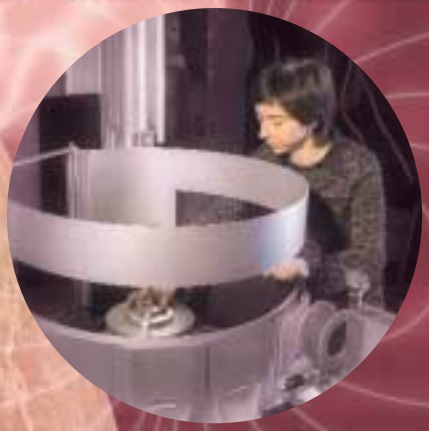
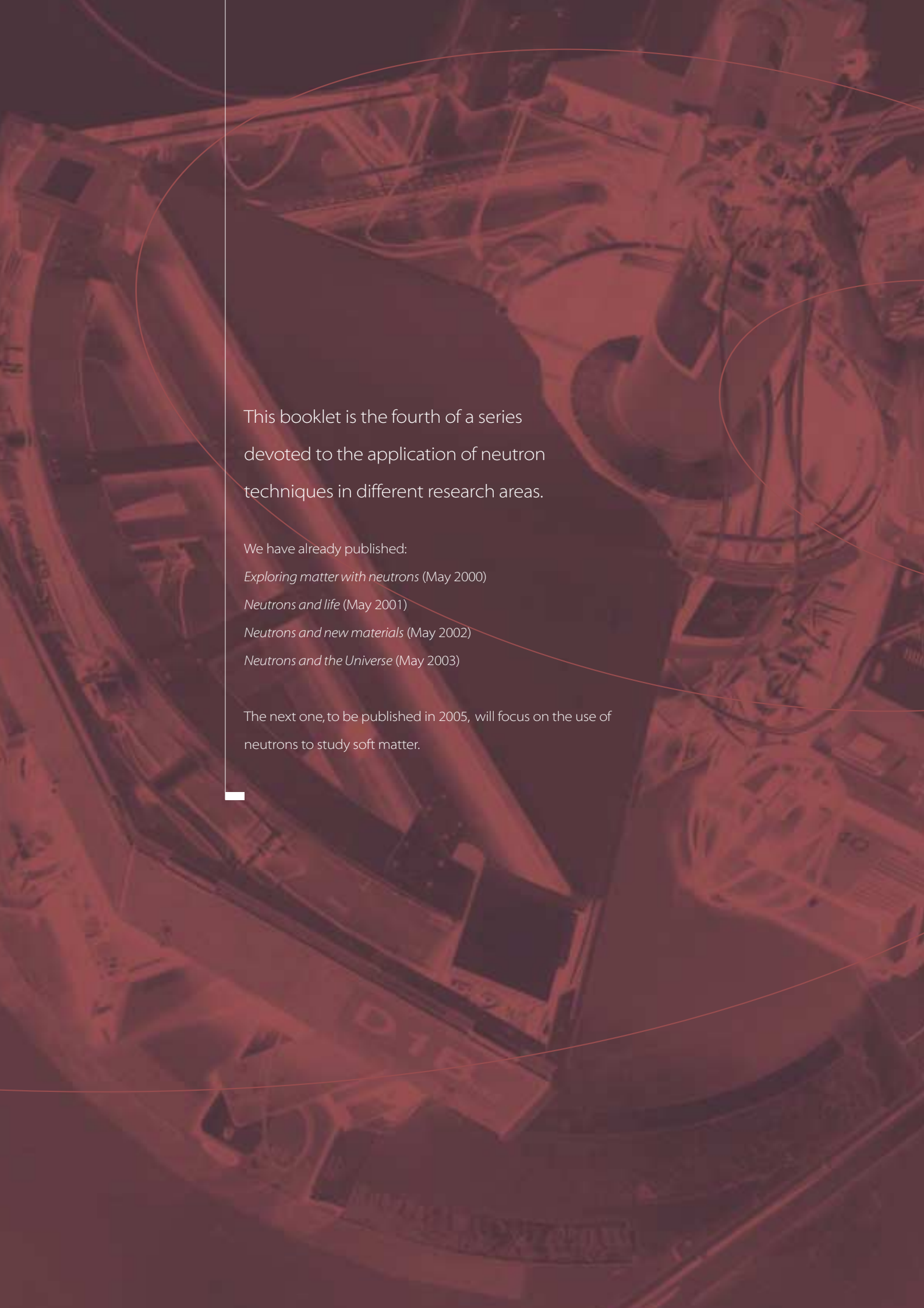
HIGHLIGHTS OF ILL RESEARCH



Neutrons and magnetism

A review of ILL research on magnetic materials and phenomena

NEUTRONS FOR SCIENCE



This booklet is the fourth of a series devoted to the application of neutron techniques in different research areas.

We have already published:

Exploring matter with neutrons (May 2000)

Neutrons and life (May 2001)

Neutrons and new materials (May 2002)

Neutrons and the Universe (May 2003)

The next one, to be published in 2005, will focus on the use of neutrons to study soft matter.

Foreword

For centuries, people have been aware of magnetic materials – the effects of a magnetic force are easily observable. In everyday life, magnets are found everywhere from cars, through mobile phones, to high-speed trains. But magnetic systems exist on all scales: elementary particles such as the electron and neutron act like tiny magnets; planets such as the Earth, Jupiter and Saturn (and once upon a time Mars, p.9) have powerful magnetic fields generated by massive dynamos at their cores. The Earth's magnetosphere actually protects us from high-energy solar radiation so can be considered essential for life. The Sun and other stars have complex magnetic structures which generate powerful storms, and galaxies also reveal large-scale magnetic turbulence.

Back on Earth, for the past two centuries, scientists have been trying to understand the origin of magnetism. In the 19th century, the first theoretical concepts and experimental methods were developed and bulk properties of magnetic materials defined. In the 20th century, as understanding grew of the nature of magnetic interactions at the microscopic level, new kinds of magnetic behaviour were proposed. These predictions were not confirmed until the mid-1950s with the development of neutron diffraction experiments.

Because of its elementary magnetic moment, the neutron can probe the magnetic properties of materials at the atomic level and even down to the nuclear level: it acts as a tiny compass exploring the inner structure of matter. It can detect and characterise the vibrational motions of the individual magnetic moments. From the characteristics of the vibrational modes, scientists and engineers can determine the interactions between the local moments, which are so important for the bulk properties of magnetic materials. In this way they have been able to optimise and develop more efficient magnets for technological applications.

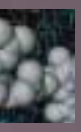
AIP Emilio Segrè Visual Archives

Louis Néel (1904-2000) played a major role in the birth and the international success of research in Grenoble. *A 2-day workshop, organised in November 2004 commemorates the 100th anniversary of his birth*

Louis Néel, who won the Nobel Prize for his seminal contributions to our understanding of magnetism, was one of the founding fathers of ILL. And so, research in magnetism has played a major role at ILL right from the beginning. Expertise in methods and techniques was developed in-house early on, bringing ILL to the forefront of research in this area.

The ILL is now engaged in an ambitious programme of instrument renewal to prepare for future experimental challenges. It is our responsibility to ensure that the laboratory offers the adequate tools needed by the scientific community to develop the materials to be used in tomorrow's technology. Thanks to these efforts, neutrons are seen to contribute to a deeper understanding of properties of matter and to the growth of advanced technology. The ILL can be proud of its achievements in the study of magnetism with neutrons.

Dr Christian Vettier
Associate Director
Head of Science Division



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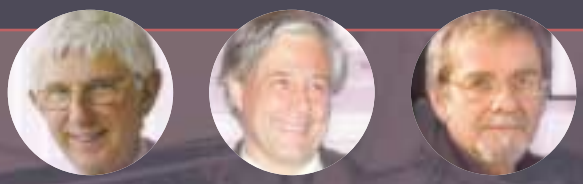
Investigating magnetism with neutrons

>> GERARD LANDER, CHRISTIAN VETTIER AND ROLAND CURRAT

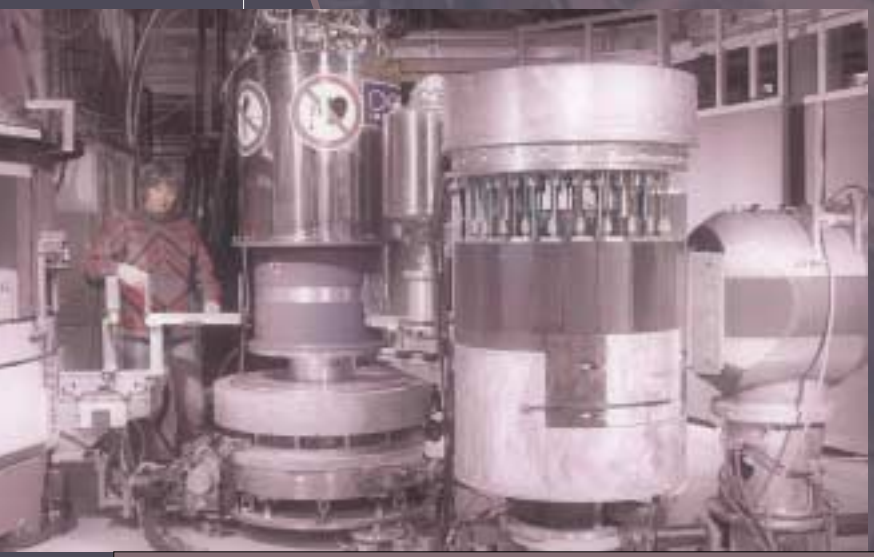
Studies of magnetism with neutrons is a vibrant research area, which is underpinning a new generation of electronic devices as well as leading to a deeper understanding of Nature at a fundamental level



People have been exploiting magnetism for more than a millennium. The ancient Greeks discovered that certain stones – lodestones – could attract iron. This magnetic force could then be imparted to an iron object by rubbing it with the stone. The Chinese showed that magnetised needles pointed north-south when suspended. Such magnetic compasses have been guiding ships across the seas ever since.

Today, magnetic materials have many more uses. Apart from obvious applications as fridge magnets and door catches, they form the central components of motors used in transport and electrically-driven machinery, and are also found in communication devices from telephones to loudspeakers. Extremely powerful magnets are used in hospital scanners, and in basic research – in huge machines to accelerate and study subatomic particles.

One of the most significant technological developments over the past decades has been the exploitation of magnetic materials in storing information as minute magnetised particles – first on tapes and then on computer disks. Indeed, the rapid growth of our information-based economy has been driven not only by the development of ever smaller electronic devices (the latest 10 gigahertz chips will have transistors 30 nanometres in size) but also of more densely packed magnetic computer memories (MRAM devices now include memory cells of 1.4 square micrometres). The next generation of computer chips, as well as memory devices, could well be based on new, exotic magnetic materials, designed and fabricated at the 'nano' scale of atoms and molecules.



The IN14 instrument

Understanding the magnetic force

These advanced ideas depend on a detailed understanding of the magnetic force at the most basic level. During the past two centuries, scientists have elucidated its subtle nature. Hans Christian Oersted in Denmark and Michael Faraday in the UK saw the link between electricity and magnetism in the early 19th century, which led Scottish physicist James Clerk Maxwell, shortly afterwards, to derive his brilliant equations explaining mathematically the combined electromagnetic force.

In the early 20th century, our insights into magnetic interactions advanced rapidly with the development of quantum theory, which built on the ideas of Maxwell amongst others. Pioneers of quantum mechanics, Werner Heisenberg, Paul Dirac and Wolfgang Pauli, were able to explain magnetism as an inherent property of the electron. According to their ideas, particles like the electron have a quantum property called spin, which carries a half-integer value. The effect is that of a bar magnet, or magnetic moment, which can be flipped up or down to give a value of +1/2 or –1/2.

Everyday matter is made up of atoms containing electrons, so what makes some materials magnetic and not others? Electrons in atoms and molecules tend to pair off so that their magnetic moments of +1/2 or –1/2 cancel, leaving no residual magnetism. However, some metals and metallic salts (and quite a few molecular materials) contain unpaired electrons. In crystalline form, the atoms or molecules carrying these unpaired electrons are arranged in a regular geometric way on a lattice. If the electrons can interact with each other (via the 'exchange' energy, as predicted by quantum theory) their moments will align to give a bulk magnetic effect.

In the familiar permanent magnet, such as iron, the moments are aligned in the same direction generating a north and south pole. Not surprisingly, this is called ferromagnetism. Ferromagnetic materials include iron,

The EVA instrument

cobalt and nickel, and a range of metallic compounds involving heavier elements – lanthanides and actinides. Above a certain temperature called the Curie temperature, the thermal energy causes the alignments to break up. In a few materials, the moments align in alternately opposite directions – an effect called antiferromagnetism. This phenomenon was first proposed by Louis Néel working in Grenoble, and the temperature below which a substance becomes antiferromagnetic is named after him.

We now know of many materials where the magnetic ordering is a good deal more complicated, depending on how the moments interact, as some of the examples in this booklet show. The ordering may vary according to direction – especially in materials with layers or chains of differing atoms. The moments may be canted to each other, or form a helical arrangement (p.14). In electron-rich molecules with unpaired electrons the moment may be spread out over several atoms (p.12). Single molecules consisting of clusters of metal atoms, each with one or several unpaired electrons, can form 'nanomagnets' where the spins combine and interact in fascinating ways (p.11). Because electrons also orbit the atomic nucleus, they may produce an additional magnetic contribution due to the moving electric charge, and this can further complicate the magnetic interactions.

Studies of these exotic magnetic properties involve a strong interplay between theory and experiment. Models of magnetic interactions often have relevance to other physical systems which can be described using a similar underlying mathematical approach. Exploring magnetic behaviour thus not only leads to new applications but also plays an important role in demonstrating the universality and beauty of the laws of Nature.

Experimental studies

Many of the models were developed, by Néel and others, before the experimental tools – or the materials – existed to test them out. It was not until beams of neutrons became available from nuclear reactors in the 1940s that it became possible to study in detail how magnetic moments are arranged in a material.

Neutrons, like electrons, have a spin 1/2, so have a magnetic moment. They can themselves therefore interact with unpaired electrons in a material, and can be scattered by the lattice of magnetic moments. The resulting diffraction pattern provides information about the magnetic structure, and even the dynamics of the interactions.

The theory of neutron scattering from magnetic solids had already been developed by Otto Halpern and Montgomery Hunt Johnson at New York University in a famous paper in 1939. A decade later, Cliff Shull and Ernie Wollan successfully applied the ideas using the reactor at Oak Ridge National Laboratory Tennessee. Neutrons have turned out to be the perfect tool for probing magnetism at a microscopic level. The models proposed by Néel were verified and new perspectives started to be explored, leading to the rich field of magnetism studies we have today, in which ILL plays a major part.

New techniques combined with ever improving instrumentation have led to a wide range of experiments. Scattering at small angles provides structural information on a larger scale – that of domains of different magnetisation in a material. Neutrons can also be reflected off surfaces and interfaces, allowing researchers to look at structures based on ultrathin magnetic layers, to be used in 'spintronic' devices in which information is carried by the electron's spin rather than by its mobility (p.18).

The availability, now, of polarised neutrons (p.6) means we can pinpoint magnetic information in experiments much more precisely, allowing us to look at other exotic materials. These include unusual superconducting materials, in which the strong interactions between electrons are reflected in the magnetic behaviour (p.13), and molecules with unusual magnetic structures. It may soon be possible to follow the paths of single electrons in biological systems as revealed through their magnetism (p. 8).

Neutron magnetic scattering remains a burgeoning field of essential technical and theoretical importance. This booklet highlights the wide range of research on magnetism tackled at the ILL. ■

The power of polarised neutrons

Magnetically aligned neutron beams are an excellent probe of magnetic materials

>> JANE BROWN

D3 diffractometer used for polarised neutron diffraction

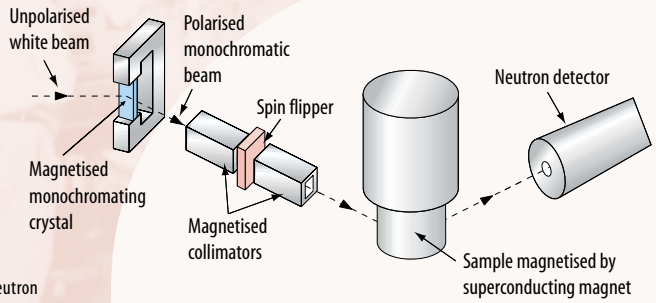


Figure 1
A simple polarised neutron diffractometer. The neutrons from a reactor source are reflected by a magnetised crystal which selects neutrons with a particular wavelength and polarised parallel to the magnetisation direction. These neutrons are then scattered by a magnetised single crystal sample and the intensities of the reflected neutrons are recorded

Both neutrons and electrons have a spin of 1/2, so have a magnetic moment and can interact magnetically with matter. The strength of the interaction depends not only on the size of the electronic magnetic moments, but also on their relative orientations. Beams of neutrons with all their spins parallel – a polarised beam – can therefore be used to study materials in which the electronic magnetic moments are ordered in a structurally interesting way. The intensities of the neutrons scattered by the sample (usually a single crystal), are measured in a detector.

However, the best way to extract precise information about the sample's magnetic properties is to compare scattering patterns obtained with neutron beams polarised in opposite directions. A device called a spin flipper reverses the polarisation of the incident neutron beam (figure 1), so that the ratio between the scattered intensities for the two orientations can be measured – the *flipping ratio*. Precise measurements of this ratio can be used to map the distribution of magnetic moments within a crystal – as was shown by Clifford Shull and his students at MIT in pioneering experiments in the 1960s investigating the classic ferromagnetic metals iron, cobalt and nickel. They demonstrated that although the electrons responsible for the magnetism are also involved in conducting electricity they are well-localised in space.

Since then, this method has been used to look at magnetisation in many materials. One of the more exotic compounds studied is a large molecule containing 12 manganese atoms linked to acetate groups, commonly known as Mn_{12}-Ac, and which has unusual low-temperature magnetic properties. The molecule contains an inner core of four manganese ions, each with three unpaired electrons, surrounded by an outer ring of eight manganese ions with a total of 32 unpaired electrons. The overall spin of the complex is obtained by summing all the magnetic moments in the molecule. Magnetisation measurements give a net spin of 10, which suggests that the spins on the outer manganese atoms (total spin,16) are oriented antiparallel to those in the inner ones (total spin, -6). Polarised neutron scattering confirmed this picture, and the magnetisation values at the various manganese sites agree well with those predicted theoretically.

Polarised neutron diffraction has also been used to pinpoint the unpaired electrons responsible for magnetism in an organic compound containing no metals. It consists of a fluorocarbon ring attached to a ring of one carbon, two sulfur and two nitrogen atoms. The unpaired electrons are found on the latter, five-membered ring (figure 2).

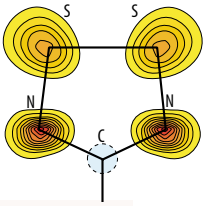


Figure 2
The magnetisation distribution in the CNSSN ring of the organic magnet, *p*-$O_2NC_6F_4CNSSN$

Polarisation analysis

Adding a second flipper and a polarisation analyser between the sample and detector allows us to carry out measurements that specifically distinguish magnetic scattering from the normal nuclear variety. Data from four combinations of measurements made by switching each flipper can be obtained: the intensities of scattered polarised neutrons both parallel and antiparallel to the incident polarised neutrons, and the same with the incident polarisation reversed. This technique can be used to study antiferromagnetism in which the direction of magnetic moments in a crystal alternate.

More sophisticated measurements of the magnitude and direction of the scattered polarisation for various orientations of the incident polarisation will give the absolute magnetic configuration of materials such as magneto-electric crystals (in which an electric field induces magnetisation or vice-versa). For example, such polarimetric experiments on the magneto-electric crystal chromium oxide (Cr_2O_3) determine the absolute orientation, relative to the surrounding oxygen atoms, of the oppositely directed moments on pairs of chromium ions. Figure 3 shows the configuration stabilised by cooling in different combinations of electric and magnetic fields. ■

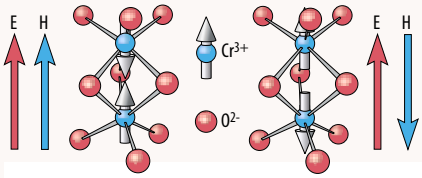


Figure 3
The crystal structure of chromium oxide showing the moment orientations stabilised by cooling in (a) parallel and (b) antiparallel magnetic (H) and electric (E) fields

A crystal for polarising neutrons on instrument IN20

Orbital order in manganites

Combined neutron and X-ray diffraction has revealed a new type of electronic behaviour in an important class of magnetic materials

>> TAPAN CHATTERJI

Compounds called manganites – derived from a structure consisting of a rare-earth element such as lanthanum combined with manganese and oxygen ($LaMnO_3$) – have caused great excitement in the past decade because they show a huge change in resistivity when a magnetic field is applied. This colossal magnetoresistance (CMR) effect could be the key to the next generation of magnetic memory devices, magnetic-field sensors, or transistors.

The key to this CMR effect is the manganites' complex electronic and magnetic structure, which depend subtly on how the outer '*d*' electrons of the manganese atoms are arranged in their orbitals. In the parent lanthanum manganite, the triply-charged manganese atom (Mn^{3+}) is bound to six neighbouring oxygen atoms in an octahedral shape (figure 1a). The Mn^{3+} ion has one electron involved in bonding; it occupies one of two possible *d* orbitals, which are geometrically different and are associated with differing bond lengths. The octahedral structure is thus actually slightly distorted. The lanthanum ions, also triply charged (La^{3+}), sit between layers of manganese-oxygen octahedra.

If a percentage of the lanthanum ions is replaced with doubly-charged metal ions such as strontium (Sr^{2+}), the electrons redistribute to give some Mn^{4+} ions with an empty *d* orbital (a hole). This 'hole-doping' allows the remaining electrons to hop from manganese to manganese atom so that the material conducts like a metal. Furthermore, when the 30 or 40 per-cent hole-doped manganite is cooled below a certain temperature, the spins of these electrons align so that the material becomes ferromagnetic. It is this that increases the resistivity of the material because the aligned electrons scatter oppositely-aligned electrons trying to pass through.

Using a combination of X-ray and neutron diffraction, we investigated the interplay between the ordering of the spins, the charge and the orbital occupancy in the 50 per-cent hole-doped, layered manganite ($LaSr_2Mn_2O_7$). Neutron studies enabled us to measure the manganese-oxygen bond lengths, which indicated which *d* orbitals were occupied. We found that this compound has equal numbers of Mn^{3+} and Mn^{4+} ions arranged alternately, and a 'staggered' arrangement of bonding orbitals (figure 2) below 225K. At 170K this charge-orbital order 'melts' as antiferromagnetic order sets in.

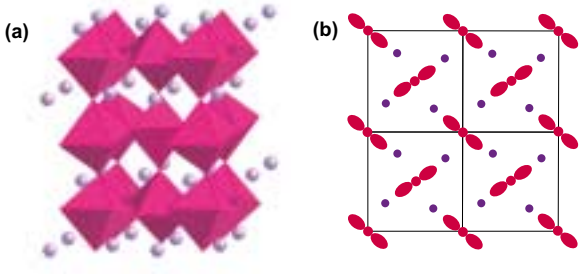


Figure 1
(a) The structure of lanthanum manganite; (b) the staggered ordering of *d* orbitals

An unusual transition

More recently, we have investigated the orbital ordering further, in the parent lanthanum manganite over a range of temperatures. The bonding *d* orbitals are again arranged in an alternate staggered pattern within each plane of manganese-oxygen octahedra (figure 1b), but unlike in $LaSr_2Mn_2O_7$, all the manganese ions are Mn^{3+} and have a bonding *d* orbital. The octahedra are distorted giving three different bond lengths. The compound retains this structure up to 750K – when something dramatic happens. The distortion disappears, the staggered arrangement of orbitals is lost, and the solid material abruptly contracts in volume. Such a transition in a solid, which depends purely on changes in the electronic arrangement, is rather unusual. We think that in the high-temperature, orbitally disordered state all the octahedra pack together more efficiently. This is similar to what happens when ice melts into water, although in that case the contraction is due to the water molecules losing positional order. ■

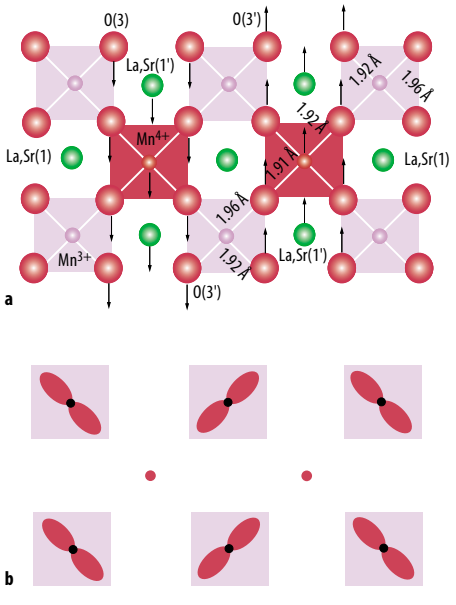


Figure 2
The structure of 50 per-cent hole-doped lanthanum strontium manganite ($LaSr_2Mn_2O_7$), at a temperature of 165K, looking down through the manganese-oxygen octahedra. Neutron diffraction allowed us to determine the position of both manganese and oxygen atoms, and thus the Mn-O bond distances. This revealed the ordering of the Mn^{3+} and Mn^{4+} ions (a) and the ordering of the bonding orbitals (b)

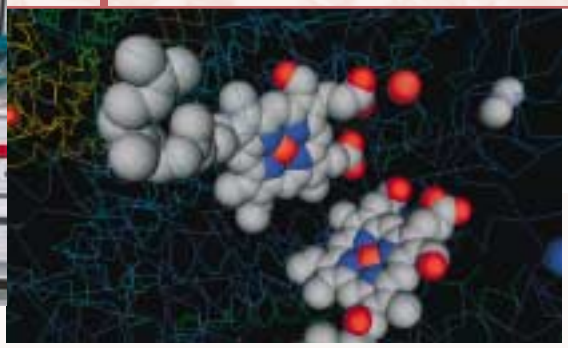
Research team T. Chatterji, G. J. McIntyre, A. Stunault and B. Ouladdiaf *(ILL)*, and F. Fauth *(ESRF, Grenoble)*

The experimental team on instrument D1B

Animal magnetism

Developing polarised neutrons to reveal the magnetic side of proteins

>> ANDREW WILLS AND EDDY LELIÈVRE-BERNA



The active site of cytochrome *c* oxidase

Reactions in biological systems, such as energy-producing respiration, rely on a helping hand from enzymes containing metal atoms. These metallo-proteins catalyse the transfer of electrons in a reduction-oxidation (redox) mechanism. A typical example is cytochrome *c* oxidase (above). Such molecular assemblies are large and complex, and the details of the redox process are still uncertain; conventional studies using X-ray scattering, resonance or spectroscopic techniques are complicated by the presence of the many atoms in the enzyme's framework and the ambiguity of the data.

Polarised neutrons, however, have the potential to provide the information to unravel these mechanisms. Most enzyme-catalysed redox reactions involve the transfer of single electrons (each with a magnetic moment). They can therefore be located and followed, via the accompanying magnetic changes in the molecular system, using polarised neutron diffraction (p.6), without the interfering effects of the multitude of framework atoms.

In fact, the main obstacle in using neutron diffraction is that proteins such as cytochrome *c* oxidase are difficult to prepare in the required single-crystal form. For this polarised neutron technique to be used, it must first be modified to deal with powder and polycrystalline samples.

Powder diffraction is a well-established method of studying such materials. Instead of measuring individual reflections in three dimensions, as happens in single-crystal diffraction, the data are obtained as a one-dimensional set of complex, overlapping peaks from which information has to be extricated by a computer. In proteins, the complexity and large size of the protein structure amplifies the overlapping peak problem, so requires an optimised powder diffractometer.

A polarisation filter

The main technical difficulty to overcome is providing an intense-enough source of polarised neutrons over a wide wavelength range. Traditionally, ferromagnetic single crystals (p.6) are used, which produce polarised beams only at specific wavelengths. A new polarisation technique has recently been developed at ILL, which has a broader application and can be used with 'white' beams of pulsed neutrons (as provided by spallation neutron sources), as well as the continuous neutron source from a nuclear reactor such as ILL's.

The method is based on spin-polarised helium-3 which absorbs neutrons of one spin type, effectively acting as a spin filter. The device is compact (only a few centimetres long) and convenient. It is ideal for using with powder diffractometers, and will be suitable for experiments using the next generation of spallation sources that aim to follow the path of redox reactions with timed neutron pulses.

In June 2003, we carried out the first experiment to determine the applicability of this approach using the powder diffractometer D1B at the ILL. Data collected from a variety of organometallic and intermetallic materials clearly indicate that experiments can be designed to detect unpaired electrons in biological systems, thus heralding a new way of probing fundamental questions in biology – using magnetism. Chemists should also be able to apply the same technique to design novel redox catalysts. ■

The helium-3 cell used as a source of polarised neutrons

Research team A.S. Wills *(University College London and The Royal Institution of Great Britain)* and E. Lelièvre-Berna *(ILL)*

How Mars lost its magnetism

Mars has a complex and patchy magnetic field; neutron experiments may explain why

>> BACHIR OULADDIAF

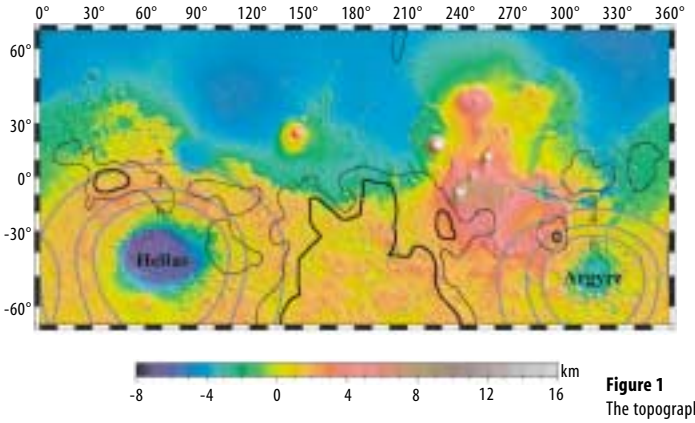


Figure 1
The topography of Mars showing the computed peak shock pressure in GPa around the Hellas and Argyre impacts (grey), and the 20 and 40 nanotesla contours of the magnetic field (black) measured by Mars Global Surveyor at an altitude of 380 to 420 kilometres

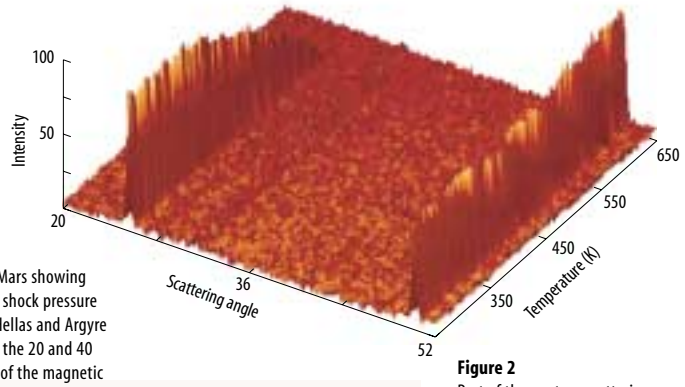


Figure 2
Part of the neutron scattering pattern collected on D1B from the pyrrhotite powder sample at room pressure and versus temperature

Our planetary neighbour Mars is currently exciting great interest as various space missions explore its surface and atmosphere. One of the key areas of interest is Mars' magnetic field and what happened to it in the distant past. Researchers believe that Mars once had a global magnetic field, like Earth's, but the iron-core dynamo that generated it shut down billions of years ago leaving behind only patches of magnetism due to magnetised minerals in the Martian crust.

NASA's Mars Global Surveyor spacecraft mapped these magnetic left-overs in 1999. The results were mysterious. While crustal magnetisation in the northern lowlands was negligible, it was much stronger in the older highlands of the southern hemisphere – with an especially strong magnetic field in a strip between longitudes 130°E and 240°E, but almost no magnetisation around the giant impact craters of Hellas and Argyre (figure 1).

The north-south divide probably arose because, when the Martian dynamo shut down, the younger, thinner northern crust had not yet solidified and thus became demagnetised – while the solid southern crust's magnetisation was already 'frozen' in. However, there is no apparent difference between the magnetised and non-magnetised areas in the southern terrain. One explanation is that the Hellas and Argyre impacts occurred after the dynamo shut down, and that the accompanying pressure shock-waves (rather than heat) demagnetised the crust around those areas.

Possible evidence for this scenario lies with one of the minerals identified in Martian meteorites as carrying the remanent Martian magnetisation – pyrrhotite, Fe_7S_8. This mineral is ferromagnetic below a transition temperature of 325°C. This is due to alternate stacking of partially and fully-filled iron layers in the mineral which, although coupled antiferromagnetically, results in a residual magnetic moment. At moderately high pressures, however, pyrrhotite loses this magnetism, but the exact pressure at which this happens was not known.

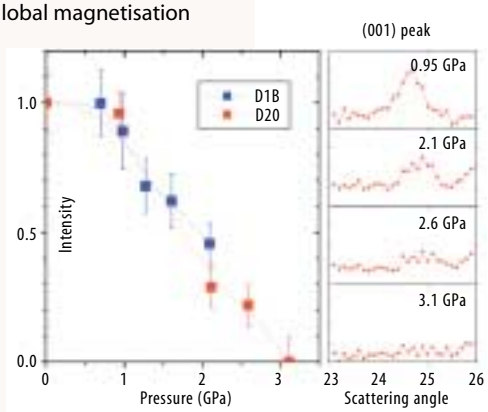
Pyrrhotite under pressure

We decided to pin down the pressure-demagnetisation relationship more precisely using neutron diffraction. Samples of natural pyrrhotite were placed in pressure-clamp cells of up to 2 and 3 gigapascals (GPa), using deuterated ethanol as a medium to transmit even pressure, and placed on diffractometers D1B and D20 respectively. Two sets of peaks were isolated as being from the mineral; one set could be ascribed to magnetic scattering since it disappeared above the transition temperature (in an independent experiment, figure 2). The study then showed that this magnetic peak decreases with pressure and vanishes between 2.6 and 3.1 GPa, figure 3. An independent experiment based on a remanence measurement after pressure-release led to the same result.

Calculations indicate that the shock waves from impacts on the Martian surface would have indeed resulted in a maximum pressure contour of 3 GPa at the distance that coincides with the boundary between magnetised and non-magnetised crust. This strengthens the case of pyrrhotite as the mineral responsible for the Martian remanent magnetic field.

Besides nicely predicting the global magnetisation map, the results also have a major implication for the paleomagnetic signal of the Martian meteorites. All Martian meteorites have been shocked to pressures above 3 GPa, and since their remanence is also carried by pyrrhotite, they would have been demagnetised when they hit the Earth. Therefore, their paleomagnetic signal postdates shock. ■

Figure 3
The neutron scattering pattern versus pressure: (a) showing how the intensity of the magnetic peak goes down with pressure; and (b) its evolution with increasing pressure, as measured on D20



Research team B. Ouladdiaf *(ILL)*, R. Ballou and G. Fillion *(Louis Néel Laboratory, Grenoble, France)*, P. Rochette *(CEREGE University of Aix, France)* and L. Hood *(University of Arizona, USA)*

Magnetism chills out

Materials that behave as magnetic refrigerants have surprisingly complex structures

>> CLEMENS RITTER

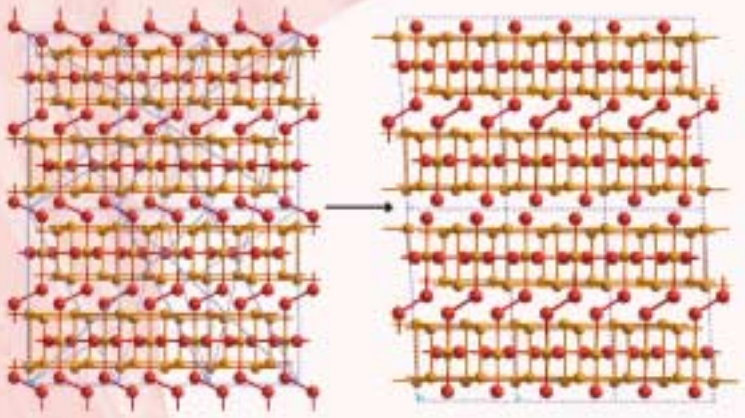


Figure 1
The transition from monoclinic to orthorhombic structure in the alloy, $Tb_5Si_2Ge_2$. The red balls are silicon or germanium atoms, yellow balls represent terbium atoms. The arrow marks where a strong shear movement leads to breaking of the silicon or germanium bonds

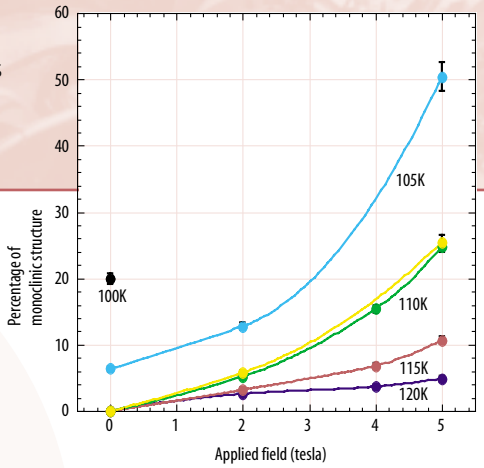


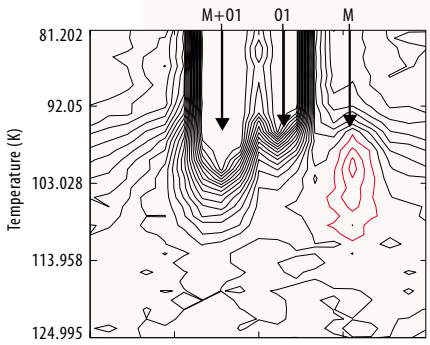
Figure 2
The percentage of monoclinic phase induced by increasing the magnetic field at selected temperatures as determined from high-resolution D2B data

When a magnetic field is applied to a magnetic material, the constituent magnetic moments align, and the material warms up. When the field is switched off, the moments become disorderly again and the material cools. In certain alloys, this magnetocaloric effect is substantial – large enough to suggest a novel type of refrigeration based on cycling the magnetic field-switching and allowing the heat given off to escape. Companies are already interested in applying this environmentally-friendly technology to air-conditioning and supermarket chillers.

The giant magnetocaloric effect was first discovered in 1997 in the gadolinium silicon germanium alloy, $Gd_5(Si_{1-x}Ge_x)_4$, and has since been found in similar metal compounds. A field of 1 tesla (20,000 times the Earth's field) can produce a change of 3 to 4 degrees in these materials, and depending on the proportion of germanium contained, the effect can be tuned to appear across a range of temperatures between 20 and 295K.

The extent of the magnetocaloric effect is believed to depend on an intimate coupling between the material's crystal structure and its magnetism. X-ray and magnetisation measurements indicate that as the temperature drops, a strong magnetic moment appears alongside a change in crystal structure from monoclinic to orthorhombic. Figure 1 shows how bonds between silicon or germanium atoms of every second layer break, allowing the layers to shift sideways to a new structure.

Figure 3
Neutron diffraction contour plot of $Tb_5Si_2Ge_2$ in a selected angular and temperature range as recorded on the high-intensity D1B diffractometer. The diffraction peaks marked are of purely magnetic origin coming from the monoclinic (M), the orthorhombic (O1), or both crystallographic structures



Changing phases

The obvious question is whether the structural transition strictly coincides with the onset of magnetism, and if so which triggers which. We set about finding out using neutron diffraction. We chose a variant of the alloy containing terbium rather than gadolinium because the latter strongly absorbs neutron energy; the terbium compound still shows the magnetocaloric effect.

Starting at a temperature of 110K, well above the magnetic transition temperature, we found that applying a field as high as 5 tesla induced little change from the monoclinic to the orthorhombic structure (figure 2). Even when lowering the temperature to 105K, only half the sample changed. But what was surprising was that the magnetic scattering pattern obtained indicated that the remaining monoclinic phase had become magnetic as well.

To explore this unexpected magnetic phase, we decided to do a slow and detailed scan with an intense neutron beam, in a zero field, lowering the temperature at a rate of about 2 degrees an hour. The resulting diffraction pattern in figure 3 shows the magnetic peaks for the monoclinic (M) and orthorhombic (O1) structures, revealing that magnetism first emerges in the former and only at about 104K does the latter appear. The monoclinic peaks disappear at about 92K, marking completion of the structural transition. We also found that the monoclinic phase was largely ferromagnetic, similar in nature to the magnetic structure of the orthorhombic phase. Neutron studies are the only way that could distinguish between the two magnetic phases.

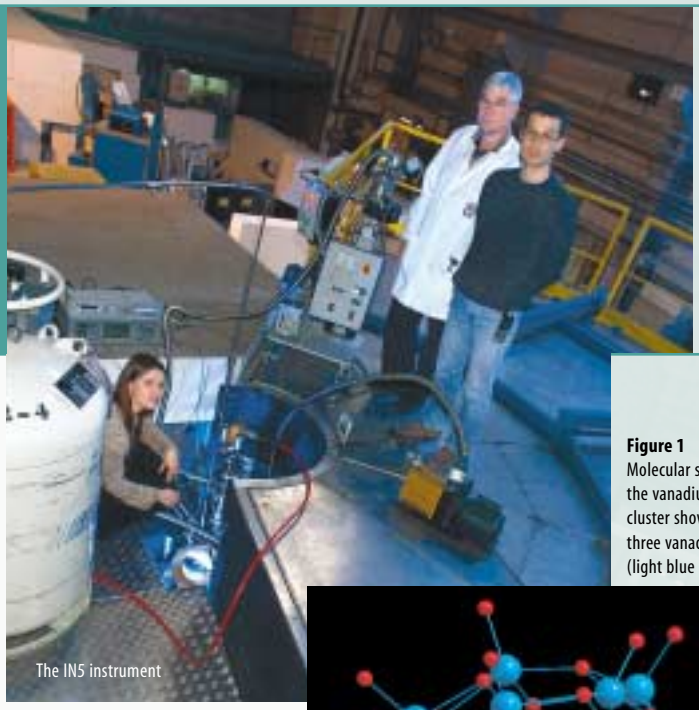
Clearly, these results are significant in understanding the magnetocaloric effect. The magnetic phase transition happens at a higher temperature (about 112K) than the structural phase transition (about 105K). Even an applied field of 5 tesla could not induce the change of more than 50 per cent in the crystal structure, showing that the interplay between crystal structure and magnetic properties is more complex than previously thought. ■

10 **Research team** C. Ritter *(ILL)*, L. Morellon, C. Magen, P. A. Algarabel and M. R. Ibarra *(University of Zaragoza, Spain)*

Single molecule magnets can display unusual magnetic interactions in which their local environment plays a significant role

>> GRÉGORY CHABOUSSANT

The vanadium triangle



The IN5 instrument

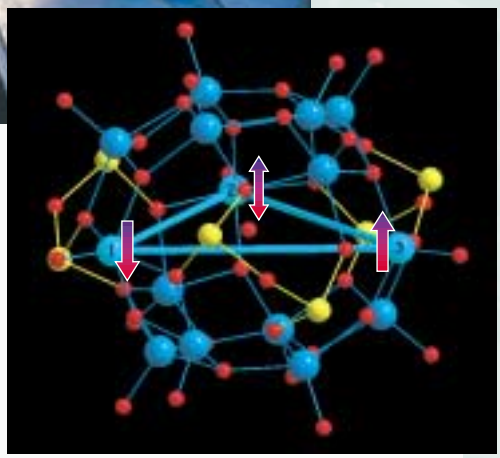


Figure 1
Molecular structure of the vanadium (V_{15}) cluster showing the three vanadium ions (light blue balls)

Molecules that contain a cluster of magnetic metal atoms are fascinating physicists and chemists alike because of the surprising ways in which the constituent spins can interact. Such a molecule is a heavily hydrated complex of 15 vanadium atoms ($K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$). Each vanadium ion has a spin 1/2. However, the spins arrange themselves antiferromagnetically to give a total molecular spin of only a 1/2 in the lowest energy, or ground state.

The reason behind this weak magnetic effect is shown in figure 1. The vanadium atoms are arranged as two hexagons with a triangle sandwiched between. The spins in the separate hexagons form strongly coupled non-magnetic pairs, which also interact weakly with individual vanadiums of the central triangle, so that these vanadiums are also weakly coupled with each other. At very low temperatures (2 to 3K), the system is effectively a magnet made up of three indirectly interacting spins. Since at least two of these spins are always forced to be parallel, while they would prefer to be antiparallel, the system is said to be 'frustrated'. It also means that there are two possible lowest quantum energy levels for the molecule, depending whether the spins are up or down.

Magnetisation experiments exploring this coupling have shown that the situation is actually more complicated. First, increasing and then reversing an applied magnetic field at different rates produces a peculiar kind of hysteresis effect (the lag in magnetisation/demagnetisation of the molecule behind the changing field) which suggests that the alignment of spins is affected by the vibrations of the crystal lattice (phonons). Secondly, at zero field the two ground states are not equivalent but differ by a small amount of energy.

Inelastic neutron scattering

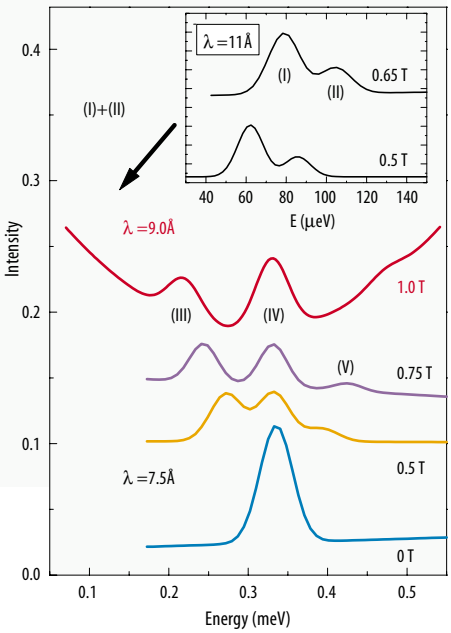
While magnetisation experiments have successfully explored the phonon-coupling phenomenon, high-resolution neutron scattering, combined with magnetic fields, offers the best method to investigate the origin of the split ground state. When neutrons scatter off molecules they can exchange energy – inelastic scattering – so that the atoms jump to another energy state, for example, by changing spin direction. Measuring the energies of the inelastically scattered neutrons thus gives the energy of the transition and identifies the quantum state.

By investigating the various transitions at different neutron wavelengths and magnetic fields, we could determine the energies of the vanadium cluster's lowest magnetic states. First, however, the hydrogen atoms of the water molecules in the vanadium complex had to be replaced by deuterium to reduce the 'background' from the strongly scattering hydrogens. The sample was cooled to between 40 and 50 millikelvin and the experiment was carried out with magnetic fields going up to 1 tesla.

Figure 2 shows the main experimental results at different wavelengths. They reveal five types of inelastic transitions, which can be explained by three sets of unequal couplings between the vanadiums making up the triangle of antiferromagnetic spins. There is a tiny but significant energy gap of 30 microelectronvolts between the two lowest states. The gap is most likely induced by the fact that the vanadium triangle is spatially distorted as a result of one water molecule sitting inside the cluster and disordered water molecules in the crystal lattice.

The data also suggest that the ground states are 'entangled' – a property of quantum systems in which states are intrinsically linked. Entangled states are of great interest in the burgeoning field of quantum computing as a future way of encoding and processing large amounts of data. ■

Figure 2
Inelastic neutron scattering spectra at different wavelengths and applied magnetic fields showing the five transitions, I, II, III, IV and V. The two lowest-energy peaks are shown in the inset

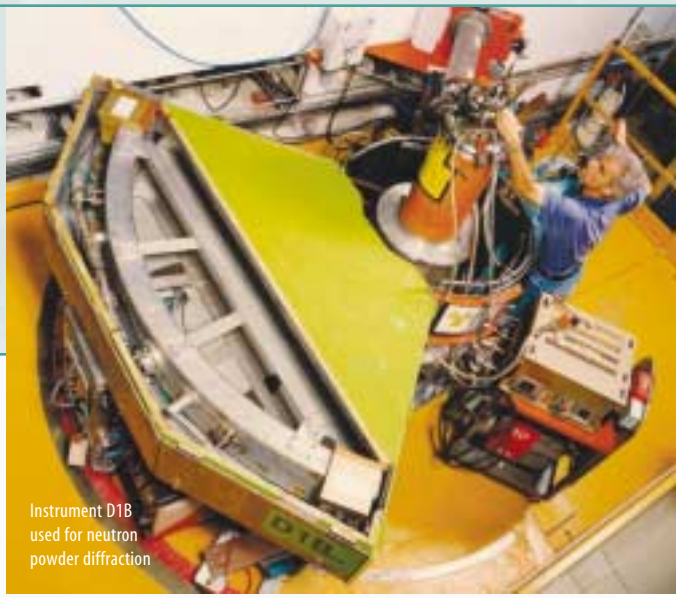


Research team G. Chaboussant, S. T. Ochsenbein, A. Sieber, R. Bircher and H.-U. Güdel *(University of Bern, Switzerland)*, B. Barbara *(Louis Néel Laboratory, Grenoble, France)*, A. Müller *(University of Bielefeld, Germany)* and H. Mutka *(ILL)*

Molecules seize the moment

Molecules with unpaired electrons offer a new type of magnetic material

>> DANTE GATTESCHI



Instrument D1B used for neutron powder diffraction

Magnets based on molecular building blocks have the potential to produce materials with novel characteristics of both theoretical and practical interest. The advantages of molecular magnets are that they can be altered by fine-tuning their structure chemically, they are soluble in organic solvents so can be processed easily, and they may interact with light in a technologically useful way. One intriguing application is in the new field of quantum computing which relies on encoding information in superposed quantum states.

Contrary to classical magnets, where the magnetisation density is localised on the atoms of metallic lattices, in molecular magnets the density may be spread across several of the constituent atoms. It is often difficult to understand the magnetic interaction without a detailed knowledge of how this magnetisation density is distributed. Here, polarised neutron diffraction techniques (p. 6) provide the most significant results.

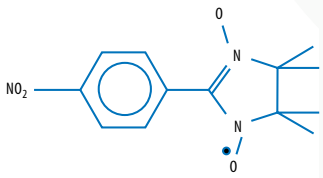


Figure 1
A nitroxide-based organic magnet

Organic magnets

The first materials investigated in this way were organic molecules containing a nitrogen-oxygen single bond carrying an unpaired electron – a nitroxide radical (to be magnetic, molecules must have unpaired electrons). Normally, radicals are very reactive, as the unpaired electron tries to seek a mate to form a stable chemical bond, but the radical can be stabilised by protecting the nitroxide bond with surrounding bulky groups of atoms. The first genuine ferromagnet made, with no metal atoms, is shown in figure 1 – although it was magnetic only below 0.6K. It contains a six-membered carbon ring (a benzene ring) attached to a nitrogen with attendant two oxygens (a nitro group). Polarised neutron studies showed that the unpaired spin density is not limited to the nitroxide bonds but actually spreads through the benzene ring to the nitro group. The nitro group of one molecule can then couple ferromagnetically with the nitroxide group of a neighbouring molecule. The measured spin density confirms this and agrees well with theoretical predictions.

Another fascinating class of magnetic molecules contain metal ions bound to flat, ringed organic structures called semiquinones, which again have an unpaired electron. When bound to a nonmagnetic titanium ion (Ti^{4+}), they generate moderately strong ferromagnetic coupling. Figure 2 shows a beautiful example, with two semiquinone-based structures attached to the titanium so that their planes are perpendicular to each other. The unpaired electrons responsible for the magnetism are smeared out in orbitals above and below the rings. We still do not understand how they couple ferromagnetically: the smeared-out orbitals could overlap directly; or the unpaired electrons could couple through the intervening orbitals of the metal ion. Polarised neutron data suggest that the latter is the case, as unpaired spin density is observed on the titanium atom.

Clusters of metal atoms bound in a molecular framework to create 'single molecule magnets' have also generated enormous interest. As described on p.6, the magnetic spins of the metal atoms can combine in complex ways. One of the first single molecule magnets discovered was a cluster of eight iron ions bridged by oxide and hydroxide ions – basically a fleck of rust enclosed in a flower-like organic structure. Magnetic measurements showed that the total spin of the molecule is 10. This suggests that since each iron atom has five unpaired electrons (spin 1/2 each, so total 5/2), six iron atoms must have their spins up (spin 15) and two must have their spins down (spin 5). Polarised neutron analysis of the magnetisation density as in figure 3 confirms this arrangement. ■

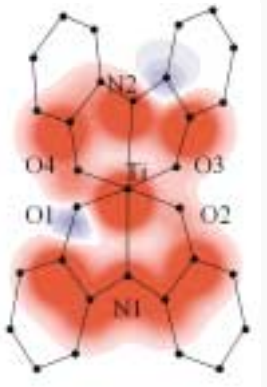


Figure 2
Map of the spin density of a titanium semiquinone radical-ion

KEY
Red: positive spin density
Blue: negative spin density

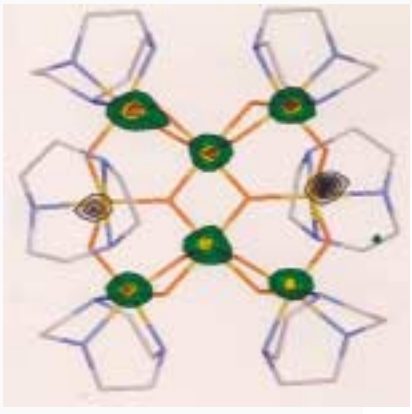


Figure 3
Map of the spin density of the single molecule magnet with a cluster of eight iron atoms

Research team D. Gatteschi, A. Dei, A. Caneschi and R. Sessoli *(University of Florence, INSTM, Italy)*, B. Gillon *(Laboratoire L. Brillouin, Saclay, France)*, D. Ressouche, J. Schweizer and Y. Pontillon *(DRMFC, CEA Grenoble, France)*

Two of a kind

How do spins pair up in superconductors?

>> JIRI KULDA AND STEPHEN HAYDEN

Metals become superconducting when an attractive interaction causes the conduction electrons to couple into 'Cooper pairs'. The paired electrons can combine their 1/2 spins to give an integer total spin of either 0 or 1. According to quantum theory, such particles are able to share the same energy state, unlike the individual constituent electrons, and it is this quantum property that gives a superconductor its unique properties – like the absence of electrical resistivity. In the earliest superconductors discovered – mercury and lead – the pairing interaction is mediated by vibrations of the metal's crystal lattice (phonons). It is strongest for electrons with opposite spins, so that they align antiparallel with their total spin equal to 0. Such materials are known as 'conventional superconductors'.

In recent years, many new forms of superconductivity have been discovered such as the high-temperature cuprates (p.16) and 'heavy fermion' compounds – heavy-metal alloys in which the electrons interact in a strong and complex way. Many of these materials have properties which are fundamentally different from conventional superconductors. In particular, the pairing interaction in these 'unconventional' superconductors seems to be different in nature. The crystal lattice appears to play little part in the interaction, and spins have a parallel arrangement.

Probing Cooper pairs

An excellent way of probing the type of pairing in superconductors is to measure how easily the spins are influenced by an applied magnetic field – the spin susceptibility. A conventional magnetometer, however, cannot be used because electric currents on the surface of a superconducting sample screen out the magnetic response inside the bulk of the material (the Meissner effect). So, to find out about the spatial distribution of the magnetisation inside a superconductor, polarised neutron diffraction is the method of choice. Neutrons scatter off the periodic arrangement of induced magnetic moments within the superconductor's crystal lattice to produce a series of diffraction peaks, whose intensities are then measured.

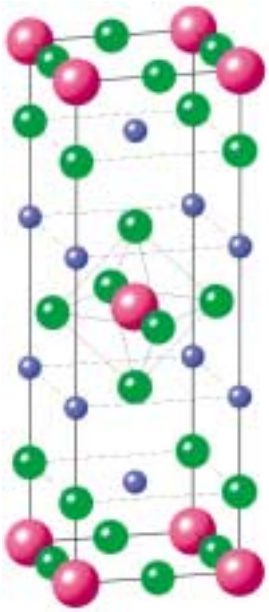
In the conventional superconductors, the electrons are paired antiparallel; their magnetic moments cancel so they are not affected by a magnetic field. This means that at zero temperature the spin susceptibility must be zero. However, as the temperature rises, the increasing thermal energy starts to break up some of the Cooper pairs into normal electrons, and the spin susceptibility rises. Neutron scattering data from experiments on the conventional vanadium-silicon superconductor (V_3Si) confirm this picture (figure 1a).

In a superconductor with parallel spins, when the field is applied along certain directions, the spin susceptibility actually remains finite even at zero temperature. A recently discovered superconductor strontium ruthenate (Sr_2RuO_4) was thought to show this behaviour. Indeed, carrying out the same kinds of measurements, we found that there was no drop in the spin susceptibility when strontium ruthenate became superconducting at 1.5K (figure 1b), as would be expected with conventional superconductors. This suggests that the electrons constituting the Cooper pairs have a non-zero spin moment, indicating that their spin states are the same.

This is particularly interesting because strontium ruthenate (figure 2) appears structurally similar to the high-temperature superconducting cuprates, which, however, exhibit a spin-1/2 pairing. Strontium ruthenate behaves much more like helium-3 in its superfluid state in which the two electrons are in equal spin states. ■

The IN20 instrument

Figure 2
Strontium ruthenate is a recently discovered superconductor which has many unusual physical properties such as a very large electronic specific heat at low temperatures. It also has very strong magnetic fluctuations (excitations)



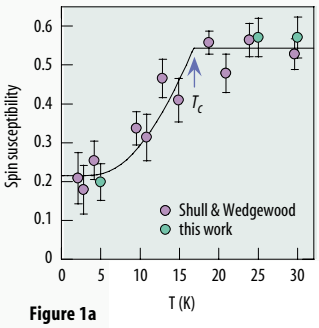


Figure 1a
The spin susceptibility in the conventional superconductor V_3Si measured by neutron scattering. This experiment was first performed by F. A. Wedgwood and Clifford Shull at MIT. Shull received the Nobel prize in 1994 for his contributions to neutron scattering

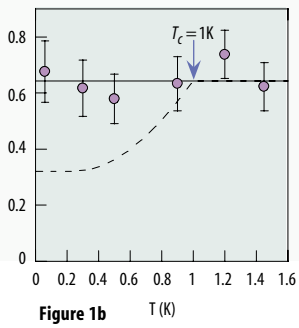


Figure 1b
The temperature dependence of the susceptibility in Sr_2RuO_4 measured by neutron scattering

Research team S. M. Hayden and J. A. Duffy *(University of Bristol, UK)* and J. Kulda *(ILL)*

Spin chains with a chiral twist

One-dimensional magnetic systems, called spin chains, show unusual dynamic behaviour that may shed light on how high-temperature superconductors work

>> JIRI KULDA AND HANS-BENJAMIN BRAUN

1

Figure 1
A domain wall, or soliton, separates the two types of antiferromagnetic order in a spin chain. They have equal energies so without quantum fluctuations, the domain wall can be placed at any point along the chain without changing its energy.

Figure 2
Quantum fluctuations induce transitions between spin states shown in figure 1 and lead to a soliton band. The states of lowest energy are left- and right-handed

Drawing hands by M.C. Escher

Chiral objects are those that cannot be superimposed onto their mirror images, such as our right and left hands. They occur at every scale in Nature from spiral seashells to molecules and elementary particles. Some of the most intriguing systems studied by condensed-matter physicists – like the high temperature cuprate superconductors (p.16) or low-dimensional spin chain systems – have no magnetic order in the traditional sense. However, the spins of their magnetic atoms do behave in a much more complicated way, than would correspond to simple disorder. This situation is thought to be linked to possible chiral arrangements of their quantum states.

This motivated us to study a simple prototype of a spin-chain system, caesium cobalt bromide ($CsCoBr_3$), in which chirality might emerge and be observed experimentally. In this compound, the spins of the cobalt ions are arranged in an up-down fashion along one crystal axis, forming an antiferromagnetic chain, and point in the opposite direction to those in the neighbouring chains. A similar arrangement with all the spins reversed has the same energy, so both states can be present, separated by a 'domain wall' as in figure 1. In fact, as a result of thermal fluctuations, one spin will occasionally flip over, triggering the neighbouring spins in the chain to flip sequentially. This creates a dynamic domain wall like a travelling solitary wave, or soliton, which destroys the antiferromagnetic order.

Spiral solitons

In the classical picture, these domain walls are just an abrupt switch-over between two neighbouring atoms (figure 1). Researchers have demonstrated previously, by neutron scattering, that because of 'quantum fluctuations' (due to the quantum uncertainty principle) the solitary wave joining the two possible spin arrangements is actually spread over a large number of adjoining atoms. Using spin-polarised neutrons, we have now demonstrated that this transition range has a well-defined internal structure: the spins turn in one direction or the other, creating a spin chain with a moving right-handed or left-handed twist (figure 2). As a result, the moving solitary waves have a clear handedness.

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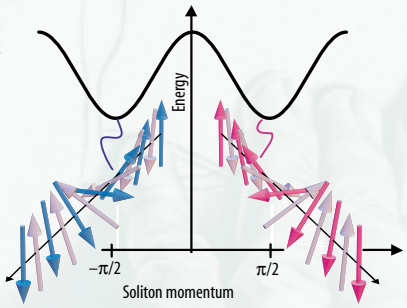


How spin-polarised neutrons scatter from a spiral structure depends on its handedness. If the neutron spin is parallel to the helicity, the neutron passes unaffected but is scattered if the spin is antiparallel. The spiral thus acts like a spin filter for neutrons. While this is a simple way to distinguish a static magnetic structure of fixed helicity, detecting the chirality of moving domain walls is far more challenging.

As long as the right-handed and left-handed solitons in the spin chain have the same range of energies, the neutrons cannot distinguish the two chiral states of the solitons since their effects cancel. This explains why chirality has remained undetected so far. We overcame this problem by applying an external magnetic field, which induces a slight energy difference between the populations of the right and left-handed solitons. In accordance with theoretical predictions, the response then shows a small asymmetry between neutrons, which had their spins parallel to the field and those with spins in the opposite direction.

This proves that quantum fluctuations induce a surprising metamorphosis, whereby the antiferromagnetic order is not simply lost by an appearance of moving domain walls but is replaced by a chiral arrangement of the magnetic moments.The discovered chirality may therefore shed new light on the behaviour of systems with exotic magnetic states at the limit between order and disorder, including those that lie at the heart of the still unexplained high-temperature superconductors. ■

The IN14 instrument

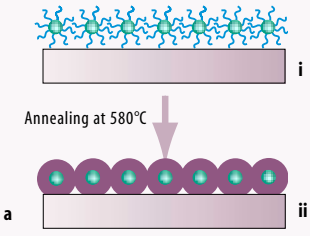
Research team H. B. Braun *(ETH, Zurich, Switzerland)*, P. Boeni *(TU Munich, Germany)*, B. Roessli *(PSI Villigen, Switzerland)* and J. Kulda *(ILL)*

The D11 small angle neutron scattering diffractometer

Magnetic nanoparticles could be the next medium for data storage

>> THOMAS THOMPSON, STEPHEN LEE AND CHARLES DEWHURST

Towards better recording media



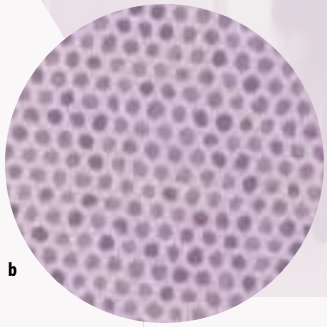


Figure 1
(a) Polymer-mediated self-assembly of nanoparticles, (i) is the polymer and (ii) shows the surfactant-coated particles; (b) electron micrograph of the evenly-sized, evenly-spaced nanoparticles

Nanotechnology – manipulating matter at the scale of a billionth of a metre – offers the potential for many exciting applications. In particular, creating ferromagnetic particles just a few nanometres across would allow data to be recorded and stored at densities of around 0.16 terabit per square centimetre (1 terabit per square inch) – 10 times that currently available on magnetic disks and tapes.

However, there is a problem: as the particles get smaller, thermal motions are more likely to prevent them from remaining magnetically aligned. This means that they can't be magnetised and demagnetised as is needed for recording data – the *coercivity* goes to zero. The hunt is now on to find ways of creating magnetically ordered arrays of nanoparticles that remain thermally stable at room temperature. Clusters of roughly equal numbers of iron and platinum atoms in a highly magnetically ordered arrangement (L10 phase), 4 nanometres across, turn out to be good candidates.

Recently, researchers at IBM developed a method for preparing the L10 phase by depositing the metal particles on a surface in a polymer matrix to give evenly-sized nanoparticles arranged in well-behaved layers. Following deposition, the films must be annealed at more than 500°C for about half an hour to form the desired phase. This burns off the organic material, leaving behind particles embedded in a carbon-containing matrix. However, the annealing process also tends to cause the particles to agglomerate into larger, less-ordered clusters. To optimise the films for data storage, it is vital to understand just how the final structural and magnetic properties of the particles are affected by the annealing conditions.

SANS reveals all

Small angle neutron scattering (SANS) was able to reveal the extent of agglomeration at different annealing temperatures. The nanoparticles were first deposited on double-sided silicon substrates to create films consisting of three layers of particles with composition $Fe_{58}Pt_{42}$ as in figure 1. The films were annealed over a range of temperatures (580 to 800 °C) and times (2 to 120 minutes); the magnetisation of the films was also measured. Figure 2 shows the neutron diffraction pattern for the as-deposited film. The coherent diffraction ring obtained confirms their regularity. The size of the particles is 4 nanometres and the average interparticle distance is 6.5 nanometres.

After annealing this diffraction ring disappears, indicating that the process has disrupted the ordering of the particles and that they have started to agglomerate. To estimate the sizes of the particle clusters formed, we compared the diffraction results with those predicted from theory. The SANS data indicate that significant agglomeration occurs for all three samples. The particle-cluster size increases from 4 nanometres for the as-deposited film to 6.2 nanometres for the film annealed at 580°C for 30 minutes, and to 16 nanometres for the 650°C/5 minutes film. In the case of the film annealed at 700°C for 5 minutes, the median size appears to increase rather dramatically to 66 nanometres.

The challenge of understanding and inhibiting particle agglomeration is currently the goal of a number of research groups worldwide, as is synthesising the L10-phase nanoparticles without the need for annealing. Although many hurdles must be overcome, the high coercivities found at room temperature demonstrate that these nanoparticles do indeed offer significant potential as very high-density recording media. ■

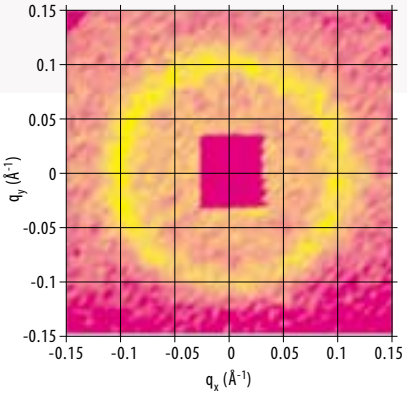
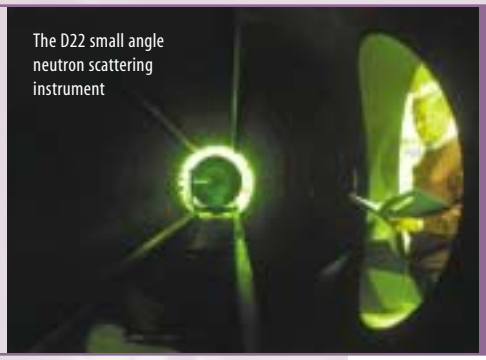


Figure 2
Diffraction image measured at room temperature for as-deposited nanoparticles with a diameter of 4 nanometres and a separation of 6.5 nanometres

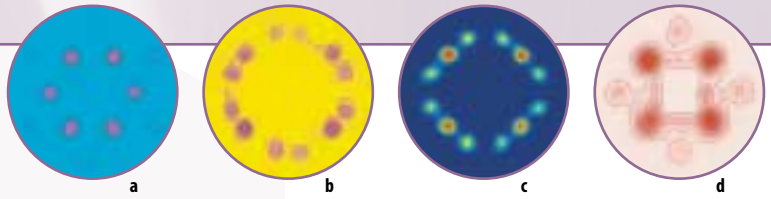
Research team T. Thomson and S. Sun *(IBM Almaden Research Center, USA)*, S. L. Lee and C. J. Oates *(University of St Andrews, UK)*, F. Y. Ogrin *(University of Exeter, UK)* and C. D. Dewhurst *(ILL)*



The D22 small angle neutron scattering instrument

The behaviour and motion of magnetic fields in superconductors is paramount in determining their usefulness for carrying large resistance-free electrical currents and generating strong magnetic fields

>> ROBERT CUBITT AND CHARLES DEWHURST



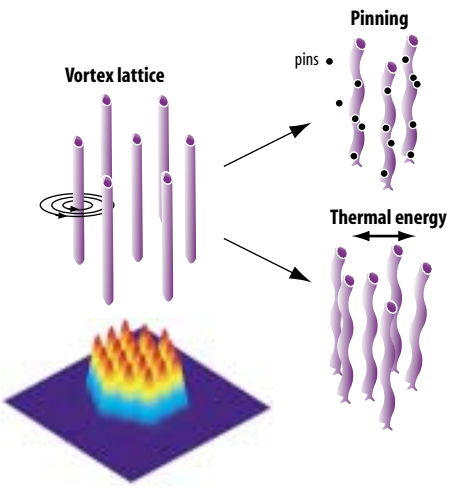
Small-angle neutron diffraction images showing peaks from the vortex lattice (VL) in (a) niobium, $T_c = 9.2$K and (b) the recently discovered magnesium diboride superconductor ($T_c = 38$K) where the VL splits into two equivalent domains of hexagonal lattice. If the currents around vortices are not circular due to the underlying crystal symmetry, the VL can become rhombic as in yttrium nickel boron carbide (c), $T_c = 15.5$K; or even square as in strontium ruthenate (d), $T_c = 1.5$K

Superconductivity: resistance is useless

Superconductors are materials that conduct electricity without resistance when cooled below a critical temperature, T_c. They can therefore transmit power with minimal loss as well as generate strong magnetic fields.

Until recently, the only superconducting materials exploited commercially (in powerful magnets) were alloys with T_cs not much above absolute zero. They had limited use because they required expensive liquid helium as a coolant. Then in 1987 a new class of superconductors was discovered – the ceramic cuprates – some of which have T_cs ranging upwards from 92K. These high-temperature (HTC) materials are revolutionising superconducting applications because they can be cooled with much cheaper liquid nitrogen. Indeed, they are already being exploited in power transmission, and in high-field magnets for levitating trains and medical imaging machines.

Their efficient application, however, requires an understanding of their superconducting properties at the microscopic level, in particular the behaviour of magnetic fields generated within them. The magnetic field is bundled into tubes called flux-lines or vortices sustained by circulating currents. Each vortex repels its neighbours, like bar magnets aligned in the same direction, and they naturally arrange themselves in a solid, hexagonal vortex lattice (VL).



The vortex lattice (VL) in superconductors creates an undulating magnetic field, much like the shape of the inside of an egg-box. The vortices are like threads of magnetic field. They repel each other and usually form a hexagonal lattice. Material defects can act as 'pins' to tack-down the VL and stop it from moving when an electrical current is passed. 'High' temperatures close to the T_c can violently shake the VL from its pinning centres and even melt the VL into a vortex liquid

The ability of superconductors to carry large currents depends crucially on the response of the VL. When a current passes perpendicular to the vortices they feel a force, in the same way as a current-carrying wire in an electrical motor feels a force in a magnetic field. If there is nothing to resist this force, the VL moves and energy is lost in dragging vortices though the material, so that the electrical resistance returns. Fortunately, real materials are often full of defects that form sites where the superconductivity is locally weaker than in the surrounding material. Vortices prefer to sit on these weak regions or 'pinning centres'. Only if the VL is 'tacked down' by these pinning centres can a significant bulk current pass though the superconductor without resistance. For high-current applications, manufacturers go to great lengths to introduce impurities in order to improve the electrical characteristics.

Seeing vortices

A neutron beam provides an excellent probe of these effects. The rows of vortices reflect neutrons to form a pattern of diffraction peaks characteristic of their arrangement. Vortex-pinning can be observed directly as broadened peaks in the diffraction images.

Of particular interest are the newer HTC materials with higher operating temperatures. In these cases, the increased thermal energy can shake the vortices so violently that the whole vortex 'solid' becomes unpinned and may even melt into a liquid of vortex lines. Such vortex liquids are useless for high-current applications. In most materials, the melting happens only at temperatures approaching the T_c, but a notable exception is a bismuth-containing cuprate – a favoured material for making superconducting tapes. Small-angle neutron diffraction experiments on this material have provided one of the first confirmations of this theoretically predicted phenomenon.

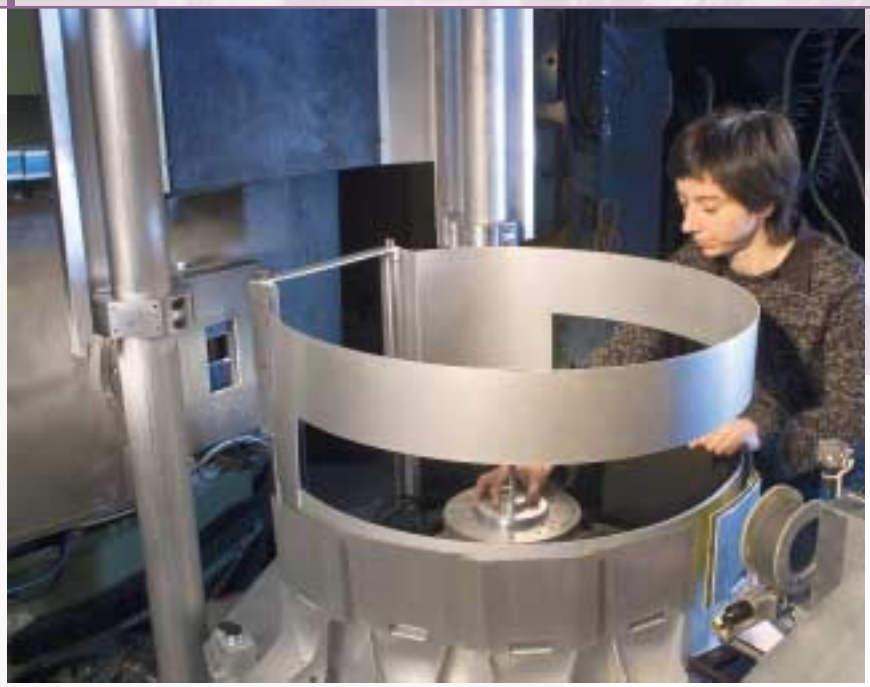
The 'Holy Grail' of superconductivity is thus not only to discover a material that superconducts at room temperature but also one in which the vortices can be rigidly pinned so as to support a large current. Neutron diffraction will continue to play a pivotal role in this technologically important quest. ■

16 **Research team** R. Cubitt, C. D. Dewhurst and S. Levett *(ILL)*, E. M. Forgan *et al (University of Birmingham, UK)*, D. McK. Paul *et al (University of Warwick, UK)*, S. L. Lee *et al (University of St. Andrews, UK)*, M. R. Eskildsen *et al (Notre Dame University, USA)*

Inside modern magnets

Neutron experiments combined with X-ray studies are leading to better permanent magnets

>> GERARD LANDER



IN8 – one of the instruments involved in the experiment, which has recently been rebuilt

Although iron is the most familiar magnetic material, many of today's 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 fully understand how. 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.

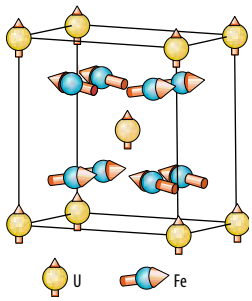
One such magnetic material is a compound containing iron, aluminium, and a rare earth (M) such as dysprosium (Dy) or holmium (Ho), or an actinide such as uranium (U). The formula is MFe_4Al_8, where M = Dy, Ho or U. The electrons responsible for iron's magnetism sit in the so-called 3*d* electronic shell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

A complex structure

We have been studying in considerable detail how the various electronic shells (3*d*, 4*f* and 5*f*) develop their ordered magnetic moments as the temperature is lowered. This has been the subject of considerable controversy in the past. Using polarised neutrons (p.6), we could obtain information about the orientation of magnetic moments. From these results, coupled with magnetic X-ray measurements made at the neighbouring European Synchrotron Radiation Facility, emerges a unified picture of the magnetic ordering process.

As we expected, the magnetic ordering is dominated by the 3*d* 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 remains disordered. In contrast, in the uranium compound, the iron 3*d* and uranium 5*f* electron shells interact enough to cause the two sets of atoms to order at the same temperature.

The X-ray studies show that ordering in the 4*f* electrons is more complicated and involves the information being transmitted to the 4*f* shells via the intermediary 5*d* electrons of the rare-earth element, but they do order when the temperature is low enough. Through polarised neutron measurements, we showed that the 4*f* magnetic moments dance along with the (dominant) iron 3*d* moments, but with their spins oriented at an angle to those of the 3*d* moments depending on temperature. This phase angle is different for each element, and its origin is not understood. At the lowest temperatures, the rare earth moments try and 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 good examples of how neutron and X-ray studies together can analyse the complex magnetic structure of strategically important materials. ■



The unusual magnetic configuration of the uranium iron aluminium (UFe_4Al_8) compound

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

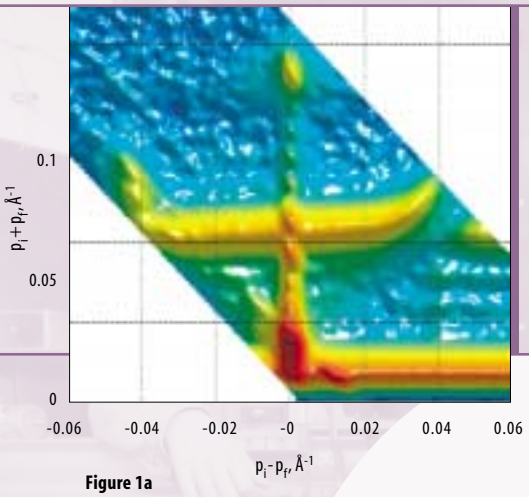


Figure 1a
Experimental two-dimensional map of the intensity scattered from an iron-chromium multilayer

Reflections on magnetic multilayers

Nano-sized magnetic films have huge commercial potential but have complex characteristics; polarised neutron reflectometry offers the best way to see inside them

>> VALERIA LAUTER

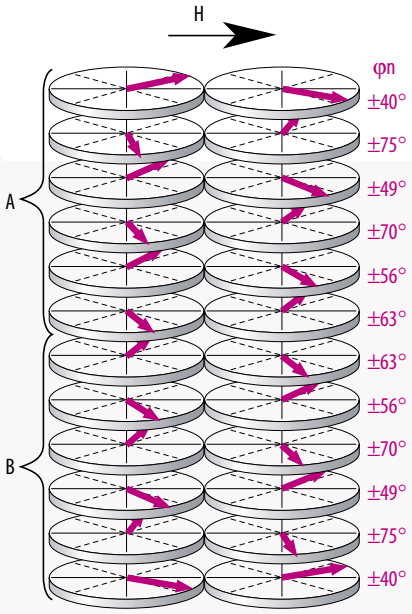


Figure 1b
Configuration of magnetisation orientation within the iron layers in an iron-chromium multilayer fitting the experimental data. The only possible two types of magnetic domains are depicted. Brackets A and B indicate the two transverse antiphase parts of one lateral domain

Magnetic films and multilayers, just a few atoms thick, are used in a wide variety of applications including magnetic media, recording heads, magnetic random access memory, sensors, and actuators. The interfaces and surfaces of these thin structures often introduce novel and useful characteristics. Indeed, most of the recent explosive growth in magnetic data storage has been due to new discoveries and a better understanding of the magnetic and electronic properties of complex magnetic thin films.

Studying the magnetism of these systems is extremely challenging. Most experimental methods give information averaged over all the layers. However, the technique of polarised neutron reflectometry – in which polarised neutrons are reflected off the surface and interfaces – provides an excellent method of probing in detail their complete magnetic and nonmagnetic structure both across and along the layers.

This analysis is achieved via two types of simultaneous measurement: that of normal, or specular, reflection of polarised neutrons – which gives information about the *transverse* structure of layers; and that of diffuse, or off-specular, scattering – in which differences in the *lateral* structure (magnetic and nonmagnetic) cause the reflected neutrons to deviate from the specular direction.

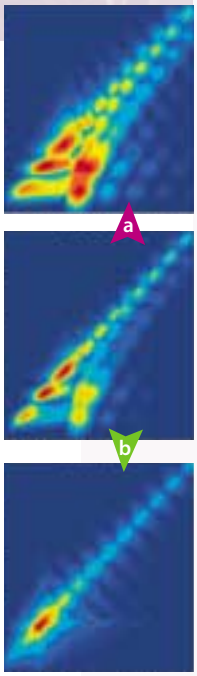


Figure 2
Reversing the magnetic field in an exchange-biased spin valve (CoO/Co/Si) as 'seen' by neutrons

Giant magnetoresistance

Using this approach we investigated a phenomenon of considerable commercial significance, giant magnetoresistance (GMR), whereby an external magnetic field induces a very large change in electrical resistance in a material with alternating magnetic and non-magnetic layers. The effect results from changes in magnetisation alignment in the layers which correspondingly influence the degree of scattering of electrons (responsible for resistance) passing through the layers. GMR materials are revolutionising data storage since they can be used in the devices that read the magnetised areas of computer disks.

One material we studied consisted of alternating iron (magnetic) and chromium (nonmagnetic) layers. We were able to determine how the magnetisation was oriented across and along the layers, from analysing the line shape in the specular and off-specular reflectivity patterns (figure 1a). This revealed that in the presence of a magnetic field the direction of magnetisation of the iron atoms is twisted up through the layers in a complex way – the first time this had been seen. The magnetisation within the layers falls into lateral domains about 200 to 300 nanometres across. Within each vertical domain column, the magnetisation orientation twists in alternate directions in alternate iron layers, with the difference in tilt increasing from the centre towards the top and bottom layers. The resulting configuration, figure 1b, has no net magnetic moment perpendicular to the external field and therefore is stable.

Polarised neutron reflectometry can also be used to study GMR multilayer devices, with potential in read-head applications, called exchange-biased spin valves. These consist of two ferromagnetic layers separated by a nonmagnetic spacer. An additional antiferromagnetic layer is coupled to one of the layers, effectively 'pinning' down its orientation. When the ferromagnetic layers are aligned parallel the resistance is low, but when an applied magnetic field reverses the magnetisation of the 'free' layer the resistance rises dramatically.

Figure 2 shows what can happen during the magnetisation reversal of an exchange-biased structure based on cobalt oxide-cobalt-silicon layers. The spins in the magnetic cobalt layers can re-orient to the new field direction either starting in small clumps which rapidly grow in size (the domain walls therefore move), or rotating all together. The two scenarios produce different off-specular reflectivity patterns (a and b). ■

 Research team V. Lauter *(TU Munich and ILL)*, H.J. Lauter *(ILL)*, B. Toperverg *(PNPI, St Petersburg, Russia)* and V. Ustinov *(MPI, Ekaterinburg, Russia)*

Interleaved layers of iron and vanadium exposed to hydrogen offer a new experimental approach to study magnetic systems with variable coupling between layers

>> VINCENT LEINER


The ADAM instrument

A new way to study magnetic multilayers

Devices based on ultra-thin multilayers of magnetic and nonmagnetic materials have important applications in the burgeoning area of 'spintronics' whereby information is transmitted or stored by manipulating electrons' spin. An important aspect of current research is to determine how the magnetic interactions between the layers can be tuned – for example, by altering the inter-layer spacings – to create useful properties. We have prepared a multilayer system that offers a new experimental tool for this kind of investigation.

More than 30 years ago Robert Griffiths, when at Carnegie-Mellon University in Pittsburgh, proposed, in a thought-experiment, a model system of spins arranged on a cubic lattice (figure 1). This lattice could be regarded as a series of planes of magnetic moments with a fixed, ferromagnetic coupling within the planes but a variable coupling between moments in adjacent planes. The interlayer coupling strength can be varied from positive, through zero, to negative. A positive coupling denotes that the magnetic interaction between the sheets causes the moments in adjacent planes to align and the whole system becomes a ferromagnet. If the coupling is negative, however, neighbouring ferromagnetic planes align in an antiparallel way so that the material becomes an antiferromagnet. With zero coupling there's no interaction between the magnetic sheets – the ferromagnetic planes no longer 'see' each other – and each layer becomes an isolated two-dimensional magnet.

Griffiths presented the properties of this system as a 'phase diagram' plotting the point at which the overall magnetic order vanishes in the system (critical temperature) against the strength of the magnetic coupling (figure 2a). This reveals that as adjacent layers decouple, the critical temperature also drops towards a minimum value at zero coupling – the system displays a strongly reduced but finite ordering temperature of a two-dimensional magnet. Interestingly, in the absence of an external magnetic field, the phase diagram is symmetrical around the temperature axis, indicating that the coupling behaviour over temperature is the same for both the ferromagnetic and antiferromagnetic regimes.

This kind of model which presents what happens as the interlayer coupling is varied is highly suitable for studying real 2D magnetic systems, and also for exploring the gradual transition from both a ferromagnetic and antiferromagnetic bulk magnet to a planar system.

A real experiment

We have now succeeded in realising this thought experiment of a fixed intra- and variable interlayer coupling for the first time, and have established the phase diagram. First, we prepared a multilayer system of two planes of iron atoms (ferromagnetic) and 13 planes of vanadium atoms (nonmagnetic) – repeated in a series of 200 composite layers. Neutron reflectivity and magnetometry studies show that the interlayer coupling is antiferromagnetic.

We could then alter this coupling by introducing hydrogen gas. Previous work had shown that the vanadium layers readily and exclusively take up hydrogen, expanding the metal lattice, which has a strong effect on the electronic properties of the host metal. In our experiment, a very small amount of hydrogen was sufficient to alter the strength and indeed the sign of the interlayer coupling.

We combined neutron reflectivity experiments with magnetometry studies to investigate the properties of our iron-vanadium multilayer system at different hydrogen concentrations and temperatures, and then mapped out a phase diagram (figure 2b). This showed that the experimental phase diagram is in very good agreement with Griffiths' theoretical one.

We think that metallic multilayer systems in which hydrogen is incorporated in one of the sublayers offers a new experimental approach to the investigation of magnetic phase diagrams, changes in the dimension of a magnetic system, and the critical conditions at which magnetic properties change. ■

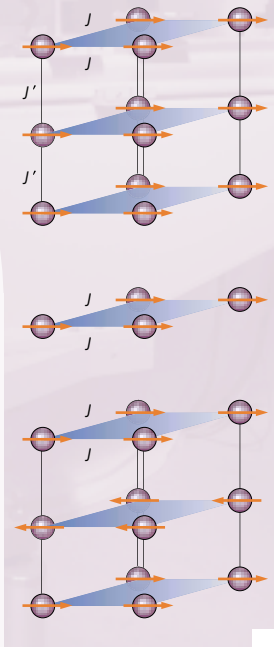
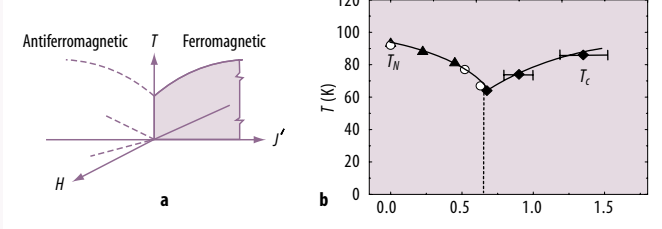


Figure 1
Spins placed on a cubic lattice with fixed intralayer coupling (J) but variable interlayer coupling (J')

Figure 2
a Griffiths' schematic magnetic phase diagram of a model system of spins on a cubic lattice (T is temperature, J' is the interlayer coupling strength and H is the external magnetic field)

b The experimental phase diagram of an iron-vanadium Fe_2/V_{13} multilayer as a function of hydrogen concentration and temperature



Research team V. Leiner *(ILL and University of Bochum, Germany)*, K. Westerholt and H. Zabel *(University of Bochum, Germany)*, A. M. Blixt and B. Hjörvarsson *(Uppsala University, Sweden)*

Glossary

Antiferromagnetism
A type of magnetic order in which the magnetic moments are alternately oppositely aligned.

Chirality
The notion of 'handedness', referring to an object whose mirror image cannot be superimposed on it.

Colossal (or giant) magnetoresistance
A phenomenon in which certain materials show very large changes in electrical resistance with magnetic field. The effect was first seen in europium chalcogenide thin films, where it is referred to as giant magnetoresistance (GMR). Even larger resistance changes, colossal magneto-resistance (CMR), have since been observed in a family of doped manganese oxides.

Coercivity
The magnetic field intensity needed to demagnetise a fully magnetised material.

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

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

Electron orbital
The quantum state of an electron in an atom or ion.

Electron shell
Atomic electrons are arranged in shells composed of specific orbitals – *s, p, d, f*.

Domain
A region in a magnetic material in which all the magnetic moments are aligned; domains with different alignments are separated by walls.

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

Giant magnetoresistance
See left: colossal magnetoresistance.

Gigapascal (GPa)
A unit of pressure – 1 gigapascal is a billion pascals, or 9870 atmospheres.

Ground state
The lowest quantum energy level a system can occupy.

High temperature superconductors (HTCs)
A class of ceramic oxides which become superconducting at temperatures above the boiling point of liquid nitrogen.

Hysteresis
The effect whereby the resulting change due to a force lags behind its application – particularly the magnetisation of a material in a changing magnetic field.

Magnetic moment
An 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 multilayers
Advanced materials consisting of alternating ultrathin layers of magnetic and nonmagnetic materials. Some of these materials behave as spin valves showing giant magnetoresistance.

Magnetic scattering
Neutrons have a magnetic moment which interacts with the magnetic moment of an unpaired electron in an atom. The arrangement of electron magnetic moments in a crystal lattice therefore produces a characteristic magnetic diffraction pattern.

Magnetocaloric effect
An effect whereby some magnetic materials heat up when placed in a magnetic field and cool down when removed.

Magnetoelectric crystal
A crystal that develops a magnetisation when immersed in an electric field and a dielectric polarisation when immersed in a magnetic field.

Molecular magnet
Single molecules with one or several unpaired electrons which show a variety of magnetic behaviours.

Molecular orbital
The quantum state of an electron associated with a molecule.

Monoclinic crystal
A crystalline structure with three axes of unequal length, two of which are perpendicular to the third axis, but not to each other.

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

Nanotechnology
The manipulation of materials and their physical and chemical properties at the scale of a nanometre.

Neutron
One of the two particles found in the atomic nucleus. Like all quantum particles, the neutron has both particle-like (mass, velocity, kinetic energy, gravitational effects) and wave-like (wavelength, diffraction and refraction effects) properties.

Neutron diffraction
Neutrons can be 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.

Off-specular reflection
See 'Specular reflection', right.

Orthorhombic crystal
A crystalline structure with three perpendicular axes of different length.

Permanent magnets
Materials such as iron that remain magnetic, with the constituent moments aligned, even in the absence of an external magnetic field.

Phase transition
The abrupt change in the properties of a material under defined conditions such as temperature and pressure.

Phonon
A quantum of atomic vibration in a crystal lattice.

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

Polarised neutron diffraction
A class of neutron experiments using polarised neutrons to investigate the magnetic properties of materials.

Polarised neutron reflectometry
A technique using polarised neutrons to investigate magnetic properties at surfaces and interfaces.

Powder diffraction
Coherent scattering from a polycrystalline material.

Quantum computing
A new type of computing based on manipulating quantum states which are intrinsically connected in a way that allows much more information to be processed.

Quantum fluctuations
The mathematics underpinning quantum theory predicts that there is always a small uncertainty in connected properties such as position and momentum, or energy and time. This results in inherent fluctuations in quantum states, for example, spin states that are similar in energy.

Quantum state
The defined energy state of a quantum system.

Small angle neutron scattering
The measurement of neutron scattering at small angles used to investigate large-scale structures such as polymers or biological molecular arrangements.

Specular reflection
Normal reflection from an interface or a multilayer structure in which the angle of incidence of the neutron beam equals the angle of reflection. Specular reflection gives information about the *transverse* structure of layers. In addition, the *lateral* layer structure (magnetic and nonmagnetic roughness) causes the reflected neutrons to deviate from the specular direction (diffuse or off-specular reflection).

Spin
The term describing the internal angular momentum of a quantum particle such as the electron or neutron. It has the value of 1/2 or multiples of that value.

Spintronics
A new technology in which information is transferred or stored using the spin of electrons.

Spin valve
A novel device that operates by allowing electrons with one spin state, but not the other, to pass a junction.

Superconductor
A material that has no electrical resistance below a certain temperature.

Contacts

Scientific Coordination Office (SCO)
Institut Laue Langevin
6 rue Jules Horowitz
BP 156
F-38042 Grenoble Cedex 9
France
Email: cicognani@ill.fr or kjenkins@ill.fr

Page 6
Dr Jane Brown
Email: brown@ill.fr

Page 11
Dr Grégory Chaboussant
Laboratoire Léon Brillouin
(LLB-CNRS-CEA)
CEA Saclay
91191 Gif-sur-Yvette Cedex, France
Email: chabouss@llb.saclay.cea.fr

Page 7
Dr Tapan Chatterji
Email: chatt@ill.fr

Pages 16
Dr Robert Cubitt
Email: cubitt@ill.fr

Page 4
Dr Roland Currat
Email: currat@ill.fr

Page 15 and 16
Dr Charles Dewhurst
Email: dewhurst@ill.fr

Page 12
Professor Dante Gatteschi
Department of Chemistry
University of Florence
Polo Scientifico Universitario
via della Lastruccia 3
I-50019 Sesto Fiorentino
Italy
Email: dante.gatteschi@unifi.it

Pages 13 and 14
Dr Jiri Kulda
Email: kulda@ill.fr

Pages 4 and 17
Dr Gerard Lander
Institute for Transuranium Elements
PO Box 2340
D-76125 Karlsruhe
Germany
Email: gerard.lander@cec.eu.int

Page 18
Dr Valeria Lauter
Email: vlauter@ill.fr

Page 19
Dr Vincent Leiner
Institute for Experimental Physics 4
Ruhr University of Bochum
D-44780 Bochum
Germany
Email: vincent.leiner@gkss.de

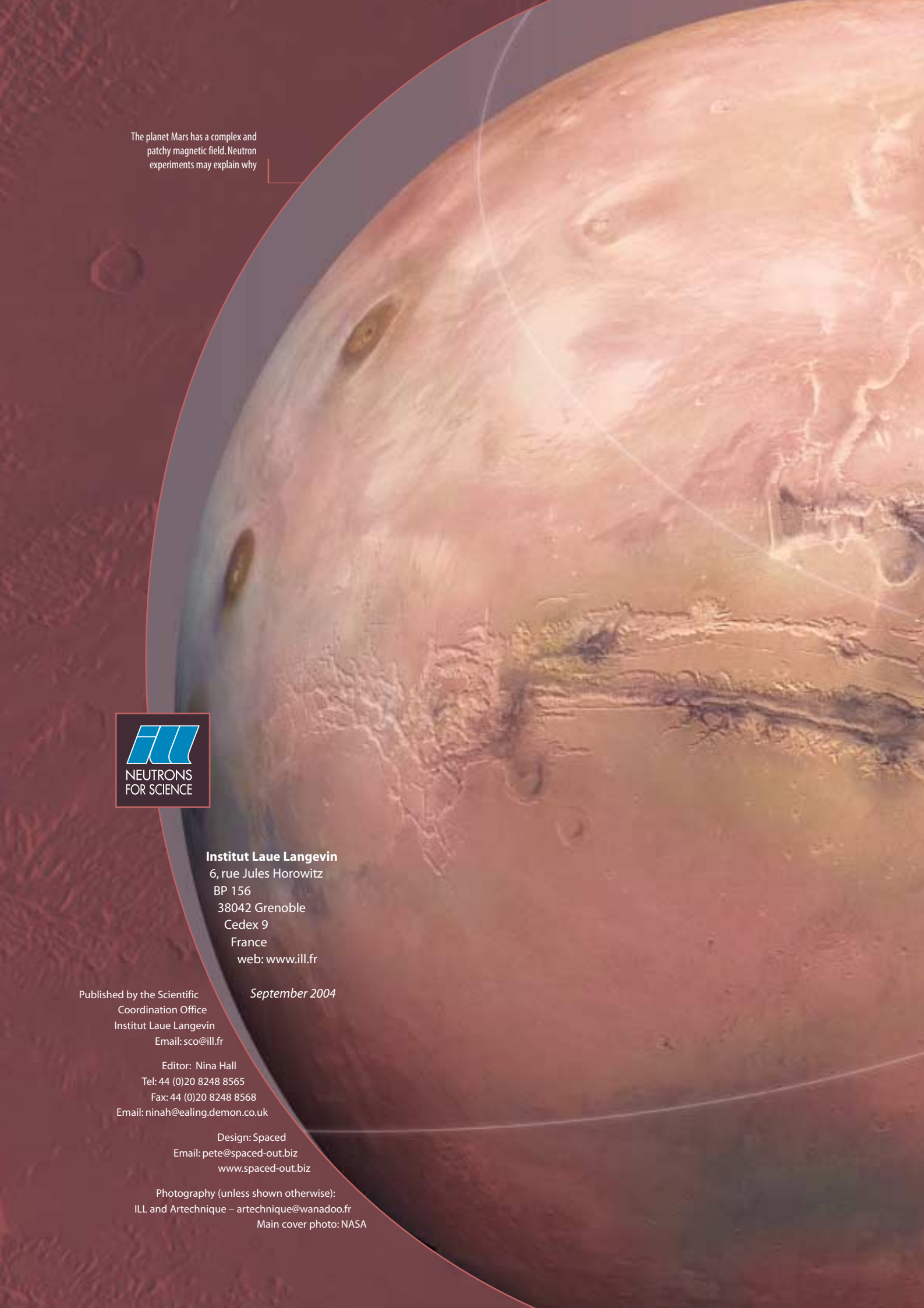
Page 8
Dr Eddy Lelièvre-Berna
Email: lelievre@ill.fr

Page 9
Dr Bachir Ouladdiaf
Email: ouladdia@ill.fr

Page 10
Dr Clemens Ritter
Email: ritter@ill.fr

Page 1 and 4
Dr Christian Vettier
Email: vettier@ill.fr

The authors are based at ILL unless otherwise stated



The planet Mars has a complex and patchy magnetic field. Neutron experiments may explain why

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Institut Laue Langevin
6, rue Jules Horowitz
BP 156
38042 Grenoble
Cedex 9
France
web: www.ill.fr

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www.spaced-out.biz

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