of the rare-earth element, but they do order when the temperature is low enough. Using the neutron polarimeter, we showed that the 4f magnetic moments dance along with the (dominant) iron 3d moments, but with their spins oriented at an angle (which depends on temperature) to those of the 3d moments. This phase angle is different for each element, and its origin is not understood. At the lowest temperatures, the rare-earth moments try to align themselves ferromagnetically (all in the same direction), but the iron prevents them from doing so, and the subsequent competition gives rise to unusual behaviour in a magnetic field. These experiments are an excellent example of how neutron and X-ray studies together can analyse the complex magnetic structure of strategically important materials. 1



The unusual magnetic configuration of the UFe_4Al_8 compound

Research team J. A. Paixão (University of Coimbra), P. J. Brown (ILL), B. Lebech (Risø National Laboratory), G. H. Lander (Institute for Transuranium Elements, Karlsruhe)

Magnetic materials called spin glasses in which the spins are highly disordered are used as universal models of complexity. However, there is still much to learn about their dynamic behaviour

magnetism

Relaxing spins in glassy magnets

ROBERT CYWINSKI

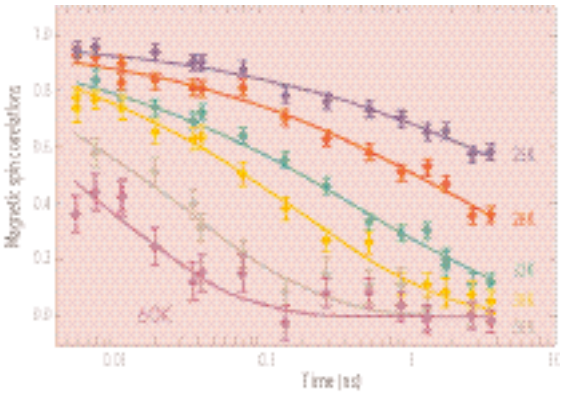


Figure 1 (right) These neutron spin echo measurements show how the alignment of the magnetic spins in glassy Er_7Fe_3 decay with time, and how this decay changes as the sample is cooled the solid lines represent a theoretical model describing complex spin relaxation processes

Look closely at an ancient stained glass window and you might notice that the glass at the bottom of the window is thicker than at the top. This is because the material has flowed a little, like a liquid. In molten (liquid) glass the molecules move randomly but when it cools to a certain temperature (the glass transition) and solidifies, the random positions of the molecules become frozen in.

A question interesting scientists is whether the glass transition is a true transition. Enormous amounts of work have been done on trying to understand the behaviour of glasses since they are a classic example of a complex system. Even more intriguing, however, are magnetic materials in which the spins interact randomly to give a highly disordered magnetic state a so-called spin glass. Spin glasses also undergo a glass transition to a state in which the random orientations of the spins are frozen in.

Physicists are fascinated by spin glasses. They are, in many ways, easier to theorise about than structural glasses, and mathematical models of spin glass behaviour have been applied in areas dealing with complexity as diverse as protein folding and biological evolution. However, there is still significant controversy regarding the spin glass transitions. Again, some physicists ask: does a spin glass transition really exist; and how universal is the nature of glass transitions? To investigate further, we have been studying a particular model spin glass system a non-crystalline or amorphous alloy of erbium and iron (Er_7Fe_3). The best way to investigate the spin glass transition is to follow what happens to the spins at various temperatures around the glass transition. When individual spins in the sample align how long does it take for them for them to become unaligned? Does this spin relaxation decay away exponentially as for many analogous physical processes, or does it take longer with a stretched exponential time dependence as found in some complex and strongly interacting systems?

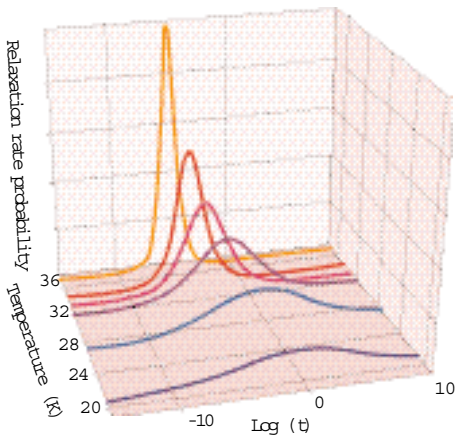


Figure 2 The evolution of the distribution of magnetic relaxation rates close to the glass transition in amorphous Er_7Fe_3 as determined by a combination of neutron spin echo, dynamic susceptibility and magnetisation measurements. Notice the dramatic broadening of the distribution as we go below the glass temperature

Neutron spin echo

Spin relaxation happens over a period of between a hundred-millionth to a million-millionth of a second, which exactly matches the time window that can be probed by a technique called neutron spin echo. Here, polarised neutrons are passed down a fixed-length tube in a very uniform magnetic field. Their spins precess , and the number of precessions achieved depends on their velocity, or the time spent in the tube. After being scattered by the sample the neutrons are spin-flipped and then travel down a second tube of similar length and magnetic field. The precession is therefore reversed and the neutron spins should end up back as they were originally. If, however, there is a slight change in neutron energy due to interactions with the spin relaxation process in the sample then there will be a change in their velocity and their spins will not have wound back to what they were. The spin echo experimental set-up is such that the energy changes can be measured more precisely than with any other neutron technique, and it has been possible to follow the evolution of very slow magnetic spin relaxation not only down to the spin glass transition, but also below it.

Our measurements have provided important new insights. For example, we find that the relaxation processes continue to evolve through the glass temperature, although with different time-scales on either side of the transition. The measurements also show quite clearly that the spin relaxation follows the complex stretched exponential time dependence, just as predicted by several theoretical models of strongly interacting disordered systems. 1

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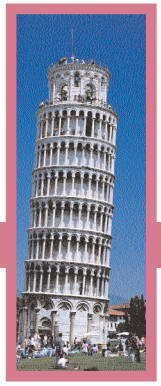
Dropping neutron waves

How does gravity affect a particle obeying quantum laws? Scientists at the University of Vienna and ILL have been investigating how neutron waves respond to gravity



fundamental physics

GERBRAND VAN DER ZOUW

By dropping masses off the tower of Pisa, Galileo Galilei for the first time demonstrated that all bodies fall the same way, when starting from the same position with the same velocity. This observation forms the basis of Einstein s General Theory of Relativity describing gravity.

It is interesting to ask what happens when you drop an object, such as the neutron, that is governed by the laws of that other great physical theory of our time: quantum mechanics. This theory predicts that very small particles can behave either as waves or as particles, depending on how you look at them. Wave-like behaviour has been observed in several beautiful experiments for increasingly heavier particles electrons, neutrons and atoms. Recently Markus Arndt and colleagues at the University of Vienna showed that even so-called fullerenes football-shaped molecules consisting of 60 or 70 carbon atoms behave as waves.

The COW experiment

Until 1975 there had been no experiment that demonstrated what happens when you drop a particle in the quantum limit, that is, while it is behaving as a wave. In that year R. Collela, A.W. Overhauser and S.A. W erner (COW) at the University of Missouri (Columbia) observed just that using a neutron interferometer. This is a device that specifically exploits the wave-like aspect of the neutron. Inside the instrument the neutron wave is split and goes two separate ways. When the two parts of the neutron wave come together again this leads to interference, as with water-waves behind a rock. At some places the neutron wave becomes stronger, while at other places it disappears. COW observed how the gravitational force shifts this interference pattern (see Figure 1).

Unfortunately the shifts in the interference pattern observed in the COW experiment and in later, more sophisticated versions of it did not quite agree with what quantum theory predicted. Does this mean theoreticians should start to worry? Probably not. Another team recently showed using an atom interferometer that theory and experiment agree almost perfectly on a level of 7 parts in a billion.

This leaves us with the very unlikely hypothesis that the neutron might be somehow different when it comes to gravity. Because all COW-type experiments so far have been carried out using essentially the same neutron interferometer, it is much more likely that the intricate theoretical aspects of this instrument are not yet fully understood.

To verify this hypothesis we have repeated the COW experiments with a completely different type of neutron interferometer: our interferometer for very cold neutrons at ILL. This one-metre-long interferometer uses particularly slow neutrons flying at only about 40 metres per second (144 kilometres per hour). This makes it very sensitive to gravity. Thanks to adding a neutron filter to our interferometer in 1999, we managed to determine all parameters in our experiment with high enough accuracy to be able to decide whether the earlier experiments or the theory were right.

Our experiment consisted of measurements of the shift of the interference pattern (gravitational phase-shift) at different amounts of tilt of the interferometer (Figure 2). The measurement of the velocity distribution of the neutrons and of some other parameters results in a theoretical prediction with which we can compare our experimental results. We find that our experiment agrees with theory on the experimental level of error of about 0.4 per cent. At the same time it excludes the earlier results that did not agree with theory.

W e think we can now safely say that neutrons drop as theory predicts; also when they happen to be behaving like waves. 1

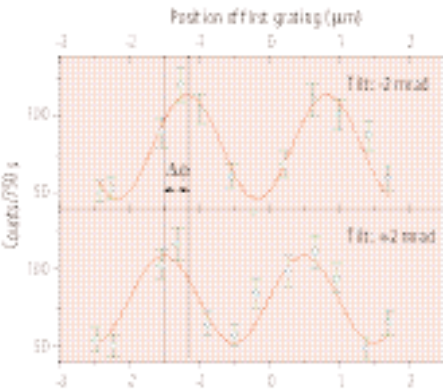


Figure 2 This graph shows that an interference pattern (which here looks like a sine) is shifted by tilting the interferometer. The amount of this phase-shift is predicted by theory

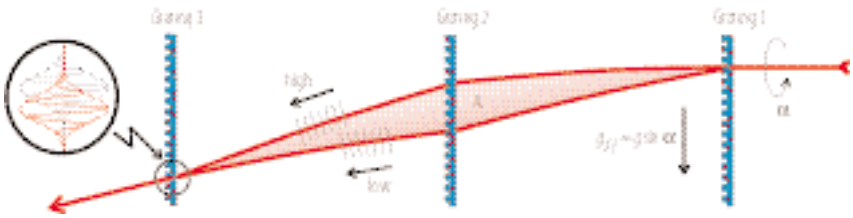


Figure 1 The COW experiment: when a neutron interferometer is tilted one path travels at a greater height than the other. This causes a shift (phase-shift) of the interference pattern at the exit of the interferometer where the two paths come together

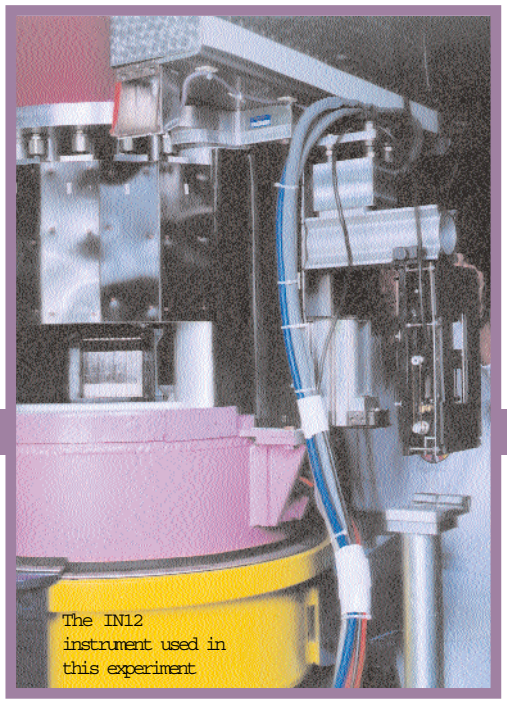
Research team G. van der Zouw and A. Zeilinger (Univ. Vienna), P. Hghlj, R. G hler, P. Geltenbort and J. Butterworth (ILL)

Superfluid helium in porous media

Pure superfluid helium is well-known for its bizarre quantum properties. When confined in porous silica, its behaviour is even stranger

quantum systems

BJORN FAK



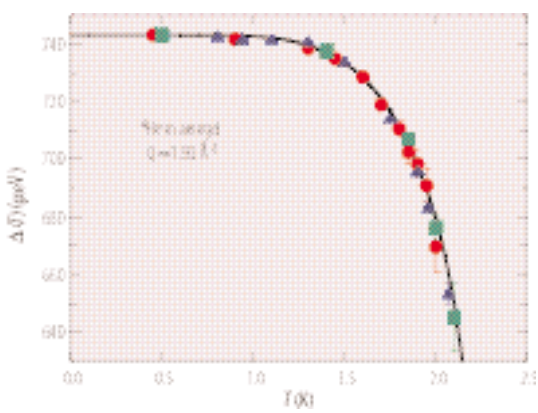
The IN12 instrument used in this experiment

Helium is the only material that does not freeze, even close to absolute zero temperature. Instead, it undergoes some extraordinary changes. At a temperature of 2.17K, bulk liquid helium-4 (the normal isotope with two neutrons and two protons) changes to a superfluid – a bizarre form of matter which flows without friction or viscosity and can even climb out of its container!

This state is the result of the helium-4 atoms undergoing a change predicted by quantum theory called a Bose-Einstein condensation (BEC). According to quantum mechanics, at a low enough temperature, certain kinds of indistinguishable particles like helium-4 will all collect together in the lowest quantum energy state (ground state) and behave as a single quantum entity. Like microscopic quantum particles, this macroscopic quantum state can be excited to higher energy levels; in the case of superfluid helium, these excitations are density fluctuations called phonons and rotons. Rotons in particular have been well studied and their energy spectra related to the large-scale physical properties of liquid helium such as specific heat, the superfluid transition temperature, and the fraction of the liquid that is in a superfluid state.

Introducing disorder

Recently, researchers have become interested in studying superfluid helium adsorbed on surfaces and in porous solids. These confined systems are expected to show some disorder, and could offer insights into technologically important quantum systems such as high temperature superconductors (which conduct electricity without resistance). These materials have complex disordered structures whose electronic behaviour is still not well-understood.



Temperature dependence of the roton energy measured for different aerogels (symbols). No deviations are found from bulk helium-4 (line)

The large-scale properties of superfluid helium are known to be modified by immersion in porous media, and we wanted to relate these changes to the quantum excitations using inelastic neutron scattering. We examined superfluid helium in two forms of porous silica – aerogel and Vycor. In the aerogel the superfluid transition is lowered by a few millikelvin whereas in Vycor it is lowered to 1.95K.

What we found was that while the roton energies and the roton life times in both systems were the same as in bulk superfluid helium, there were additional two-dimensional excitations associated with the layers of helium atoms that are adsorbed and held in place on the silica surfaces. These layer modes had lower energies than the three-dimensional bulk rotons and accounted for the modifications in physical properties.

Vycor showed a further peculiar effect. In bulk helium the intensity of the rotons should drop more or less proportionately with the superfluid fraction as the temperature is raised to the superfluid transition. At this point the rotons should disappear. They don't! There is still a roton peak in the neutron spectrum above the superfluid transition. In fact, theoretical work has suggested that the roton intensity should relate directly to the number of helium atoms that have undergone BEC rather than the superfluid fraction. We therefore think that in Vycor the temperature at which the BEC occurs is actually above the superfluid transition. In other words, superfluidity sets in only after the BEC fraction has reached a certain level as the temperature is dropped. This separation of the superfluid and BEC transition points is very strange indeed but must related to the disorder induced by the confined environment furnished by Vycor. We still have a lot to learn about these intriguing quantum systems. l

Research team B. Fåk and O. Plantevin (CEA Grenoble), H.R. Glyde and N. Mulders (University of Delaware), G. Coddens (LLB Saclay), H. Schober (ILL)

Amorphous state A state of solid matter in which the atoms or molecules are arranged randomly rather than in a regular crystalline array.

Angstrom (Å) A unit of length equal to 10^{-10} metres.

Antiferromagnetism A type of magnetic order in which the magnetic moments of the atoms or molecules are alternately aligned in opposite (antiparallel) directions, giving a null net magnetisation.

Bilayer A term most often applied to double layers of lipid molecules.

Bose-Einstein condensation A quantum phenomenon in which particles which have a whole-number spin (bosons) drop into a single quantum state usually at very low temperatures. Particles with half-integer spin (fermions) such as electrons cannot occupy the same state and must spread themselves over a series of states as in an atom. Examples of bosons are helium-4 nuclei and Cooper pairs – the electron pairs responsible for superconductivity.

Cellulose A natural carbohydrate consisting of a chain of simple sugar molecules in a complex configuration.

Contrast variation A technique in which particular atoms in a sample are substituted by another isotope with different scattering strength in a way that preferentially enhances the scattering pattern of particular components of interest.

Crystal lattice The regular three-dimensional array of atoms or molecules in a crystal.

Critical exponent A quantity used to classify substances according to the type of phase transitions they undergo. Close to a phase transition, certain properties vary with the difference between the temperature of the material and the phase transition temperature raised to some characteristic power – the critical exponent. These coefficients reflect the symmetry of the material.

d electrons The electrons occupying the d orbitals in an atom. Atomic electrons sit in orbitals, s, p, d, f, classified according to the laws of quantum mechanics.

Deuterium A heavier isotope of hydrogen having a neutron as well as a proton in the nucleus.

Electronic shell Electrons in atoms are arranged in concentric shells subdivided into orbitals (see d electrons).

Electron spin One of the quantum properties of electrons (and other subatomic particles). It has a value of one-half. Electrons prefer to form pairs with spins in opposite directions; unpaired electrons in atoms or molecules are responsible for the magnetic properties of materials.

Enzyme A type of protein responsible for mediating a specific biochemical reaction in living systems.

f electrons The electrons occupying the f orbitals in an atom. Atomic electrons sit in orbitals, s, p, d, f, classified according to the laws of quantum mechanics.

Ferromagnetism A type of magnetic order in which the electron spins are all aligned.

Fractal A type of complex structure that is the same on any scale. Fractals are classified according to the way they scale.

Giant magnetoresistance A phenomenon shown by certain complex magnetic materials in which an applied magnetic field produces a large change in electrical resistance.

Gigapascal Unit of pressure equal to a billion newtons per square metre and equivalent to 10 000 times the atmospheric pressure.

Glass A solid material in which the atoms or molecules are randomly arranged.

Glass transition The change at a certain temperature from a glass to a liquid or vice versa.

Heavy water Water in which hydrogen has been replaced by its heavier isotope deuterium

Hexagonal ice The normal form of ice in which each water molecule has four nearest neighbours.

Hydrogen bonding A weak form of bonding in which the proton of a hydrogen atom is electrostatically attracted to pairs of electrons on atoms like oxygen and nitrogen.
It plays a crucial part in the structure of water and also of many biological materials.

Incommensurate structure A term applied to materials in which a periodic ordering (for example, magnetic spins) does not match that of the crystal lattice.

Inelastic scattering Scattering of particles like neutrons from a sample in which there is an exchange of energy between the neutrons and the molecules or atoms in the sample, thus giving information about the dynamics of the sample molecules or atoms.

Lipid A molecule consisting of a long hydrocarbon chain with an electrically charged group of atoms at one end. Lipids arrange themselves in layers and are the basis of biological membranes.

Magnetic moment Magnetic effect arising from a spinning electric charge. Atoms have magnetic moments as a result of the spin and orbital motions of any unpaired electrons. Neutrons also have a magnetic moment.

Magnetic susceptibility The ease with which a material can be magnetised by an external magnetic field.

Nanometre One billionth of a metre (10^{-9} metres).

Neutron One of the two particles found in the atomic nucleus. It is electrically neutral, but has a spin of a half and a mass of 1, equal to that of the proton.

Neutron reflectivity A technique in which neutrons are reflected off a surface or interface. It is used to characterise the structure of surfaces and thin layers.

Neutron diffraction or scattering Like other subatomic particles, neutrons have a characteristic wavelength depending on energy. When reflected, or scattered, off a material in which the interatomic distances are similar to the neutron wavelength, the scattered waves interfere to produce a characteristic diffraction pattern.

Neutron spin echo A method of measuring very small changes in energy in a neutron beam after interacting with a sample, and thus subtle aspects of dynamics in the material, from changes in precession of neutron spin after passing through two successive magnetic fields which oppose each other.

Nonspecular scattering Reflection of neutrons from a surface or interface in which the angle of reflection is different from the angle of incidence. It gives information about the lateral structure of the surface.

Phase diagram A schematic representation of the various structures adopted by a material over a range of temperatures and pressures.

Phonon A quantum of atomic vibration in condensed matter.

Phospholipid A class of lipid containing a phosphate group.

Plasma A hot gas composed of charged particles.

Polarised neutrons A beam of neutrons whose spins are all aligned.

Polymer Large molecules consisting of chains of similar chemical units.

Polysaccharide A polymer made up from sugar units.

Quantum energy levels Systems obeying the laws of quantum mechanics can occupy only certain energy levels.

Quantum mechanics The theory that describes the behaviour of matter at the microscopic level in terms of probability waves.

Quantum tunnelling A phenomenon in which a quantum system can tunnel through an energy barrier as a result of the Uncertainty Principle which allows for a small probability that the system can exist on the other side of the barrier.

Quasielastic neutron scattering Measurement of very small changes in neutron energy after scattering, which relate to subtle dynamic changes in the sample.

Rare-earth elements A large group of heavy metals in the Periodic Table from cerium (atomic number 58) to lutetium (atomic number 71) with similar chemical and physical properties.

Roton A type of quantum energy excitation found in superfluid helium.

Silica Silicon oxide.

Small angle neutron scattering Measurement of neutron scattering at small angles used to investigate structures with large interatomic distances such as polymers or biological structures.

Specific heat The ratio of heat supplied to a material to its subsequent rise in temperature.

Specular scattering Reflection of waves in which the angle of reflection equals the angle of incidence.

Spin glass A magnetic material in which the ordering of spins is random.

Superalloy A group of metal alloys often containing nickel with high strength at elevated temperatures.

Superconductivity The property of conducting electricity with no resistance.

Supercooled water Liquid water cooled below its normal freezing point.

Superfluidity A property in which liquid helium flows without friction and viscosity.

Synchrotron radiation The electromagnetic radiation produced when charged particles are accelerated and bent in a magnetic field. Synchrotron radiation is coherent and can be produced in intense narrow beams suitable for X-ray analysis experiments.

Transition metal A large group of heavy metals in the Periodic Table with a rich variety of chemical and physical properties derived from the fact that they have unfilled d orbitals.

X-ray scattering A technique used to determine the structure of materials. X-rays are reflected, or scattered, off a material in which the interatomic distances are similar to the X-ray wavelength such that the scattered waves interfere to produce a characteristic diffraction pattern.

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