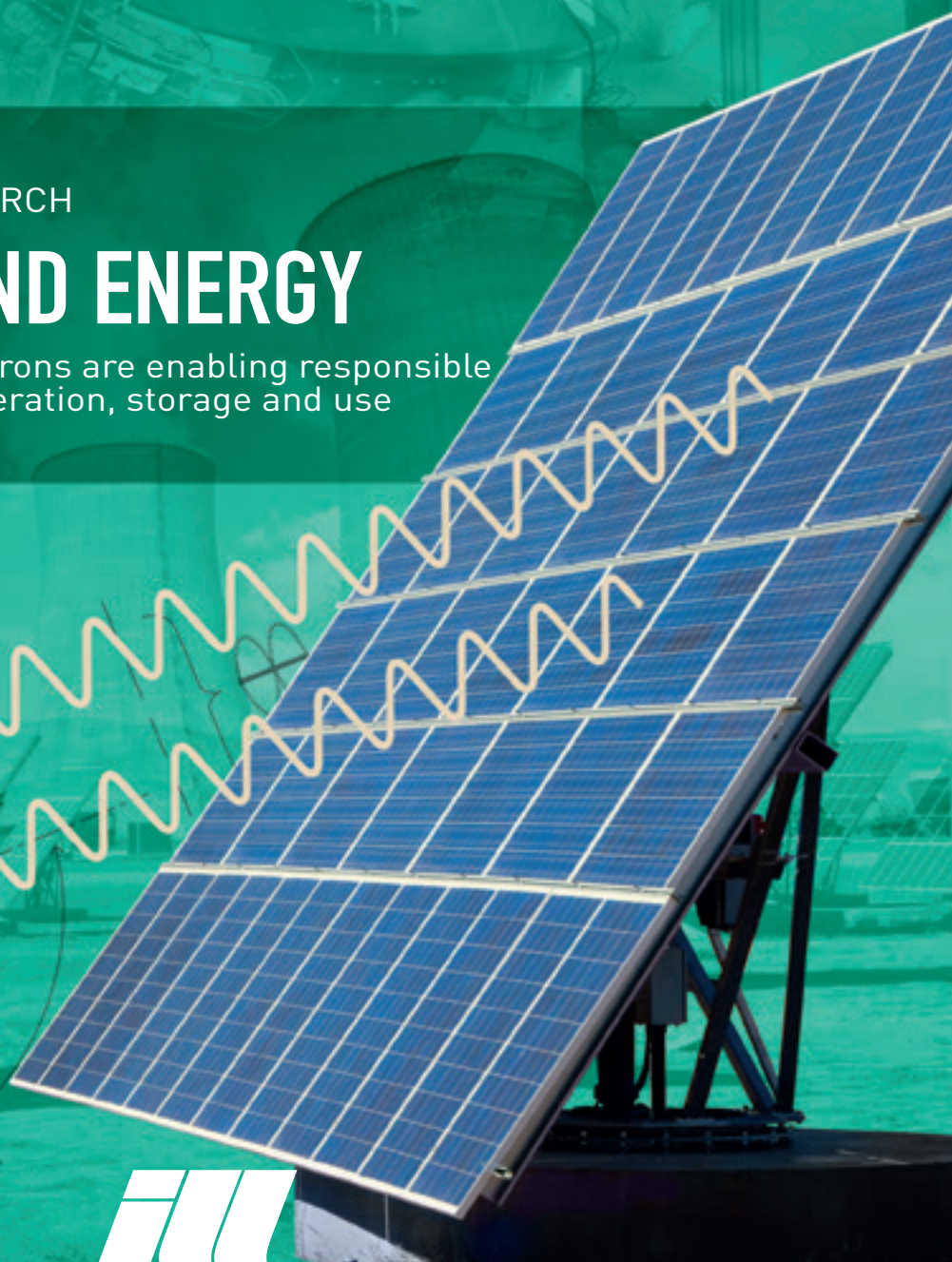
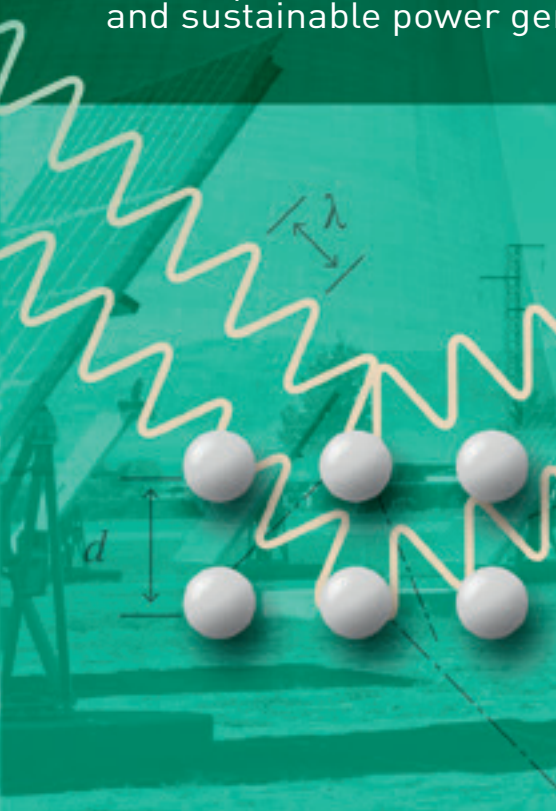


HIGHLIGHTS OF ILL RESEARCH

# NEUTRONS AND ENERGY

How experiments with neutrons are enabling responsible and sustainable power generation, storage and use



NEUTRONS  
FOR SCIENCE



# FOREWORD

Manipulating the resources of energy provided to us by Nature empowers us with the faculty of changing our environment. All through human history, progress in exploiting energy resources has triggered important societal changes. As citizens of the economically developed world, we each have, on average, several thousand watts of power at our disposal. To get a feeling for this abstract number, we can note that a human being can sustain a continuous effort at a rate of a few tens of watts, while that for a strong domestic animal may approach 500 watts. The power consumption in the developed world thus corresponds to about a dozen sturdy beasts of burden perpetually working for each citizen. This provision of external power liberates us from the necessity of spending most of our own energy on tasks essential for our subsistence – as it was the case for our ancestors, the majority of whom were forced to labour in the fields to grow food. We thus are free to dedicate the bulk of our time to tasks that we, as a society, consider important for our wellbeing and future development.

To maintain the current model of our civilisation, we have no other option than to make the provision of energy sustainable – and this, for reasons of fairness, in such a way that the totality of mankind can profit from similar standards of living. Making energy use more efficient will help. On its own, it will, however, be insufficient to reach this objective. We have to succeed in developing sustainable power delivery at current levels. In the Universe – and even on Earth – energy is actually not in short supply. Within about 2 hours, we receive from the Sun the equivalent of a year's global energy consumption – human energy needs are actually tiny on the cosmological scale. The problem is, therefore, harvesting and properly distributing power in a way that does not jeopardise our delicate terrestrial biosphere.



Physical and chemical processes are at the heart of this problem – whether it is in solar cells, nuclear and fusion reactors, or modern batteries. In order to optimise current technology – or even better, develop new technology – it is, in all cases, essential to understand the processes and the concomitant evolution of materials on the atomic level. Neutron scattering is the perfect analytical probe to add unique bits of this information. This especially holds true when the materials involved contain elements that are particularly visible with neutrons, like hydrogen or lithium. Neutron-induced gamma spectroscopy is another, very potent probe if the physical process is itself a nuclear reaction that can be triggered by the capture of a neutron.

In this brochure, we have chosen representative examples of current research performed at the ILL on scientific questions related to the energy question. They cover the whole energy pipeline, ranging from energy production to storage and efficient use, providing insight that either is unique or cannot be obtained with the same quality and ease by other probes. I am confident that you will be as impressed as I am by the possibilities offered by neutron science in a field that provides the key to the sustainability of human societies.

*Helmut Schober*

Helmut Schober  
Associate Director  
Head of Science Division

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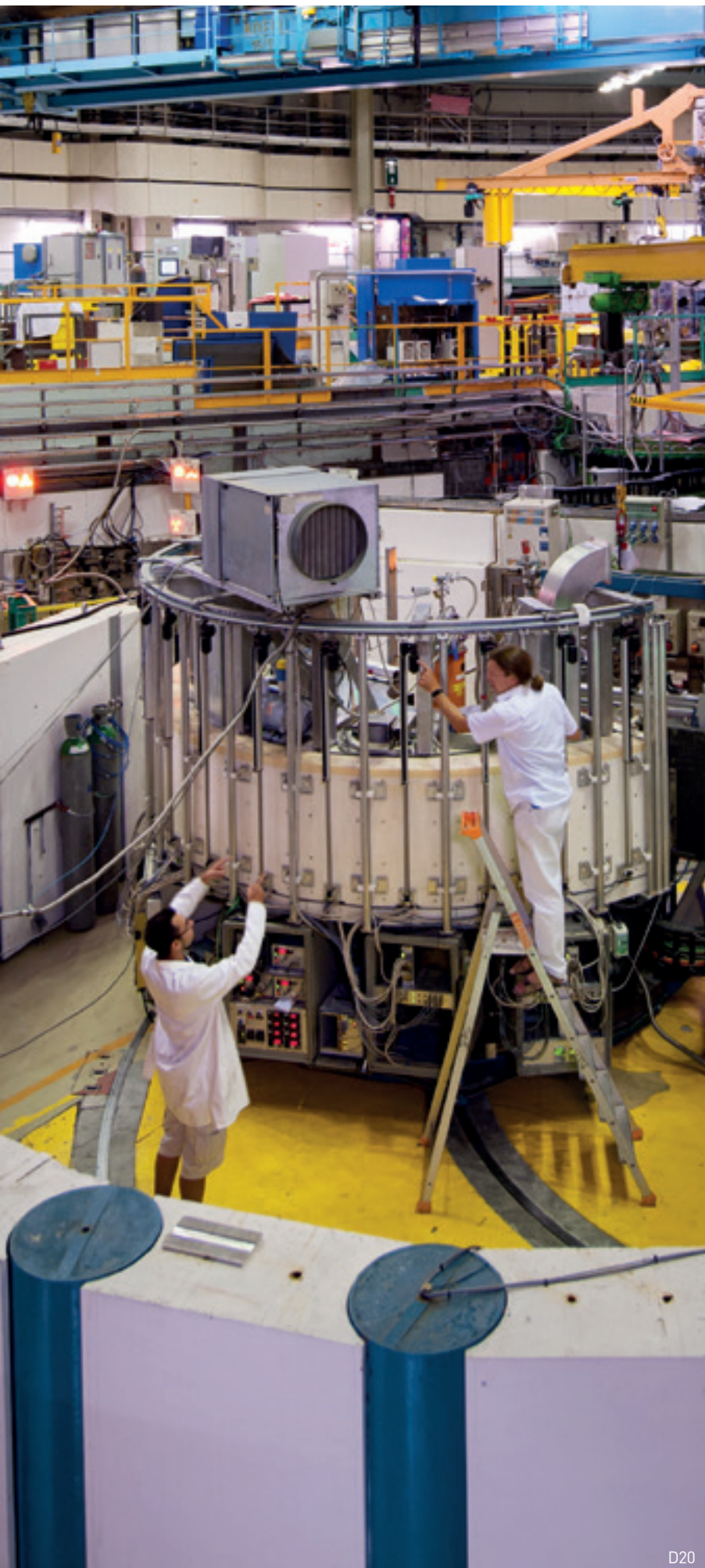
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# INTRODUCTION

## NEW MATERIALS FOR SUSTAINABLE ENERGY

GROWING ENERGY DEMANDS AND SERIOUS ENVIRONMENTAL CONCERNS MEAN THAT NEW AND MORE EFFICIENT FORMS OF ENERGY GENERATION AND CONSERVATION ARE REQUIRED – OFTEN BASED ON ADVANCED MATERIALS WITH CAREFULLY TAILORED COMPLEX STRUCTURES. NEUTRONS OFFER THE PERFECT TOOL TO STUDY THEM

Mohamed Zbiri and Thomas Hansen

Over the past two centuries, the industrial revolution has reshaped the destiny of humanity. It marked a major step towards seemingly unstoppable technological progress, reflected in our continuously evolving lifestyle. The practical realisation of advances in technology is strongly coupled to available energy resources, and the way in which they are generated, stored and used.

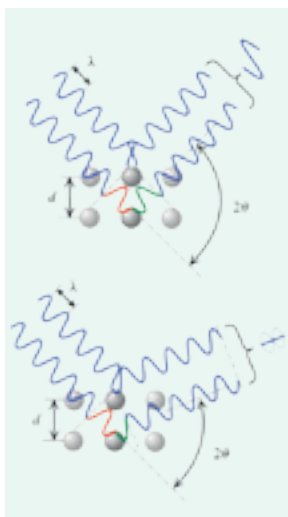
Energy sustainability is now a global issue. It is also a multifaceted challenge since it requires scientists, economists and politicians to cooperate in the search for solutions that, for example, reduce dependence on fossil fuels, and explore other options such as solar energy or the safe exploitation of nuclear power. Designing new, often highly sophisticated materials to achieve these goals has emerged as a significant field of scientific research, in which astonishing findings are being – and will be – achieved, at both applied and fundamental levels.

## DIFFRACTION REVEALS THE STRUCTURE OF MATERIALS

To optimise how these materials perform in energy applications requires careful engineering design, which in turn means studying their structure and behaviour at the level of atoms and molecules, as well as the bulk properties. Fortunately, Nature has provided a range of fantastic and powerful tools – in the form of various kinds of radiation, which allow us to ‘see’ the detailed atomic arrangements in a material, particularly if they are regular, as in the periodic geometry of a crystal lattice. For example, X-rays – a type of electromagnetic wave able to penetrate many materials – encompass the range of wavelengths that match interatomic distances (at the scale of nanometres). When the waves interact with regularly spaced similar atoms in a sample, they are scattered such that they combine, either positively to enhance their intensity, or negatively to reduce it. This creates a pattern of peaks (known as Bragg peaks) and troughs, in a strategically placed detector, that is characteristic of the atomic arrangement. From this diffraction pattern, researchers can work out the position of atoms in the crystal structure.



IN8



### THE POWER OF NEUTRONS

While X-ray diffraction is a powerful technique for studying materials, radiation composed of beams of subatomic particles – neutrons – is also an extremely valuable tool in materials research. Neutrons, which are found in the atomic nucleus, behave not just as particles but also as waves (according to quantum mechanics). Furthermore, they are also penetrating and, depending on their energy, their wavelengths can be adjusted to match the microscopic distances between atoms and molecules in a crystal. They are similarly scattered, producing diffraction patterns that provide significant structural information, which is complementary to that from X-rays.

While the arrangement of the Bragg peaks gives information about the overall crystal structure, much more data can be gleaned from the shapes of the peaks and the more diffuse signals lying in between. They may give information about localised irregularities in the structure such as missing or extra atoms (so-called defects), pores in solids and bubbles in liquids, or surface effects. These may have a critical significance in controlling a material's performance.

There are a number of variations of the diffraction technique employed for specific experiments. Larger-scale structures such as fibres, or polymers can be investigated using small-angle neutron scattering (SANS), see box, while thin films and layers, and their roughness, can be explored in reflectivity experiments in which neutrons are 'bounced' off sample surfaces and interfaces. If samples are composed of many small crystals instead of one large crystal (as is often the case for some materials), special equipment, combined with sophisticated computer techniques can be used to analyse the structure – a method known as powder diffraction.

### WHAT NEUTRONS DO PARTICULARLY WELL

- Low and medium-energy neutrons penetrate most materials but do not damage their structure. They can be employed to investigate even quite delicate materials, and can follow relevant structural changes in a sample over a given period of time.
- The main advantage of neutrons is that they are actually scattered by the central nucleus of an atom, unlike X-rays which interact only with the surrounding atomic electrons. This means that X-rays do not easily detect very lightweight atoms with low numbers of electrons (such as hydrogen). Neutrons, however, are readily scattered by light atoms such as hydrogen or oxygen, the strength of the scattering being dependent only on the nature of the scattering nucleus. Many materials important in energy generation contain light elements whose structural arrangement may be critical to performance, so neutrons are particularly useful for these studies.
- Another hugely important outcome of this scattering process is that neutrons can distinguish between different isotopes of an element (which nevertheless have the same chemical and electronic properties). This allows researchers to replace significant atoms in a structure with an isotopic variation so that they can be 'picked out' in an experiment. Hydrogen is often replaced by its heavier isotope, deuterium, which gives a different scattering signal that is easily seen. 'Deuteration' is one of the most powerful techniques in the neutron-scattering toolbox. Selected components of a sample can be deuterated so that they are specifically highlighted.
- Experimental setups can be arranged so that diffraction is measured over specific ranges of angles of the scattered neutron beam. Measurements made at very small angles provide information about larger structural features in a material.
- Neutrons can also be reflected off surfaces and interfaces to provide information about thin films and layers.
- The energies (speed) of neutron beams can be adjusted so that their wavelength is appropriate for specific studies. The energies can be measured before and after passing through a material; any change in energy will be the result of an interaction triggering a specific dynamical change (for example, rotation), which provides information about its behaviour.
- Neutrons also have a magnetic moment or spin, which can be exploited in experiments to look at the magnetic and electronic properties of a material.



## INELASTIC SCATTERING REVEALS HOW MATERIALS BEHAVE

Of crucial importance in developing better or novel energy sources is the probing of details of processes by which materials transfer or convert energy from one source to another. This involves understanding a wide variety of subtle motions at the atomic scale, with the aim of tuning the structural, chemical and electronic properties of a material or device to give the most efficient performance. So-called inelastic neutron-scattering spectroscopy provides the perfect way of uncovering these dynamics.

Inelastic scattering happens when neutrons exchange (either by gaining or losing) energy with a sample's material. By analysing the angular spread and energies of the scattered neutrons, insights can be gained into dynamical changes across a range of spatial and time-scales. For example, discrete magnetic excitations and vibrations of the crystal lattice can be measured. Diffusive motions such as small rotations and translations (p14), which involve very small energy changes over periods from picoseconds (covering the fast dynamics of small atomic groups and macromolecules) to nanoseconds (slow dynamics of large-scale molecular structures) are investigated via quasi-elastic neutron scattering, QENS.

A specific neutron technique known as neutron spin echo is particularly suitable for probing slow dynamics at the macromolecular scale by measuring changes in the spin of the neutrons following their interaction with the sample. The complexity of materials used in energy applications means that their behaviour involves many different kinds of dynamics, which can affect each other. In this context, experiments are frequently combined with computer atomistic modelling and molecular dynamics simulations to help in the analysis and interpretation of the neutron data.

## THE ROLE OF THE ILL

The Institut Laue-Langevin in Grenoble, France is one of the world's main facilities for neutron-based science. It employs a research reactor to supply neutron beams over a wide range of energies. State-of-the-art instruments designed for different types of diffraction and spectroscopy experiments can be operated with specific geometrical configurations of samples, and under a variety of environmental conditions (phase, temperature, pressure, magnetic field or chemical), often to simulate real working conditions as closely as possible.

## APPLICATIONS IN ENERGY STUDIES

Many kinds of energy-related experiments are carried out at the ILL using its suite of diffractometers and spectrometers, some of which are designed for particular kinds of measurements.

## ALTERNATIVES TO FOSSIL FUELS

The need to reduce dependency on fossil fuels has resulted in major global efforts to improve the efficiency and life-cycles of batteries and fuel cells for electric vehicles, as well as for portable power sources. New electrode compositions for advanced lithium batteries can be very effectively investigated using diffraction (p12), since lithium is a light element and is easily seen by neutrons. The performance of various fuel-cell designs can be optimised by using diffraction and spectroscopy to monitor changes in distributions of materials during operation, or to assess the effect of varying the chemical composition (p8 and 15). Water (H<sub>2</sub>O) in particular is easily detected because neutrons are sensitive to hydrogen (unlike X-rays) and when selectively substituted by heavy water (D<sub>2</sub>O) is even better distinguished. Fuel cells for vehicles may rely on the efficient storage of hydrogen (as a fuel). Complex light-metal hydrides are potential storage materials, whose efficiency in absorbing and releasing hydrogen can be effectively followed using a combination of neutron powder diffraction and judicious deuteration (p13).

Solar energy holds huge promise as an environmentally-friendly power source, and there is currently a great deal of interest in devices that convert sunlight into electricity using novel organic (carbon-containing) materials. However, their somewhat poor efficiency needs to be improved considerably. One type of organic solar cell relies on structured thin, electron-rich carbon films, which can readily be probed using neutron reflectivity (p9), while QENS has been used to identify the subtle molecular motions that affect electrical conductivity in a model organic solar material based on liquid crystals (p10).

Another process that makes use of an alternative energy source is the thermoelectric effect, which can be exploited to convert waste heat into electricity. Establishing the ideal material requires the identification of a suitable crystal structure with the right heat-flow and electrical properties – which can be investigated in neutron experiments (p16).

D16



# ABOUT THE ILL

The ILL is an international research centre at the leading edge of neutron science and technology. It is located in a setting of outstanding beauty in the cosmopolitan city of Grenoble in south-east France.

The Institute operates the most intense neutron source in the world, feeding neutrons to a suite of 40 high-performance instruments that are constantly upgraded.

As a service institute, the ILL makes its facilities and expertise available to visiting scientists. Every year, about 2000 researchers from more than 30 countries visit the ILL. Over 800 experiments, which have been selected by a scientific review committee, are performed annually. Research focuses primarily on fundamental science in a variety of fields; these include condensed matter physics, chemistry, biology, materials science, engineering, nuclear physics and particle physics.

Neutron-scattering experiments have made significant contributions to our understanding of the structure and behaviour of biological and soft condensed matter, to the design of new chemicals such as drugs and polymers, and to materials used in electronics and structural engineering. Neutron studies also offer unique insights into the nature of complex systems at the most fundamental level.

## NEUTRONS FOR EUROPE

The ILL was founded in 1967 as a bi-national enterprise between France and Germany with the UK joining later in 1973. As well as these three Associate Members, 11 Scientific Members now participate in the ILL: Spain, Switzerland, Austria, Italy, the Czech Republic, and more recently Sweden, Hungary, Belgium, Slovakia, Denmark and Poland.

## NEW ENERGY-RELATED MATERIALS

Nanoporous materials with frameworks that allow small molecules to diffuse through them have many applications that relate to the energy industry. They can separate hydrocarbon molecules relevant to oil refining, and again QENS can detect small molecular motions and forces that affect the diffusion process (p14). Such structures can also store hydrocarbons. Remarkably, water forms a natural porous framework hosting the hydrocarbon, methane. These clathrate hydrates are found as subterranean deposits and could be a future source of fuel. Neutron diffraction is ideal for probing these potentially important lightweight structures (p11).

The properties of engineering materials are significant in many areas of energy use and generation. For example, inefficient lubrication can result in energy losses. Neutron spectroscopy experiments allow researchers to uncover at the molecular level how new, improved carbon-based lubricants might do a better job (p17).

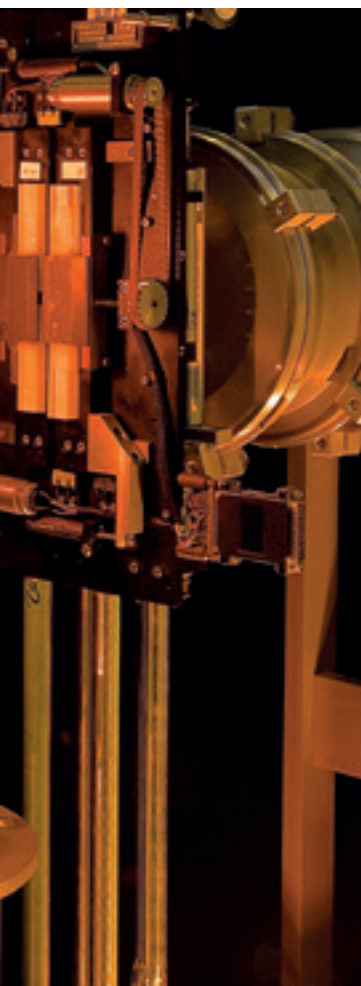
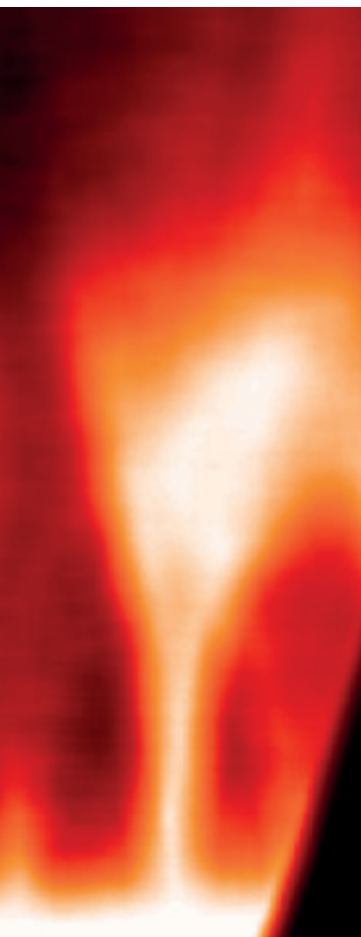
## SAFER NUCLEAR POWER

Stress corrosion cracking affects the life-span of large-scale engineering components. Here, neutron diffraction offers a unique tool in that it can measure directly the changes in interatomic distances due to stress in the crystal structure of a bulk item. The ILL has a dedicated instrument for this purpose called SALSA. It has successfully been used to assess the robustness of nuclear reactor components (p18).

Also crucial to the nuclear industry is the safe disposal of nuclear waste, which depends on the oxidation state of the spent uranium oxide fuel. Fortunately, neutron experiments focusing on capturing the diffuse scattering between the Bragg peaks in the diffraction pattern highlight the irregularities in the oxide structure that are relevant to understanding the oxidation mechanism (p19).

Finally, the ILL has one more trick up its sleeve that is highly relevant to the future of nuclear power. The facility has a strong nuclear physics programme that exploits high-energy neutrons from its reactor to make exotic isotopes of choice. As advanced and novel nuclear fuel cycles are explored, which are safer and produce less waste, more information on the relevant nuclear reactions, decay modes and amounts of nuclear fission products generated is needed. The ILL's LOHENGRIN spectrometer, and eventually its upgrade, are providing some of these important data (p20).

The following pages provide more details of all these experiments.





# FUEL CELLS GET COOL

**SOLID-OXIDE FUEL CELLS ARE CLEAN AND ENERGY EFFICIENT, BUT THE ZIRCONIUM OXIDE CURRENTLY USED REQUIRES HIGH OPERATING TEMPERATURES; NEW VERSIONS OF BISMUTH OXIDE MATERIALS COULD BRING THOSE TEMPERATURES DOWN**

Mark Johnson

The key materials component of solid-oxide fuel cells (SOFCs) is the solid-oxide electrolyte membrane. As in other fuel cells, fuel (for example, hydrogen) is supplied at the anode and oxygen at the cathode. In SOFCs, negative oxide ions that form at the cathode flow through the solid electrolyte membrane towards the anode, where they react with hydrogen to form water, generating a current around an external circuit.

SOFCs are one of the most efficient methods of generating energy (up to 85 per cent efficiency, compared with only 30 to 40 per cent for conventional power plants). In addition, they minimise emissions from pollutants such as carbon monoxide, nitrogen and sulfur oxides, and can utilise a wide range of fuels – including natural gas, petroleum, coal, biofuels, and hydrogen generated from renewable sources.

A crucial property of the electrolyte membrane is that it must be impermeable to fuel and oxygen gases under operating conditions, but permeable to oxide ions. Almost all practical SOFCs still use zirconium oxide stabilised by yttrium oxide ( $Zr_{1-x}Y_xO_{2-x/2}$ , or YSZ), first demonstrated to meet these criteria in the 1930s. However, to conduct effectively, YSZ requires temperatures of at least 750 °C, so SOFCs based on it need a large power input, suffer from mechanical degradation during thermal cycling and require the use of materials that are stable at high temperatures.

## STABILITY VERSUS MOBILITY

One way to reconcile the competing requirements of overall chemical (thermal) stability and the necessary chemical flexibility for conduction is to use oxides with much more complex structures than YSZ. Their crystal structures have regions with well-ordered arrangements of ions that act as 'scaffolds' for wide, continuous channels with more irregular arrangements that allow oxide ions to pass through.

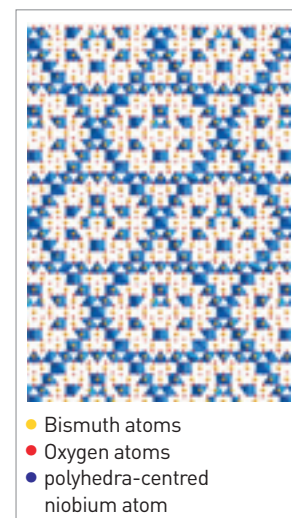
An important class of materials in this context is derived from the high-temperature form of bismuth oxide,  $\delta$ - $Bi_2O_3$ . This is the best solid-oxide ionic conductor known. A quarter of the oxygen sites in the crystal are empty, and these vacancies are randomly spread

throughout the structure, so allowing oxide ions to hop across the membrane. Pure  $\delta$ - $Bi_2O_3$  has never been seriously considered for practical applications because of its limited thermal stability. However, its useful characteristics can largely be preserved down to room temperature by introducing smaller heavy-metal ions into the structure. The resulting stabilised  $\delta$ - $Bi_2O$ -type phases have genuine technological potential and have been extensively investigated since the 1970s.

We recently explored the most effective of these phases, known as Type II, which shows the highest conductivities across the widest ranges of chemical and thermal stability. Type-II phases were poorly understood because their structures (p23) had never been fully analysed, due primarily to a lack of adequate data. We overcame this to achieve the most complete determination ever of a '3+3' dimensional incommensurately-modulated structure, by collecting neutron diffraction data from a large crystal of bismuth niobium oxide ( $Bi_2O_3-xNb_2O_5$ ) in the Type-II region. The result (right) revealed strings of ordered, niobium-rich regions separating continuous, disordered, oxygen-deficient channels, which are the basis of the very high conductivity.

In parallel, we investigated a molybdenum-containing oxide superstructure ( $Bi_{26}Mo_{10}O_{69}$ ), using a combination of inelastic neutron scattering and molecular dynamics calculations (p23). Our results suggest a new explanation for its high oxide-ionic conduction. They showed that some of the molybdenum ions could bond flexibly with extra oxygen to form different structural building blocks, which allowed the oxygen ions to travel through the crystal lattice. We also observed this behaviour with other metal ions that behave similarly, such as rhenium ( $Re^{7+}$ ) and vanadium ( $V^{5+}$ ). We are now carrying out further studies on similar structures and over various length- and time-scales.

A typical flat solid-oxide fuel cell, which converts chemical energy in the form of a fuel into electricity; a stack of these cells can thus provide a power supply



The refined crystal structure of bismuth niobium oxide obtained from neutron diffraction

**RESEARCH TEAM:** Ivana Evans (Durham University, UK), Chris Ling (University of Sydney, Australia) and Mark Johnson (ILL)

**ILL INSTRUMENT USED:** Single crystal diffractometer D19, and time-of-flight spectrometers IN4 and IN5

**REFERENCES:** C. D. Ling *et al.*, *J. Am. Chem. Soc.*, 2013, **135**, 6477; C. D. Ling *et al.*, *Chem. Mater.*, 2012, **24**, 4607; X. Kuang *et al.*, *Angew. Chem. Int. Ed.*, 2012, **51**, 690.



# PROLONGING THE LIFETIME OF ORGANIC SOLAR CELLS

LIGHT AND HEAT ARE THE KEY TO MORE EFFICIENT PHOTOVOLTAIC DEVICES BASED ON POLYMER-FULLERENE THIN FILMS

João Cabral

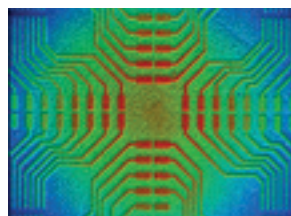
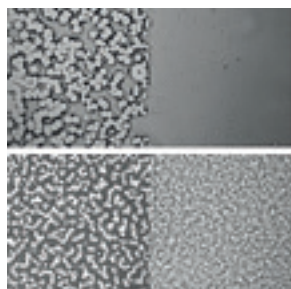
Solar-energy harvesting has the potential to meet rising global energy demands, which stands at approximately 18 terawatts, and is projected to double by 2050. Despite their promise, the devices that capture sunlight and convert it into electricity – solar cells – currently generate only about 0.2 per cent of our energy needs. This is because they are less efficient, have a short lifetime and apparently cost more, compared with other energy sources such as fossil fuels (which also have huge, hidden health, environment and safety costs).

One kind of cell that would be cheaper, as well as lightweight, utilises photosensitive organic materials. An organic solar cell contains an 'active' layer, about 100 nanometres thick, which can absorb a large amount of light, and is a balanced blend of two materials, an electron donor and an electron acceptor. When a photon of sunlight is absorbed, it excites the electron-donor molecule, so that an electron is released and moves to the acceptor. The resulting charges generated must then make their way to the appropriate electrode of the cell to create the electric current. The processes involved are dependent on the exact structure of the layer: the relative locations of the donor and acceptor molecules, and the pathways through the structure along which the charges can travel.

In order for organic solar cells to fulfil their promise, they must increase their efficiency to between 10 and 15 per cent, and their lifetime to many years.

An attractive thin active film being studied consists of a semiconducting polymer and  $C_{60}$  fullerene (football-shaped carbon 'buckyballs') that act as donor and acceptor respectively. The ideal 'heterojunction' film is structured at the nano-level to maximise chances of charge separation – and in an interconnected way, so that no charges are lost in 'dead-ends' before reaching the electrodes; each component should also be enriched close to the respective electrode. However,

Composites containing ball-shaped  $C_{60}$  molecules could tap into the Sun's energy



A small amount of light stabilises the structure of fullerene-polymer films (above) such that selective illumination and thermal annealing can be used to pattern nano-structured circuits (below)

cost-effective fabrication means that these films must rely on spontaneous assembly from solution, and it is extremely difficult to fabricate – and especially maintain – the optimised nanostructure. They are not particularly stable; environmental factors including heat, light, humidity and oxygen exposure can result in dynamic changes in the nanostructure, resulting in degradation in performance.

## THE BINDING POWER OF BUCKYBALLS

We used neutron reflectivity and small-angle neutron scattering (p5) to study and elucidate the structure and distribution of the components, how they were affected by the processing involved, and how they changed over time. We focused on the effect of light on fullerene chemistry, and subsequent changes in the morphology of the active layer. Fullerene molecules can oxidise and polymerise under light exposure, depending on the environment, and their relative position and orientation to each other. This then affects how they behave when the film is thermally annealed during fabrication.

We found that even gentle illumination seems to stabilise the structure by triggering a certain amount of chemical binding between fullerene molecules. Conveniently, the process is reversible with temperature. As a proof-of-concept, we also spatially modulated the light exposure and added heat, thus demonstrating that electrically-conducting fullerene nano-circuits could be patterned in this way (above left).

By careful processing of the polymer-fullerene films, we were able to increase the stability of these model solar cells by up to 200 times. This approach is thus a clearly promising route not only for increasing their efficiency and lifetime, but also generally for creating thin patterned films that remain stable over time.

**RESEARCH TEAM:** Him Cheng Wong, Zhe Li, James Durrant and João Cabral (Imperial College London, UK), Jack Douglas (National Institute of Standards and Technology, US), Anthony Higgins (Swansea University, UK) and Andrew Wildes (ILL).

**ILL INSTRUMENT USED:** D17 vertical reflectometer

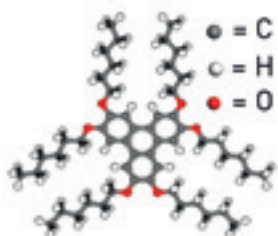
**REFERENCES:** H. C. Wong *et al.*, *Advanced Materials*, 2013, **25**, 985; Z. Li *et al.*, *Nature Communications*, 2013, **4**, 2227; H. C. Wong *et al.*, *ACS Nano*, 2014, **8**, 1297.

# LIQUID-CRYSTAL SOLAR CELLS

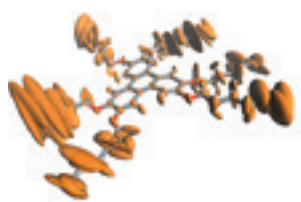
**RESEARCH AT THE ILL HAS SUCCESSFULLY UNCOVERED THE FUNDAMENTAL MECHANISMS THAT INFLUENCE CONDUCTIVITY IN A NEW TYPE OF POTENTIAL SOLAR-ENERGY MATERIAL**

Mohamed Zbiri

The Nellis Solar Power Plant array, Nevada, US



The planar symmetrical structure of the flat liquid-crystal molecule, HAT6 (above), which then twists and tilts giving the dynamically averaged structure shown below



Sunlight is the most abundant energy source on Earth, and a great deal of research is going into photovoltaic devices, or solar cells, that harness incident solar energy. They employ materials in which a charge separation is induced by photons of light to create a flow of charge carriers (negative electrons and the positive 'holes' they leave behind). Thanks to their low cost, inherent flexibility and relative ease of processing, photovoltaics composed of organic materials (carbon-based compounds) are potential candidates for the next generation of solar cells.

One particular group of organic materials that is of interest are so-called discotic liquid crystals (DLCs). These have a molecular structure consisting of a planar core composed of several conjoined, electron-rich hexagonal (aromatic) carbon rings, to which are bound a symmetrical arrangement of hydrocarbon tails that spread out from the core (above left). The resulting disc-like molecules self-assemble into stable columnar superstructures, which possess both solid and liquid-like properties arising from the rather stiff aromatic cores and 'floppy' hydrocarbon tails respectively. The columns act as one-dimensional 'molecular wires' that allow charges to 'hop' across overlapping electron-rich cores when combined with an electron acceptor. The charge separation results in an electric current when connected to an external circuit.

However, organic photovoltaics tend to suffer from a poor dissociation of charges, limiting their solar conversion efficiency. In the case of DLCs, the overall conductivity is strongly affected by the local conformation of the molecules, the presence of structural irregularities in the columns, and the disorderly

motions induced by the fluidic tails. Knowledge of how each of these three factors limits the hopping of the charge carriers along the columnar stack is valuable for the rational design of discotic compounds with optimal device performance. This calls for a careful study of structure-*versus*-dynamics property relationships at the microscopic level.

Neutron scattering is a convenient tool for studying this relationship in molecular organic systems, especially because deuteration (p5) can be used to highlight selected structural and dynamical components. Neutron diffraction can reveal the structural arrangements within the system, while quasi-elastic neutron scattering (QENS, p6) experiments can probe molecular motions on the required picosecond (ps) timescale. In this way, we could elucidate the morphology and motions in a prototype discotic liquid crystal, hexakis(alkyloxy)triphenylene (HAT<sub>6</sub>), and determine the effect of the dynamical disorder on its conductivity.

## LESS FIDGETING, MORE HOPPING

Using the time-of-flight (p23) spectrometer IN6, we observed motions on two timescales from the QENS spectra, which we assigned to molecular translations (0.2 ps), and tilt-and-twist motions (7 ps) of the whole HAT<sub>6</sub> molecule. They indicated that the motion of the hydrocarbon tails was driven by the core dynamics. The diffraction data, obtained with the diffractometer D16, highlighted considerable conformational disorder, which caused displacements of the planar aromatic cores along the stacking axis. These displacements act as structural traps for the charge carriers because they persist for several tens of picoseconds, which is longer than the characteristic timescale for the charge-hopping.

It turned out that the large disorder in the core-core distances is the major factor limiting the conductivity of HAT<sub>6</sub>. The charge-hopping rate decreases exponentially as adjacent cores get further apart. Using larger discotic molecules, which have higher conductivities, as a benchmark, we found that the structural defects resulting from variations in core-core distances reduce conductivity by a factor of about 100.

**RESEARCH TEAM:** Lucas Haverkate and Fokko Mulder (Delft University of Technology, The Netherlands), Gordon Kearley (ANSTO, Australia), and Mohamed Zbiri and Mark Johnson (ILL)

**ILL INSTRUMENT USED:** IN6 time-of-flight spectrometer, D16 diffractometer

**REFERENCES:** M. Zbiri *et al.*, "Organic Solar Cells", pp. 109-135, in *Neutron Applications in Materials for Energy. Series: Neutron Scattering Applications and Techniques*, (ed.), Springer 2015.

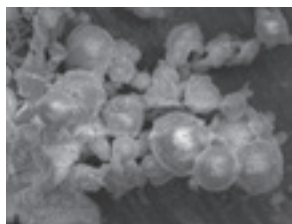


# INSIDE CLATHRATE HYDRATES

**NEUTRON STUDIES ARE PROVIDING A BETTER UNDERSTANDING OF GAS HYDRATES, WHICH COULD BE THE KEY TO FUTURE ENERGY SUPPLIES THAT OFFSET GLOBAL WARMING**

Andrzej Falenty, Thomas Hansen and Werner Kuhs

An empty clathrate structure composed of just water molecules



A neon clathrate hydrate sample



Methane hydrate burning

Clathrate hydrates, or gas hydrates, are crystalline solids, in which 'guest' atoms or molecules are enclosed inside cages formed by a three-dimensional 'host' network of hydrogen-bonded water molecules. They are known to store enormous quantities of methane and other gases in the permafrost, and in vast layers of hundreds of metres of sediment on the ocean floor. There are both negative and positive consequences of this. On the one side, methane is a powerful greenhouse gas, and climate change could trigger its release from the hydrates; on the other side, the total amount of methane stored within clathrates far exceeds the remaining exploitable reserves of 'conventional' carbon in the form of coal, petrol or natural gas. The gas-hydrate reservoirs are difficult to access at present – but are the subject of intensive research.

Clathrate hydrates can also be formed with carbon-dioxide gas, and these are stable under ocean-floor conditions. There is, thus, at least the theoretical possibility of extracting methane from the gas hydrates for energy and then replacing it with carbon dioxide pumped down into the ocean floor. The technical challenges are large and the feasibility is still questionable, but it remains an intriguing possibility worth exploring. The University of Göttingen is a member of the SUGAR project funded by the German government, whose aim is to explore the scientific, technical and economic possibilities for such an undertaking. Similar activities are currently underway in Japan, China, India and elsewhere.

A more immediate benefit of clathrate research is in assuring flow in gas pipelines. The gas is transported at high pressures and low temperatures – conditions that can lead to the formation of gas hydrates. These cause substantial blockages, the prevention of which costs the energy industry half a billion dollars per year worldwide. This is a significant cost that better predictions of clathrate stabilities could help reduce.

## CRYSTALLINE WATER CAGES

We set out to study the stability and physical chemistry of clathrate hydrates by preparing the first empty clathrate hydrate – that is, a framework of water molecules with all guest molecules removed, and long-thought to be purely hypothetical. We first synthesised a clathrate filled with neon gas. Such small atoms allow the clathrate to be emptied by pumping, without compromising its fragile structure. The neon clathrate was exposed to vacuum at temperatures up to about 140 K over several days, while neutron diffraction was carried out simultaneously with the high-intensity diffractometer D20. The powder-diffraction patterns obtained allowed us to follow the process of cage emptying, *in situ*, and to confirm when the clathrate had been fully emptied.

The diffusion constants and activation energy of the gas migration could be determined by analysing how the leaching process was affected by temperature. The fundamental structural and thermodynamic properties could thus be obtained experimentally for the first time. These are invaluable in underpinning theoretical calculations of clathrate behaviour needed by geologists and chemical engineers.

In addition, the empty clathrate, being composed entirely of water molecules, also represents a new phase of ice. Ice XVI is the 17th form of ice discovered, and is the least dense of all known crystalline forms of water. This discovery provides a new jewel in the crown of fascinating ice phases. Predicting the properties of ice XVI is thus not only an important step forward in understanding clathrates and their potential role in securing the world's energy resources, but also in understanding the most important resource for life – water.

**RESEARCH TEAM:** Thomas Hansen (ILL), Andrzej Falenty and Werner Kuhs (University of Göttingen, Germany)

**ILL INSTRUMENT USED:** High-intensity two-axis diffractometer D20

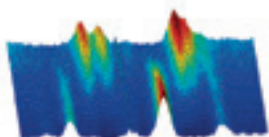
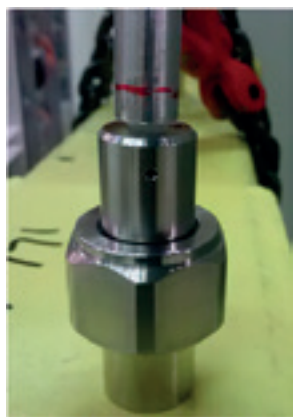
**REFERENCES:** A. Falenty, T.C. Hansen and W.F. Kuhs, *Nature*, 2014, **516**, 231; doi:10.1038/nature14014.

# TOWARDS A BETTER LITHIUM BATTERY

**A NEUTRON-TRANSPARENT BATTERY DESIGN CAN VISUALISE THE STRUCTURE AND BEHAVIOUR OF ADVANCED ELECTRODE MATERIALS**

Matteo Bianchini  
and Emmanuelle Suard

The novel battery developed at the ILL to study electrode materials during operation



The neutron diffraction results reveal the changes in the working lithium battery electrode: on charging, the initial lithium iron phosphate ( $\text{LiFePO}_4$ ) material disappears and is replaced by the iron phosphate ( $\text{FePO}_4$ ) charged phase

During the past three decades, lithium-ion batteries have become the leading technology for powering consumer electronics. Energy is stored in the battery when positively charged lithium ions flow through an electrolyte from a positive lithium-containing electrode to a more negative electrode; electrons then pass through an external circuit to balance the charge. Power is generated from the battery when the process is reversed. More recently, the use of lithium batteries has been spreading to the automotive market. However, the required improvement in their efficiency has been slow, and has somewhat held up the development of the electric car.

One of the key factors to improving their performance is to understand how the lithium ions are exchanged between the electrode materials during the charge/discharge cycle. This requires being able to 'visualise' the changes in the crystal structure of the electrodes. Neutron diffraction is an excellent technique for seeing lithium ions moving through the electrodes, because neutrons are readily scattered by light elements such as lithium (unlike X-rays).

## REAL-TIME MOVIES

For this reason, we developed a novel battery to study what happens in the electrode materials while it is actually operating. The aim was to obtain a high-quality, real-time movie of the entire process. The cell had larger-than-normal electrodes so as to obtain the optimum quality neutron-diffraction patterns for analysis. The most important feature was the use, in the fabrication of the cell, of a titanium-zirconium alloy, which is known for being neutron-transparent. In this way, only the signal from the electrode of interest was collected, while

avoiding other unwanted contributions from the cell. Moreover, the use of a deuterated version of the electrolyte further reduced the incoherent scattering and improved the signal obtained.

The studies were carried out on the D20 high-flux diffractometer – the high neutron flux being an extremely important feature, given that the samples were small in terms of what is normally required for neutron-diffraction experiments.

The working of the cell, the methodology and the quality of the diffraction patterns were first evaluated using relatively well-understood electrode materials such as lithium iron phosphate ( $\text{LiFePO}_4$ ). We were then able to study some newer electrode materials based on lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ). This is an interesting positive-electrode material, with a high capacity and charge/discharge rate. However, its capacity quickly fades upon cycling, thus thwarting commercial application.

The problem can be solved, however, by incorporating more lithium into the structure at the expense of manganese during synthesis, to give rise to compositions  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ , where  $x$  is the amount of extra lithium. This reduces the usable capacity but eliminates the problem of capacity-fading. We synthesised three compounds where  $x$  is 0, 0.05 and 0.10, and studied how their structure is modified as the lithium ions flow.

The study showed that not only is the volume change induced by the loss of lithium ions reduced as the proportion of lithium in the electrode material is increased, but also that the mechanism by which this happens is modified. As a result, the materials with the highest amount of lithium is a much better battery-electrode material.

Given these promising results, the study of this material type is expanding to different compositions such as those containing additional nickel ( $\text{LiMn}_{1.6}\text{Ni}_{0.4}\text{O}_4$ ), operating at higher voltages and thus having more energy. The cell will be also used for studies on new positive and negative electrode materials – thus establishing neutron diffraction as the ideal technique for understanding the behaviour of lithium ions and structural modifications in lithium-ion batteries.

**RESEARCH TEAM:** Matteo Bianchini and Emmanuelle Suard (ILL), Christian Masquelier (CRCS, Amiens, France) and Laurence Croguennec (ICMCB, Bordeaux, France)

**ILL INSTRUMENT USED:** High-intensity two-axis diffractometer D20

**REFERENCES:** M. Bianchini *et al.*, *J. Phys. Chem. C*, 2014, **118**(45), 25947; M. Bianchini *et al.*, *J. Electrochem. Soc.*, 2013, **160** (11), A2176.



# COMPOSITE COMPOUNDS FOR HYDROGEN STORAGE

COMPOSITE HYDRIDES ARE PROMISING CANDIDATES FOR STORING HYDROGEN FUEL; NEUTRON DIFFRACTION UNCOVERS HOW THEY WORK

David Grant, Gavin Walker and Thomas Hansen

Hydrogen is a clean fuel for transport; its successful use depends upon developing a compact, light, safe and mobile way of storing it on-board. Metal hydrides are potential hydrogen carriers, thanks to their relative stability, and ability to take up and then release large amounts of the gas.

Much research has focused on hydrides of aluminium and boron in form of complex anions,  $[\text{AlH}_4]^-$  and  $[\text{BH}_4]^-$ , bound to light-metal cations such as lithium,  $\text{Li}^+$ , or sodium,  $\text{Na}^+$ , offering high hydrogen-storage capacities (18.5 per cent by weight for lithium borohydride). Unfortunately, the high stability of many complex hydrides means that the temperatures at which they decompose are too high – for example, lithium borohydride does not fully decompose until it reaches 600 °C. Adding another hydride or an element can destabilise the composite (or multicomponent) system and lower the decomposition temperature. The related reaction pathway is often complex and can vary depending on the circumstances of decomposition.

Several experiments on the ILL's high-intensity powder diffractometers, D20 and D1B, have shed light on the decomposition pathways of two composite systems: lithium borohydride combined with magnesium hydride ( $\text{MgH}_2$ ) to form a mixture  $2\text{LiBH}_4:\text{MgH}_2$ ; and a binary hydride ( $\text{LiH}$ ) combined with germanium. Neutron diffraction detects light elements more reliably than X-rays. Modified mixtures, with deuterium replacing hydrogen, yield even more clearly the changes in crystal structure and composition during a reaction's progress.

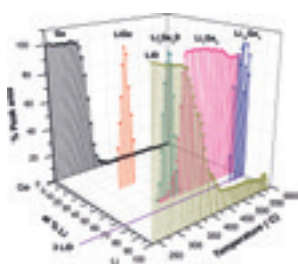
## REAL-TIME INVESTIGATIONS

The decomposition of  $2\text{LiBH}_4:\text{MgH}_2$ , under a partial pressure of hydrogen greater than 1 bar, was already accepted ( $2\text{LiBH}_4 + \text{MgH}_2 \rightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$ ). Under a pumped vacuum, a fully de-hydrogenated magnesium–lithium alloy forms quickly and the reaction is easily

reversible, which is favourable for hydrogen storage. Nonetheless, there was a puzzle; some researchers had found that a mixture of magnesium metal and lithium hydride formed instead – with poor reversibility. Our investigations, carried out in real time, discovered why: different vacuum systems offer different partial pressures of hydrogen, which affects the decomposition pathway.

We explored further the reaction pathways of more magnesium-rich composites ( $\text{LiBD}_4:\text{MgD}_2$ ) in various ratios – 0.3:1, 0.23:1 and 0.44:1. All the samples decomposed to lithium–magnesium alloys regardless of the vacuum system or the ratios of the constituents. However, upon cooling, if a low-to-medium vacuum system was used, then the partial pressure of hydrogen was sufficiently high to allow lithium hydride to form. This is significant for investigations of lithium-containing, multi-constituent systems, and the reproducibility of results achieved with different vacuum pump systems, since the amount of evolved hydrogen changes. Our results have also helped to explain differences in the reported reversibility of the systems with lithium-rich samples, which form a passivating hydride layer that hinders further hydrogenation.

Another example of the importance of the *in-situ* exploration of dehydrogenation pathways of new composites is the lithium-hydride–germanium system. Adding germanium greatly increases the ease of dehydrogenation for lithium hydride, so that hydrogen evolves at much lower temperatures, around 270 °C. We found that the reaction pathway goes through a sequence of steps involving germanium-rich compounds, but with the content of lithium gradually increasing ( $\text{LiGe}$ ,  $\text{Li}_4\text{Ge}_2\text{H}$ ,  $\text{Li}_9\text{Ge}_4$  and  $\text{Li}_7\text{Ge}_2$ ). Further studies measuring the heats of formation associated with the various compositions showed that such hydride systems could be optimised to work at low working temperatures.



Powder neutron diffraction experiments on a lithium-hydride/germanium sample ( $3\text{LiD}/\text{Ge}$ , *ie* with deuterium replacing hydrogen) beautifully reveal the phases that form as it decomposes when slowly heated to 600 °C under dynamic vacuum

**RESEARCH TEAM:** David Grant, Gavin Walker, Tobias Price, David Weston, Xuebin Yu and Marwa Abbas (University of Nottingham, UK), Dorthe Ravnsbæk, Torben Jensen and Lene Arnbjerg (Århus University, Denmark), Vincent Legrand, Michela Brunelli (ILL at the time) and Thomas Hansen (ILL)

**ILL INSTRUMENT USED:** High-intensity two-axis powder diffractometers, D20 and D1B

**REFERENCES:** E. C. Price *et al.*, *J. Am. Chem. Soc.*, 2011, **133**, 13534; doi:10.1021/ja204381n. M. A. Abbas *et al.*, *Phys. Chem. Chem. Phys.*, 2013, **15**, 12139; doi:10.1039/c3cp51330k.

# SPEED FREAKS IN MOLECULAR SIEVES

SMALL MOLECULES WHOSE SIZE MATCHES THE WIDTH OF CHANNELS IN NANOPOROUS MATERIALS CAN MOVE THROUGH THEM IN SPECTACULAR AND UNEXPECTED WAYS

Hervé Jobic

Nanoporous materials, which are characterised by an open molecular framework of regularly arranged channels, behave as 'molecular sieves'. They readily adsorb small molecules, and can be used to separate gases. Minerals such as zeolites (nanoporous aluminosilicates) are already employed in the energy industry to separate methane ( $\text{CH}_4$ ) – the major component of natural gas – from other short-chain hydrocarbons. Removing carbon dioxide from the gas mixture is also important, since its presence leads to pipe corrosion and to reduced energy content.

A great deal of effort is going into designing new nanoporous materials with dimensions and chemical properties tailored to do a particular job. They include not only inorganic materials such as zeolites but also networks of organic molecules held together with clusters of metal atoms. These metal-organic frameworks (MOFs) have attracted immense interest, because of their fascinating structures and potential applications for adsorbing and separating gases and liquids. Carbon molecular sieves are also promising as adsorbents or membrane filters.

In nanoporous materials, the width of the pore is very similar to the size of the molecule diffusing through. The result can be unusual and lead to unexpected behaviour, which is clearly important to understand. So, over the past few years, we have been exploring unusual diffusion effects using a combination of theoretical studies and quasi-elastic neutron scattering (QENS, p6), which we describe below.

■ *Quantum kinetic sieving.* Surprisingly, a carbon molecular sieve can be used to separate hydrogen and its heavier isotope, deuterium because of the isotopes' quantum properties. According to quantum mechanics, the molecules behave as waves as well as particles. The wavelength associated with hydrogen is larger than that of deuterium, which means that it diffuses more slowly through pores of similar size at temperatures below 100 K.

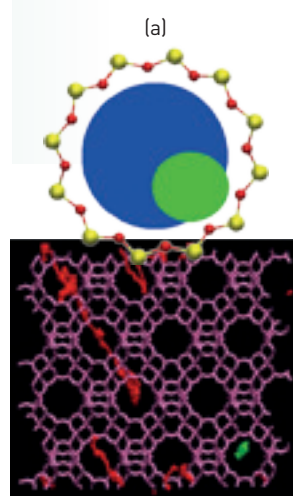
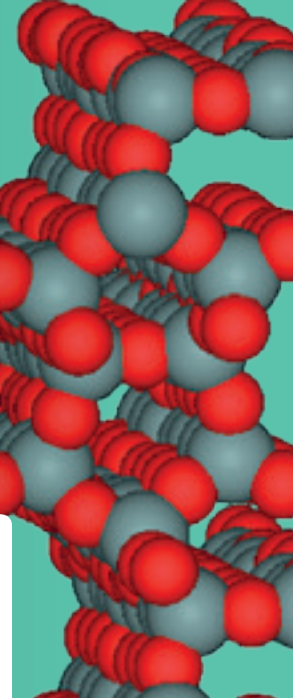
■ *The levitation effect.* Another counterintuitive diffusion phenomenon was seen in three

versions of pentane, a five-carbon hydrocarbon ( $\text{C}_5\text{H}_{12}$ ): straight-chain *n*-pentane, singly-branched isopentane, and neopentane in which one carbon is bound to the four other carbons so is more ball-like and 'fatter'. Studies of diffusion through the zeolite, NaY, in which the narrowest part of the network of cavities is comparable to the size of the molecules, showed that the largest pentane diffused faster than the smaller ones. This is because it does not adsorb onto the zeolite 'windows' as readily, being buoyed up by the external balancing forces around its more symmetrical structure (right).

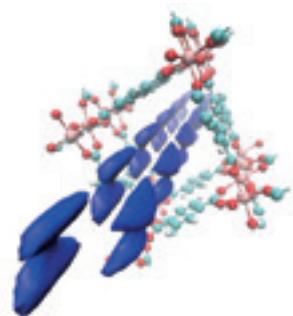
■ *The blowgun effect.* A study of the diffusion of hydrocarbons of increasing chain-length, methane, ethane, propane and *n*-butane, in a MOF called MIL-47(V), also provided an unusual result. The longest molecule, *n*-butane, diffuses faster than propane, because it can keep the same orientation in a long thin channel, behaving like a dart flying down a tube, while the shorter molecule tumbles around and thus loses more momentum.

■ *A corkscrew motion.* The separation of benzene and other aromatic (ring-shaped) hydrocarbons, is also of great industrial interest. Studies of the diffusion of benzene in the same MOF showed that it rotates as it travels down a channel, in effect moving with a corkscrew motion (right).

■ *The microwave effect.* Microwave heating is increasingly used in chemical processing but the actual energy transfer is not well understood. We investigated the motions induced in methanol molecules confined in a zeolite structure, silicalite, at various microwave powers. At high powers, we found that the energy is transferred to the rotations of the molecule, before partly being dissipated as translational motion. The zeolite itself stays cooler. This offers the possibility of selective heating of molecules in nanoporous systems.



The biggest molecule, in blue in (a) and in red in (b), diffuses faster than the small one (in green) between the cavities of NaY zeolite



Benzene moves in a corkscrew fashion in the MIL-47(V) MOF material. It jumps between free-energy pockets forming a spiral inside the channels

**RESEARCH TEAM:** Suresh Bhatia (University of Queensland, Brisbane), Subramanian Yashonath (IISc, Bangalore), Guillaume Maurin (Université de Montpellier), Thomas Devic, Christian Serre and Gérard Férey (Institut Lavoisier, Versailles), Daniil Kolokolov and Alexander Stepanov (BIC, Novosibirsk, Russia), Andrew Harrison (ILL at the time), William Conner and Scott Auerbach (University of Massachusetts, Amherst, US).

**ILL INSTRUMENT USED:** Time-of-flight spectrometers IN5 and IN6

**REFERENCES:** T. X. Nguyen *et al.*, *Phys. Rev. Lett.*, 2010, **105**, 085901; H. Jobic *et al.*, *Phys. Rev. Lett.*, 2011, **106**, 157401; H. Jobic *et al.*, *J. Phys. Chem. B*, 2009, **113**, 12635; H. Jobic *et al.*, *Chem. Eur. J.*, 2010, **16**, 10337; D. I. Kolokolov *et al.*, *J. Phys. Chem. C*, 2012, **116**, 15093.

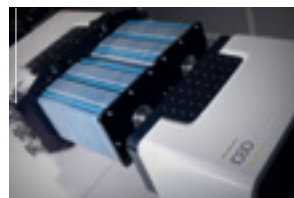


# INSIDE AN OPERATING FUEL CELL

**NEW RESULTS FROM NEUTRON EXPERIMENTS PROVIDE INVALUABLE AND UNIQUE INFORMATION THAT CAN BE USED TO OPTIMISE THE DESIGN OF THE NEXT-GENERATION OF HIGH-PERFORMANCE FUEL CELLS**

Arnaud Morin, Gérard Gebel and Sandrine Lyonnard

The neutron-transparent fuel cell developed at the CEA for carrying out SANS experiments under operating conditions



A stack of PEMFC fuel cells as would be used in a car

Fuel cells are one of the key 'green-energy' technologies currently being developed as an alternative to burning fossil fuels. They convert chemical energy – derived from the oxidation of a fuel such as hydrogen – into electricity and heat. The proton exchange membrane fuel cell (PEMFC) is one such electrochemical device, and is an ideal power source for electric vehicles, because its components are relatively light, it is fast-starting at room temperature, and has a high power-density.

The PEMFC has a complicated layered system. It converts hydrogen and oxygen to water using catalytic electrodes separated by a polymer-membrane electrolyte. Oxygen (air) is fed to the cathode, while hydrogen is fed to the anode, where it splits into positive hydrogen ions (protons) and negative electrons. The protons selectively pass through the polymer membrane to the cathode, whereas the electrons must travel to the cathode through an external circuit, thus generating the power. Bipolar plates are used to supply the gases (in channels) and to collect the current (under ribs). The protons and electrons then react with the oxygen at the cathode to form water.

Increasing the PEMFC's performance and longevity, as well as reducing its cost, are still crucial issues to address for the large-scale application of fuel cells – and require a deep understanding of the system's components and behaviour. One of the main issues affecting the power output, stability and lifetime is the amount and distribution of water within the cell. The water distribution in the active areas should be as homogeneous as possible. Moreover, a critical problem for operation is maintaining the dynamic balance of water within the membrane, so as to maintain the right level of hydration while avoiding drying out or flooding the electrodes.

## MEASURING WATER CONTENT

The distribution of water varies considerably both within and across the various layers of the fuel cell. Locally, the in-plane and through-plane hydration mostly depend on two factors: first, the cell design – in particular the design of the gas distribution channels and the specific membrane-electrode assembly chosen; and secondly, the operating conditions, such as the current density, the hydration/flow of the inlet gases, temperature and pressure.

Recently, a very effective methodology was developed to diagnose how the water content is partitioned across the different components of a working cell. Small-angle neutron scattering (SANS, p5), when used on a specially constructed state-of-the-art, neutron-transparent fuel cell, has proved to be a non-intrusive, highly-sensitive proton probe. We found that it was the only method that could measure simultaneously the variation in water content in both vertical and horizontal planes throughout the cell.



The Hyundai ix35 FCEV car powered by PEMFCs

We have now carried out several SANS experiments at the ILL on the D22 diffractometer, to screen systematically the impact of operating conditions on local water distribution. We varied the membrane thickness (20 to 200 micrometres), gas composition, temperature (–10 to 80 °C), current density (up to 0.8 A.cm<sup>-2</sup>), pressure (up to 3 bars) and relative humidity of the fed gases (from 0 to 100 per cent), and investigated transient regimes during on/off cycles. We were able to record a series of 3D water-distribution maps with unprecedented spatial and temporal resolutions. After developing a specific method to analyse the SANS data in a working cell, we could very precisely correlate the water content and distribution to both the operating conditions and cell design. These data provide unique information to feed into advanced modelling of fuel cells and to optimise the system.

**RESEARCH TEAM:** Arnaud Morin and Gérard Gebel (CEA-LITEN, Grenoble), Lionel Porcar (ILL) and Sandrine Lyonnard (CEA-INAC, Grenoble)

**ILL INSTRUMENT USED:** Small-angle scattering diffractometer D22

**REFERENCES:** A. Morin *et al.*, *Int. J. Hydrogen Energy*, 2011, **36**, 3096; A. Morin *et al.*, *Fuel Cells*, 2012, **12**, 156; A. Morin *et al.*, in preparation.

# MAKING THE MOST OF WASTE HEAT

**THE DEVELOPMENT OF MORE EFFICIENT THERMOELECTRIC MATERIALS, WHICH CONVERT HEAT INTO ELECTRICITY, IS RESULTING IN A RENEWED INTEREST IN UTILISING THEM FOR POWER GENERATION**

Michael Marek Koza

Today, power generation and energy consumption rely on inefficient processes, resulting in high-energy losses through waste heat. For example, most electrical power is still generated through combustion processes, and electricity – however it is used – creates waste heat. So it makes economic sense to harness waste heat for further power generation.

A promising way of converting waste heat to useful energy is offered by so-called thermoelectric materials (TEMs). The principle is that an electric current is induced when one side of a slab of the material is heated (for example, by waste heat) and the other side is kept cold. Electrical energy is propagated from one side to the other, and can then be harvested.

To achieve the highest electric currents requires maintaining the steepest thermal gradient across a TEM. This means that the inevitable, accompanying heat flow across the gradient must be suppressed as much as possible. This heat is transported in two ways: first, via the actual flow of the electrons; and secondly, via the collective vibrations of the atoms forming the crystal lattice of the TEM – the so-called acoustic phonons. The aim is therefore to identify materials in which heat transport by acoustic phonons is kept to a minimum, while maintaining the electron flow.

It turns out that semiconductors are the most efficient TEMs because their electrical conductivity increases with increasing temperature, and the heat flow mediated by phonons can be minimised by tailoring their vibrational states.

## OBSTRUCTING BAD VIBRATIONS

To achieve the highest efficiencies in TEMs, there are several strategies that can be followed. In general, the more complex the crystal structure is, the fewer of the heat-carrying excitations are present, and the more likely they are scattered and stopped from propagation. So-called host-guest materials such as cobalt- and iron-antimonide-based skutterudites are proving to be of particular

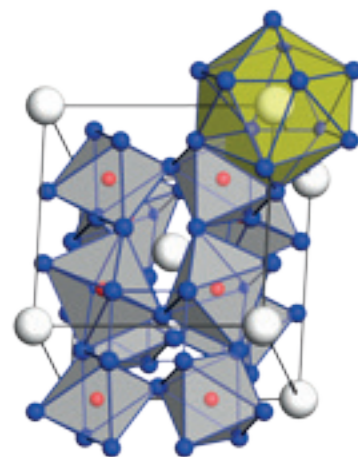
interest. These materials are characterised by having voids in their host structures, which can accept heavy rare-earth atoms as guests. These guests act as 'rattlers' and dissipate the vibrational energy, but do not obstruct the electrical current. Heat-carrying collective vibrations are also reduced in materials that are layered or have a variable nanostructure. Another successful approach is to create selective disorder in the crystalline lattice, thus forming random scattering channels for the acoustic phonons.

Optimising the efficiency of such TEMs requires a comprehensive understanding of their dynamics on a microscopic scale. Inelastic neutron scattering (INS, p6) is a unique tool for meeting this requirement. The characteristic energies and momenta of neutrons in INS experiments perfectly match the kinematics of lattice vibrations in TEMs. In this way, not only can the global distribution of vibrational states be accurately measured, but also the specific modes that work against the overall lattice thermal conductivity. We can determine whether or not the vibrational excitations are of collective heat-carrying character, as well as shed light on the material's velocity of sound, elastic properties and heat capacity. The energy resolution of modern neutron spectrometers renders the measurement of the lifetime of the relevant excitations feasible, and allows us to discern directly the effectiveness of TEMs in atomic detail.

We can even go a step further and monitor the response of vibrational excitations to external effects such as temperature and pressure changes, and so obtain information about chemical bonding needed to model the dynamics and transport properties of TEMs theoretically. Nonetheless, the full exploitation of INS depends on the quality of the specimen. TEMs are complex compounds and deciphering their thermal conductivity is often a challenging task.



Siemens is investigating the thermoelectric generation of electricity using waste heat from industry



The incorporation of rare-earth 'guest' atoms (white balls) into the iron-antimony skutterudite crystal structure reduces its thermal conductivity

**RESEARCH TEAM:** Michael Marek Koza (ILL), Andreas Leithe-Jasper (Max Planck Institute for the Chemical Physics of Solids, Dresden, Germany) and Romain Viennois (Institute Charles Gerhardt, University of Montpellier, France)

**ILL INSTRUMENT USED:** Time-of-flight spectrometers IN4 and IN6, and three-axis spectrometer IN8

**REFERENCES:** G. J. Snyder and E. S. Toberer, *Nature Materials*, 2008, **7**, 105; M. M. Koza, *et al.*, *Nature Materials*, 2008, **7**, 805; D. J. Voneshen *et al.*, *Nature Materials*, 2013, **12**, 1028.



# A CLOSE LOOK INTO FRICTION AND LUBRICATION

**MOTORS, WHEELS, BEARINGS AND OTHER MOVING DEVICES ARE INTRINSIC TO OUR TECHNOLOGICAL WORLD, AND THERE IS ONE UNIVERSAL PHYSICAL PHENOMENON THAT AFFECTS HOW WELL THEY WORK – FRICTION**

Peter Fouquet

**F**riiction is the resistance to a driving force, and is the cause of considerable energy expenditure in both industry and transport. Experts have calculated that the effects of friction-driven wear, loss of efficiency, and the use of lubricants, cost industrialised countries as much as 6 per cent of their gross national product. With such a high economic impact, the nature of friction and wear – and how to reduce their negative effects – has been a hot scientific topic for some decades.

Nevertheless, our knowledge of friction processes has remained very shallow up to now. This is because friction is a highly complex phenomenon involving the dynamic interactions of molecules at connecting surfaces hidden from view, which are thus not easily probed using most microscopy and spectroscopy techniques.

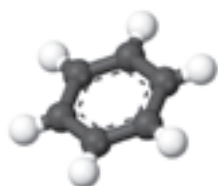
Neutrons, however, provide ideal tools for such studies. They penetrate deep into matter, and allow us to investigate buried interfaces with atomic resolution. In particular, the ILL hosts a suite of neutron spectrometers that are able to do this over a particularly wide spectral range – that is, these instruments can measure the dynamics of molecules at all imaginable speeds. They are therefore highly suitable for analysing the complex motions of molecules at an interface.

In our recent studies, we used two of these instruments, a neutron spin-echo spectrometer (p6), and a neutron time-of-flight spectrometer (p23), to unravel the dynamics of molecular structures that are significant in moderating friction between surfaces. One such material is graphite, a form of the element carbon. It consists of electron-rich (aromatic) hexagonal networks of carbon atoms – like chicken wire – which pack into layers that easily slip over each other to provide a lubricating effect. Recently, physicists have prepared just single atomic layers of this carbon structure, called graphene, which could provide the ideal lubricant, lasting thousands of ‘wear cycles’. Aromatic structures such as these also have intriguing electrical and mechanical properties, so have great technological potential.

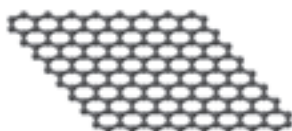
In a proof-of-principle experiment, we looked at the interactions between graphite surfaces and the simplest hexagonal hydrocarbon molecule, benzene. The combination of the spin-echo and the time-of-flight techniques allowed us to study all the diffusive dynamics happening on a molecular scale, over a timescale from pico- to nanoseconds.

## MOLECULAR ICE-HOCKEY

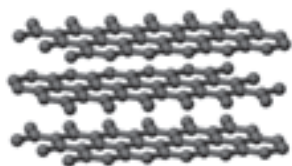
It turns out that benzene molecules like to cling to a surface with a flat geometry, which they move over with very little resistance, just like tiny ice hockey pucks. In fact, the friction against the surface is so small that the benzene molecules serve as a model system for what physicists call a two-dimensional ideal gas (in which the gas particles bounce off each other perfectly in just two dimensions). With this test system, we have been able to develop and justify a new theoretical formula that allows us to calculate the loss of energy during the collision of the molecules with each other. Using this bottom-up approach, we can now predict much better the lubricating properties of technologically interesting materials like aromatic hydrocarbons and graphene.



Benzene



Graphene



Graphite

**RESEARCH TEAM:** Peter Fouquet, Emanuel Bahn, Thomas Hansen, Michael Marek Koza, Mohamed Zbiri (ILL), Irene Calvo-Almazán, Andrew Jardine (University of Cambridge, UK), Holly Hedgeland (University College London, UK), Salvador Miret-Artés (CSIC, Madrid, Spain), Mark Telling (ISIS, UK) and Paul Henry (ESS, Sweden).

**ILL INSTRUMENT USED:** Spin-echo spectrometer IN11 and time-of-flight-spectrometer IN6

**REFERENCES:** H. Hedgeland, P. Fouquet *et al.*, *Nature Physics*, 2009, **5**, 561; I. Calvo-Almazan, E. Bahn *et al.*, *Carbon*, 2014, **79**, 183; E. Bahn *et al.*, *Physical Chemistry Chemical Physics*, 2014, **16**, 22116.

# KEEPING NUCLEAR REACTORS SAFE

**NEUTRON DIFFRACTION HELPS DETERMINE THE OPERATING LIFETIME OF CRITICAL COMPONENTS IN A NUCLEAR INSTALLATION**

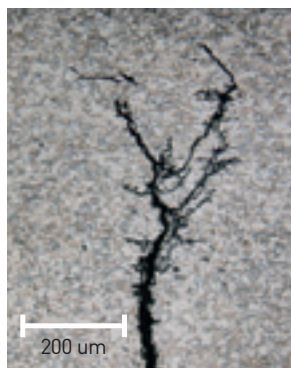
Gonghao Qiu and Thilo Pirling

A key issue in operating and maintaining a nuclear reactor is safety. Reactor components have to operate in a high-radiation, corrosive environment, and ensuring their complete reliability and robustness over a given lifetime is a major challenge for nuclear engineers. A profound knowledge of the structure and behaviour of a component is required, including their thermal and mechanical history during fabrication as well as in operation.

Reactor components for which there are safety issues are the partition plates within the steam generators that provide superheated steam for the electrical power generator. This is done in a heat exchanger between the nuclear reactor's primary circuit and the secondary circuit feeding the generator. The water in the primary circuit has a temperature of about 315 °C at a pressure of 15 MPa, while that in the secondary circuit is at 275 °C at a lower pressure of 6.2 MPa in order to produce saturated steam. The partition plates separate the inlet and outlet of the primary circuit, and so play an important role in confining the activated elements in the primary circuit.

These plates are, however, susceptible to a widely known and annoying problem in engineering: stress corrosion cracking. Three factors come together to create cracks: a corrosive environment; the material used (a nickel-chromium alloy that is susceptible to this kind of cracking); and the presence of severe tensile stresses applied during operation and residual in the material from manufacture. Although we need avoid only one of these factors to eliminate stress corrosion cracking, it is not so easy to achieve. In the case of a

A replacement steam generator being installed at the Davis-Besse nuclear power plant near Toledo, Ohio, US



Stress corrosion cracking



SALSA

nuclear reactor, the environment is given and cannot be changed (hot water, for instance, is highly corrosive to most materials), the choice of materials is limited because of mechanical and thermo-mechanical requirements, and residual stresses can never be completely avoided.

## WATCHING STRESS EVOLVE

Recently, we at EDF launched a study of these partition plates. The first step was to model the partition plates on a computer using a widely-used engineering technique called the 'finite-element' method (p23), to simulate the thermal fields in the component, the effect of welding processes, and the development of stresses. Such calculations are able to reveal the evolution of stress and plastic deformation during both the welding stages and operation. However, there are no reliable data available on changes induced by welding during fabrication to put into the model, and there is a large uncertainty in the behaviour of the alloy at the high temperatures achieved in the reactor. These data have to be obtained in the laboratory.

Neutron diffraction steps in here, offering a unique tool to study stress and deformation in materials experimentally because it can measure the resulting changes in distances between atoms in the crystal structure. The results can then be compared to the finite-element model, and so validate it.

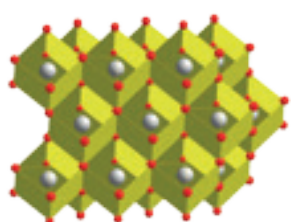
Samples were cut out from dismantled steam generators, and their microscopic structure investigated using the ILL's stress imager, SALSA. Although SALSA is constructed to receive relatively large samples – up to 1.5 metres across and 1000 kilograms in weight – the cutting of such large parts was unavoidable. Moreover, the radioactivity of the samples necessitated a reduction in size, so that the operating personnel were not put in danger. Because cutting causes stress relaxation, this step had to be calculated as well before a comparison was possible. Although the stress levels were much reduced due to cutting, a model could be developed that is in good agreement with measurements.



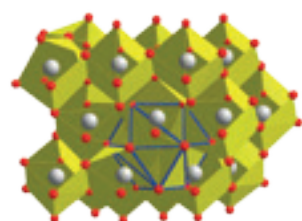
# DISPOSING OF SPENT NUCLEAR FUEL

THE SUBTLE OXIDATION MECHANISMS IN URANIUM DIOXIDE ARE UNCOVERED BY NEUTRON DIFFRACTION EXPERIMENTS

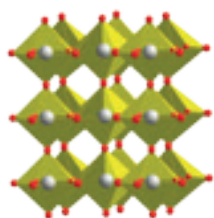
Henry Fischer



UO<sub>2</sub>



U<sub>4</sub>O<sub>9</sub>



U<sub>3</sub>O<sub>8</sub>

- Oxygen atoms
- Uranium atoms

The crystal structures of uranium dioxide (UO<sub>2</sub>), of which spent nuclear fuel is composed, and two uranium higher oxides that form as a result of oxidation

The fate of spent nuclear fuel is a major challenge for our society. Nuclear fuel consists of ceramics containing uranium dioxide (UO<sub>2</sub>) wrapped in a protective metal skin. This oxide has characteristics that allow it to be used safely as nuclear fuel: a high melting temperature, good resistance to water corrosion, and an ability to trap the radioactive isotopes produced during the operation of a nuclear power plant.

However, during the long-term storage of spent nuclear fuel, that situation could change: UO<sub>2</sub> could be exposed to an oxidising environment and be converted to a higher oxide, U<sub>3</sub>O<sub>8</sub>. Unfortunately, this compound forms a fine-grained powder that is highly soluble in water. It could therefore readily be dispersed, thus substantially increasing radioactive contamination of the environment. Obviously, the formation of U<sub>3</sub>O<sub>8</sub> must be avoided, or at least controlled.

We have therefore been studying the oxidation mechanism of UO<sub>2</sub> in terms of structural changes at the atomic level, using neutron diffraction. Neutrons are the most suitable probes for revealing the positions of oxygen, a light atom with only eight electrons, in the presence of uranium, a heavy atom with 92 electrons. Experimental techniques that rely on interactions with electrons, such as X-ray or electron diffraction, can hardly detect oxygen in UO<sub>2</sub> because its diffraction signal is overwhelmed by that of uranium. Neutrons, however, interact only with the atomic nuclei, and thus can 'see' oxygen almost as easily as uranium. This unique property of neutrons makes it possible to determine how oxygen is structurally incorporated into UO<sub>2</sub> during oxidation.

## THE OXIDATION PROCESS

As UO<sub>2</sub> oxidises, it passes through two crystalline phases, U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>7</sub>, before U<sub>3</sub>O<sub>8</sub> is formed. The accompanying neutron diffraction patterns we obtained could be interpreted using a well-established theoretical modelling

technique, which enabled us to determine the structures of these phases. The results showed that additional oxygen atoms were incorporated into UO<sub>2</sub> by displacing regular oxygen atoms and forming clusters containing 13 oxygen atoms (see left). Each U<sub>4</sub>O<sub>9</sub> unit cell contains 12 clusters, while each U<sub>3</sub>O<sub>7</sub> unit cell contains 16 clusters. We thus learned that UO<sub>2</sub> oxidation could be considered basically as an accumulation of clusters of interstitial oxygen atoms that eventually lead to the formation of U<sub>3</sub>O<sub>8</sub> above some saturation threshold.

We are now interested in the very first steps of oxidation from UO<sub>2</sub> to U<sub>4</sub>O<sub>9</sub>, and we would like to know if the oxygen clusters appear immediately in the UO<sub>2</sub> structure as it begins to oxidise, and then simply grow in number on approaching the U<sub>4</sub>O<sub>9</sub> structure, or if another type of (intermediate) structure is involved.

We therefore have been studying samples whose oxygen content lies between UO<sub>2</sub> and U<sub>4</sub>O<sub>9</sub>, and with compositions that vary locally on a length-scale of nanometres or more – meaning that there could be clusters of interstitial oxygen atoms in some unit cells but not in others. We wanted to study this local structure and find out whether there is, in fact, some order to it.

Normally only the sharp 'Bragg' peaks (p4) in diffraction patterns are analysed, but this gives information only on the overall average atomic structure. In order to probe the local variations in structure, we needed to analyse as well the broad diffuse scattering between Bragg peaks, for which we made use of relatively new modelling techniques. The results we obtained confirmed that the clusters of interstitial oxygen atoms appear as soon as UO<sub>2</sub> begins to oxidise more, but they can be arranged either in a regular or disordered manner depending on temperature. These results also validate the theoretical models we have proposed to describe the oxidation of nuclear fuels.

**RESEARCH TEAM:** Gianguido Baldinozzi (CNRS Paris, France) and Henry Fischer (ILL).

**ILL INSTRUMENT USED:** Liquids and amorphous diffractometer D4

**REFERENCES:** L. Desgranges *et al.*, *Inorganic Chemistry*, 2011 **50**, 6146.

# FISSION STUDIES FOR NUCLEAR APPLICATIONS

**GROWING GLOBAL DEMANDS FOR ENERGY, AND CONCERNS ABOUT CLIMATE CHANGE, HAVE RE-VITALISED INNOVATIVE PROGRAMMES TO DEVELOP NUCLEAR FISSION AS A MAJOR SOURCE OF POWER**

Gregoire Kessedjian, Aurelien Blanc and Olivier Serot

Nuclear power has so far been based on the nuclear reactions of uranium isotopes, particularly the uranium-235 isotope (which accounts for just 0.72 per cent of this radioactive, naturally-occurring element). Uranium-235 is a fissile element: when bombarded with neutrons, it captures a neutron to form uranium-236, which then splits into lighter nuclei. More neutrons are released, which trigger further fissions in a sustainable way to create a chain reaction. The result is the release of a large amount of energy in the form of fast-moving particles and gamma-rays (p23). Also created by neutron capture are small amounts of artificial elements heavier than uranium, including isotopes such as those of plutonium, americium and curium (collectively known as minor actinides). All of these reaction sequences produce a vast number of radioactive isotopes, both lighter fission products and long-lived actinides – the latter mostly responsible for creating the well-known waste-storage problems, regarded by many as a strong reason for not exploiting nuclear energy.

## ADVANCED NUCLEAR FUEL CYCLES

The major component of uranium ore, uranium-238, is not a fissile nucleus, but nevertheless could be exploited advantageously. Following the capture of a neutron and two successive beta-decays (p22), uranium-238 is transformed into plutonium-239, which is a fissile element. Theoretically, all the uranium can be 'burned' in this way to produce energy. Future nuclear-power generation will most likely employ so-called breeder reactors based on this principle, since they would exploit the limited, natural resources of uranium in the most efficient way, so preserving them for as long as possible. Reactors could also be designed to burn up the radio-toxic actinides produced.

NRC



A nuclear fuel pellet

Another potential breeder nuclear fuel that could be used in these reactors, which is now of great interest, is thorium-232. When irradiated with neutrons, it is eventually transmuted to uranium-233, which is an excellent fissile material. Thorium is higher in abundance in the Earth's crust relative to uranium – and since this fuel cycle produces barely any actinides heavier than uranium, it could provide cleaner nuclear energy (Indeed, the thorium cycle does not produce anything heavier than the actinide, neptunium). However, it does produce waste and we estimate that, actually, during the first 200 years, the thorium cycle would be more of a problem for waste storage (since the waste would be much more active). It is only after two centuries of storage that the benefits of the thorium cycle over the uranium cycle are seen.

In the future, both fuel cycles will be exploited in the nuclear industry. The uranium-plutonium cycle will be developed further in the next generation of reactors (so-called Generation IV), because the basic technological concepts have been well-studied, and it allows plutonium to be re-cycled. The technology for the thorium-uranium cycle is much less well developed, but it is acknowledged as having huge potential.

## NEW DATA NEEDED

The design of new reactor concepts, and improving the efficiency and safety of these fuel cycles, as well as storage, require a much better understanding of all the key nuclear reactions involved.

Information is needed on the yields of fission products, particularly the heavy nuclei for which data are still sparse. Over the past 10 years, a mammoth campaign of measurements has been initiated to improve our knowledge of neutron-induced reactions of key nuclei (thorium-232, protactinium-233 and uranium-233) to the level of those of the uranium-plutonium cycle. For plutonium recycling, knowledge of the properties of all plutonium isotopes produced in the cycle are needed for fuel management. Moreover, in the framework of waste management, the burning of minor actinides has to be studied. Some fission products called neutron poisons readily absorb neutrons and obstruct the breeder aspect of a fuel cycle, so their properties need to be characterised. Data on how the various forms of radiation are





released – which affect the heating and integrity of the reactor structure and vessel, and the safe handling of spent fuel – are also required.

### THE LOHENGRIN SPECTROMETER

The ILL is able to provide many of these measurements with its unique Lohengrin fission-fragment spectrometer. Fissile materials of interest such as uranium-235 can be made into thin targets that are placed in a beam-tube under vacuum, near the core of the ILL's high-flux reactor. The neutrons impinging on the target material induce fission to produce fast-moving fragments. These lose many of their electrons to form highly-charged ions, which are separated, according to their velocity and mass-to-charge ratio, using a combination of a large dipole magnet and huge electrostatic deflector.

The Lohengrin separator provides access to hundreds of fission products up to a mass of 160. Various detectors, such as ionisation chambers to measure nuclear charge, and germanium detectors to measure gamma-ray spectra, allow nuclei to be identified and their yields calculated.

### CURRENT PROGRAMME

A collaboration of the French CEA and CNRS laboratories, together with the ILL, is driving an experimental programme to extend and improve the existing fission-yield data for key nuclei of innovative fuel cycles, for which there is a severe lack of data. During the past decade, we have been working on the development of precise measurement methods in order to respond to the nuclear data needs within the framework of the OECD/Nuclear Energy Agency assessment programme.

Using efficient high-resolution gamma-ray detectors coupled to Lohengrin, we have obtained much better measurements of the yields of the major fissioning nuclei (uranium-235, plutonium-239 and uranium-233). Accurate measurements of fission yields from plutonium-241 and americium-242 are ongoing – and will be extended to curium isotopes. Other significant measurements include measuring the yields of additional light isotopes produced through fission processes, such as tritium (the radioactive hydrogen isotope).

Another important issue for fuel management is the control and evaluation of the residual power from the heat generated by radioactive isotopes just after a reactor shut-down. Decay-heat calculations must take account of all the isotopes produced in the process, including those created in only small amounts. These cover products of so-called symmetric fission whereby an actinide scissions into two fragments of similar mass. We are studying this range of products, which includes certain rare but technically significant isotopes such as antimony-125.

We are also involved in the development of a new instrument in the context of the ILL's instrument-renewal programme, ENDURANCE. FIPPS (Fission Product Prompt gamma-ray Spectrometer) consists of a high-efficiency gamma-ray detector array coupled to a fission-fragment spectrometer based on a gas-filled magnetic device. It will give us access to the study of gamma-rays and neutrons emitted just after fission, which play an important role in the heating and integrity of the reactor structure and vessel.



The Lohengrin spectrometer

**RESEARCH TEAM:** Adeline Bail, Olivier Serot, Ludovic Mathieu, Florian Martin and Olivier Litaize (CEA, DEN-Cadarache, Saint-Paul-lez-Durance, France), Thomas Materna, Ulli Köster, Waldemar Urban and Herbert Faust (ILL), Alain Letourneau, Charlotte Amouroux and Stefano Panebianco (CEA, DSM-Saclay, IRFU/SPhN, Gif-sur-Yvette, France), Adrian Bidaud, Nicolas Capellan, Sébastien Chabod, Christophe Sage, Grégoire Kessedjian, Annick Billebaud and Olivier Méplan (LPSC, Grenoble, France), Jean-Marc Regis, and Mattias Rudigier (IKP, University of Cologne, Germany), and Charles-Olivier Bacri and Xavier Doligez (IPN, CNRS/IN2P3, University Paris-Sud, France).

**ILL INSTRUMENT USED:** Lohengrin spectrometer

**REFERENCES:** A. Bail *et al.*, *Phys. Rev. C*, 2011, **84**, 03405.; O. Serot *et al.*, *Nucl. Data Sheets*, 2014, **119**, 320; F. Martin *et al.*, *Nucl. Data Sheets*, 2014, **119**, 328.

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P8 (Fuel cells get cool)

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P9 (Prolonging the lifetime of organic solar cells)

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P11 (A future for clathrate hydrates)

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P12 (Towards a better lithium battery)

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P13 (Composite compounds for hydrogen storage)

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P14 (Speed freaks in molecular sieves)

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P15 (Inside an operating fuel cell)

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P17 (A close look into friction and lubrication)

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P18 (Keeping nuclear reactors safe)

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P19 (Disposing of spent nuclear fuel)

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P20 (Fission studies for nuclear applications)

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# GLOSSARY

**Actinides** Elements with atomic numbers between 89 (actinium) and 103 (lawrencium); they are all radioactive and include thorium, uranium and plutonium.

**Alkali metal** Highly reactive metals that readily lose the single electron sitting in the outermost orbital of each atom to form a singly-charged positive ion.

**Alkaline earth metal** Reactive metals which readily lose the two electrons that sit in the outermost orbital of each atom to form a doubly-charged positive ion.

**Aromatic compound** A compound consisting of electron-rich carbon rings, which are stable and in which the negative electron charge is spread around the ring.

**Bar** The atmospheric pressure at sea level (100,000 pascals).

**Battery** A device consisting of several electrochemical cells (see below).

**Beta decay** A type of radioactive decay in which either a neutron in the nucleus is converted into a proton, and an electron (beta-ray) is emitted together with an antineutrino, or a proton is converted into a neutron with the emission of a positron and neutrino.

**Bragg peaks** The characteristic sharp peaks in a diffraction pattern produced when neutrons (or X-rays) are scattered off a crystal lattice.

**Clathrate hydrates/gas hydrates** Materials consisting of cage-like, frozen water structures in which are trapped gas molecules such as methane. These are found in large quantities in permafrost regions.

**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.

**Diffuse scattering** The additional weak scattering effects in a diffraction pattern resulting from various kinds of disorder within a crystalline material.

**Electrochemical cell** A device that generates electricity from a chemical reaction. It consists of two electrodes composed of materials that can readily release or accept electrons to form ions, when immersed in a suitable conductive electrolyte. Ions flow through the electrolyte, while the electrons flow through an external circuit connected to the electrodes.

**Electrode** A material that electrons can flow in and out of when immersed in an electrolyte.



**Electrolyte** A material that splits into electrically charged 'ions' when in a dissolved or molten state to produce a medium that conducts electricity.

**Finite-element method** A numerical method for analysing a complex problem by first breaking it up into 'elements' with discrete properties. It is used extensively to model engineering structures.

**Friction** The force associated with resistance to motion exerted by surfaces or particles in contact with each other.

**Fuel cell** A device that converts chemical energy into electricity when a chemical (fuel) reacts with an oxidising agent such as oxygen. It is similar to an electrochemical cell but relies on a continuous supply of fuel to generate the power.

**Fullerene** A molecule made of carbon atoms shaped like a hollow sphere or ellipsoid consisting of fused hexagonal and pentagonal units. The most common fullerene is buckminsterfullerene, C<sub>60</sub>.

**Gamma-ray** Very high-energy electromagnetic radiation, which is emitted in nuclear reactions such as nuclear fission.

**Generation IV reactors** A new generation of nuclear reactors currently being developed, which are designed to be safer, with more efficient fuel use, and with the potential to produce very little nuclear waste.

**Germanium detector** High-purity germanium crystals produce an electrical signal when gamma-rays impinge on them, which depends on their energy. They are therefore used to analyse gamma-ray spectra that characterise nuclear processes being investigated.

**Greenhouse gas** An atmospheric gas that absorbs infrared radiation, thus trapping heat. Carbon dioxide and methane are greenhouse gases. While essential for maintaining the Earth's surface temperature, excessive anthropogenic greenhouse emissions could cause radical changes in the Earth's climate.

**Heterojunction** An interface between two semiconductors with different electronic properties. It is a significant feature in the functioning of microelectronic devices.

**Hydrogen-storage materials** Hydrogen for fuel applications can be stored chemically as hydrides of various elements or in the microporous structure of various absorbents.

**Incoherent elastic scattering** Scattering without any energy transfer, in which incident neutrons interact with each individual nucleus in a sample, resulting in a random, almost smooth scattering pattern.

**Inelastic scattering** A neutron technique in which there is an exchange of energy between the neutrons, and the atoms and molecules being studied, thus giving information about their motion and flexibility. (When a neutron is scattered elastically, there is no energy transfer.)

**Ion** An atom or molecule that has gained or lost electrons so that it has become electrically charged.

**Incommensurate structure** A periodic structural characteristic of a crystal that does not coincide with its basic regular lattice.

**Interstitial site** A position that is not part of the regular atomic lattice of a crystal, but which is sometimes occupied by, for example, an impurity atom. Interstitial atoms can have important effects on the physical properties of a material.

**Isotope** A version of an element whose nuclei contain a particular number of neutrons. Each element is characterised by the number of protons present in its nuclei but the number of neutrons can vary.

**Liquid crystal** A material in which the molecules have orientational order (as in a crystal) but no translational order (as in a liquid).

**Molecular dynamics simulation** A type of computer simulation that can predict how a material behaves by modelling the motions of its constituent atoms over time. The system is pushed out of equilibrium so as to simulate the dynamical situation at the temperature of interest, and then, using Newton's laws, the evolution of the atoms' motions is calculated.

**Molecular sieve** Porous materials through which molecules or ions can selectively pass.

**Nanocomposite** A material composed of more than one compound organised at the nano-level.

**Nanometre** One billionth of a metre (10<sup>-9</sup> metres).

**Neutron** One of the two particles found in the atomic nucleus. They have a characteristic wavelength depending on energy.

**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. In standard neutron diffraction, a single crystal is oriented over a range of angles to collect diffraction patterns from different planes of atoms in the crystal.

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

**Neutron spin echo** A neutron technique that measures the changes in the spins of neutrons passing through a material, caused by small changes in energy associated with molecular movements over relatively long timescales.

**Neutron time-of-flight spectroscopy**

The times of arrival and locations of neutrons with initial fixed energy are measured at the detector after they have been scattered by a sample. This allows any energy changes due to inelastic scattering to be calculated.

**Nuclear fission** Process by which heavy nuclei break up to produce smaller nuclei.

**Phonon** A quantum of atomic vibration in a crystal lattice.

**Picosecond** One million millionth of a second (10<sup>-12</sup> seconds).

**Polymer** A molecule composed of repeating molecular units (monomers) usually in long chains.

**Powder diffraction** Coherent scattering from a polycrystalline material.

**Proton** One of the constituents of the nucleus. The number of protons characterises an element.

**Quasi-elastic neutron scattering (QENS)**

Scattering processes that are almost elastic but where there is a broadening of the signal caused by slow random motions such as diffusion.

**Residual stress** Internal forces exerted within the structure of a material that remain after it has been processed.

**Small-angle neutron scattering (SANS)**

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

**Solar cell /photovoltaic cell** A device that converts sunlight into electrical energy. They exploit materials that absorb photons of light and then release electrons.

**Thermoelectric materials** Materials demonstrating the thermoelectric effect whereby a temperature difference across the material causes a flow of electrons.

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

**Zeolite** Natural or synthetic mineral with a porous aluminosilicate framework through which ions and molecules can pass.



NEUTRONS  
FOR SCIENCE

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