ANNUAL REPORT
2013
INSTITUT LAUE - LANGEVIN

This report has been printed using FSC certified paper (http://www.fsc.org/)
The world’s leading facility in neutron science and technology
# ILL Annual Report 2013

## CONTENTS

**DIRECTOR’S FOREWORD**

*ABOUT THE ILL*

*WHY NEUTRON SCATTERING IS USEFUL*

**WHAT IS THE ILL**

**SCIENTIFIC HIGHLIGHTS**

**INTRODUCTION**

**ILL IN THE PRESS**

**MAGNETISM**

**CHEMISTRY AND CRYSTALLOGRAPHY**

**MATERIALS SCIENCE**

**LIQUIDS AND GLASSES**

**SOFT MATTER**

**BIOLOGY**

**HEALTH**

**NUCLEAR AND PARTICLE PHYSICS**

**THEORY**

**THE ENDURANCE PROGRAMME**

**MILLENNIUM PROGRAMME AND TECHNICAL DEVELOPMENTS**

**INTRODUCTION**

**MILLENIUM PROGRAMME**

**TECHNICAL DEVELOPMENTS**

**EXPERIMENTAL AND USER PROGRAMME**

**INTRODUCTION**

**USER PROGRAMME**

**USER AND BEAMTIME STATISTICS**

**INSTRUMENT LIST**

**REACTOR OPERATION**

**MORE THAN SIMPLY NEUTRONS**

**THE EPN - CAMPUS**

**SCIENTIFIC SUPPORT LABORATORIES**

**ADMINISTRATIVE MATTERS**

**INTRODUCTION**

**FACTS AND FIGURES**

**ORGANISATION CHART**

**WORKSHOPS AND EVENTS**

**ILL WORKSHOPS AND SCHOOLS IN 2013**

**ILL CHRONICLE 2013**

**A YEAR IN PHOTOS**

**PUBLICATIONS**

**PUBLICATION IN 2013**

---

**PUBLISHING INFORMATION**

*Editors:* Giovanna Cicognani and Helmut Schober  
*Production team:* Giovanna Cicognani, Alison Mader, Robert Corner and Susan Tinniswood  
*Design:* www.synthese-eca.com - *Printing:* Imprimerie du Pont de Claix  
*Photography:* ILL (unless otherwise specified)  
Further copies can be obtained from Institut Laue-Langevin  
Scientific Coordination Office (SCO)  
BP 156 F-38042 Grenoble Cedex 9 (France)  
Email: sco@ill.eu – web: www.ill.eu
It is now more than 40 years since the first neutron experiments were conducted at ILL, and although accounts vary over what the first sample to be studied, and who carried out the measurement, there is no dispute that by the end of the 1970s the ILL had established itself as a worldwide centre for science. That remarkable success is a testament to the vision and skill of ILL’s founding fathers and the band of pioneering scientists, engineers and technicians who created it. What is also remarkable is how well ILL has stood the test of time: it still leads the field of neutron science and technology and far from being an ‘old’ or even ‘middle-aged institute’, almost every technical component between the source and the detectors on our instruments has been upgraded at least once.

The latest cycle of reincarnation – the Millennium Programme - has brought astonishing gains, increasing the average detection rate across the instrument suite by a factor of more than 24 already, and transforming the scope and capacity of the science we support.

The latest cycle of reincarnation – the Millennium Programme - has brought astonishing gains, increasing the average detection rate across the instrument suite by a factor of more than 24 already, and transforming the scope and capacity of the science we support.

The Millennium Programme still has two years to run, but the process of renewal should not end there. It is vital to the health both of our Institute and the broader scientific community that we continue to explore and exploit the limits of what is possible in instrumentation. To this end, four years of consultation and planning will deliver in 2013 the case for the next wave of our upgrade Programme, christened ‘Endurance’ to signal our aim to continue to lead for years to come. 2013 will therefore be crucial for ILL approval and funding for the Endurance Programme will not only lever significant further improvements in performance, but much of the technical development we propose should also be applied further afield in other neutron centres. Not least among these will be the next-generation European Spallation Source in Lund as it ramps up to full scientific strength. In Lund as it ramps up to full scientific strength by the end of the next decade.

Elsewhere at the ILL other major projects abound. Post-Fukushima work is well underway to strengthen our defences further against yet more improbable circumstances: in this way we are very fortunate to be able to receive prompt and generous additional funding from our Associates, strong political support from our host country, France, and tremendous expertise and determination on the part of many ILL staff to deliver this project. We will also soon have a new ‘Science Building’, funded by the city of Grenoble and the Rhône-Alpes region, to house facilities shared with the ESRF; a common theory group, joint chemistry laboratories and the Partnership for Soft Condensed Matter will all be housed therein, together with members of both institutes to establish a vigorous new scientific community, particularly for largescale structures. Further afield, the set of the ‘Planète Scientifique’ is also in the midst of major reconstruction, with new facilities for research, innovation and education promised for the members of the CHANT partnership (ILL, ESRF, EMBL), with the laboratories of the CEA and CNRS as well as local universities. The accent on ‘innovation’ marks a new departure for ILL, with additional funding to establish with ESRF new interface facilities for industrial users.

Of course the real strength of ILL is human — represented both by expert staff and a vibrant user community — and we paid tribute to some of them in 2012. We celebrated two 80th birthdays in 2012: that of the neutron itself — or rather its first public announcement by James Chadwick — as well as Philippe Nizialek, the first head of our theory group and still playing a key role in the intellectual life of the ILL. We noted the remarkable contribution of his successor, Emile Kats, as well the many and varied contributions of Alan Hewat — one of that original pioneering band referred to above — and Joe Zaccari, whose has done so much to bring biology to the ILL, and vice versa. We also saw the departure of José Luis Martinez Patiño, who came to the end of his term of office as French Associate Director. José Luis brought great clarity and rigour to the planning and delivery of the Millennium Programme — indeed to all aspects of the life of ILL in which he was involved — and we salute him for that. Muchas gracias y hasta pronto! He gives way to Charles Simon, a long-term user of ILL who brings much savoir-faire in matters scientific, technical and political. Finally, we note the passing of the “baton” from Martin Walter to Manuel Rodriguez-Castellanos as Head of Administration. Martin held the fort magnificently during an unexpected interregnum period, while Manuel brings decades of experience working for our neighbours, the ESRF: bienvenido!

Of course this is all part of the much broader renewal of staff who have contributed in very different but no less crucial ways. This point is made most clearly each year at the General Assembly for retired ILL staff: looking out towards old friends and colleagues in our Chadwick Amphitheatre it is humbling to be reminded of the roles they have played in ILL’s success. This success is all the more remarkable for the diversity of the actors, with very different skills and cultural backgrounds yet bound through the generations to a common purpose: truly an example of a ‘Europe that works’.

Prof. W.G. Stirling
Director of the ILL
ABOUT THE ILL

The Institut Laue-Langevin (ILL) is an international research centre at the leading edge of neutron science and technology, where neutrons are used to probe the microscopic structure and dynamics of a broad range of materials at molecular, atomic and nuclear level.

The ILL is owned by the three founding countries - France, Germany and the United Kingdom. The three Associate member countries contributed a total of about 63% to the Institute in 2013, a sum enhanced by significant contributions from the ILL’s Scientific Member countries, Austria, Belgium, the Czech Republic, Denmark, Hungary, India, Italy, Poland, Spain, Slovakia, Sweden and Switzerland. ILL’s overall budget in 2013 amounted to approximately 100.5 M€.

The Institute operates the most intense neutron source in the world, based on a single-element, 58.3 MW nuclear reactor designed for high brightness. The reactor normally functions round-the-clock during four 50-day cycles per year, 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. Our user community is world-wide: every year, about 2000 researchers from more than 30 countries visit the ILL to perform over 800 experiments selected by a scientific review committee.

The ILL monitors the papers published as a result of the use of our facilities, of which there are – on average – about 600 per year. We pay particular attention to papers published in high-impact journals. About 80 such papers are published per year from data taken on ILL instruments. This is a factor of two higher than the second most productive neutron source in the world.

The ILL has a Director and two Associate Directors who represent each of the Associate countries and are appointed on short-term contracts, normally for five years. A Scientific Council, comprising external scientists from the member countries, advises the Directors on scientific priorities for the Institute and how to develop the instrument suite and technical infrastructure in order to best meet the needs of the user research programme. It also assesses the scientific output of the Institute. Our governing body is the Steering Committee, which meets twice yearly and is made up of representatives of the Associates and the Scientific Members together with the Directors and Staff Representatives. Within the framework of the Intergovernmental Convention, the Steering Committee has the ultimate responsibility for determining operational and investment strategies for the Institute.

NEUTRONS AND SOCIETY

The scope of the research carried out at the ILL is very broad, embracing condensed matter physics, chemistry, biology, materials and earth sciences, engineering, and nuclear and particle physics. Much of it impacts on many of the challenges facing society today, from sustainable sources of energy, improved healthcare and a cleaner environment to new materials for information and computer technology. For example, neutron scattering experiments have given us new insights into the structure and behaviour of biological and soft condensed matter, important in designing better drug delivery systems or the molecular magnets that may provide the technology on which the computers of the future are based.

PREPARING FOR THE FUTURE

In 2001, the ILL launched an ambitious programme to modernise its instruments and infrastructure called the ILL Millennium Programme, whose aim was to optimise the ILL’s instrument suite (Phase M0: 2001-2008, Phase M1: 2008-2014). We are now looking forward to and setting the scene – in the framework of our ENDURANCE programme - for developments still further into the future, in order to maintain the Institute’s world-leading position for another 20 years.

WHY NEUTRON SCATTERING IS USEFUL

When used as a probe for small samples of materials, neutron beams have the power to reveal what is invisible using other radiations. Neutrons can appear to behave either as particles or as waves or as microscopic magnetic dipoles and it is these specific properties which enable them to uncover information which is often impossible to access using other techniques.

WAVELENGTHS OF TENTHS OF NANO METERS

Neutrons have wavelengths varying from 0.01 to 100 nanometers, which makes them an ideal probe of atomic and molecular structures ranging from those consisting of single atomic species to complex biopolymers.

ENERGIES OF MILLIELECTRONVOLTS

The associated energies of millielectronvolts are of the same magnitude as the diffusive motions of atoms and molecules in solids and liquids, the coherent waves in single crystals (phonons and magnons) and the vibrational modes in molecules. An energy exchange between the incoming neutron and the sample of between 1µeV (even 1 neV with spin-echo) and 1eV can easily be detected.

MICROSCOPICALLY MAGNETIC

Neutrons possess a magnetic dipole moment which makes them sensitive to magnetic fields generated by unpaired electrons in materials. Precise details of the magnetic behaviour of materials at the atomic level can be investigated. In addition, the scattering power of a neutron by an atomic nucleus depends on the orientation of the spin of both the neutron and the atomic nucleus in a sample, thereby providing a powerful tool for detecting the nuclear spin order.

NEUTRONS AND SOCIETY

Neutrons are electrically neutral and so can penetrate deep into matter, while remaining non-destructive. This makes them an ideal probe for studying, for example, biological samples or engineering components under extreme conditions of pressure, temperature or magnetic field, or within chemical-reaction vessels.

HIGH SENSITIVITY AND SELECTIVITY

The variation of scattering power from nucleus to nucleus in a sample varies in a quasi-random manner, even in different isotopes of the same atom. This means that light atoms are visible in the presence of heavy atoms and atoms that are close to one another in the periodic table may be distinguished from each other. This introduces the possibility of using isotopic substitution (for example deuterium for hydrogen or one nickal isotope for another) to allow contrast to be varied in certain samples thereby highlighting specific structural features.

In addition, neutrons are particularly sensitive to hydrogen atoms and therefore they are a powerful probe of hydrogen storage materials, organic molecular materials, and biomolecular samples or polymers.

WHAT IS THE ILL
If we had to draw up an organisation chart of human society, research facilities would most certainly occupy a prominent position. The importance of knowledge for human development has deeply penetrated our collective consciousness. The task of preserving and expanding this knowledge has been entrusted to a network of academic institutions which provides society with its rational intelligence. It is, as is generally accepted, a high degree of interconnectivity is a sign of increased intellectual capacity, tremendous progress has been achieved in recent decades. Thanks to modern communication technologies and human mobility, researchers can now interact almost instantaneously on a global scale. This interaction has boosted the productive exchange of ideas and, among many other things, has broken down barriers between scientific disciplines. Large research infrastructures play a crucial role in the network of academic institutions. Offering unique services across a broad array of disciplines, they are an essential stopover destination for scientists at every step and can thus be considered the true crossroads of academic exchange.

The founding fathers of the ILL clearly anticipated the enormous potential of research infrastructures for interconnecting the scientific community. They insisted from the start on an organisational structure that places collaboration with outside academic institutions at the very heart of the ILL’s mode of operation. They also defined as broad a scope as possible for the science to be carried out at the Institute, thus laying the foundations for intense interdisciplinary cross-fertilisation. When reading the scientific highlights in this report, you will quickly realise that the ILL has remained true to its original vocation.

Like all infrastructure, roads are best when they are safe and easy to use. Knowledge-based infrastructure is no exception to this rule. It must be the aim of all responsible and easy to use. Knowledge-based infrastructure is no exception to this rule. It must be the aim of all responsible and easy to use. Knowledge-based infrastructure is no exception to this rule. It must be the aim of all responsible and easy to use. Knowledge-based infrastructure is no exception to this rule. It must be the aim of all responsible academic exchange.

The key to this enduring success has been the succession of modernisation programmes initiated by the ILL. 2012 and 2013 saw the commissioning of a number of highly innovative instruments, such as IN1-ULAGRANGE, D33, and the new IN16B. The user experiments performed on these instruments have confirmed their tremendous potential. The last projects to be completed within the Millennium Programme will be the high-resolution spin-echo instrument IN1.5 and the wide-angle spin-echo instrument WASP. In this context, we very much appreciate the support we have received via third-party funding from the BMBF and FZ-Jülich.

With the Millennium Programme in its final phase, the ILL has spent the last few years preparing the successor programme. The 2020 Vision user meeting in 2010 gave ILL scientists an opportunity to confront their ideas for modernisation with the expectations of the user community. Driven by the support of the community, the project teams then set out to elaborate their proposals, making them suitable for evaluation. The evaluation phase of what has since become the Endurance programme started in 2012 under the close scrutiny of the Instrument Subcommittee, with the programme taking final shape in 2013. Enthusiastically endorsed by the Scientific Council, Endurance has been proudly presented to the ILL Steering Committee and is now awaiting funding approval.

The scientific highlights presented in this report are a glowing testament to the success of the ongoing process of rejuvenation at the ILL. I am sure you will be as impressed as I am by the breadth and depth of the results achieved. Alongside articles on work dealing with very fundamental scientific questions, you will also find reports on investigations with immediate practical implications. I hope you enjoy reading them!
The presence of theorists at the ILL sometimes leads to the bringing to light the underlying mechanism of multiferroicity. Although some theories of high-temperature cuprate superconductors link charge-stripe order and on-high-glass phase, from epitaxial thin films to glassy superconductors that are the origins. By using the full capabilities of the TAS IN4, Raymond et al. (p. 24) gained valuable insight into the spin-polarised spallation neutron-scattering measurements. They used the instrument in the polarised neutron set-up to investigate the fascinating experiment (which could confirm a new species of multiferroic compound: joining forces for which SALSA, the dedicated instrument for residual stresses, is an example) in collaboration with theorists from Rutgers, showing the effect of spin-orbit interactions and the highlight on the hour-glass spectrum of heavy-fermion superconductors. Li and collaborators (p. 30) gained valuable insight into the spin-polarised spallation neutron-scattering measurements. In the framework of the Endurance upgrade programme, our College has one flagship project: SuperSAC. Although SuperSAC’s performance is outstanding in terms of capture rate, precision, lateral resolution and flexibility of sample manipulation, stress is only one parameter in the spectrum of materials characterisation. The proposed new instrument will add the analysis of textures and phases, and the in situ determination of elements in an object at a given stage in its manufacture, by offering a white beam option. By placing the sample in the white beam and analysing the scattered intensity using the two large crystal analysis set-ups, selected parts of the diffraction pattern will be recorded in acquisition times as short as 1 s. This new instrument will provide new opportunities not only for materials scientists and engineers, but also for other user groups, such as geologists and archaeologists who also need to analyse complex, bulky samples non-destructively. The use of the College is not restricted to the conducting of experiments. Our users also come to give talks on their results or to present new techniques or instrumentation for neutron scattering. One particularly successful year saw the arrival of Ferenc Mészáros give an excellent talk on low-dimensional neutron moderators for enhanced source brightness. The seminar attracted an exceptional number of scientists interested in the development of new moderators for spallation sources.

In the framework of the Endurance upgrade programme, our College has one flagship project: SuperSAC. Although SuperSAC’s performance is outstanding in terms of capture rate, precision, lateral resolution and flexibility of sample manipulation, stress is only one parameter in the spectrum of materials characterisation. The proposed new instrument will add the analysis of textures and phases, and the in situ determination of elements in an object at a given stage in its manufacture, by offering a white beam option. By placing the sample in the white beam and analysing the scattered intensity using the two large crystal analysis set-ups, selected parts of the diffraction pattern will be recorded in acquisition times as short as 1 s. This new instrument will provide new opportunities not only for materials scientists and engineers, but also for other user groups, such as geologists and archaeologists who also need to analyse complex, bulky samples non-destructively. The use of the College is not restricted to the conducting of experiments. Our users also come to give talks on their results or to present new techniques or instrumentation for neutron scattering. One particularly successful year saw the arrival of Ferenc Mészáros give an excellent talk on low-dimensional neutron moderators for enhanced source brightness. The seminar attracted an exceptional number of scientists interested in the development of new moderators for spallation sources.

In the framework of the Endurance upgrade programme, our College has one flagship project: SuperSAC. Although SuperSAC’s performance is outstanding in terms of capture rate, precision, lateral resolution and flexibility of sample manipulation, stress is only one parameter in the spectrum of materials characterisation. The proposed new instrument will add the analysis of textures and phases, and the in situ determination of elements in an object at a given stage in its manufacture, by offering a white beam option. By placing the sample in the white beam and analysing the scattered intensity using the two large crystal analysis set-ups, selected parts of the diffraction pattern will be recorded in acquisition times as short as 1 s. This new instrument will provide new opportunities not only for materials scientists and engineers, but also for other user groups, such as geologists and archaeologists who also need to analyse complex, bulky samples non-destructively. The use of the College is not restricted to the conducting of experiments. Our users also come to give talks on their results or to present new techniques or instrumentation for neutron scattering. One particularly successful year saw the arrival of Ferenc Mészáros give an excellent talk on low-dimensional neutron moderators for enhanced source brightness. The seminar attracted an exceptional number of scientists interested in the development of new moderators for spallation sources.
fields and polarisation analysis offered by the recently commissioned SANS machine. Examples of what can be done using polarised neutrons in small-angle scattering is given by one of our highlights (p. 18), in which the distortion of the vortex lattice in Sr$_2$RuO$_4$ as a function of the angle between the applied magnetic field and the Ru-O basal plane was determined to obtain the superconducting anisotropy.

In the past, studies on magnetic defects or short-range magnetic order or correlations were rare. Now things have changed dramatically thanks to the availability of polarised neutron beams, allowing for example the detection of magnetic monopoles (see Annual Report 2009). The availability of the dedicated reflectometers D17 and SuperD3 has had an enormous impact on the science conducted in College 5B, in parallel to a strong shift in scientific interest towards thin films, multilayers and nanoparticles, the newly developed polarisation-analysis reflectometers, which demand the accuracy of measurements and is underpinned increasingly frequently by molecular modelling that can be predicted by conventional equations used for the dynamics of simple liquids.

The organisation provides a key platform to assist scientific visitors in the pre-characterisation, analysis and interpretation of scattering data. At the start of 2014, the PSCM and chemistry laboratories will move into the new Science Building adjacent to SDS, where they will provide modern, state-of-the-art facilities for future soft matter research using neutron, x-rays and complementary techniques carried out on the EPN platform.

A neutron is an ideal probe for the structure and dynamics studies of soft condensed matter (SCM), which allows the investigation of partially ordered systems, such as biological and model membranes, to study the interactions between gold nanoparticles and floating lipid bilayers to the surface charge (p. 66). Findings from soft matter experiments at the EIL have featured in the popular press, in articles dealing with such diverse topics as health and crime prevention. For example, work on understanding beating difficulties from studying the elasticity of polymers in the deformation of living surfactant laden in the New Scientist and the new approach for fingerprint detection mentioned above was publicised on the BBC website. There continues to be emphasis on combined neutron experiments with site techniques, such as dynamic light scattering combined with small-angle neutron scattering (D11) and neutron reflectometry combined with infrared reflection absorption spectroscopy (D17). Furthermore, a great effort has been made to promote the use of neutron reflectometry in material science and biology. The measurement of the structure factor $S(Q)$ allows the detection of magnetic monopoles (see Annual Report 2009). The availability of the dedicated reflectometers D17 and SuperD3 has had an enormous impact on the science conducted in College 5B, in parallel to a strong shift in scientific interest towards thin films, multilayers and nanoparticles, the newly developed polarisation-analysis reflectometers, which demand the accuracy of measurements and is underpinned increasingly frequently by molecular modelling that can be predicted by conventional equations used for the dynamics of simple liquids.

**SCIENTIFIC HIGHLIGHTS**

**College 6 – Liquids and Glasses**

**Author: V. Czjzek (College 6 Secretary)**

Non-crystalline materials are characterised by the loss of long-range order. However, chemical and internal motions can be identified by diffraction and dynamics observed by quasi-elastic and inelastic scattering from which we can draw conclusions about their glassy and plastic state. This is a powerful tool in this field. It complements other techniques based on X-ray and neutron scattering.

**SCIENTIFIC HIGHLIGHTS**

**College 7 – Spectroscopy and Modelling**

**Author: M. Zhibo (College 7 Secretary)**

The atomic world is subject to perpetual dynamics that define its characteristics and shape its evolution in time and space. Neutron spectroscopy is a perfect tool for revealing the dynamic fingerprints of atoms and molecules in the material and nanoregime. This paves the way for a comprehensive understanding of the microscopic level, of the chemical and physical processes that dominate the material. In the solid state, various interesting and societally relevant phenomena can be observed. These need to be studied and/or explored for their potential applications. The activities of College 7’s “Spectroscopy in solid-state physics and chemistry” are situated precisely within this framework and are aimed at dealing with topics of boundaries of various domains ranging from materials science and condensed matter to energy and life sciences. This can be clearly seen from the highlights presented in this article. Neutron spectroscopy offers exactly the right time-window for observing these movements. In addition, incoherent neutron spectroscopy provides unambiguous answers to questions of intra and intermolecular motions. The IL’s NSF-funded reflectometer D16 is today second-to-none, and now includes the neutron-diffusing and backscattering spectrometer PIV-10, which accesses biomolecular dynamics with unprecedented precision.

The final importance of deuteration in sample preparation for biological studies cannot be overstated. From $^{2}$H/$^{1}$H exchange and contrast variation methods to selectivity or even complete isotope scrambling, biological molecules produced in the D-lab, researchers are able to prepare ever more sophisticated experiments using neutron reflectometry to provide insights into the functional and exciting insights for a vast array of biological processes.

**College 9 – Soft Condensed Matter**

**Authors: R. Campbell (College 9 Secretary) and L. Percor (College 9 Secretary)**

Soft condensed matter is a key growth area at the EIL with the number of experiments exceeding 20% of the total in 2013. Research covers a broad range of fundamental areas in physical chemistry, condensed matter physics and biology. Topics under investigation include colloids, micelles, soft and complex biological systems. Neutrons are an ideal probe for the structure and dynamics of soft matter and contrast variation is of critical importance. Can neutron scattering continue to generate a great deal of research interest? For example, work on $D_{11}$ has revealed the mechanism of deformation for lipid bilayers with reverse micelles (p. 51). Also, electrochemical polymerisation of surface films has been characterised on FIGARO and the detection of invisible fingerprints (p. 34). Bio-related soft matter experiments continue to thrive and recent highlights include work on $D_{10}$ and $D_{17}$ concerning the trend of growing interest into phospholipid monolayers and bilayers by ring-shaped cyclodextrin molecules (p. 52), as well as work on $D_{17}$ linking the interactions between gold nanoparticles and floating lipid bilayers to the surface charge (p. 68). From soft matter experiments at the EIL have featured in the popular press, in articles dealing with such diverse topics as health and crime prevention. For example, work on understanding beating difficulties from studying the elasticity of polymers in the deformation of living surfactant laden in the New Scientist and the new approach for fingerprint detection mentioned above was publicised on the BBC website. There continues to be emphasis on combined neutron experiments with site techniques, such as dynamic light scattering combined with small-angle neutron scattering (D11) and neutron reflectometry combined with infrared reflection absorption spectroscopy (D17). Furthermore, a great effort has been made to promote the use of neutron reflectometry in material science and biology.
SCIENTIFIC HIGHLIGHTS

ILL IN THE PRESS

1. Published in BBC News Science & Environment on 21 August 2013.
3. Published in Scientist Live on April 2013.
4. Published in Laboratory News on 10 April 2013.
6. Published in DIE WELT on 16 July 2013.
7. Published in Chemicals-technology on 17 July 2013.
8. Published in Physics World on 21 August 2013.

More articles on:

Small-angle diffractometers D11, D22 and D33

Anisotropy of the superconducting state in Sr$_2$RuO$_4$

While superconductors continue to find an increasing range of practical applications, they still hold an even greater, untapped potential. In this regard, it appears that some of the most significant advances will be precisely in those materials that are the most complex to understand and control.

Strontium ruthenate (Sr$_2$RuO$_4$) can in many ways be considered a paradigm for unconventional superconductivity. We have measured the anisotropy of the superconducting state in Sr$_2$RuO$_4$, providing significant constraints on models of superconductivity in this material.

The superconducting state emerges due to the formation and condensation of Cooper pairs made from charge carriers (electrons and/or holes). That said, the exact microscopic mechanism responsible for the pairing in different materials varies and, in many cases, remains elusive.

A prominent example of this is found in Sr$_2$RuO$_4$, where the two carrier spins in the Cooper pairs are believed to form a triplet that introduces an additional degree of freedom and complexity [1,2]. As a result, the exact nature of the order parameter in this compound remains unresolved despite being studied extensively for almost 20 years.

We have used the D11, D22 and D33 small-angle neutron scattering (SANS) instruments to study the vortex lattice [VI] in Sr$_2$RuO$_4$ [3]. The distortion of the VI, arising when the field is applied parallel to the Ru-O planes, provides a direct measure of the anisotropy, $\Gamma_{VI}$ of the superconducting state. This anisotropy is of particular interest in comparison to earlier measurements of the upper critical field ($H_c2$) ratio for magnetic fields applied parallel and perpendicular to the basal plane. This $H_c2$ ratio ($H_c2(\perp)/H_c2(\parallel)$) is much smaller than expected from the Fermi surface anisotropy [1,2], suggesting a suppression of the upper critical field perpendicular to the basal plane, possibly due to Pauli limiting, in turn raising questions concerning triplet pairing in Sr$_2$RuO$_4$ [2].

While measurements with the field parallel to the basal plane are conceptually simple, they require a novel approach to SANS VI studies. This is evident from a simple estimate of the VI scattering intensity that turns out to be several orders of magnitude too weak to be measurable, even at a high intensity neutron facility such as the ILL. However, due to the large anisotropy of Sr$_2$RuO$_4$, applying the field close to, but not perfectly within, the Ru-O planes causes a significant current to run in the basal plane along the field direction [4].

This greatly enhances the field modulation and hence the scattered intensity, making the VI Bragg reflections easily observable as shown in Figure 1. The increased magnetisation is perpendicular to the field directions (and hence the neutron spin) causing spin-flip scattering and a Zeeman splitting of the VI rocking curves as shown in Figure 2.

The lines show the calculated VI anisotropy for $\Gamma_{VI} = 58.5$ ± 2.3 as shown by the dashed line. In comparison the $H_c2$-anisotropy of 20 (dotted line) yields a very poor fit to our measurements.

In conclusion we have used SANS to measure the anisotropy of the superconducting state in Sr$_2$RuO$_4$ in a narrow range of field angles close to, but not perfectly aligned with, the Ru-O basal plane. The superconducting anisotropy greatly exceeds that of the upper critical field and imposes significant constraints on the possible pairing of carriers in this material. Any model aimed at describing the superconducting phase must provide a satisfactory explanation for this observation.
In this work, we studied a 40 % hole-doped single-layer perovskite cobaltate \( \text{La}_{1.6}\text{Sr}_{0.4}\text{CoO}_4 \) which is isostructural to the high-temperature superconducting cuprates. In the ideal half-doped "parent compound", the charges are known to order in an alternating \( \text{Co}^{2+}/\text{Co}^{3+} \) arrangement with an antiferromagnetic structure that resembles a checkerboard (see figure 1a). In contrast, the incommensurate magnetic peak positions in our 40 % hole-doped cobaltate should, in principle, be compatible with a phase where the charges arrange into diagonal stripes. Due to the comparably high sharpness of the magnetic peaks in our high-quality single crystals, we would also expect relatively sharp charge-stripe ordering superstructure reflections. It should be noted that magnetic-stripe phases cannot easily be decoupled from charge-stripe phases in this insulting and localised system containing non-magnetic \( \text{Co}^{2+} \) ions. The movement of one electron from a \( \text{Co}^{2+} \) to a \( \text{Co}^{3+} \) site would require several 100 meV.

However, in detailed neutron scattering experiments, we were not able to detect any indication of charge-stripe ordering reflections in our 40 % hole-doped cobaltate material [2]. Instead, we observed superstructure reflections located at half-integrals in reciprocal space and indicative of the checkerboard charge-ordering exhibiting by the half-doped "parent compound". In fact, this is not entirely surprising, because the half-doped compound exhibits a very robust checkerboard charge-ordering pattern that persists up to very high temperatures (above 800 K). It would therefore seem quite natural that such an extremely stable checkerboard charge-order also persists in a certain doping regime around half-doping. In addition, it is unlikely for these stripes to occur at lower temperatures, since the charges cannot easily re-arrange themselves once they are frozen in a disordered checkerboard arrangement due to their insulating properties ("spin blockade" mechanism). Finally, the results of the study we performed at the spectrometer IN8 of high-energy cobalt-oxide [3], where the charges within the copper oxygen planes segregate into stripes or on purely itinerant models where Fermi surface effects are significant. However, a recent observation of this type of magnetic excitation spectrum in an insulating cobalt oxide showed that Fermi surface effects are not necessarily needed for an understanding of the hour-glass spectrum [1]. We have now been able to synthesise an insulating cobalt oxide with this spectral shape that does not exhibit charge stripes either, thus suggesting that "hour-glass"-shaped magnetic excitations may have a completely different origin [2].

**SCIENTIFIC HIGHLIGHTS**

**MAGNETISM**

Three-axis spectrometer IN8

**Hour-glass spectrum in a stripeless insulating transition metal oxide**

The magnetic excitations in high-temperature copper oxide superconductors are believed to be crucial for superconductivity. The most promising models able to describe these "hour-glass"-shaped magnetic excitation spectra are currently based either on models where the charges within the copper oxygen planes segregate into stripes or on purely itinerant models where Fermi surface effects are significant. However, a recent observation of this type of magnetic excitation spectrum in an insulating cobalt oxide showed that Fermi surface effects are not necessarily needed for an understanding of the hour-glass spectrum [1]. We have now been able to synthesise an insulating cobalt oxide with this spectral shape that does not exhibit charge stripes either, thus suggesting that "hour-glass"-shaped magnetic excitations may have a completely different origin [2].

**AUTHORS & REFERENCES**

Y. Drozd and A.C. Komarek (Max-Planck-Institute for Chemical Physics of Solids, Germany)
D. Lamago (ILL, France)
A. Plowman (LLB, France)

As a major interaction in rare earth compounds, the crystalline electric field (CEF) reflects directly the electrical and magnetic potential on the rare-earth site, which is created by the neighbouring ions. Interestingly, in the case of NdFeAsO, the neighbouring ions are more than just a point charges since they include the magnetic Fe cations. The determination of structure and parameters of CEF is therefore an attractive issue to be addressed for a better understanding of the physical properties of these systems.

We have studied the CEF excitations of NdFeAsO by performing detailed temperature-dependent (1.6 to 200 K) inelastic neutron scattering (INS) measurements on IN4, using two neutron incident wavelengths (2.11 and 2.22 Å). Simulations based on a single ion crystal field model Hamiltonian were carried out to help analysis and interpretation of the INS data. The structure of the crystalline field levels are constructed for both the high-temperature paramagnetic tetragonal (local point group symmetry C4v) and the low-temperature antiferromagnetic orthorhombic (local point group symmetry C2v) phases. The crystal field parameters are obtained from the analysis of the CEF interactions.[1]

The local structure surrounding the Nd3+ ion is illustrated in figure 1a. A schematic diagram of the obtained splitting of the Nd3+ ground multiplet, at 5 and 160 K, is presented in figure 1b. We note that the ground state at 5 K and at 160 K is a magnetic singlet and doublet, respectively.

The obtained CEF spectra at 5 and 160 K are shown in figure 2a and figure 2b, respectively. The solid lines represent a relevant modeling based on a crystal field model Hamiltonian. The simulations allowed extracting reliable CEF parameters which are used to describe the behaviour of the CEF excitations. Good agreement is found between the results of the fits and the experimental data. With increasing temperature, the intensities of all peaks decrease, indicating that these features are excitations occurring between the ground state and the excited states. Moreover, few new peaks are observed and can be assigned to the CEF transitions between the populated excited states. Further, the de-excitation transition from the excited states to the ground state can also be observed on the neutron energy gain side (negative energies) of the spectra in figure 2b. The assignment of the peaks is depicted in figure 1b. We notice that, while four CEF excitation peaks were expected at 5 K, we observe in fact five (A–E). The additional splitting of CEF peaks in the low-temperature orthorhombic phase indicates that the molecular field, i.e. the effective exchange magnetic field induced by the Fe magnetic sublattice, is correlated with the magnetism of NdFeAsO, leading to a further lifting of the degeneracy.

The interplay between Nd and Fe magnetism in NdFeAsO is complex and becomes significant as the order-order transition of the Fe magnetic sublattice exhibits a close proximity to the onset of the Nd magnetic order. In order to gain deeper insights into the effect of the molecular field of the magnetic Fe sublattice on the CEF excitations, we consider the temperature-dependent INS measurements presented in figure 3a. Two peaks are clearly observed at 7.24 meV (labeled as B) and 8.59 meV (labeled as C). We define the splitting parameter, \( P = [EC(1-C)B]/[B(1-C)E] \), whose temperature dependence is shown in figure 3b. The SDW transition temperature is found at ~140 K, which is associated with a long-range antiferromagnetic order of the Fe moments. Further, the splitting parameter reaches its maximum at 2 K and its amplitude is reduced below 2 K. In the inset of figure 3b, we also note the magnetic quadrupole moment of the Nd atom is reduced at lower temperatures, which is consistent with the magnetism of Nd3+ in NdFeAsO.

Figure 1 illustrates the local structure of the Nd3+ ion at 5 K. Figure 2a schematically shows the energy-level diagram of NdFeAsO for the lowest J multiplet, under the tetragonal (C4v) and orthorhombic (C2v) structural environments. The arrows denote a few representative CEF transitions as extracted from our inelastic neutron spectra.
Spin waves excited by the electric component

There has been increasing interest in so-called multiferroic materials, which simultaneously display spontaneous ferroelectric polarisation and (anti)ferromagnetic ordering. Electromagnons are spin waves excited by the electric component of electromagnetic radiation due to dynamic magnetoelectric coupling in multiferroics.

Figures 1 and 2 show the time-of-flight (TOF) spectrometer IN4 and time-domain THz spectroscopy and inelastic neutron scattering measurements, respectively.

The crystal lattice has a temperature-independent non-collinear ferrimagnetic antiferromagnetic structure with the Pr2O3 space group. Its low-temperature phase diagram is complex—below 150 K, a series of magnetic phase transitions occur. Below \( T_s \approx 110 \) K, an incommensurate magnetic ordering appears, where the magnetic structure modulation has a periodicity of about 10 unit cells.

The results of our infrared (IR) and THz measurements are given in Figure 1, showing polar optical phonons. Upon cooling, all phonons above 12 meV exhibit the usual behaviour: their intensity increases due to reduced phonon damping at low temperatures. In contrast, the phonon near 11 meV exhibits an anomalous behaviour on cooling; its intensity only increases down to 115 K. Below this temperature, it weakens notably, while a supplementary broad reflectivity peak develops below \( E \approx 10 \) meV and becomes more intense upon cooling. This transfer of strengths evidences a coupling between these two polar modes.

At the same time, we confirmed that the crystal symmetry of \( \varepsilon\text{-Fe}_2\text{O}_3 \) does not change with temperature. In other words, no new polar phonons should appear.

As the nanopowder does not allow us to determine directly the magnetic and magnon dispersion branches in the BZ, we used the time-of-flight technique on IN4. The resulting intensity maps of inelastic neutron scattering (INS) taken at selected temperatures are depicted in Figure 2a, 2b, and 2c. Upon cooling, all phonons above 12 meV exhibit the usual behaviour; their intensity increases due to reduced phonon damping at low temperatures. In contrast, the phonon near 11 meV exhibits an anomalous behaviour on cooling; its intensity only increases down to 115 K. Below this temperature, it weakens notably, while a supplementary broad reflectivity peak develops below \( E \approx 10 \) meV and becomes more intense upon cooling. This transfer of strengths evidences a coupling between these two polar modes.

The data reveal a steep column of intense scattering, emanating from magnetic Bragg peaks at \( Q = 1.4 \) Å\(^{-1}\) and extending up to \( E \approx 10 \) meV. The weaker columns at \( Q > 2 \) Å\(^{-1}\) are due to scattering in higher-order BZs. The fact that the area of most intense scattering is located at low \( Q \) shows unambiguously that the dominant contribution to the low-\( Q \) scattering comes from spin waves.

Since the observed spin-wave excitation is coupled with the lowest-energy TO1 phonon, it must be excited by the electric component of the electromagnetic radiation; at the same time, it has to contribute to dielectric permittivity. Therefore, the excitation seen near 10 meV must be an EM. EMs were previously only identified in single crystals using a thorough polarisation analysis of measured spectra. Here we have determined an EM from unpolarised IR and THz spectra of nanograined ceramics showing its coupling with a TO1 phonon. At the same time, we have shown from INS experiments conducted on powder that the EM in \( \varepsilon\text{-Fe}_2\text{O}_3 \) comes from the BZ boundary. The combining of experimental methods in this way provides a guideline for an unambiguous determination of EMs in materials where sufficiently large single crystals for polarised IR and THz measurements are not available.

The results of our infrared (IR) and THz measurements are given in Figure 1, showing polar optical phonons. Upon cooling, all phonons above 12 meV exhibit the usual behaviour: their intensity increases due to reduced phonon damping at low temperatures. In contrast, the phonon near 11 meV exhibits an anomalous behaviour on cooling; its intensity only increases down to 115 K. Below this temperature, it weakens notably, while a supplementary broad reflectivity peak develops below \( E \approx 10 \) meV and becomes more intense upon cooling. This transfer of strengths evidences a coupling between these two polar modes.

At the same time, we confirmed that the crystal symmetry of \( \varepsilon\text{-Fe}_2\text{O}_3 \) does not change with temperature. In other words, no new polar phonons should appear.

As the nanopowder does not allow us to determine directly the magnetic and magnon dispersion branches in the BZ, we used the time-of-flight technique on IN4. The resulting intensity maps of inelastic neutron scattering (INS) taken at selected temperatures are depicted in Figure 2a, 2b, and 2c. Upon cooling, all phonons above 12 meV exhibit the usual behaviour; their intensity increases due to reduced phonon damping at low temperatures. In contrast, the phonon near 11 meV exhibits an anomalous behaviour on cooling; its intensity only increases down to 115 K. Below this temperature, it weakens notably, while a supplementary broad reflectivity peak develops below \( E \approx 10 \) meV and becomes more intense upon cooling. This transfer of strengths evidences a coupling between these two polar modes.

The data reveal a steep column of intense scattering, emanating from magnetic Bragg peaks at \( Q = 1.4 \) Å\(^{-1}\) and extending up to \( E \approx 10 \) meV. The weaker columns at \( Q > 2 \) Å\(^{-1}\) are due to scattering in higher-order BZs. The fact that the area of most intense scattering is located at low \( Q \) shows unambiguously that the dominant contribution to the low-\( Q \) scattering comes from spin waves.

Since the observed spin-wave excitation is coupled with the lowest-energy TO1 phonon, it must be excited by the electric component of the electromagnetic radiation; at the same time, it has to contribute to dielectric permittivity. Therefore, the excitation seen near 10 meV must be an EM. EMs were previously only identified in single crystals using a thorough polarisation analysis of measured spectra. Here we have determined an EM from unpolarised IR and THz spectra of nanograined ceramics showing its coupling with a TO1 phonon. At the same time, we have shown from INS experiments conducted on powder that the EM in \( \varepsilon\text{-Fe}_2\text{O}_3 \) comes from the BZ boundary. The combining of experimental methods in this way provides a guideline for an unambiguous determination of EMs in materials where sufficiently large single crystals for polarised IR and THz measurements are not available.

The results of our infrared (IR) and THz measurements are given in Figure 1, showing polar optical phonons. Upon cooling, all phonons above 12 meV exhibit the usual behaviour: their intensity increases due to reduced phonon damping at low temperatures. In contrast, the phonon near 11 meV exhibits an anomalous behaviour on cooling; its intensity only increases down to 115 K. Below this temperature, it weakens notably, while a supplementary broad reflectivity peak develops below \( E \approx 10 \) meV and becomes more intense upon cooling. This transfer of strengths evidences a coupling between these two polar modes.

At the same time, we confirmed that the crystal symmetry of \( \varepsilon\text{-Fe}_2\text{O}_3 \) does not change with temperature. In other words, no new polar phonons should appear.

As the nanopowder does not allow us to determine directly the magnetic and magnon dispersion branches in the BZ, we used the time-of-flight technique on IN4. The resulting intensity maps of inelastic neutron scattering (INS) taken at selected temperatures are depicted in Figure 2a, 2b, and 2c. Upon cooling, all phonons above 12 meV exhibit the usual behaviour; their intensity increases due to reduced phonon damping at low temperatures. In contrast, the phonon near 11 meV exhibits an anomalous behaviour on cooling; its intensity only increases down to 115 K. Below this temperature, it weakens notably, while a supplementary broad reflectivity peak develops below \( E \approx 10 \) meV and becomes more intense upon cooling. This transfer of strengths evidences a coupling between these two polar modes.

The data reveal a steep column of intense scattering, emanating from magnetic Bragg peaks at \( Q = 1.4 \) Å\(^{-1}\) and extending up to \( E \approx 10 \) meV. The weaker columns at \( Q > 2 \) Å\(^{-1}\) are due to scattering in higher-order BZs. The fact that the area of most intense scattering is located at low \( Q \) shows unambiguously that the dominant contribution to the low-\( Q \) scattering comes from spin waves.

Since the observed spin-wave excitation is coupled with the lowest-energy TO1 phonon, it must be excited by the electric component of the electromagnetic radiation; at the same time, it has to contribute to dielectric permittivity. Therefore, the excitation seen near 10 meV must be an EM. EMs were previously only identified in single crystals using a thorough polarisation analysis of measured spectra. Here we have determined an EM from unpolarised IR and THz spectra of nanograined ceramics showing its coupling with a TO1 phonon. At the same time, we have shown from INS experiments conducted on powder that the EM in \( \varepsilon\text{-Fe}_2\text{O}_3 \) comes from the BZ boundary. The combining of experimental methods in this way provides a guideline for an unambiguous determination of EMs in materials where sufficiently large single crystals for polarised IR and THz measurements are not available.
Chirality of the spin resonance excitation in an unconventional superconductor under magnetic field

Promises of superconductivity are moderated by important gaps separating technology from basic science in terms of temperature of operation and critical currents achieved. This notwithstanding, the diversity of materials and the understanding of phenomena has been unprecedented in the past decades. The spin resonance is an ubiquitous magnetic excitation that appears in many unconventional superconductors: cuprates, iron pnictides and chalcogenides as well as heavy fermion systems.

This magnetic mode is observed in inelastic neutron scattering experiments below the superconducting transition temperature $T_c$. It appears at a specific wave-vector for which the superconducting gap changes sign and at an energy of several $k_B T_c$.

The measurements were performed on the cold neutron three-axis spectrometer IN14 with the polarised neutron set-up shown in figure 1. In this set-up the initial neutron beam is polarised and the polarisation is adiabatically kept toward the sample located in a dilution fridge inside an horizontal field magnet. The field is applied along the scattering vector $Q$ and the polarisation is either parallel ($P^+)$ or antiparallel ($P^-$) to the horizontal magnetic field.

The corresponding scattered intensity measured is $I^+$ for $P^+$ and $I^-$ for $P^-$. With such a set-up, different contributions to the magnetic excitation spectrum can be enhanced or suppressed whereas an unpolarised neutron scattering experiment measures the sum of both contributions [3]. This is due to the so-called chiral correlation function that enters the scattering cross-section for such polarised neutron scattering experiment and that is directly obtained by the difference $I^+ - I^-$. In particular, a clockwise spin precession leads to non-vanishing intensity only for $P^-$ and an anticlockwise precession for $P^+$ (see figure 1). A given handedness is therefore associated to a given neutron beam polarisation only.

The spectra obtained for the unconventional superconductor CaCoIn$_5$ at a temperature of 50 mK and for a field of 2 T applied along $Q$ are shown in figure 2.

The energy dependence of the signal depends on the initial polarisation indicating the presence of chirality. Figure 2a shows the excitation spectrum for $P^+$ and figure 2b for $P^-$. The difference between the two measured intensities, $I^+ - I^-$, is shown in, figure 2c. This chiral response has similar spectral weight, but with opposite sign, above and below $k_B T_c = 0.6$ meV, which is the zero field resonance energy. The minima and maxima located at $\Delta = \hbar \omega$ and $(\Delta + \hbar \omega)$, with $\hbar \omega = 0.08$ meV at 2 T, establishes the Zeeman splitting of the resonance, each mode having a different handedness. The peculiar feature is that the symmetry of the chiral contribution figure 2c does not reflect the signal in each polarisation channel figure 2a and 2b. At an energy around $\hbar \omega$, both polarisation channels contribute to the scattering while around $(\Delta + \hbar \omega)$ scattering occurs almost only for the $P^-$ channel. Without any model so far, this asymmetry can be accounted for by the presence of another contribution to the spin dynamics that has no polarisation dependence and therefore no chiral nature. This low energy mode exists on the top of the Zeeman split contribution that exhibits the chirality shown in, figure 2c. This possibility may be related to a dominant crystal field anisotropy allowing several kinds of fluctuations (transverse and longitudinal) and such scenario must be addressed by relevant theoretical studies [4].

In summary, two modes of the Zeeman split resonance of CaCoIn$_5$ are observed for different incident neutron polarization evidencing their chiral nature. An unexpected additional non-chiral contribution must be added in order to account for the asymmetry arising in the individual polarisation channel measurement. This complexity tightens the more theoretical scenario for the spin resonance mode. These are necessary steps for understanding the mechanisms of unconventional superconductivity in view of tailoring new materials in the future.

Authors & References

K. Komiya, Japan Atomic Energy Agency, Japan
A. Mess (ESS, Lund, Sweden)
P. Stoffels (UANN)

SCIENTIFIC HIGHLIGHTS
Magnetic correlations in multilayers and monolayers of iron oxide nanoparticles

Chemically synthesised magnetic nanoparticles (NPs) are promising materials for the bottom-up approach to nanodevice fabrication [1]. They can be self-assembled in a 2-dimensional (2D) monolayer or in a three-dimensional (3D) multilayer with tunable magnetic and electrical properties. In particular, the interaction between NPs can lead to collective magnetic behaviour manifesting itself in superparamagnetic, superspin-glass, and superferromagnetic states [2]. These states depend on the ordering of the NPs and the type and strength of magnetic interaction between the NPs.

We show here that hexagonally ordered spherical NPs with a pure magnetic dipolar coupling can lead to the formation of long-range magnetic order. The understanding of these interactions has implications for data storage media and spintronics devices.

Using spin-coating techniques, we promoted the self-assembly of iron oxide NPs of 20 nm in diameter on silicon substrates. The NPs were dispersed in toluene and separated by oleic acid surfactant. The samples were heated at 80°C to evaporate the solvent and annealed at 230°C in vacuum to enhance magnetite as the major phase. Figure 1 shows SEM images of as-prepared monolayer and multilayer films. The NPs show a hexagonal close-packed arrangement with a long-range structural ordering. This long-range ordering leads to the collective magnetic behaviour of the self-assembled system. The respective measurements were carried out using the SuperADAM instrument at the ILL.

Figure 2 shows the polarised neutron reflectivity from a multilayer sample for up and down polarisation at an applied field of 5 kOe, respectively, along with best fits (solid lines). The fitting reveals a 5-layer system with an out-of-plane hexagonal periodicity of 13.5 nm, as confirmed by the Bragg peak (arrow). Furthermore, the fitting reveals several novel features in the multilayer. The nuclear SLD indicates that the out-of-plane NP layering improves from bottom to top, unlike many other self-assembled NP systems.

The fitting also provides insight into the microscopic magnetic structure. The splitting of the reflectivities for up and down polarised neutrons at high fields confirms a finite magnetisation of the multilayer, which is expressed in a finite magnetic SLD, as shown in Figure 2c, top left panel. At remanence the splitting disappears, which implies that the magnetic SLD value, shown in the bottom left panel of Figure 2c, remains finite and identical to the value at high fields. This can be explained if the system is assumed to have a domain-like structure as shown in the sketch (bottom right panel of Figure 2c). At the applied field of 5 kOe, the NPs' magnetic moments are aligned mainly along the field axis and a finite magnetisation is observed. When the field is removed, the net magnetisation falls to zero. However, due to strong dipolar interaction between the NPs, their magnetic moments are heavily correlated over microscopic regions. These regions are much smaller than the sample area, but greater than the lateral projection of the neutron coherence length. Within such regions, the NPs' magnetic moments are aligned ferromagnetically forming quasi-domains (shown as brown lines in the bottom right panel) and project a finite magnetic SLD. Arising purely due to dipolar interaction, they are different from usual ferromagnetic domains and have no well-expressed domain walls [3].

In summary, the multilayer shows hexagonal ordering with out-of-plane layering achieved using spin-coating. The structural ordering leads to quasi-domain-like long-range magnetic order mediated by pure dipolar coupling.

Figure 1 shows SEM images of NPs spin-coated on silicon substrate with hexagonal ordering forming (a) monolayer and (b) multilayer.

Figure 2 shows polarised neutron reflectivity taken at room temperature and at (a) 5 kOe and (b) remanence for two polarisation states, along with best fits. The arrow indicates the Bragg peak of the five-layer stack of NPs. The inset shows the nuclear SLD obtained from fitting. (c) Plot of magnetic SLD at 5 kOe (top left panel) and at remanence (bottom left panel). The corresponding sketches of the superlattice arrangement at 5 kOe and at remanence are shown in the right-hand panels, respectively. The quasi-domains are highlighted by the brown lines. Figure published in ref [3].
A proton chain in a molecular solid

The movement of water and protons, including transport in confined spaces, is of considerable importance in a number of key areas of science and technology. Water transport can be observed in a wide variety of media from solids, such as zeolites and clays, to living cells, and in various contexts, such as molecular storage materials, catalysis, soil science and many others. Proton migration, which is often related to water transport, is currently of interest in energy applications, while water transport is of particular importance in biology, especially in cell membranes in which the sophisticated structures permit the passage of water while blocking ion transport.

A common form of proton migration is the diffusion of water into absorbing materials, either via channels and cavities or via some sort of pathway which involves a proton cascade. When trying to explain electrolysis in water solutions some 200 years ago, Grotthuss already proposed concepts which over time have taken the form of a hopping-reorientation mechanism in which the movement of anionic H\(^+\) is assumed to involve concerted proton 'hand-off' from one water molecule to the next in the chain [1]. This type of mechanism has been put forward to explain proton mobility in a number of different processes, very often in solution, but has not always been supported by experimental evidence.

The complete exchange of protium for deuterium on mobile and immobile water molecules in a non-porous crystal of a manganese citrate cubane coordination polymer, \([\text{Mn(H}_2\text{O})_6]^2n{[\text{Mn(H}_2\text{O})_5]}\), has been observed through single-crystal neutron diffraction analysis [2].

When a partially dehydrated crystal of the manganese citrate cubane polymer is exposed to D\(_2\)O vapour at room temperature for few hours, all of the 21 H\(_2\)O units per polymer link, attached to four independent Mn\(^{II}\) centres in the form of aqua ligands, and the additional 9 free solvent water sites, become D\(_2\)O units.

The primary goal of studying the Mn-containing citrate cubane polymer was to understand the non-destructive, fully reversible single-crystal-to-single-crystal transformation that this non-porous system exhibits upon physical solvent loss and reuptake. The structures of the fully H\(_2\)O-hydrated, the dehydrated, and the H\(_2\)O-rehydrated compounds were first analysed by single-crystal X-ray diffraction in the home laboratory. The experiments revealed the principal structural changes occurring at the solid-state transformations. However, because of the size of the structure and the small scattering power of hydrogen in X-ray diffraction, the hydrogen atoms of the water molecules could not be located.

Neutron diffraction measurements carried out at 20 K on the thermal neutron single-crystal diffractometer D19 have enabled us to locate the hydrogen atoms in the fully H\(_2\)O-hydrated structure and in the D\(_2\)O-rehydrated structure. All the H by EXAFS atomic positions have been identified by neutron Fourier difference maps and fully refined with isotropic displacement parameters. Of the 30 water sites, 8 are found to have 3 hydrogen atoms at bonding distance from the oxygen atom, 2 of which are half-occupied. The fully occupied oxygen forms two chemically perfectly acceptable H\(_2\)O units with either of the half-occupied hydrogen atoms. Two additional oxygen atoms are surrounded by four half-occupied hydrogen atoms. Again two water molecules with correct geometry can be formed by the oxygen atom and the two pairs of hydrogen atoms.

The hydrogen-atom disorder implies a superposition of two orientations of water molecules frozen in place at the low temperature of the data collection. The disorder can therefore be interpreted in terms of two chains of double-minimum hydrogen potentials which fit with the two states of a Grotthuss mechanism (Figure 1).

The enormous difference in scattering length between protium and deuterium makes neutron diffraction an essential probe for studying proton migration and isotopic substitution phenomena in molecular solids.

**SCIENTIFIC HIGHLIGHTS**

**CHEMISTRY AND CRYSTALLOGRAPHY**

**Single-crystal diffractometer D19**

A proton chain in a molecular solid

The movement of water and protons, including transport in confined spaces, is of considerable importance in a number of key areas of science and technology. Water transport can be observed in a wide variety of media from solids, such as zeolites and clays, to living cells, and in various contexts, such as molecular storage materials, catalysis, soil science and many others. Proton migration, which is often related to water transport, is currently of interest in energy applications, while water transport is of particular importance in biology, especially in cell membranes in which the sophisticated structures permit the passage of water while blocking ion transport.

A common form of proton migration is the diffusion of water into absorbing materials, either via channels and cavities or via some sort of pathway which involves a proton cascade. When trying to explain electrolysis in water solutions some 200 years ago, Grotthuss already proposed concepts which over time have taken the form of a hopping-reorientation mechanism in which the movement of anionic H\(^+\) is assumed to involve concerted proton 'hand-off' from one water molecule to the next in the chain [1]. This type of mechanism has been put forward to explain proton mobility in a number of different processes, very often in solution, but has not always been supported by experimental evidence.

The complete exchange of protium for deuterium on mobile and immobile water molecules in a non-porous crystal of a manganese citrate cubane coordination polymer, \([\text{Mn(H}_2\text{O})_6]^2n{[\text{Mn(H}_2\text{O})_5]}\), has been observed through single-crystal neutron diffraction analysis [2].

When a partially dehydrated crystal of the manganese citrate cubane polymer is exposed to D\(_2\)O vapour at room temperature for few hours, all of the 21 H\(_2\)O units per polymer link, attached to four independent Mn\(^{II}\) centres in the form of aqua ligands, and the additional 9 free solvent water sites, become D\(_2\)O units.

The primary goal of studying the Mn-containing citrate cubane polymer was to understand the non-destructive, fully reversible single-crystal-to-single-crystal transformation that this non-porous system exhibits upon physical solvent loss and reuptake. The structures of the fully H\(_2\)O-hydrated, the dehydrated, and the H\(_2\)O-rehydrated compounds were first analysed by single-crystal X-ray diffraction in the home laboratory. The experiments revealed the principal structural changes occurring at the solid-state transformations. However, because of the size of the structure and the small scattering power of hydrogen in X-ray diffraction, the hydrogen atoms of the water molecules could not be located.

Neutron diffraction measurements carried out at 20 K on the thermal neutron single-crystal diffractometer D19 have enabled us to locate the hydrogen atoms in the fully H\(_2\)O-hydrated structure and in the D\(_2\)O-rehydrated structure. All the H by EXAFS atomic positions have been identified by neutron Fourier difference maps and fully refined with isotropic displacement parameters. Of the 30 water sites, 8 are found to have 3 hydrogen atoms at bonding distance from the oxygen atom, 2 of which are half-occupied. The fully occupied oxygen forms two chemically perfectly acceptable H\(_2\)O units with either of the half-occupied hydrogen atoms. Two additional oxygen atoms are surrounded by four half-occupied hydrogen atoms. Again two water molecules with correct geometry can be formed by the oxygen atom and the two pairs of hydrogen atoms.

The hydrogen-atom disorder implies a superposition of two orientations of water molecules frozen in place at the low temperature of the data collection. The disorder can therefore be interpreted in terms of two chains of double-minimum hydrogen potentials which fit with the two states of a Grotthuss mechanism (Figure 1).

The enormous difference in scattering length between protium and deuterium makes neutron diffraction an essential probe for studying proton migration and isotopic substitution phenomena in molecular solids.

**SCIENTIFIC HIGHLIGHTS**

**CHEMISTRY AND CRYSTALLOGRAPHY**

**Single-crystal diffractometer D19**

A proton chain in a molecular solid

The movement of water and protons, including transport in confined spaces, is of considerable importance in a number of key areas of science and technology. Water transport can be observed in a wide variety of media from solids, such as zeolites and clays, to living cells, and in various contexts, such as molecular storage materials, catalysis, soil science and many others. Proton migration, which is often related to water transport, is currently of interest in energy applications, while water transport is of particular importance in biology, especially in cell membranes in which the sophisticated structures permit the passage of water while blocking ion transport.

A common form of proton migration is the diffusion of water into absorbing materials, either via channels and cavities or via some sort of pathway which involves a proton cascade. When trying to explain electrolysis in water solutions some 200 years ago, Grotthuss already proposed concepts which over time have taken the form of a hopping-reorientation mechanism in which the movement of anionic H\(^+\) is assumed to involve concerted proton 'hand-off' from one water molecule to the next in the chain [1]. This type of mechanism has been put forward to explain proton mobility in a number of different processes, very often in solution, but has not always been supported by experimental evidence.

The complete exchange of protium for deuterium on mobile and immobile water molecules in a non-porous crystal of a manganese citrate cubane coordination polymer, \([\text{Mn(H}_2\text{O})_6]^2n{[\text{Mn(H}_2\text{O})_5]}\), has been observed through single-crystal neutron diffraction analysis [2].

When a partially dehydrated crystal of the manganese citrate cubane polymer is exposed to D\(_2\)O vapour at room temperature for few hours, all of the 21 H\(_2\)O units per polymer link, attached to four independent Mn\(^{II}\) centres in the form of aqua ligands, and the additional 9 free solvent water sites, become D\(_2\)O units.

The primary goal of studying the Mn-containing citrate cubane polymer was to understand the non-destructive, fully reversible single-crystal-to-single-crystal transformation that this non-porous system exhibits upon physical solvent loss and reuptake. The structures of the fully H\(_2\)O-hydrated, the dehydrated, and the H\(_2\)O-rehydrated compounds were first analysed by single-crystal X-ray diffraction in the home laboratory. The experiments revealed the principal structural changes occurring at the solid-state transformations. However, because of the size of the structure and the small scattering power of hydrogen in X-ray diffraction, the hydrogen atoms of the water molecules could not be located.

Neutron diffraction measurements carried out at 20 K on the thermal neutron single-crystal diffractometer D19 have enabled us to locate the hydrogen atoms in the fully H\(_2\)O-hydrated structure and in the D\(_2\)O-rehydrated structure. All the H by EXAFS atomic positions have been identified by neutron Fourier difference maps and fully refined with isotropic displacement parameters. Of the 30 water sites, 8 are found to have 3 hydrogen atoms at bonding distance from the oxygen atom, 2 of which are half-occupied. The fully occupied oxygen forms two chemically perfectly acceptable H\(_2\)O units with either of the half-occupied hydrogen atoms. Two additional oxygen atoms are surrounded by four half-occupied hydrogen atoms. Again two water molecules with correct geometry can be formed by the oxygen atom and the two pairs of hydrogen atoms.

The hydrogen-atom disorder implies a superposition of two orientations of water molecules frozen in place at the low temperature of the data collection. The disorder can therefore be interpreted in terms of two chains of double-minimum hydrogen potentials which fit with the two states of a Grotthuss mechanism (Figure 1).

The enormous difference in scattering length between protium and deuterium makes neutron diffraction an essential probe for studying proton migration and isotopic substitution phenomena in molecular solids.
The design of molecular multiferroic materials where electric and magnetic order coexist can be achieved by including electrically polarisable guest molecules into a flexible porous host lattice where long range magnetic order resides. Such multifunctional materials have recently aroused much interest with a view to development of new materials with very large magnetoelectric effects [1-4].

**Authors & References**

O. Fabris and J.A. Rodríguez-Velamazán (IKERBASQUE, Spain and IJLL)

L. Canelles-Delgado (IKERBASQUE University of Zaragoza, Centro Universitario de la Defensa de Zaragoza, Spain and IJLL)

M.-H. Lemieux-Collereux, S.A. Mason and J. Rodríguez-Carvajal (IJLL)

F. Pardo and F. Llont (University of Valencia, Spain)

J.-P. Zhao and X.-H. Bu (Harbin University, Harbin, China)

V. Simonet and C.V. Collin (Institut Néel, CNRS and UJF, Grenoble, France)

**References**


**Neutron diffraction studies have been carried out to shed light on the unprecedented order-disorder phase transition observed in the mixed-valence iron(III)-iron(II) framework compound \([\text{NH}_2\text{CH}_2\text{CH}_3\text{]}_n[\text{Fe}^{III}\text{Fe}^{II}(\text{HCOO})_6]_n\).** The initial studies were performed using laser neutron diffraction at the VIVALDI instrument at two different temperatures above and below the transition. The comparison between the two patterns shows the appearance of new Bragg reflections at low temperature, which is a clear sign of a structural phase transition. This nuclear phase transition is associated with an electric phase transition, from paraelectric to antiferroelectric, as corroborated by means of dielectric measurements.

In order to determine the crystal structure in the low temperature phase, a neutron diffraction experiment was carried out at the D19 monochromatic single crystal diffraction apparatus, where the new phase was accurately characterized (see figure 1). These results reveal the occurrence of a structural phase transition from P-31c space group at room temperature to P-3c: space group at low temperature. This phase transition involves small distortions in the rigid [\text{Fe}^{III}\text{Fe}^{II}(\text{HCOO})_6]_n framework, while a more dramatic change is observed in the dimethylammonium cations, which are weakly anchored in the cavities. These cations are disordered at room temperature but become ordered below the phase transition temperature. The length of the c-axis in the ordered phase is about three times the length at room temperature, due to the loss of the 3-fold rotation axis that passes through the cations in the high temperature phase, therefore the three possible equivalent of the dimethylammonium ions observed at high temperature are split into three well-differentiated positions at low temperature (see figure 1c).

Once the crystal structure of the low temperature phase was properly characterized, our objective was to determine the magnetic structure below the ordering temperature (37 K). In order to elucidate the correct magnetic model, a multi-pattern approach based on simultaneous refinement of neutron powder diffraction (instrument D1B) and neutron single-crystal data (instrument D9) was carried out. Among the different magnetic models compatible with the possible irreducible representation, only the magnetic structure shown in figure 2 gives a solution compatible with the neutron diffraction measurements. The spin moment of the Fe\(^{III}\) atoms lies strictly along the c-axis while the Fe\(^{II}\) atoms have two different components: the main contribution along the c-axis, which is coupled antiferromagnetically with the spin moments of the Fe\(^{III}\) atoms, and a second one, a small component in the ab plane that produces a rotation of the magnetic moments along the c-axis. This model produces a ferrimagnetic layered structure, where the magnetic moments are non-compensated along the c-axis in agreement with the results previously observed using macroscopic magnetic measurements.

In this work we have determined, using complementary neutron diffraction techniques, the crystal and magnetic structures of the molecular multiferroic [\text{NH}_2\text{CH}_2\text{CH}_3\text{]}_n[\text{Fe}^{III}\text{Fe}^{II}(\text{HCOO})_6]_n compound. The combination of laser neutron diffraction studies and monochromatic neutron diffraction has allowed us to determine the structural model after an unprecedented order-disorder phase transition.

The order-disorder phase transition is triggered by the occurrence of an extensive network of hydrogen bonds; and neutron diffraction techniques have directly contributed to understand the role of this weak interaction in the physical properties of this material. Finally, the refined magnetic structure below 37 K corresponds to a weakly non-collinear ferrimagnetic structure, due to the non-compensation of the magnetic moments of the Fe\(^{III}\) and Fe\(^{II}\) sites, which are antiferromagnetically coupled.
High-resolution diffractometer D2B
Powder diffractometer 11-8M
at Argonne National Laboratory

Synthesis and structure determination of CaSi1/3B2/3O8/3, a new calcium borosilicate

Boron, alkali and alkaline earth oxides are key additives used to tune properties in technologically important bioactive and optical glass materials. In particular, boron oxide is added to glass compositions (typically silicate-based compositions) in order to optimise the melting and forming stages [1]. This work has led to the identification, synthesis and in situ structure determination of a new crystalline calcium borosilicate phase, namely CaSi1/3B2/3O8/3, using neutron and X-ray powder diffraction and recent advanced high-resolution solid-state NMR techniques.

To obtain initial crystallographic information, electron diffraction analysis was performed on several CaSi1/3B2/3O8/3 crystallites. The reconstruction of the reciprocal space showed an orthorhombic cell with a = 12.1 Å, b = 5.2 Å and c = 3.7 Å, and a space group that is either Pmn21 or Pna21. No isostructural compound could be found in the ICSD database using these space groups and similar sets of cell parameters.

The crystallographic structure of the calcium borosilicate was then determined ab initio using the charge flipping algorithm [3] performed on neutron powder diffraction data collected in situ at high temperature. The X-ray scattering of light elements characterised by a low electronic density, such as boron and oxygen, is actually much lower than their neutron scattering power. Moreover, the good contrast between boron and silicon elements using neutrons diffraction (whose scattering cross-sections are 5.24 and 2.17 barn, respectively) allowed us to determine precisely the position of each element within the structure. In order to reduce the absorption by natural abundance of our 10B-containing sample (whose absorption cross-section is 7.10^9 times greater than 11B), a powder sample was prepared from purified commercial products containing only 11B. The absence of 10B made it possible to reduce the acquisition time considerably. Moreover, due to the poor peak shape of the CaSi1/3B2/3O8/3 phase at ambient temperature (due to ordering at the nanometric scale, as evidenced by high-resolution transmission electron microscopy [4]), the high-resolution neutron powder diffraction diagram was collected at 650 °C on the D2B diffractometer at the ILL.

At the final stage of structure determination, the crystallographic parameters such as unit cell, atomic positions and site occupancy factors were refined with high levels of precision using the REEF method on the neutron diffraction powder diagram (figure 1). Due to the high resolution and the high counting level of the data, very good reliability factors (Rw = 3.05 %, R = 2.30 %, χ^2 = 1.57) were obtained. The average long-range structure of the CaSi1/3B2/3O8/3 phase consists of an array of linear chains of TO4 tetrahedra (figure 2a) with a mixed composition of 1/3 silicon and 2/3 boron for the 7 sites and a partial occupancy of 2/3 for the bridging oxygen sites (figure 2b). From the average structure, the TO4 tetrahedra appear to be severely distorted, and exhibit large and anisotropic atomic displacement parameters, which indicate deviations from a perfectly ordered structure. The local arrangement, and more especially the Si/B ordering, was then described based on data from 29Si and 11B solid-state Nuclear Magnetic Resonance (NMR) experiments and first-principles calculations.

A one-dimensional (1D) 11B MAS solid-state NMR experiment shed light on the local structure, showing a line-shape characteristic of three-coordinated B sites forming planar BO3 units, each associated with an oxygen vacancy and thus interrupting the chain. The average TO4 chain thus consists of an arrangement of SO4 tetrahedra and BO3 planar units, in a 1:2 ratio, and the atomic displacement parameters translate the departure from an ideal tetrahedron. The results of a two-dimensional experiment allowed us to discard the presence of B-O-B chemical bonds. The structure of the calcium borosilicate is thus composed of CaSi3O8 (B2O3/5-SiO2)8 units.

The simplest structural models characteristic of CaSi1/3B2/3O8/3 must consist of multiple unit cells of the average structure determined by neutron diffraction. This leads to two possible structures: (a) and (d), which differ in the topology of the chain arrangements. DFT methods then allow (i) the optimisation of the geometry of these two models, and (ii) the computation of their 11B NMR signatures. Remarkably, these two models, both involving similar CaSi3O8 units (figure 2d), yield very similar 11B signatures, both compatible with the observed spectrum. The actual situation is certainly more complex and probably consists of combinations of different topologies of the inter-chain arrangements at the scale of tens of nanometres. Indeed, non-equivalent domains exhibiting superstructures are evidenced by high-resolution electron microscopy images [4]. This study shows the existence of a new calcium borosilicate compound, CaSi1/3B2/3O8/3, in the CaO-SiO2-BO3 ternary system that is of considerable interest to both the glass industry and the geology community. The synthesis of this new material was achieved by full crystallisation from glass. Its crystal structure was solved ab initio from synchrotron and neutron powder diffraction data collected in situ at high temperature. The orthorhombic structure (Pna21, a = 10.026(4) Å, b = 5.267(6) Å and c = 3.713(2) Å) contains one CO, one mixed Si/B and three inequivalent O crystallographic sites located on 4a Wyckoff positions. The combination of 11B solid-state NMR and DFT calculations suggests that the CaSi1/3B2/3O8/3 structure is composed of BO3/5-SiO2-BO3 units with different arrangements along the [001] direction.

In this article, we report the synthesis of CaSi1/3B2/3O8/3, a new calcium borosilicate compound obtained by crystallisation from a corresponding glass composition using a simple heat treatment. This so-called “X-phase” had been known since the sixties but until now its structure had never been solved. Interestingly, this new compound is located on the tie-line between the Ca2SiO4 and CaB2O4 phases in the CaO-SiO2-BO3 ternary diagram [2], and is only the fourth reported calcium borosilicate oxide phase, despite their importance within the mineralogy, glass and ceramics communities.

Authors & References

E. Véron, M.M. Garaga, S. Cadars, M. Allix (ENSICAEN, Caen, France)
D. Pelloquin (National Graduate School of Engineering and Research Center ENSICAEN, Caen, France)
M. Suchomel (CNRS and University of Orléans, Orléans, France)
G. Matzen (ILL)
E. Véron (Argonne National Laboratory, Argonne, USA)

References


SCIENTIFIC HIGHLIGHTS
CHEMISTRY AND CRYSTALLOGRAPHY

ANNUAL REPORT 2013
33
Controlling fluorophore spatial distribution in polymer films for latent fingerprint visualisation

Latent (non-visible) fingerprints are a primary source of forensic evidence, but require physical or chemical treatment to visualise them. Despite a range of such treatments, the success rate is low. Recent work has shown how spatially controlled deposition of electrochemical polymers provides a powerful means of visualising fingerprints in “difficult” scenarios. In a novel extension of this strategy, we have used neutron reflectivity to monitor and optimise a multi-stage interfacial assembly process that yields electroactive films with optical absorption and emission characteristics with the potential for highly sensitive latent fingerprint enhancement.

The spatial pattern of a fingerprint uniquely identifies an individual. Despite the use of optical, magnetic and electrochemical methods, fingerprints are central to criminal investigations and civil identification applications [1]. Indeed, the power of fingerprint evidence is anecdotally recognised in other contexts – DNA “fingerprinting” and the “fingerprint” region of X-ray spectra. Forensically, most fingerprint evidence derives from latent fingerprints (those for which material exchanged between the finger and the surface is not visible to the eye), but these fingerprints require some means to visualise them. Although diverse reagents have been developed for this purpose – from powders that adhere mechanically to the sticky residue to chemicals that interact with specific components of the residue – the low power of fingerprint evidence is anecdotally recognised in other contexts.

Reflectivity profiles acquired during PPy-FMOC hydrolysis (to generate the free volume within the film) are shown in figure 4. Within each profile, there are fringes with distinct periodicities. One set is associated with the Au film electrode; those independently of time and, as a consequence of its flat surfaces, are more evident than on the Au film electrode. The other is associated with the polymer film; these fringes stretch out as hydrolysis progresses, corresponding to spatial film collapse. Detailed fitting of data obtained for a range of reaction scales (figure 5) was facilitated by two external constants, namely a geometric decay of the total amount of electroactive polymer (for the data shown, $\Gamma_{PPyNH} = 20 \text{ mmol cm}^{-2}$) and FTIR spectroscopic verification of FMOC removal and fluorophore binding (via the disappearance and reappearance of a characteristic amide band; see figure 3). These spatially integrated insights into “how much” and “what” facilitate NR addressing the question “where?” The data revealed that FMOC solution resulted in film shrinkage by ca. 30%, but in an increase in solvent volume fraction from 0.04 to 0.60 – an effect of the size of the leaching group. Following polymer relaxation, the solvent volume fraction respectively fell to 0.52. In relative terms these changes can profoundly alter polymer mobility and in all practical terms the replaceable solvent volume fraction permits a high fluorophore population – one fluorophore entity for every ca. five pyrolysis monomer units.

Fingerprints play an important role in criminal investigations, security applications, and identifications of unknown individuals following natural disasters. The fundamental scientific challenge underlying these societal issues is that successful visualisation of the fingerprint involves observation of lateral structure at the nanometre (whole print) to 100 μm (ridge feature size) length scales, but accomplishment of this involves control of vertical interfacial chemistry at the nanometre to micrometre scale. We have separately optimised the lateral control of polymer deposition (figure 2 and of the vertical control of fluorophore functionalisation (figure 4 and 5) on a laterally uniform surface. Their combination is the next step. The interplay of (electro)chemistry on different length scales in lateral and vertical directions provides novel challenges to which neutron science will undoubtedly contribute significantly in the near future.

**Authors & references**

R.M. Sapstead, K.S. Ryder, A.R. Hillman and C. Fullarton (University of Strathclyde, UK)
M. Skoda and R.M. Sapstead (Rutherford Appleton Laboratory, UK)
E. Watkins, C. Beech and R. Barker (UL) A. Gilden (Glasgow University, UK)


**Materials science**

**Scientific highlights**


**A. Glidle**

**Illooms science**

**Scientific highlights**


**A.R. Hillman**

**Materials science**

**Scientific highlights**


**A.R. Hillman**

**Materials science**

**Scientific highlights**


**A.R. Hillman**

**Materials science**

**Scientific highlights**


**A.R. Hillman**

**Materials science**

**Scientific highlights**
Liquids and amorphous diffractometer D4

Fragile glass-formers reveal their structural secrets

Calcium aluminates CaO-Al2O3 form a significant component of the Earth’s mantle and are an important ingredient in several materials having great utility [1]. They are, for example, an integral component of aluminous cement, the glasses have optoelectronic applications in the infra-red spectrum, and the rare-earth doped materials exhibit persistent luminescence.

Aerodynamic-levitation with laser-heating allows for the containerless processing of refractory liquid oxides and for the formation of new families of glass forming materials. Here we combine this technique with the method of isotope substitution in neutron diffraction to elucidate the structure of liquids and glasses, but its application to aerodynamic-levitation experiments is hindered by the need to use single levitated droplets, typically small spheres formed. The isotope substitution method is a site-specific tool that avoids the use of a container material, thus allowing liquid droplets to be deeply supercooled and new families of glass to be formed. The isotope substitution method is a site-specific tool that avoids the use of a container material, thus allowing liquid droplets to be deeply supercooled and new families of glass to be formed.

The levitation method has the advantage that it avoids the use of a container material, thus allowing liquid droplets to be deeply supercooled and new families of glass to be formed. The isotope substitution method is a site-specific tool that avoids the use of a container material, thus allowing liquid droplets to be deeply supercooled and new families of glass to be formed.

To tackle this problem, the combined methods of (i) aerodynamic-levitation with laser-heating and (ii) neutron diffraction with Ca isotope substitution were used to investigate the detailed structure of CaAl2O4 as a liquid at 1973 K and as a glass at room temperature [3]. The ILL diffractometer D4 was employed with the setup illustrated in figure 1.

The levitation method has the advantage that it avoids the use of a container material, thus allowing liquid droplets to be deeply supercooled and new families of glass to be formed. The isotope substitution method is a site-specific tool that avoids the use of a container material, thus allowing liquid droplets to be deeply supercooled and new families of glass to be formed.

The experimental information was interpreted with the aid of molecular dynamics computer simulations using a polarisable ion model, and the results reveal dramatic and unexpected changes in the material’s structure during glass formation.}

Photograph of the laser heating set-up installed at the neutron diffractometer D4 (a) and a schematic of the levitation device mounted in the instrument belljar (b).

Figure 1

Figure 2

Snapshot from molecular dynamics simulations showing the structure of liquid (a) and glassy (b) CaAl2O4. On quenching the liquid, a reorganisation of Al-centred structural motifs is accompanied by the formation of extended branched chains of edge- and face-sharing Ca-centred polyhedra. Different chains are represented by the connected yellow, blue and green coloured units, and involve many more Ca atoms in the glass than in the liquid.
Figure 2 shows the refined angle of the spin-direction relative to (a) at three different isotherms, as well as the pressure dependence of the internal atomic coordinates. It is seen that the Morin transition shifts dramatically under pressure to higher temperatures. Figure 3 illustrates the shift of $T_M$ over a pressure range of 3 GPa, giving a massive pressure coefficient of $dT_M/dP = -27$ K/GPa, which can also be expressed by a 'Grüneisen parameter' $\gamma = -\partial\ln T_M/\partial\ln V \approx -20$. For comparison, the Grüneisen parameter of Néel temperature of hematite is typically about 3 (Bloch's 10/3 rule).

Although the pressure dependence of $T_M$ was investigated before, including by several high pressure neutron experiments [3], the ILL study is the first one which carried out the measurements under strictly hydrostatic conditions, thereby avoiding the spurious effects which have been reported before [3] and allowing a meaningful comparison with theory.

The currently accepted understanding explains it by a competition between two contributions to the total anisotropy energy, $K$ [4]: the magnetic dipolar anisotropy energy $K_{MD}$, arising from the dipole interaction of the spins, and the fine structure anisotropy energy $K_{FS}$, also called the single-ion anisotropy. At 0 K the two quantities $K_{MD}$ and $K_{FS}$ have opposite sign and cancel each other to within 2%. Since they follow different temperature dependencies, the total anisotropy energy $K$ changes sign at a temperature $T_M$, where $|K_{MD}| = |K_{FS}|$, which defines the temperature $T_M$ where the spin flop occurs. The ILL measurements give structural parameters which allow the pressure dependence of $K_{MD}$ to be calculated exactly. It turns out that this contribution is negligible, i.e. the massive pressure effect observed on $T_M$ is entirely due to the increase of $K_{FS}$, i.e. the change in the splitting of the Fe$^{3+}$ ground state levels.

The Morin transition is the textbook example of a spin-flop transition. Hematite is antiferromagnetic with a Néel temperature of 960 K. At low temperature and ambient pressure, the Fe$^{3+}$ moments are aligned along the rhombohedral (111) axis, pointing in opposite directions in adjacent iron-layers. At 260 K, the spins flip by 90° into the hexagonal layer. There is also a slight residual canting of the spins by 0.04° which leads to a very small ferromagnetic component.

In recent experiments carried out at ILL, the variation of the Morin transition was investigated under pressure. Such experiments ought to give insight into the microscopic origin of the Morin transition, and spin-flop phenomena in general. To achieve such pressures the group from the University Pierre and Marie Curie (Paris) and the Paul Scherrer Institute (Villigen, Switzerland) used the ILL Paris-Edinburgh pressure cell to compress samples of Fe$_2$O$_3$ under strictly hydrostatic conditions up to 8 GPa (80 000 bar).

Figure 2 illustrates the shift of $T_M$ over a pressure range of 3 GPa, giving a massive pressure coefficient of $dT_M/dP = -27$ K/GPa, which can also be expressed by a ‘Grüneisen parameter’ $\gamma = -\partial\ln T_M/\partial\ln V \approx -20$. For comparison, the Grüneisen parameter of Néel temperature of hematite is typically about 3 (Bloch’s 10/3 rule).
Single-crystal neutron diffraction D19 Time-of-flight spectrometers IN4 and IN5

Single crystal neutron scattering and ab initio calculations reveal the mechanisms of oxide-ionic conduction in modulated structures

Solid-state oxide-ionic conductors are of great current (and greater potential) importance as membrane materials in solid-oxide fuel cells (SOFCs). SOFCs use hydrocarbons and other chemical fuels far more efficiently than any other device, by obtaining electricity directly from their oxidation by O2 ions. They are therefore not subject to the laws of the Carnot cycle, which fundamentally limit the efficiency of thermal power plants to 30–40%. SOFCs minimise pollutants such as carbon, nitrogen and sulfur oxides, and can use a wide range of fuels – including natural gas, petroleum, coal, bioliquids, and hydrogen generated from renewable sources – with efficiencies of up to 85%.

The key design requirement for SOFC membrane materials is to be impermeable to fuel and oxygen gases under operating conditions, but permeable to oxide ions, which must pass through and react with the fuel. Almost all practical SOFCs still use yttria-stabilized zirconia (YSZ), which was first demonstrated to meet these criteria in the 1970s. Because YSZ is an oxide conductor at high temperatures (>950 °C), YSZ-based SOFCs require a large power input, suffer from mechanical degradation during thermal cycling, and require the use of high-temperature-stable materials in components such as casings, seals and inter-connects.

One way to reconcile the competing requirements of net chemical stability and local chemical flexibility is to use materials with much more modulated structures than YSZ, which well-ordered regions can act as ‘scaffolds’ supporting wide and continuous channels that become locally disordered in the ionic conducting temperature regime. However, it is difficult to study the structure and dynamics of materials with large and complex unit cells by neutron scattering from conventional polycrystalline (powder) samples. Consequently, such materials remain too poorly understood to be systematically optimised for applications.

These limitations can be overcome to a large extent by applying the same neutron scattering methods to single crystals. In practice, this is usually done for ionic conducting materials due to the difficulty of obtaining sufficiently large crystals (of the scale). Furthermore, while much more detailed information can be obtained, the experiments and data treatment are also much more difficult.

We have recently made some progress in this direction, growing large single crystals of a number of oxide-ionic conductors for the first time, and studying them at the ILL. We have been using single-crystal neutron diffraction (SCND) to study these structures, phase transitions, and ionic conduction pathways; inelastic neutron scattering (INS) to investigate the dynamics of ionic conduction in different directions with respect to the crystal lattice, and ab initio molecular dynamics (AIMD) calculations to verify and interpret experimental data.

An important class of materials in this context is derived from the high-temperature form of bismuth oxide, 12Bi2O3. This is the best solid-state oxide-ionic conductor known, due to the 25% oxygen vacancies evenly distributed throughout its disordered fluorite-type structure. Pure 12Bi2O3 has never been seriously considered for practical applications due to its limited thermal stability, and the fact that lower-temperature polymorphs eliminate the critical oxygen vacancies. However, the fluorite-type average structure of 12Bi2O3 (along with a significant fraction of its conductivity) can be preserved at room temperature by doping with smaller rare earth cations that can support flexible coordination environments, notably Nd3+ and Er3+ in addition to Y3+ and Yb3+.

Another class of oxide-ionic conductor on which we have been working is the bi-2223 and Bi-2212 superconductors. These are superconducting oxide and perovskite structures, respectively, that allow for oxygen doping, and thus provide for a wide variety of structures with different oxygen contents. The high oxide-ionic conduction of this phase is generally associated with the presence of oxygen vacancies, which are thought to play a role in the transport of oxide ions through the structure. The high-temperature stability of these phases is further enhanced by the presence of additional phases that can serve as ‘scaffolds’ supporting the oxide ion conduction pathways.

The results of these studies support the conjecture [7] that high ionic conductivity in stabilised 12Bi2O3 phases comes from four structural features: (1) a highly polarizable Bi–O sublattice, (2) dipolar cations that can support variable coordination geometry, (3) a superstructure that permits a high degree of rotational freedom to MoO6 polyhedra, and (4) a pseudo-cubic ordered superstructure. Such mechanisms probably govern the behaviour of all the oxide-ion conducting phases studied by doping with cations that can support flexible coordination environments, notably Nd3+, Y3+, and Er3+ in addition to Y3+ and Yb3+.

Another class of oxide-ionic conductor on which we have been working is the brownmillerite-type structures, which consist of alternating layers of corner-connected MoO6 octahedra and MoO4 tetrahedra, and can be thought of as oxygen vacancy ordered superstructures of the ubiquitous perovskite-type structure. This creates continuous one-dimensional channels of oxygen vacancies, which are thought to play a role in the transport of oxide ions through the structure. The brownmillerite Sr3FeO4 phase displays particularly high oxide ion conductivity in the absence of atmospheric oxygen (>0.1 S cm−1 at 775 °C) and offers additional advantages of relatively low toxicity and cost.

Some of us together with Paulus et al. [8] had previously investigated the nature of oxide ionic mobility in Sr2FeO4 using INS data collected from polycrystalline (powder) samples, in conjunction with AIMD. We observed quasistatic neutron scattering (QENS) around the Bragg peak, which we ascribed to fast oxygen diffusion, and proposed a model in which dynamics of the cationic oxygen atoms (those connecting the octahedral and tetrahedral layers) triggers disorder in the tetrahedral layers. The model can be loosely interpreted as dynamic switching of the orientations of tetrahedra at temperatures lower than 80 °C.
In our latest study on IN5 [9], we used single-crystal samples that allowed a clearer separation of the QENS part of the INS signal, allowing us to characterise it in detail and providing direct information about the anisotropy of the oxygen ion motions.

We found clear evidence for disordering of the tetrahedral layers at 600 °C, just below the onset temperature for conduction, strongly suggesting that such disordering is a prerequisite for ionic conduction. However, we saw no quasielastic broadening until higher temperatures (750 °C). We also found that the QENS signal is isotropic. AIMD calculations confirmed this interpretation and also showed good agreement for the characteristic time-scale of the oxygen ion dynamics, measured to be 4.2 ps and calculated to be 4.5 ps at 875 °C. This presents a compatible but somewhat simpler picture of ionic conductivity compared to our previous work. It appears that tetrahedral rotations are essentially isotropic, but that they are a precondition for the anisotropic motion that moves oxide ions into the tetrahedral layers from the octahedral layers. This continual but incoherent movement of oxide ions in turn creates conduction pathways and activates long-range diffusion at the interface between layers, which appears to be largely isotropic in two dimensions on the pico-second timescale.

These results of all these studies show what can be achieved with a single-crystal sample on modern, high-flux, time-of-flight spectrometers, even when measuring the weak scattering from mobile oxide ions (compared to the more usual case of scattering from hydrogen). However, according to our simulations, the length scales we are probing are still only of the order of 1 Å, indicating that local rather than long-range diffusion is being observed. In the context of ionic conduction, it would of course be of more interest to investigate long-range diffusion and look for any associated anisotropy.

Accurate AIMD simulations are still challenging to run on such timescales, given that the spatial extent of the simulation box should ideally be extended beyond that used in this work, and more approximated electronic structure calculation methods should be considered.

Experimentally, however, backscattering and spin-echo spectrometers do extend the dynamical range of neutron scattering to and beyond the nanosecond timescale and new instruments with higher flux (IN16b and WASP) will offer opportunities to extend this work in the near future.

**Figure 2**

Structure of Bi$_2$Mo$_{10}$O$_{69}$ in the ionic-conducting temperature regime, from ab initio molecular dynamics calculations. Clouds show the space explored by four oxygen atoms on the edge of a Bi$_2$O$_3$-like column, plus four forming a MoO$_4$ tetrahedron over the course of 40 ps. Bi atoms are blue, Mo atoms are orange and O atoms are red. The green arrows illustrate the interplay of rotational and translational diffusion.

**Figure 3**

AIMD and QENS results for Sr$_2$Fe$_2$O$_5$ at temperatures below (600 °C) and above (875 °C) the onset of oxide-ionic conduction. (a) Colour scales (blue-green-yellow red) represent increasing mean square displacements (MSDs) of oxygen atoms from the AIMD simulation at each temperature as a function of their fractional coordinate along the b (layering) axis. (b) Clouds represent the space sampled by individual oxygen atoms over the course of each entire AIMD simulation. (c) S(Q,ω) plotted on a logarithmic scale.
Time-of-flight spectrometer IN6

Translational and Rotational diffusion in hot dense water

Water’s exceptional behavior mainly derives from the directionality of the hydrogen bond, and from the open geometry of the water molecule. Therefore water represents a paradigm for associated liquids, due to the simplicity of its electronic structure, and the clear influence of the hydrogen bond network in determining the structural properties of the system. The structure of water is now well known for a large portion of the p,T phase diagram [1]. Conversely, knowledge of water dynamics is limited to moderate p,T conditions, in particular for what concerns the diffusive and rotational dynamics [2].

Despite, the diffusion of water at pressures of a few GPa, typical of the transition zone of the Earth’s mantle, has strong incidence on the processes governing volcanic eruptions and intermediate-depth seismicity; water diffusion and re-orientation under extreme conditions is essential to characterize new exotic properties, such as the predicted plastic and superionic phases in water, and thus to interpret observations and develop models of planetary interiors, to cite few examples.

Neutrons are the most suited probe to investigate diffusive and re-orientational dynamics in water because of their sensitivity to hydrogen. The quasi-elastic neutron scattering (QENS) technique offers the unique possibility of analysing both atomic and molecular motion on the picosecond timescale and on the scale of atomic distances.

Taking advantage of the new toroidal high pressure chamber of the Paris-Edinburgh press, specially conceived for QENS measurements [3], and of the high flux and low background of the time-of-flight (TOF) spectrometer IN6, we measured the self-dynamics of liquid water along isotherms in the 400-450 K range up to ice VII crystallization (0.3-6 GPa), at pressures one order of magnitude higher than previously studied [2]. An example of the spectra collected along the 400 K isotherm at 0.6-1.8 GPa for a selected Q value is shown in Figure 1 [4].

Two well distinguished components can be observed: a translational (narrower) and a rotational (broader) contribution from which we extracted [4] the diffusion coefficient (D) and the molecular rotational time (τ), reported in Figure 2.

We readily see that D is strongly reduced under pressure, though its variation is definitively slower than that of shear viscosity (η), reported in the inset. Along the 400 K isotherm, the product DR is approximately constant at moderate pressures (P<1 GPa), while it decreases by a factor 2 in the high-pressure regime. Thus, the Stokes Einstein (SE) relation, D=η/ρC, which predicts a constant product of diffusion and shear viscosity at constant temperature is violated [4]. Violation of the SE equation has already been observed in glass forming liquids when approaching the dynamical arrest, i.e. in conditions of extremely high viscosity, when dynamical heterogeneities take place. Here we investigated a complementary situation where the viscosity of the system is comparable to that of water at ambient conditions, while a strong density variation (40% T) is produced by pressure. The observed failure of the SE equation is thus most likely related to the free volume reduction, the consequent enhancement of cage dynamics and the onset of hopping phenomena [4].

The breakdown of the Debye equation, which establishes a direct relation between the molecular rotational time and the shear viscosity, is still more striking: τr turns out to be almost pressure independent and translational and rotational dynamics completely decouple under pressure. This unexpected result can be understood relying on the structural data available for hot dense water [2] and on the mechanism of reorientation of a water molecule in a H-bond network: the first shell of neighbours of a water molecule shows a density-independent O-O distance for the nearest neighbour oxygen atoms, while the radial distribution function of the second coordination shell reveals, instead, a difference between ambient and elevated P,T, associated with the gradual transformation towards a high-density configuration (which is totally achieved for pressures higher than 1 GPa at 400 K, see also Figure 2). Under further compression the number of nearest neighbour oxygen atoms do not change anymore, and as the number and strength of H-bond per water molecule remains almost constant [4], τr turns out to be almost pressure independent.

To summarise, we measured the translational diffusion coefficient and the rotational time of water molecules under unprecedented high-pressure conditions.

We observed a decoupling of the translational and rotational dynamics under pressure.

SCIENTIFIC HIGHLIGHTS

Pressure dependence of the translational diffusion coefficient D1 and of the molecular rotational time τr along the isotherm 400K as derived by our QENS experiment. Black stars represent the available low pressure data [5] on D1, as measured by NMR at 403 K. In the inset we show the shear viscosity dependence on pressure along the 400 K isotherm (red curve), interpolated from data [4] at 373 K (green dot) and at 437 K (cyan dot). The blue-yellow color boundary indicates the region of collapse of the second coordination shell on the first one [4]. The two simulations snapshots indicate the first neighbours (blue lines in yellow) and the second neighbours (cyan lines in light blue) of a central water molecule at 0.3 GPa (a) and at 2.3 GPa (b).

We readily see that D1 is strongly reduced under pressure, though its variation is definitively slower than that of shear viscosity (η), reported in the inset. Along the 400 K isotherm, the product DR is approximately constant at moderate pressures (P<1 GPa), while it decreases by a factor 2 in the high-pressure regime. Thus, the Stokes Einstein (SE) relation, D=η/ρC, which predicts a constant product of diffusion and shear viscosity at constant temperature is violated [4]. Violation of the SE equation has already been observed in glass forming liquids when approaching the dynamical arrest, i.e. in conditions of extremely high viscosity, when dynamical heterogeneities take place. Here we investigated a complementary situation where the viscosity of the system is comparable to that of water at ambient conditions, while a strong density variation (40% T) is produced by pressure. The observed failure of the SE equation is thus most likely related to the free volume reduction, the consequent enhancement of cage dynamics and the onset of hopping phenomena [4].

The breakdown of the Debye equation, which establishes a direct relation between the molecular rotational time and the shear viscosity, is still more striking: τr turns out to be almost pressure independent and translational and rotational dynamics completely decouple under pressure. This unexpected result can be understood relying on the structural data available for hot dense water [2] and on the mechanism of reorientation of a water molecule in a H-bond network: the first shell of neighbours of a water molecule shows a density-independent O-O distance for the nearest neighbour oxygen atoms, while the radial distribution function of the second coordination shell reveals, instead, a difference between ambient and elevated P,T, associated with the gradual transformation towards a high-density configuration (which is totally achieved for pressures higher than 1 GPa at 400 K, see also Figure 2). Under further compression the number of nearest neighbour oxygen atoms do not change anymore, and as the number and strength of H-bond per water molecule remains almost constant [4], τr turns out to be almost pressure independent.

To summarise, we measured the translational diffusion coefficient and the rotational time of water molecules under unprecedented high-pressure conditions.

We observed a decoupling of the translational and rotational dynamics under pressure.

Authors & References

L.L. Beve, S. Kluter and A.M.J. Sautter (University Pierre & Marie Curie, Paris, France)

T. Strässl, (Institut Laue-Langevin, Grenoble, France)


L. E. Bove [4].


Bioactive glasses have the ability to chemically bond to bone and stimulate new bone growth [1]. Consequently they are widely used for a range of biomedical applications including periodontal repair, facial reconstruction and orthopaedic bone grafting. Under physiological conditions these materials dissolve, releasing Ca, P and Si, at a controlled rate which promotes the formation of hydroxyapatite (the mineral component found in teeth and bones). The release rate of these ions is determined by the glass structure and in order to better understand and control these processes a detailed knowledge of the atomic scale arrangement is necessary.

However, understanding the structure of glass and the role individual elements play within the glass matrix is not trivial. Glasses are complex materials that lack long range order or periodicity making it hard to unambiguously determine their local structure. Furthermore glasses of technological or commercial importance typically consist of a large number of components making it difficult to unravel the structure factors of individual elements. In this study we have examined the structure of 45S5 Bioglass® and its derivatives. Bioglass®, (SiO2)46.1(Na2O)24.4(CaO)26.9(P2O5)2.6, is the archetypal bioactive glass and has been used in more than one million bone graft operations [1].

Recently it has been reported that incorporating small concentrations of additional elements into 45S5 may increase bioactivity of these materials. For example, Miyata et al. [2] have reported that incorporating titanium to bioactive glasses can improve hydroxyapatite formation. Our laboratory based studies have confirmed that Ti Bioglass® is indeed bioactive and that hydroxyapatite forms on the glass surface (Figure 1). Other reports have stated that incorporating transition metals such as nickel or cobalt can improve vascularisation, i.e. increase blood vessel formation. However it is not possible to estimate a priori the structural role these ions adopt within the glass matrix. For example, Ti can form 4-, 5- or 6-fold geometries acting as either a network former or a network modifier; this would have a significant impact on the dissolution and hence bioactivity of the glass. It is difficult to unambiguously determine the co-ordination of Ti from spectroscopic techniques such as XANES. We therefore undertook two experiments to determine the structural role selected elements would adopt when incorporated into Bioglass®.

The first experiment investigated the structure of Ti within Bioglass® using the method of isotopic substitution. Exploiting the scattering length difference between 46 Ti and 48 Ti meant that by employing difference methods we were able to isolate only those correlations containing Ti. Besides the isotopic substitution, the highly dilute system (less than 1.5 % of Ti) makes the task even more difficult. Of these correlations Ti-O present within the glass (Figure 2). The results showed that Ti occupies a range of environments with a maximum of 40 % being tetrahedrally coordinated [3].

The second experiment employed the method of isomorphic substitution to investigate the structural role Ni and Co adopt when incorporated into bioactive glasses. In an analogous fashion this experiment exploited the scattering difference between natural abundant Ni and Co. The results showed that Ni and Co adopt a significantly different local environment compared to Ti. It was found that two thirds of the Ni (or Co) occupies a five-fold geometry with the remaining third in a tetrahedral environment [4].

In conclusion, we have demonstrated that the methods of isotopic and isomorphic substitution can be applied to dilute glass systems. The results have shown that first order coordination shells can be determined for systems containing concentrations of less than 1.5 atomic %.

Figure 1
Scanning electron microscopy images of (a) Ti-doped bioactive glass surface and (b) the surface after 7 days in culture media.

Figure 2
Schematic of tetrahedral (4-fold) and octahedral (6-fold) titanium oxide.

AUTHORS & REFERENCES

R.A. Martin (Aston University, UK)  
G.J. Cuello (UII)  
J.M. Smith, R.M. Mass and R.J. Newport (University of Kent, UK)


SCIENTIFIC HIGHLIGHTS

Liquids and glasses diffractometer D4

Isotopic and isomorphic substitution applied to dilute glassy systems

Bioactive glasses are of great importance for biomedical applications due to their ability to promote bone regeneration.

The structural sites present in the glass will be intimately related to their dissolution properties in physiological fluids such as plasma and saliva, and hence to the bioactivity of the material. Detailed structural knowledge is therefore a prerequisite for optimising material design. Here we employ the method of isotopic and isomorphic substitution to unravel the structural role of several key elements.
Collective dynamics of liquid gold: a truly golden neutron study combining BRISP measurements and simulations by the Computing for Science group

The propagation of acoustic-like excitations in the form of very-short-wavelength collective motions is a fundamental phenomenon in the physics of liquids. In the recent literature [1] the question has been raised as to whether the behaviour of these excitations differs in metals because of the presence of the conduction electron sea. In fact, until now liquid metals have been described by resorting to models of the dynamic structure factor more complex than those typically employed for other systems. Searching for the possible presence of a "universal" behaviour, we turned our attention to previously unstudied liquid gold.

Available dispersion curves and damping rates for the translational collective modes of conducting (e.g. Au and Cd) and insulating (e.g. CO₂ and CD₄) systems show remarkable similarities, provided the damping-to-frequency ratio zₛ/ωₛ of sound modes is analysed as a function of the normalised wave vector. Figure 2 shows this ratio for the four above-mentioned systems properly scaled to the CO₂ values. The results were beyond our expectations. We found a nearly universal behaviour for liquids of different nature, suggesting quite a remarkable picture where collective excitations at meV energies and on a mesoscopic scale, show overall equivalent properties, irrespective of the presence or absence of conduction electrons. The behaviour of liquids at exploratory scales thus appears to be dominated by those features of the nucleus-nucleus interaction which are common to both metal and non-conductive systems [1].

For decades, the microscopic dynamics of fluids has been a canonical field of application of standard simulation techniques. However, in the case of metals, a great incentive for performing such studies has come from the development of ab initio methods, much better suited to the treatment of the electronic degrees of freedom. The quality of the neutron data makes a significant comparison with the simulation results possible. The resulting good agreement [2] not only confirms the effectiveness of ab initio simulations of metals, but also allows the valuable exploration of collective dynamics at Q values that are difficult to access experimentally. As a result, we have found that an even better description of the dynamics is obtained by analysing the calculated spectra in terms of the more refined viscoelastic model that even better description of the dynamics is obtained by analysing the calculated spectra in terms of the more refined viscoelastic model that accounting for detailed-balance asymmetry and resolution.

Figure 1 Dynamic structure factors of gold at different Q values as obtained by the BRISP spectrometer. The fit (solid red line) is a generalised hydrodynamics model accounting for detailed balance asymmetry and resolution.

Figure 2 Ratio of damping to frequency of acoustic excitations for four different liquids. Data for Au (red stars), Cd (green squares) and CD₄ (blue dots) largely follow the same curve as CO₂ (pink diamonds) if multiplied by 3.20, 3.05 and 2.00 respectively. Data are plotted as a function of Q/Qp where Qp is the position of the main peak of the static structure factor, with Qp = 6 nm⁻¹ for Au and Cd, and Qp = 12 nm⁻¹ for CO₂ and CD₄. The dashed line shows the hydrodynamic behaviour of zₛ/ωₛ for CO₂.
Small-angle scattering diffractometer D11

Shear-induced macroscopic "Siamese" twins in soft colloidal crystals

Soft materials such as micelles or polymers can form highly ordered crystals which are inherently very susceptible to shear.

Large shear strains lead to the formation of macroscopic Siamese twinning in lyotropic fcc crystals formed by block copolymer micelles. The twins exist over the whole gap of the shear cell with the twin boundary located inside the gap. Our experiment indicates that the deformation twinning mechanism is analogous to the plastic deformation of nanocrystalline metals under high shear stress and high deformation rates.

In recent progress in instrumentation it has become possible to use sub-millimeter neutron beams to scan through samples with high resolution. Using the instrument D11 and the Bohlin CVO120 HR stress controlled rheometer with a Searle-type quartz shear cell (1 mm gap size) the crystalline structure of a fcc block copolymer was mapped in detail. The samples were constantly sheared until a stationary scattering pattern was developed. Abrupt cessation of shear allowed twin formation. The crystalline structure was scanned with a stilbite neutron beam of 300 μm width at different positions in the gap. The spatial arrangement of set-up and sample is shown in Figure 1. The radial beam position is parallel to the [111] direction, whereas for the tangential beam position the beam passes parallel to the [110] plane. Additionally the spatial orientation of the unit cells corresponding to both twins is defined. The location of twin B can be obtained from twin A via a rotation around the [111] axis by 60° [1]. In the [111] direction the scattering patterns of both twins are identical and a characteristic 6-fold symmetry is observed. In the [110] direction a 2-fold rotational symmetry of distorted hexagons is obtained in the scattering patterns. This feature allows distinguishing clearly between both twins.

In Figure 2 the small-angle neutron scattering data of a shear oriented fcc phase are shown. The measurements are recorded with a lyotropic micellar phase of a poly(isoprene-b-ethylene-oxide) block copolymer after shear orientation at 500 s⁻¹ in the shear cell of D11. In the radial direction the pattern is characterized by a large number of Bragg peaks corresponding to a fcc crystal. Most of them are caused by the finite domain sizes of the macroscopically oriented crystal and are crystallographically forbidden. As mentioned above the volume ratio of the twins cannot be determined in the [111] direction. The following patterns correspond to different tangential positions and therefore probe the [110] direction of the fcc lattice. In this direction most Bragg spots are allowed. A characteristic feature on the outer gap is the distorted hexagon, with is characteristic for the scattering of twin B. In the center of the gap a regular hexagon with considerable smearing in the horizontal direction occurs. As expected for the twin boundary location both twins occur with equal probability, i.e. the twin ratio is 0.5. Inside the gap near the inner rotor the scattering pattern exhibit a hexagon as expected for twin A. Model calculations reveal a twin ratio of 0.8 for twin A. Very similar results have been obtained with synchrotron-SANS experiments at ESRF.

The observation of such macroscopic "Siamese" twins is surprising due to the fact that normally only small twinned domains are reported. The existence of macroscopic twins is explained as follows. At high shear rates in continuous shear the stationary velocity gradient leads to a layer sliding of the closed-packed micellar layers in shear direction [110]. Abrupt cessation causes locally high stress in the center of the gap. Fast deformation twinning quickly relaxes the local stress. The twins grow toward the outer regions until the macroscopic twin is formed. The proposed mechanism is similar to the deformation twinning known for the plastic deformation in metals. Note that this twin formation occurs without breaking the material, a fact that is interesting for crash energy absorption or forging processes.

AUTHORS & REFERENCES

S.M. Taheri, S. Rosendahl, S. Fischer and S. Förster
(University of Bayreuth, Germany)
P. Blissard and T. Narayanan (European Synchrotron Research Facility - ESRF, Grenoble, France)
P. Lindner (ILL)


Soft colloidal crystals consist of building blocks such as micelles that interact via soft interaction potentials. The crystalline order tolerates imperfections because the related increase in the potential energy is very small. Hence, the mechanical properties of soft crystals are determined by the number and mobility of defects. This makes them quite different from inorganic crystals. A special defect is the occurrence of twins, where two adjacent crystals share common lattice points in a symmetrical manner such that a twin boundary surface exists between the two crystals. Fcc crystals, which are often found in lyotropic (water soluble) systems, can exist in two different stacking orders of the (111) planes corresponding to ABCABC (twin A) or ABCCAB (twin B) stacking (Figure 1). Usually, twins or twinned domains occur as small adjacent grains within large multidomain crystals.

Rheo-SANS data of a shear oriented fcc-phase at 16 wt % poly(isoprene-b-ethylene-oxide) blockcopolymer (PI55PEO170).

Above the scattering patterns the different positions of the neutron beam for the tangential configuration are indicated. The panels on the bottom show the calculated scattering intensities. For experimental positions with the beam passing through the center of the gap or near to the inner cylinder the resulting peaks are considerably smeared because the beam probes the FCC lattice and both twins with slightly different orientations due to the curvature of the shear cell. This effect is taken into account in the model calculations (bottom panel).
Our SAPs were obtained by inclusion of a PEG polymer into a cyclodextrin ring modified with a cholesterol group (Figure 1), allowing further anchoring into a lipid membrane. By using a wide range of surface probing techniques as Atomic Force Microscopy (AFM), Brewster Angle Microscopy (BAM), Langmuir-Blodgett, and neutron reflectometry at air/water and solid/water interfaces we have studied the insertion properties of this new class of molecules. Neutron reflectivity experiments were performed on the ILL on both FIGARO and D17 reflectometers. They provided not only structural information on the sliding polymer layers but also guidance for molecular design of the spacer at any stage of the project. In the biological realm, the end-grafted chain has been studied as a mimetic system for the spacers that provide for control of the range and strength of interactions in bio-recognition events promoted by ligand–receptor pairs.

Thanks to neutron reflectivity, a detailed understanding of the insertion matrix properties of SAP is now to perform Surface Force Apparatus experiments on supported bilayers (ICS, M3 team, P. Kékicheff).

A first series of experiments allowed us to investigate the amphiphilic behaviour of a new Cholesterol- Cyclodextrin and their insertion properties in lipid monolayers and bilayers, before investigating the membrane insertion of SAPs. At first we have shown that the cholesteryl-CD is suitable for anchoring the SAPs at the air-water interface and for insertion into phospholipid monolayers and bilayers. For sufficiently high polymer surface densities they form polymer brushes, which follow the scaling laws predicted by polymer theory. The dense SAP layers display the conventional behaviour of end-grafted polymer brushes, in agreement with the theoretical description for grafts of sliding polymers, where asymmetric chain conformations are predicted for high surface densities. Neutron reflectometry allowed us to achieve a detailed understanding of the interfacial properties of SAPs as well as the insertion properties into phospholipid membranes. It is expected that the polymeric chain of the SAPs is able to slide through the CD ring, and the associated modified distribution of chain ends, will translate into a new type of tethered ligand–receptor pairs. The study of such interactions, driven by sliding tethered ligands, could be made e.g. by force measurements between two phospholipid bilayers, the first containing SAPs modified with a ligand end-group and the second, opposite bilayer, anchoring a complementary receptor moiety. This project is presently in a phase where we are investigating the adhesive properties and the binding kinetics of model membranes decorated with SAP. A major objective is now to perform Surface Force Apparatus experiments on supported bilayers (ICS, M3 team, P. Kékicheff).

Thanks to neutron reflectivity, a detailed understanding of the insertion properties of this new potential ligand into phospholipid membranes has been obtained. We have demonstrated that the cholesteryl CD is suitable for anchoring the SAPs into phospholipid monolayers and bilayers, forming polymer brushes for sufficiently high polymer surface densities. We believe that the concept of variable spacer length and internal adaptability will open a considerable field of new perspectives. An interesting possibility would for instance be to use diblock copolymers as the spacer, which could provide sensitivity of this technology to environmental conditions such as the pH or the quality of the solvent.

**Authors & References**


G. Fragneto (ILL)

C. Fajolles and M. Bauer (CEA, IRAMIS, NIMBE, LIONS, UMR 3299 CEA / CNRS, CEA - Saclay, France)

T. Charitat, M. Bernhardt (MPI for Polymer Research, Mainz, Germany)

M. Bauer and University of Strasbourg, France)

Small-angle scattering diffractometer D22

How do bacteriophages sense the presence of their host? Bacteriophages, viruses that infect bacteria, are the most abundant and diverse organisms on Earth. They play a crucial role in the ecology, evolution and pathogenicity of bacterial populations from oceans or human intestine, where they also contribute to our immunity [1]. Phages consist of a capsid, containing the phage genetic information, and a tail that allows host recognition. Following binding of the tail tip to the host receptor, the viral genome is injected into the cytoplasm of the bacterium.

The biosynthetic host machinery is then hijacked to produce new virions, killing the cell. Phage therapy is becoming an alternative to treat antibiotic-resistant bacterial infections [2], it is thus important to understand the infection mechanisms.

At the molecular level, phage infection is triggered by the interaction of the Receptor Binding Protein in the bacterial receptor, either a sugar or a protein of the surface of the cell. In the case of the Escherichia coli-infecting phage T5 (Figure 1a), the Receptor Binding Protein pb5 is present as a unique copy located at the tip of the tail. To get insights into this question, we have purified both proteins and studied the structure of each protein isolated or within the complex.

Small-angle neutron scattering (SANS) combined with contrast strategy to highlight specific parts of the protein-detergent complexes: deuterated proteins are represented in dark gray. Hydrogenated proteins and the F6-DigluM micelles are represented in light gray as the 46% D2O buffer in which they are contrast matched.

We have previously shown, using biochemical and biophysical methods, that upon binding to FhuA, pb5 reversibly binds to a chelated-iron outer membrane transporter. Detergent-solubilized pb5 is shown to be an elongated protein, whose structure, at the resolution of the technique, does not show significant conformational changes upon formation of a complex with FhuA. The SANS envelopes of the complex and the individual proteins are in excellent agreement with negative stain single particle electron microscopy (Figure 2c).

This work was recently published in the Journal of Biological Chemistry [5].
**Antimicrobial Peptides and the Mechanism of Action of the Short Antimicrobial Peptide Trichogin GA IV**

Antimicrobial peptides are natural molecules with a strong antibiotic activity and in most cases kill bacteria by creating pores in their cell membrane (figure 1) [1]. They are a promising alternative to traditional antibiotics, which are rapidly and inexorably losing their effectiveness due to the increasing spread of drug-resistant bacteria. By combining neutron reflectivity data collected on the D17 reflectometer at ILL with molecular dynamics (MD) simulations and activity measurements, we solved a long-standing riddle about the mechanism of pore formation by the peptide trichogin GA IV, which is too short to span the normal thickness of a bilayer. Our findings provide a solid basis for the rational design of a new class of short peptide antibiotics against multidrug-resistant bacteria.

Trichogin belongs to the peptaibol family of antimicrobial peptides. Several preliminary data suggested that this peptide might form pores according to a model called “barrel-stave”, in which transmembrane-orientated peptides aggregate to form a channel [2]. However, trichogin comprises only 10 amino acids, and its helix is about half the normal bilayer thickness. How could such short peptide form transmembrane channels?

Neutrons reflectivity provided the resolution and selectivity needed to answer this question. We performed reflectivity experiments on a planar phospholipid bilayer supported by a silicon crystal and submerged in a water phase, to which increasing concentrations of deuterated trichogin were added. Deuterated peptides, lipids and water were used in appropriate combinations with the hydrogenated molecules to increase the reflectivity contrast. In figure 2 the curves of the POPC bilayer in D2O at the different concentrations of deuterated peptide investigated are compared. Two main features are visible:

When trichogin is added, a decrease in reflectivity on the mid-Q region (0.05 – 0.15 Å⁻¹) is observed, due to the insertion of the deuterated peptide into the membrane. In addition, the main minimum of the profiles shifts towards higher Q, values, indicating a thinning of the overall thickness of the deposition. A detailed analysis of these data showed that the peptide inserts in the hydrophobic region of the membrane, reaching a peptide to lipid molar ratio of about 10% (which corresponds approximately to the value needed to form the pores that kill bacteria [2]), and causing a thinning of the tail region from 28 to 21 Å.

MD simulations were in agreement with these findings, and showed that transmembrane-inserted trichogin molecules can cause membrane thinning by interacting with the phospholipid headgroups through electrostatic and H-bonding interactions, enhanced in the low-dielectric constant environment of the hydrophilic membrane core. These interactions lead to thinning by drawing phospholipid headgroups deep into the membrane.

Overall, these data indicate for the first time that a barrel-stave mechanism of pore formation is possible for trichogin and for similarly short peptaibols, despite their relatively small size. Our findings are a starting point for the rational design of new peptide-based antimicrobial molecules.

**References**


[3] M. De Zotti, F. Formaggio and C. Toniolo (University of Padua, Italy)


**Authors and References**

S. Bobone, G. Bocchinfuso, A. Forattini, B. Grisendi, R. Senesi, A. Palladini and L. Stella (University of Rome Tor Vergata, Italy)

Y. Gerelli, E. Santinelli and G. Fragneto (ILL)

M. De Zotti, F. Formaggio and C. Toniolo (University of Padua, Italy)

E. Latter and J. Penfold (ISS, UK)

(a) Neutron reflectivity profiles for the phospholipid bilayer in D2O, in the absence of trichogin (violet), and after addition of deuterated peptide at concentrations 4.5 µM (black), 15 µM (green), and 30 µM (red).

(b) Neutron scattering length density (SLD) profiles derived from the data in panel A (continuous lines), and calculated from the simulations with 0 µM (violet) or 8 µM (blue) trichogin molecules (dashed lines).

**Figure 1** Electron microscopy image of the damage caused to E. coli bacterial membranes by an antimicrobial peptide, from D. Frome, University of British Columbia [http://www.cmrd.ubc.ca/cry/iod.html].

**Figure 2** Time evolution of a simulation trajectory with 4 trichogin molecules embedded in the bilayer. P, N and O atoms of phospholipids are shown as gold, blue and red spheres, respectively, while water O atoms are coloured in pink. The acyl chains of the phospholipids are omitted for the sake of clarity. Peptides are represented as ribbons, with the N- and C-termini coloured in blue and red, respectively.
small-angle diffractometer D22 Spin-echo spectrometer IN15

Observing protein cluster phase in concentrated monoclonal antibody solutions

The formation of protein clusters with a preferred finite size is critically important to understand the physics of concentrated protein solutions. Among the many applications, protein clustering plays a key role in controlling the viscosity of therapeutic monoclonal antibodies (mAb) which have been considered the closest thing to "magic bullets" for the treatment of many diseases including cancers. In particular, it is widely speculated that the formation of mAb clusters is responsible for the high viscosity observed for some mAb solutions. This undesired high viscosity is actually one of the main obstacles for the future use of subcutaneous injection for the administration of biopharmaceuticals.

However, to date, it has been difficult to directly observe these mAb clusters accurately and quantitatively characterize their microstructure in crowded environments. Many results are still hotly debated in the colloidal community. By combining small-angle neutron and X-ray scattering (SANS/SAXS), neutron spin-echo (NSE), and computer simulations, we have studied two mAbs with small difference in their primary structures to conclusively observe the protein cluster phase with preferred cluster size and establish the relation between the cluster formation and the increased viscosity [1,2].

Despite the small difference in their primary sequences, the two mAbs (denoted as mAb1 and mAb2) have markedly different solution viscosities. The solution viscosity, η, of mAb1 has an anomalously large value of 310 mPa.s at 150 mg/ml compared to many other mAbs that have much smaller viscosity including mAb2 whose viscosity is only 18 mPa.s at 150 mg/ml. Even though the η of mAb1 is not very large in comparison with many other soft materials such as polymer blends and colloidal glass/gel systems, these solution viscosities limit the allowable concentration for bulk manufacturing as well as delivery through thin needles.

The characterization of the apparent radius of mAb1 and mAb2 at relatively small concentrations (≤ 10 mg/ml) indicates that mAb2 are dispersed as monomers for this concentration range while mAb1 begins forming small clusters. The dynamic light scattering data also show that the apparent hydrodynamic radius of mAb1 proteins increases from that of a monomer at 1 mg/ml to about 1.7 times that of a monomer at 10 mg/ml. The estimated molecular mass of mAb1 clusters at 10 mg/ml is close to that of a mAb1 dimer indicating that dimers may be the dominating species at 10 mg/ml.

To accurately characterize the cluster size at high concentrations, we used neutron spin-echo (NSE) to directly probe the translational self-diffusion coefficient, D, of mAb1 samples as a function of concentration, C. It has been shown that mAb2 remains dispersed as monomers in the concentration range studied [1,2]. Therefore, the ratio of D, between mAb2 and mAb1 is an indication of the size of mAb1 clusters relative to a mAb2 monomer. This ratio as shown in figure 1 is also represented as the size of the mAb1 clusters relative to the mAb1 monomer size. Surprisingly, the results in figure 1 show that once formed at low concentrations (about 10 mg/ml), the cluster size of mAb1 remains almost constant over a large concentration range. This indicates that the clusters in mAb1 solutions have a preferred finite size. This behavior is dramatically different than that of many globular proteins such as lysozyme.

Recent study of lysozyme solutions with strong electrosstatic repulsion demonstrated that clusters only form at relatively high concentrations and the size of clusters increases with the concentration [3]. Here, the formation of mAb1 clusters shows similarities to micelle formation, which self-assemble into clusters at relatively low concentration but maintain their size over a range of concentration.

While the clusters formed at 10 mg/ml are very dense, their sizes remain very small. For example, the size of clusters of mAb1 at 10 mg/ml, which is also the ratio of mAb1 cluster size relative to its monomer size. Despite the small difference in their primary sequences, the two mAbs (denoted as mAb1 and mAb2) have markedly different solution viscosities. The solution viscosity, η, of mAb2 is about 1.6 times that of a monomer at 1 mg/ml to about 1.6 times that of a monomer at 10 mg/ml. The estimated molecular mass of mAb1 clusters at 10 mg/ml is close to that of a mAb1 dimer indicating that dimers may be the dominating species at 10 mg/ml.

As the concentration increases, the clusters become more dense with a decrease in the solution viscosity. [2] Therefore, the strong correlation of the cluster size and the solution viscosity shows that the formation of small protein clusters is indeed the driving force of the anomalously high viscosity for our mAb solutions.

These measurements were the first to experimentally demonstrate proteins can form clusters of a very small finite size. Additionally, the insights gained controlling mAb solution viscosity are useful in the development of mAbs formulations with desired solution properties, which in turn will aid their efficient production and clinical use.

**Figure 1**

The ratio of the self-diffusion coefficients for mAb2 and mAb1, which is also the ratio of mAb1 cluster size relative to its monomer size. The colored mAb protein images are drawn for illustration purposes only.
A protein is a chemical polypeptide chain folded into a dynamic three-dimensional structure with biological activity. Protein structure and dynamics are very sensitive to environment. The crowded conditions as well as the presence of extensive molecular interactions that prevail inside a living cell are believed to interfere importantly with protein folding and unfolding processes. It follows that the consequences of environmental stress on the dynamic state of a protein in the cytoplasm could be very different from that measured in vitro, under dilute conditions. Neutron scattering has been developed as a method of choice to probe protein dynamics in live cells.

We studied Haloarchaeum salinarum (Hs) as a model microorganism and characterised, in vivo, the effects of temperature stress on molecular dynamics. Hs belongs to the family of the Haloarchaea, microorganisms that require high salt concentrations to thrive. Figure 1 shows a bloom of Haloarchaea in the Lac Retba (also known as Lac Rose) in Senegal. The temperature of the lake varies between 20 °C and as high as 50 °C depending on weather, night/day and precipitation that changes the salt concentration. Even though it is not a thermophile (an organism that thrives only in high temperatures) Hs can tolerate high temperature stress quite well. This made it possible to explore a range of stress conditions without killing the cells.

Hs cultures were grown in the laboratory at 37°C and normal high salt conditions for the organism, then transferred to the desired stress temperature and cultivated under agitation for a further hour. For the neutron scattering experiment, a paste of live cells was sealed in a gold-plated sample holder (to avoid corrosion by the salt in the suspension) and mounted on the IN13 spectrometer. Whenever a biological sample is examined it is important to verify it has not been denatured during the experiment. Viability tests on the samples confirmed that the cells survived the stress conditions and were not affected by being enclosed in the sample holder or exposure to the neutron beam (Figure 2).

As in a billiard ball collision, neutrons bounce off moving nuclei exchanging energy and momentum, so that neutron scattering informs us on the molecular dynamics in the sample. Each neutron spectrometer is sensitive to a particular window in the range of motions. On IN13, the window looks at atomic displacements of the order of 1 Å, i.e. 1 nanometre in 0.100 ns, which corresponds to thermal motions in protein molecules. Atoms in a protein can be seen as being held by springs linking them to their neighbours in the structure. One of the parameters extracted from the neutron scattering data is the mean force constant or resilience (k =< k >) of the springs in the protein structures. It is plotted as a function of stress temperature in Figure 3 (right hand axis). The fall in resilience with increasing stress indicated a ‘softening’ of protein structures, as would occur if there were partial unfolding. A further important control was to make sure that the cells were responding biologically to the imposed thermal stress. Thermosome is a large complex involved in ‘housekeeping’ for the intracellular protein population, which contributes to cell survival by recycling damaged molecules. Its increased production is one of the genetic responses to stress. Thermosome levels measured in the same samples as a function of stress temperature are in Figure 3 (left hand axis). Note how the genetic response of thermosome accumulation parallels the physical response of decrease in resilience.

The neutron study provided direct insight into the folded state of the proteome (the protein population in the cell) exposed to temperature stress conditions. It established that neutron spectroscopy sensitively detects alterations in the mean molecular dynamics state of the proteome within a living cell in response to environmental changes. Despite the crowded intracellular environment and the induction of protein quality control systems such as thermosome complexes, the dynamic state of a large fraction of the proteome is strongly perturbed under thermal stress. Yet, interestingly, the cells recovered easily when replaced in optimal growth conditions.
Transposons make up a large proportion of many genomes (e.g., 45% of the human genome). These genes were originally believed to have no purpose and were described as “junk DNA.” However, it is now emerging that transposons are powerful drivers of genetic change; some transposons can move from one place to another within a genome using a simple cut-and-paste mechanism. This DNA rearrangement shuffles the genetic code and can lead to beneficial changes in cells. For example, in the human genome, rearrangement of antibody genes enables the immune system to target infection more effectively.

The cut-and-paste property of DNA transposition is now being exploited to develop new biotechnology tools for genetic engineering and gene delivery. One family of transposons — the mariner/Tc1 family — have proved particularly useful as they are widespread in nature and can jump in a broad range of species, including mammals [1]. Only one protein — a transposase — is required to cut out the transposon and reinsert it elsewhere in the genome. Our aim is to understand how mariner/Tc1 transposons jump, with particular focus on the transposition pathway of the mariner element Mos1 (Figure 1).

By characterising the structures of the protein-DNA complexes between Mos1 transposase and the ends of its transposon, we have gained a deeper understanding of how Mos1 cuts and pastes DNA at the molecular level. These results will help us to engineer the transposase and speed the development of biotechnology applications of transposons.

We used SANS to determine the shape of the Mos1 transposase (a) before it binds to transposon DNA, and (b) when it binds to one transposon end in a single-end complex (SEC2) and before the DNA cut. We have used the powerful method of contrast variation in SANS [2] to determine the shapes and relative spatial arrangements of the individual components in the protein-DNA complex. Selective masking of either the protein or DNA is achieved simply by altering the ratio of H2O to heavy water (D2O) in the solvent. Partially deuterated Mos1 transposase (D-Mos1) was produced for these experiments in the ILL’s Life Science Group (the D-LAB). Under the Partnership for Structural Biology the SANS experiments were performed on the instrument D22 at the ILL and small-angle X-ray scattering (SAXS) experiments were performed on the beam line ID14-3 at the ESRF.

The results of SAXS and SANS experiments revealed that in the absence of DNA Mos1 transposase is an elongated homodimer, with a maximum dimension (Dmax) of 185 Å. By comparison, the transposase in the paired-end complex (PEC) crystal structure — at a later stage in the transposition pathway — has a compact crossed conformation [3] with a Dmax of 110 Å. From these data we conclude that the transposase changes shape, either upon binding one transposon end (in SEC2) or after the transposon ends are paired (in the PEC). The results of our contrast variation SANS experiments on SEC2 (Figure 2) revealed that the transposase-DNA complex is more elongated than the DNA-free Mos1 transposase dimer. Furthermore, the DNA component is associated predominantly with one transposase monomer only, and this may allow the other transposase monomer the rotational freedom to drive a change in the shape of the complex.

In conclusion, the similar architectures of the DNA-free transposase and transposase in SEC2 suggest that binding of a pre-formed transposase dimer to the first transposon end occurs without major shape changes in either the protein or the transposon DNA. We propose that these changes occur in the SEC2 to PEC transition, by rotation of one transposase monomer and its capture of the second transposon DNA end.
Quasi-Laue diffractometer LADI-III

Neutrons show their potential in drug design

Neutrons can provide drug developers with crucial details about the structure and interactions of their pharmaceuticals. After years in the shadow of X-ray based techniques, their use in a crystallographic study of an antiviral drug binding to HIV-1 protease has highlighted how recent technological progress and instrument developments at the ILL are bringing neutrons into line. The successful analysis demonstrates the wealth of new information the combination of these two techniques can provide drug developers going forward.

For several decades X-ray crystallography has been routinely used by the pharmaceutical industry to determine how their drugs interact with their protein targets. Nevertheless, a limitation of the technique is that hydrogen atoms are virtually invisible in the X-ray analysis, leaving scientists to speculate on their positions, despite their importance in drug binding through hydrogen bonding. This is where neutrons have an advantage; they allow the position of all the atoms to be determined including lighter elements such as hydrogen, and therefore neutron crystallography is particularly suited for use in drug discovery and development.

This potential has been acutely demonstrated in a recent study of interactions between a common clinical inhibitor (amprenavir) and HIV-1 protease, an enzyme essential for the replication of the HIV virus, allowing it to break polypeptide chains and create proteins used for viral maturation and the production of new infectious virus particles. After 20 years of analysis with X-rays, results published earlier this year [1] using neutrons provided a more detailed picture than ever before of how an antiviral drug used to inhibit the enzyme actually works. The team were able to identify the position of every hydrogen atom involved in the system, and which were involved in the binding of the inhibitor to the enzyme through hydrogen bonding. Critically the analysis indicated which hydrogen bonds were the weakest and how the binding, and hence the drugs performance could be improved.

This research represents a major step forward for a technique whose application in the field of pharmaceutical R&D has been held back in the past due to various technical challenges. These included the volume of sample crystals that needed to be grown, the length of time it took for the results to be collected, as well as the lack of dedicated instrumentation available around the world where scientists could carry out their studies. During this study, the neutron crystallographic experiments were carried out on the LADI-III (quasi-Laue neutron diffractometer) instrument at the ILL where developments in the last decade have addressed the technical challenges allowing crystals as small as 0.005 mm to be analysed, permitting a greater array of studies to be performed.

With the tools for the job, the study was carried out using a 0.2 mm³ single crystal of HIV-1 protease (deuterated at a level of 85%) with ampranavir bound, and data were collected to 2.0 Å resolution. Despite its decade of use as a clinical inhibitor, it was only following this first analysis using neutrons that amprenavir’s true binding behaviour was revealed, painting a rather different picture to that inferred from the X-ray studies, which had overplayed the importance of several hydrogen bonds. In fact the team suggested the presence of only two strong direct hydrogen bonds between the drug and HIV-1 protease at the catalytic site of the enzyme (Figure 1).

The findings present drug designers with a set of new sites to try and improve the drug’s chemistry significantly strengthen the binding, increasing the effectiveness of this and other inhibitors and reducing escape mechanisms. Suggestions of areas for improvement include replacing weaker water-mediated hydrogen bonds with stronger direct hydrogen bonds to increase the enthalpy of binding. This could be achieved by changing certain functional groups of the drug in order to expel water molecules present in the active site, which at the same time improves the entropy of binding. Another approach would be to increase the strength of the two direct hydrogen bonds by creation of a special type of hydrogen bond known as a “low-barrier hydrogen bond,” in which the proton is equidistant between the donor and acceptor atoms. This can be achieved by lowering the ionisation constant of the hydroxyl group of the drug to make it similar to that of the amino acids it binds to, via introduction of a strong electronegative atom such as fluorine.

The findings in this latest paper may also help address one of the biggest issues in combating HIV infection - drug resistance. Evolution of the virus over time produces the enzyme variants with weakened binding affinity to an inhibitor, a process that is actually sped up by the introduction of the drugs themselves. One way round this would be to improve the binding of the inhibitor with the main-chain atoms of HIV-1 protease rather than its side-chain atoms, as the main-chain atoms of the enzyme cannot mutate. Before this latest study it was thought the potential for advances in this area were limited because the hydrogen bond interactions with the main-chain atoms were already very strong. However, this has been shown not to be the case, creating a new avenue for the development of HIV pharmaceuticals much less affected by virus evolution and resistance.

X-ray crystallography has played a crucial role in structure-guided drug design for over two decades. Whilst its value to researchers in this field will continue for many years, combining the use of X-rays with neutrons increases the clarity of how drugs interact with their protein targets, providing the pharma industry with a powerful new tool to improve the performance of their products. It’s clear that the future of drug design will feature a combination of the two crystallographic techniques that can provide patients with newer more effective medicines to not only battle HIV infection, but for other diseases as well.

**Figure 1**

**Figure 2**

(a) The Human immunodeficiency virus (HIV) replication cycle
(b) The structure of a mature HIV virus particle
Vertical reflectometer D17

Effect of functionalised gold nanoparticles on floating lipid bilayers

The development of novel nano-engineered materials poses important questions regarding the impact of these new materials on living systems. Possible adverse effects must be assessed in order to prevent risks for the health and the environment. On the other hand, a thorough understanding of their interaction with biological systems might also result in the creation of novel biomedical applications [1].

A key issue in making use of nanoparticles (NP) for biomedical purposes is understanding of their interaction with cells beyond the designated functions. Since the first contact that all nanomaterials will always have with any living organism is through the cell membrane, this study focuses on the interaction of a particular class of NP with model cell membranes.

Many recent studies have addressed the interaction between nanoparticles and membranes. Besides size, shape, ligand structure, and composition, the way in which biological cells take up nanoparticles is significantly affected by the nanoparticles’ surface charge [2]. While cationic nanoparticles are thought to enter the cell by membrane diffusion, anionic nanoparticles probably insert through endocytosis, that is a process whereby the plasma membrane folds inward to bring substances into the cell without passage through the membrane.

To provide insight into the fate of gold nanoparticles (AuNPs) and their impact on cell membrane integrity, we analysed the interaction of two classes of AuNPs with single component model membranes. For this purpose, we brought two nanometer diameter AuNPs functionalised with cationic [N,N,N-trimethyl(11-mercaptoundecyl) ammonium] and anionic (mercaptoundecanoic acid) surface ligands into contact with single-component zwitterionic DSPC (1,2-distearoyl-sn-glycero-3-phosphocholine) bilayers. As model membrane, we chose a system composed by a solid supported double lipid bilayer, in which the second bilayer floats 20-30 Å above the first one and bypasses the interaction between the first lipid bilayer and the substrate. Our choice gives access to a highly hydrated, fluctuating bilayer that represents a membrane system with dynamic properties comparable to biological membranes and is greatly relevant for the examination of the influence of AuNPs on lipid membrane structure and integrity.

There are several advantages by using the neutron reflectivity technique for this kind of study. Neutrons have a weak interaction with matter because they are not charged and perturb soft matters systems very little. They are deeply penetrating and therefore ideal probes for buried interfaces. Last, but not least, with the use of isotopic substitution, we can vary the contrast of different regions of the system, highlighting the scattering of each component of the system. For example, in our systems this allows us to distinguish between the density variation in the bilayers due to solvent and/or NPs penetration. All these signatures of neutrons allow us a structural determination at a resolution not reachable with any other technique.

In agreement with previous experimental and theoretical results, we could confirm in the presented neutron reflectometry experiments that the charge of the AuNPs indeed affects the way nanoparticles interact with lipid bilayers. The AuNPs functionalised with cationic head groups penetrate into the hydrophobic moiety of the lipid bilayers and cause membrane disruption at an increased concentration. Furthermore, they tend to pass through the fluid phase of the lipid membrane and remain embedded in the hydrophobic moiety of the floating bilayer [3]. By a precise modelling of the reflectivity data, we could quantify the amount of AuNPs that remain embedded in the lipid bilayers. Figure 2 shows the reflectivity profile obtained by measuring a pristine lipid membrane and a lipid membrane in the presence of the AuNPs, from which we calculated the scattering length density profile of our stratified system and obtained precise information about the thickness, roughness, composition and hydration of the bilayers. The analysis of the profile indicates that the cationic AuNPs only penetrate the first bilayer. Fitting models that included AuNPs in the supported bilayer or excluded the presence of AuNPs from the complete bilayer system were not compatible with the data.

Overall, this study shows that the nature of AuNP–lipid membrane interaction depends on the AuNP surface charge. Further studies that focus on the AuNP concentration and size, as well as lipid bilayer surface charge and composition are necessary to elucidate further parameters influencing the nanoparticles–cell membrane interaction and their consequences on the membrane structure and integrity. This knowledge is crucial to effectively design safe nanoparticles for biomedical applications and also to define practices and procedures for the secure handling of nanoparticles in general. The information obtained might influence the strategy for a better nanoparticle risk assessment based on a surface charge evaluation and contribute to nano-safety considerations during their design.

**References**


Polarised cold neutron beam facility PF1B

EXILL, a campaign of measurements devoted to nuclear spectroscopy

The combination of a well collimated, intense cold-neutron beam available at the instrument PF1B and a highly efficient Germanium detector array made a unique nuclear structure physics campaign possible. The measurements were devoted to prompt γ-ray spectroscopy of stable nuclei and of medium-heavy mass neutron-rich isotopes produced in neutron induced fission. For two full reactor cycles both, stable and fissile targets (235U and 241Pu) were irradiated.

THE PHYSICS CASE

The usefulness and feasibility to study fission products with High Pure Germanium (HPGe) detector arrays has been demonstrated in the past by experiments with spontaneous fission sources such as 252Cf and 249Cm [1, 2, 3]. Neutron induced fission (with isotopes 235U and 241Pu) yields a very effective way to produce and study low-lying states of neutron-rich nuclei in the mass range A = 85-160, specifically in the scientifically interesting and so far unknown doubly magic regions of 172 \(^\text{O}\) and 172 \(^\text{N}\). The population of entire isotope chains allows a systematic study of the prediction power of the nuclear shell model. Moreover, due to their doubly magic structure, they form waiting points along the \(r\)-process nucleosynthesis path. The elementary abundances at waiting points is highly enhanced since the decay time of the unstable isotope is longer as a consequence of the increased stability of the nuclear structure. Further motivation comes from experiments focusing on the radiative neutron capture (\(n,\gamma\)) reaction itself. The non-selectivity of the capture process populates a large majority of the low spin excitations. This gives access to very rich and detailed spectroscopic information of isotopes close to the line of stability.

The high interest in the campaign is demonstrated by 120 scientific visitors from 18 laboratories submitting more than 80 different proposals and actively participating in the data taking.

THE EXILL CAMPAIGN

Experiments with HPGe detector clusters in combination with a neutron beam were so far limited to very small collections of up to 8 detectors only [4]. Within the EXILL campaign for the first time a large HPGe array has been installed around a highly collimated cold-neutron beam with a flux of \(10^8\) n.s\(^{-1}\).cm\(^{-2}\) at the target position. During the campaign 19 different samples with stable isotopes with capture cross section from 0.02 to 1,000 barns \(10^{-24}\) cm\(^2\) orders of magnitude range, have been used. Furthermore, fissile isotopes such as 235U and 241Pu have also been irradiated. In the high efficiency configuration, the detector array consisted of 10 EXOGAM [5] clover detectors from GANIL (France), 2 clover detectors from IL and 6 GASPL [6] coaxial Ge detectors from INFN (Italy). A second configuration consisted of 8 EXOGAM clovers combined with 16 LaBr\(_3\) scintillators detectors from the FATIMA collaboration [7]. This configuration profits from the excellent time resolution of the scintillators (below 200 ps) allowing lifetime measurements of nuclear states. The signals from the detectors were fed into a digital data acquisition system consisting of 100 MHz digitizer modules which allowed both, energy and time information, to be recorded. The time signals from the LaBr\(_3\) scintillators detectors were processed using analogue electronics. All data were recorded in a triggerless mode to preserve a maximum of information and resulting in about 60 TB of stored raw data.

ANALYSIS METHOD AND QUALITY OF DATA

Fission produces different nuclei as fragments of the fission process. At least one fragment must be identified in order to interpret the data. In the EXILL campaign this is done via known characteristic γ-rays, which are used to search for further γ-rays within a certain time window (coincidence). These other rays provide new information on the fission fragment. These can be the energies of unknown transitions within the same de-excitation path or the lifetime of intermediate nuclear states. This technique typically requires at least 3 γ-rays to be detected in coincidence.

Furthermore, the sensitivity of the experiment depends highly on the efficiency, the energy resolution and the granularity of the detector array. The full EXILL array had a total detection efficiency of 6% at 1.3 MeV and consisted of in total 72 individual detector channels.

The experiment produced data during 95% of the total beam time. Depending on the particular fission yield the data from spontaneous fission sources were substantially improved, which gives access to new isomers and decay schemes. For example in the case of 235U the statistical gain is in the order of 30.

In figure 2 we show the example of a \(\gamma,\gamma\) coincidence matrix of the reaction \(^{155}\text{Gd}\,(n,\gamma)^{156}\text{Gd}\). (Courtesy of L. Sengele, IPHC Strasbourg.)

A shared effort is presently ongoing in the sorting and analysis of the enormous data set. Despite the number of people involved several years of work lie ahead for this collaboration. First physics results from \((n,\gamma)\) measurements have already been presented at conferences [10].
Ultra-cold neutron facility PF2

MONOPOL – A travelling-wave magnetic neutron spin resonator for tailoring polarised neutron beams

Since the early 1960s it is known that spin resonance in undulatory static magnetic fields allows for wavelength-selective spin flip of polarised neutrons. Implementing a novel travelling-wave technique, we have developed this concept towards a resonator which does not only allow to monochromatise the neutron beam but also to chop it into a sequence of pulses short enough for time-of-flight applications. The outstanding performance of such a resonator which was optimised for very cold neutrons could be demonstrated successfully at the PF2-VCN beam line.

As shown already in the 1960s [1], the combination of a static vertical and a spatially alternating horizontal magnetic field constitutes an NMR-like system for polarised neutron beams, with the peculiarity that for given spatial period and strength of the vertical field each neutron creates its own ‘resonance’ frequency according to its individual speed. Clearly, when placed between two polarising neutron mirrors such a resonator acts as neutron monochromator. The conventional design of such a resonator employs a thin meander-shaped metal conductor foil where each turn of the foil defines a single resonator element. Increasing the number of such elements improves the achievable wavelength resolution but evidently increases also the length of the resonator. Neutron pulses may be generated by switching the foil supply current on and off with the consequence that the achievable minimum pulse length is defined by the overall resonator length.

However, in our novel ‘travelling wave’ technique the undulatory resonator field is applied in synchronisation with the resonant neutron pulse during its passage through each of the consecutive resonator elements. As a consequence, the minimum pulse length is defined only by the length of a single resonator element and hence be up to two orders of magnitude shorter than in the conventional mode. The experimental realisation of this novel technique, which allows for a complete decoupling of wavelength and time resolution, is a major step towards the development of electronically tuneable neutron monochromators and choppers of utmost flexibility. As additional feature, the concept can be applied across the complete thermal and cold neutron spectrum.

We have built a resonator composed of 48 elements (figure 1), each consisting of a 11.6 mm thick prismatic single-turn coil made of a 0.1 mm aluminium sheet and fed by an individually controllable current source which can be switched on and off within about 1 microsecond. This resonator was tested at the PF2-VCN beamline with a polychromatic beam of very cold neutrons, polarised and analysed by a pair of Fe/SiGe-based supermirrors. We established ‘Dark field’ conditions by inverting the neutron polarisation over the complete incoming neutron spectrum by means of a broad-band current sheet spin flipper. Spectral analysis was performed by employing a single-disk chopper with about 5 ms opening time when operated at 10 Hz repetition rate (chopper-detector distance: 2.7 m). The blue symbols in figure 2 represent the incoming VCN spectrum obtained with the resonator and the current sheet flipper switched off. Activating both pulses than the conventional mode. Eventually this might be of value for novel ESS instrumentation.  

ACKNOWLEDGEMENT

We acknowledge the vital contributions of T. Oda and M. Hino from Kyushu University to the experimental set-up and of S. Baumgartner, B. Berger, and R. Raab who performed their master theses on this project.

AUTHORS & REFERENCES

E. Jerich, Ch. Gösselsberger, and G. Bednarek (Institut für Physikum, Vienna University of Technology, Austria)
F. Geltenbort (Atominstitut, Vienna University of Technology, Austria)


Figure 1

Up-stream view of the experimental set-up: the resonator with 48 individual elements is shown together with the individual supply lines from the current sources on its top. A broad-band current sheet spin flipper for polarisation inversion of the neutron beam can be seen in the background. The complete experiment has been placed in a He atmosphere to reduce neutron scattering and suppress VCN absorption.

Figure 2

Time-of-flight spectra of the VCN beam as measured by means of a mechanical single-disk chopper: blue symbols show the total spectrum when the resonator is turned off, red symbols the combined effect of the neutron resonator and the broad-band spin-flipper. Black symbols indicate the neutron background due to non-polarised neutrons when the resonator is turned off.

Figure 3

Tailoring the temporal structure of the neutron beam by pulsed operation of the resonator. The typical time scale for VCN is milliseconds. In the novel travelling-wave (TW) mode the edges of the pulses are considerably sharper than in conventional mode (CM) where the resonator is switched on and off as a whole.
Analysis of the multiferroicity in the hexagonal manganite YMnO₃

Magnetoelectric material are actively studied, since they allow the cross control of magnetic and electric properties with possible applications in electronic devices. YMnO₃ is a prototype magnetoelectric compound presenting a coupling between the polarisation (P), dielectric constant (ε), and the magnetic order. Until recently its magnetic state and magnetoelectric coupling order parameters were the subject to controversies.

We analysed neutron scattering, magnetisation, polarisation, dielectric constant, second harmonic generation (SHG) experiments and proposed a comprehensive model resolving the apparent contradiction between all these experimental results. The strength of theory is also to predict new properties. We showed that the long search for a reversal of the magnetic order by a switch of the polarisation is vain, since the latter couples to P² and is thus insensitive to the polarisation sign. If such compounds are not fit to switch the magnetisation with an electric field, they however can be used to switch antiferromagnetism with an intense magnetic field, providing memories resilient to magnetic fields.

The magnetic transition of YMnO₃ occurs around Tₛ = 74 K. Neutron diffraction measurements [2-4] showed that the structure is antiferromagnetic (AFM) with moments in the ab-plane. Following Bertaut et al. [2], Muñoz et al. [3] proposed for the antiferromagnetic order the totally symmetric (Tₙ) solution of the P₆₃/mcm group, pictured as V₁ in figure 2. More recently, a neutron diffraction and polarimetry analysis performed at ILL [4] showed that the ac/bc-mirror planes are lost and that the magnetic order should rather be, either a combination of V₁ and V₃ (P₆₃ group), or of V₄ and V₆ (P₆₅ group). Finally, in a SHG experiment, Fröhlich et al. concluded to a very different order (W₃) associated with the P₆₃/mcm group [5]. Let us notice that, while Bertaut et al. [2], and Muñoz et al. [3] performed a full symmetry analysis, Brown and Chatterji [4], as well as Feibig et al. [5] only considered the Tₙ solution of the tested symmetry groups. One should however remember that while P behaves as the density matrix and thus belongs to the Tₙ representation, the magnetic order (spin part of the wave-function) can belong to any of the irreducible representations of the magnetic symmetry group.

We performed additional measurements: P and ε versus temperature and magnetic field, as well as precise magnetic measurements on a SQUID magnetometer at low magnetic field. Indeed, S. Politi observed in a non-polarised neutrons scattering experiment, a Bragg peak that was associated with a ferromagnetic (FM) component [6]. After carefully checking out the possibility of magnetic impurities, we confirmed the existence of such a component.

Let us summarise what we learned from the analysis of experimental facts. Let us consider that the AFM Bragg peaks intensity present similar temperature dependence, showing the existence of a magneto-electric coupling between the AFM and the ferroelectric (FE) orders.

• ε and the AFM Bragg peak intensity present similar temperature dependence, showing the existence of a magneto-electric coupling between the AFM and the ferroelectric (FE) orders.

Figure 1

Figure 2

YMnO₃ possible AFM orders. The blue Mn sites are in the z=0 layer and the red sites in the z=1/2 layer.
After the great success of the Millennium Programme, a new initiative to continue to upgrade ILL instruments and scientific infrastructure is being planned: the Endurance programme is built on the solid foundation and experience gained during the work carried out over the past years. The recently produced ILL 20/20 Endurance brochure [1] presents the detailed plan for the programme, which is shortly summarised in this article.

The ILL has led the world in neutron science for almost 40 years - a remarkable record that has been achieved by offering state-of-the-art instruments served by the brightest neutron source, and by attracting many of the most talented neutron scientists and technical staff to work with us. This, in turn, has meant that the instrument suite has had to evolve continuously by exploiting new technology - much of it developed in-house - to redefine the limits of what is measurable and offer new scientific opportunities.

The latest such development, stretching over more than a decade, is the Millennium Programme, which has delivered an increase of more than a factor of 25 in average instrument brightness for less than one year's budget. This has not only enabled us to increase the number of experiments and thus users that we can support, but has also opened up completely new avenues of science.

Recent achievements include the first in situ measurement of the structure of a fluid as it passes through a microfluidic cell, thus providing direct insights into key manufacturing processes. Also observed for the first time is the relaxation of magnetisation in single crystals of a single-molecule magnet, which has provided unique information relevant to its potential for data storage and quantum computing. However, there is still great potential to improve our facilities further by upgrading those instruments not yet boosted by the Millennium Programme.

The Endurance programme is dedicated to improving the performance, fitness and long-term potential of the ILL instrument suite. To achieve its scientific goals and open up new science, a challenging technical programme is being implemented to manage the design and construction of up to seven future world-leading instruments.

In addition, seven existing instruments will be extensively modernised and four existing neutron guides completely re-designed.

The Endurance instrument vision cannot be separated from two ambitious companion programmes: NESSE - a vision for future sample environments, and BASTILLE - a new approach to data treatment. These will be put in place during the Endurance programme.

**THE CHARTREUSE AND VERCORS ENSEMBLES**

The four existing neutron guides concerned by these projects were installed just over 40 years ago. Their replacement by state-of-the-art neutron distribution systems will provide optimal experimental areas for four new instruments and will boost the performance of four other refurbished ones. The new guide systems will provide additional capabilities for the implementation of instruments that are under evaluation following the Scientific Council advice (Phase II), as well as better neutron beams for technical instruments used for advanced R&D on detectors and neutron optics.

In both the Vercors and Chartreuse projects (see table 1), a typical gain factor of two to four is expected from the guides installed upstream of each instrument depending on the instrument acceptance of the beam divergence.

**AUTHOR & REFERENCE**

H. Schober (ILL)
(1) The pdf of the brochure can be downloaded from http://www.ill.eu/quick-links/publications/
The Millennium Programme has played a major role in enabling the ILL to retain its position as world leader in neutron science. Involving a total investment of 91 M€ over the period 2001-2014, the programme represents an extremely important part of the joint undertaking by the Associates and the Scientific Members to support the ILL’s modernisation efforts.

As it approaches the end of this first phase of modernisation work, the ILL is beginning to take full advantage of the enormous benefits the Millennium Programme has brought in terms of science and user service. The instruments D33, IADI, IN11, IN12, D11, IN1-LAGRANGE, D17 and IN44 have all either been completely rebuilt or have benefitted from a new guide, making it possible to improve instrument performance considerably with respect to flux, resolution and background. The OGR-IN12 is now quite simply the best cold neutron three-axis spectrometer in the world. IADI is having a major impact in the field of structural biology. The spin-echo instrument IN11 has increased its flux considerably, thanks to its new guide. And last but not least, IN1-LAGRANGE now offers the chemistry user community an outstanding spectrometer which complements UV and IR spectrometers for the materials community.

In 2013, the backscattering spectrometer IN16B was commissioned and we are waiting for the first results to be compared to those of our competitors. The time-of-flight massive dynamic Q range small-angle diffractometer D33 is now fully operational; the first publications from this instrument are expected in the near future. 2014 will see the completion of ThALES - the ILL equivalent of the IN12 three-axis spectrometer - and the replacement of the H5 guide, which will deliver neutrons to IN15, D22, D16, SuperADAM and the future instrument WASP.

Work on preparing the next phase of the ILL modernisation programme, known as Endurance, is under way (see article on p.74). This new initiative began with the ILL 2020 Vision user meeting, which was held back in September 2010 and was attended by representatives of the user community. The programme has since been further developed in collaboration with the ILL’s Scientific Council and the Instrument Subcommittee at various meetings over the course of the past few months. Endurance, which sets the scene for the next decade and continues the momentum of the Millennium Programme, has three important components: guides, instruments and infrastructure. In addition, in close cooperation with other research centres, data acquisition, processing and analysis will be also part of Endurance. Over the coming months, the teams of the Projects and Techniques Division (DPT) will be working with the Science Division on preparing the details of this ambitious project.

The DPT is also heavily involved in innovation. In the framework of a project supported by the European Commission and involving a number of other European large-scale infrastructures, the ILL is one of the first research centres to have implemented a scientific data policy that is perfectly in line with European guidelines in terms of the valuation of and access to scientific data. In the field of detectors, monochromators and guide alignment technologies, the ILL is at the forefront of innovation in neutron technologies. Polarisation analysis is another of the ILL’s strengths, as can be seen from the regular requests we receive to supply our technology to other facilities (a detector for LLB Saclay, France, a monochromator for SNS, USA, polarisation analysis for ISIS, UK, and ANSTO, Australia). The Institute is leading efforts to develop a new boron-based technology for detectors, and other neutron facilities are also beginning to show an interest in implementing our data acquisition software NOMAD. All these projects clearly demonstrate the excellent neutron technology expertise available at the ILL.

In the coming years, the teams at the ILL will have to face the challenge of continuing to lead the world in neutron technology in the context of increasingly limited budgetary resources compared to those available to our competitors. In the past, the ILL has proved on many occasions that it is capable of meeting such challenges and I have no doubt that we will do so once again and that the Institute will remain at this cutting edge of neutron technology for at least the next decade.
Millennium Programme 2013

In 2013, work on the Millennium Programme was again extremely intense. The commissioning of the new backscattering spectrometer IN16B was completed and the instrument welcomed its first users. Progress was made with the construction of the new ILL three-axis spectrometer ThALES, which is due to be completed in 2014 and hopes to become the best instrument in its category. However, the bulk of the work being carried out during the long 2013-2014 shutdown is devoted to the guide hall ILL22 and its cold neutron guide H5, which will feed IN15, D22, D16, CRYOEDM, SuperADAM, a free position and WASP.

The commissioning of the backscattering spectrometer IN16B was completed in time for the arrival of its first users. The new and extremely challenging phase transformer is working perfectly and six full-size analysers are in the process of being installed.

The three-axis spectrometer ThALES developed in collaboration with Charles University of Prague and with the support of our Spanish Scientific Member, will be constructed in the reactor hall. Figure 1 shows the present state of the space reserved for this instrument, which we hope will prove to be the best in its category.

The bulk of the work scheduled for the long reactor shutdown (August 2013-June 2014) is devoted to the guide hall ILL22, which will house IN15, D22, D16, CRYOEDM, SuperADAM, a free position and WASP, and its guide H5. The building has been extended, a new cooling system has been built for IN15 and WASP, and the guide itself is being completely rebuilt to increase the neutron flux on the instruments and reduce the background on the detectors. D16 will also benefit from no longer being positioned behind a monochromator, which was damaging for its performance.

Each new instrument will have its own cabin for experimentalists. To date, the building is finished (but still empty), the cooling system is ready and the casemates for the guides are under construction. One of the major challenges facing the ILL teams in 2014 will be the construction of the H5 guide, which has a rather complex structure making it possible to optimise the flux on every instrument in the guide hall.

The wide-angle spin-echo machine WASP is due to be delivered in 2016. One important aspect of this instrument is the construction of the polarisation analyser, which is described in detail later in this report. The guide and the primary spectrometer are under construction. The primary cooling circuit and the supply network are ready to provide power and cooling to the giant precession coil, which is currently under construction (to be delivered early 2015).

The high-resolution spin-echo instrument IN15 will also be completely rebuilt, with new precession coils which will take advantage of the power and cooling circuits mentioned earlier. The instrument will also benefit from the fact that there are no magnetic structures in the reconstructed guide hall. This will make it easier in future to tune the phase of the instrument and should increase the resolution in time.

2013 was a year of transition for the ILL’s Millennium Programme, marking the start of a lot of new work. 2014 will be a year of achievements, with the delivery of guide hall ILL22 and its instruments.

Figure 1

The commissioning of the backscattering spectrometer IN16B was completed in time for the arrival of its first users. The new and extremely challenging phase transformer is working perfectly and six full-size analysers are in the process of being installed.

The three-axis spectrometer ThALES developed in collaboration with Charles University of Prague and with the support of our Spanish Scientific Member, will be constructed in the reactor hall. Figure 1 shows the present state of the space reserved for this instrument, which we hope will prove to be the best in its category.

The bulk of the work scheduled for the long reactor shutdown (August 2013-June 2014) is devoted to the guide hall ILL22, which will house IN15, D22, D16, CRYOEDM, SuperADAM, a free position and WASP, and its guide H5. The building has been extended, a new cooling system has been built for IN15 and WASP, and the guide itself is being completely rebuilt to increase the neutron flux on the instruments and reduce the background on the detectors. D16 will also benefit from no longer being positioned behind a monochromator, which was damaging for its performance.

The wide-angle spin-echo machine WASP is due to be delivered in 2016. One important aspect of this instrument is the construction of the polarisation analyser, which is described in detail later in this report. The guide and the primary spectrometer are under construction. The primary cooling circuit and the supply network are ready to provide power and cooling to the giant precession coil, which is currently under construction (to be delivered early 2015).

The high-resolution spin-echo instrument IN15 will also be completely rebuilt, with new precession coils which will take advantage of the power and cooling circuits mentioned earlier. The instrument will also benefit from the fact that there are no magnetic structures in the reconstructed guide hall. This will make it easier in future to tune the phase of the instrument and should increase the resolution in time.

2013 was a year of transition for the ILL’s Millennium Programme, marking the start of a lot of new work. 2014 will be a year of achievements, with the delivery of guide hall ILL22 and its instruments.

Figure 1

The “hole” in the reactor hall, which will house the three-axis spectrometer ThALES.

Current state of the almost empty guide hall ILL22.
The last two cycles in 2012 were used to commission and test new components. A gain in flux of about an order of magnitude at the sample position has been achieved compared to the previous instrument and IN12’s wavelength range now extends far into the “warmish” region. The upgraded IN12 therefore retains its position as one of the best cold three-axis spectrometers in the world.

Three-axis spectrometers (TAS) have been an essential part of a reactor’s instrument suite since the very beginnings of neutron research. The study of dynamics and elementary excitations (low energy excitations in the case of cold neutron TAS) allows insight into fundamental processes in modern materials. In recent years, substantial progress has been made in particular in neutron optics and many TAS have implemented new components to improve their performance. With the refurbishment of the H14 guide system at the ILL, IN12 has also upgraded its primary spectrometer, giving the instrument a new lease of life.

As the previous position of IN12 is now occupied by D33, IN12 has moved to the Chartreuse side of the guide hall ILL, about 115 m away from the cold source. IN12 is now located at an end position on a newly installed guide with m=2 coating. This means there is more divergence in the guide than was previously the case. To compensate for the curvature of the guide, the outer side is coated with m=2.4. The guide widens vertically from 105 mm to 140 mm to match the mosaicity of the new monochromator crystals. To be able to focus on small spots (1-2 cm²) at the sample position, we use the virtual source concept: the last 8 m of the guide focus horizontally down from 43 to 20 mm in width. At the focusing guide-end, the coating increases to m=3.2. To optimise the transport of the neutrons to the sample position, we use a new double-focusing PG monochromator, comprising 11 x 11 crystals, with a total size of 16 x 20 cm.

A velocity selector in the guide ensures a clean beam, preventing higher order reflections from the monochromator and reducing the background at the sample position. Directly behind the velocity selector, a guide changer with a normal guide element and a polarising cavity guarantees an easy-to-use polarisation set-up.

Thanks to this upgrade, the new IN12 can now access incident wavelengths from 1.4 to 6.3 Å, corresponding to a k of 1 up to about 4 Å⁻¹, and incident energies from 2 up to about 40 meV. In this way, the wavelength range extends into the thermal region compared to the old IN12, where we were limited to a wavelength of 2.3 Å in the cold wavelength range (figure 1). The same figure also shows a gain in flux of about a factor of 10 for a typical wavevector of 2 Å⁻¹. Overall we have also doubled the accessible Q-range. A scan performed with the same sample at the old and the new IN12 and then fitted in the same way confirms this gain in flux (figure 2).

An important feature is the availability of polarised neutrons. The guide changer with the polarising cavity is simple to use and results in a flipping ratio at the sample position of 20 – 27, depending on the wavelength used.

One definite advantage of the upgraded IN12 is its high flux, giving us more and better results. However, the higher energy transfers that are now achievable and the larger accessible Q-range also open up new possibilities which were not available with the previous instrument. With this upgrade, IN12 has become a modern and powerful instrument. Following its shutdown at the end of 2010 and after 2 years of upgrade work, the new IN12 successfully restarted user operation at the end of 2012.

IN12 is operated by the Forschungszentrum Jülich as a CRG-8 instrument at the ILL in collaboration with the CEA Grenoble. Our thanks go to the engineers and technicians from Jülich as well as from the ILL who contributed to the success of this upgrade project.

AUTHORS
K. Schmalzl and W. Schmidt (Jülich Centre for Neutron Science, Germany), S. Raymond and B. Vettard (CEA Grenoble, France) and T. Brückel (Jülich Centre for Neutron Science and PGI, Germany)
Co/Ti supermirror analyser with large detector area coverage for WASP

At the ILL, m = 2.8 Co/Ti supermirrors are manufactured on a large scale for polarising neutrons. Over the last four years, more than two thousand mirrors have been successfully produced with the aim of constructing the world’s largest analyser for the new spin-echo instrument WASP. For the commissioning of the instrument in 2015, we expect to complete the production of 3330 mirrors to cover the first 90° of the analyser angle.

AUTHORS & REFERENCES
P. Courtois, T. Rigault, V. Gaigme, A. Viñas and G. Delphin (ILL)
D. Bourgault (Université Grenoble 1, CNRS, Grenoble, France)

Ferromagnetic Co/Ti supermirrors provide an opportunity to build efficient spin-analyser devices for cold neutron instruments. They consist of alternating layers of cobalt and titanium with graded thicknesses varying from 50 Å to 600 Å, deposited on a glass or silicon substrate. A Co/Ti supermirror only reflects the neutron spin component that is parallel to the magnetic field applied to the mirror (the spin-up component). Spin-down neutrons are not reflected but are transmitted into the layers. To absorb the transmitted neutrons before they reach the substrate, an anti-reflecting layer of Gd/Ti is introduced between the supermirror and the substrate. Such absorbing layers make it possible to maximise the angular and wavelength range for the spin-up neutrons.

Co/Ti supermirrors with anti-reflecting layers will be used to build the large polarisation analyser for the new spin-echo instrument WASP. The analyser design, based on Schildknecht-type C-shaped benders and described in [1], is inspired by the design of the D7 analyser upgrade [2]. With a total area of 636 m², which is equivalent to the area of 3 tennis courts, it is composed of 8800 m = 2.8 Co/Ti supermirrors, double-sided coated on borated float glass. The full scale analyser covers a large solid angle of 0.197 steradians for a horizontal scattering angle of 240°. The new instrument WASP will be equipped with the largest neutron-spin analyser in the world!

Supermirrors are produced at the ILL using the magnetron sputtering machine Pi (Figure 1). An m = 2.8 Co/Ti supermirror consists of 500 layers of Co/Ti and 41 layers of Gd/Ti. Multilayers are deposited on 0.2 mm-thick glass substrates by DC magnetron sputtering at a low argon pressure of approximately 10⁻³ mbar. The substrate dimensions of 254 x 141 x 0.2 mm³ were chosen to fit the instrument geometry and to maximise the number of substrates coated per process, making it possible to produce 12 one-sided coated supermirrors per day.

The magnetic properties of m = 2.8 Co/Ti supermirrors were investigated using a vibrating sample magnetometer at the CNRS, Grenoble (Figure 2). The easy axis of magnetisation is parallel to the direction of the substrate movement during the deposition process. Such measurements indicate that an external magnetic field of at least 40 mT must be applied on the mirror in order to reach magnetic saturation.

Each production batch is checked using the ILL neutron reflectometer T3 at a neutron wavelength of 7.5 Å. Figure 3 shows the performance of a typical supermirror produced recently for the WASP project. With a neutron reflectivity of the spin-up component of better than 70 % and polarisation efficiency higher than 90 %, these Co/Ti supermirrors demonstrate high performances for polarisation analysis.

After neutron characterisation, the mirrors will be mounted into special cassettes, which hold them with a bending radius of about 7 m (Figure 4) and a spacing of 1 mm between adjacent mirrors. Each cassette contains 37 mirrors and corresponds to a horizontal scattering angle of 1° from the sample position. The cassettes will then be installed in a suitable magnetic device which provides a magnetic field strong enough to maintain full magnetisation of the supermirrors [1].

Today enough mirrors have been produced to cover about 55° of the analyser. To facilitate operations and improve the reliability of the process, a new programmable logic controller was installed on the Pi machine in 2013. As a direct result, we expect to increase the production rate by 20% in the coming years. Instrument commissioning is due to take place at the end of 2015, with 90° of analyser coverage.

With the magnetron sputtering machine Pi, it is possible to produce 0.42 m² of m = 2.8 Co/Ti supermirrors per day.
0.1 K closed-cycle four-circle dilution cryostat on D10

The full determination of magnetic ground states is a key point in understanding the fundamental properties of magnetic materials. The determination of the magnetic structure factors requires access to the three dimensions of reciprocal space using single-crystal four-circle geometry.

A four-circle dilution cryostat that avoids the influence of gravity by using a capillary dilution chamber was developed [1,2] for experiments below 2 K. This system, where the sample was cooled down to 110 mK by a gravity-insensitive dilution refrigerator, was successfully used on D10 for several years. However, it did present certain disadvantages: autonomy was limited to a few days, the re-distillation of the $^3$He was done off-site, and temperature stability was difficult to maintain when rotating the phi shaft. To overcome these difficulties, a completely new closed-cycle dilution cryostat with four-circle diffraction accessibility has been developed.

THE GRAVITY-INSENSITIVE DILUTION SYSTEM

A dilution refrigerator is commonly used to reach very low temperatures. In the so-called mixing box, where the cooling power is available, the two phases of the $^3$He-$^4$He mixture are separated by gravity, the lighter $^3$He-rich phase being above the heavier $^4$He-poor phase. For applications where the system has to support a random position on the earth or even for space applications, a gravity-independent dilution refrigerator can be made by directly mixing the two isotopes in narrow capillaries.

For D10, in order to cope with the 4-circle geometry, we adopted the original system that was developed for space applications and successfully used in the Planck mission [3]. In a conventional dilution system, only the $^3$He isochores circulate. The interface between the concentrated and the diluted phases is localized by gravity within the mixing chamber. In our cryostat, we apply the closed-cycle dilution refrigerator principle. The key idea of the dilution process is to inject and mix both helium isotopes through two capillaries in a $Y$-junction, and to recover the mixture through a third capillary.

At low temperature (< 0.1 K), the dilute phase has a finite solubility of $^3$He of at 6%. If the $^3$He concentration exceeds this value, not all $^3$He is diluted and some stays in the $^3$He-rich phase, forming $^3$He droplets. In this design, the $^3$He-rich phase droplets fill the cross-section of the capillaries, where the capillary forces play the role of gravity.

THE ISOTOPE MIXTURE SEPARATION SYSTEM

Once mixed in the dilution refrigerator, the $^3$He and $^4$He are pumped at low pressure and processed in the isotope separation system. The continuous separation process is still on conventional dilution at about 0.8 K, where the $^3$He concentration in the vapour is about 65%. In this process, originally developed for space application [4], the $^3$He is extracted by a fountain pump exploiting the unique superfluid properties of this isotope. The fully automated gas-handling system shown in figure 2 was developed in order to operate the isotope separation system. The flows required for the dilution refrigerator (figure 1) are regulated by two mass flow controllers (about 20 cc/min $^3$He and 40 cc/min $^4$He). The gases are then recompressed to the required dilution-refrigerator inlet pressure of about 2 bar.

FIRST RESULTS

The new system was commissioned in 2013 and three diffraction experiments were conducted on problems requiring access to more than one plane of reciprocal space at temperatures below 1.6 K. One of the investigations performed was the study of the long-range order in bond-disordered spin ½ antiferromagnetic Hassenberg chains. Cu$_2$(C$_5$H$_5$N)$_2$Cl$_2$ belongs to the family of S=1/2 chains compounds, where bond disorder, due to a small random variation in the Cu-X-Cu bond angle, leads to a random singlet phase. This phase is crucial for superexchange interactions between Cu$^{2+}$ ions. The magnetic ground state was studied in order to understand this bond disorder. The Cu$_2$(C$_5$H$_5$N)$_2$Cl$_2$ compound presents an incommensurate antiferromagnetic state below $T_N=1.15$ K with a propagation vector $k$=[1/3 0.4 1/3]. A set of magnetic and nuclear Bragg reflections was measured during the allocated beamtime.

As shown in figure 3, the new dilution system is capable of maintaining a base temperature of 107 mK while rotating the sample. Thanks to this excellent temperature stability, it was possible to measure the temperature dependence of the magnetic reflection and determine a magnetic transition at $T_N=1.15$ K (figure 4).

ACKNOWLEDGMENTS

We would like to thank M. Theba and E. Rassouche for providing their preliminary results.

AUTHORS & REFERENCES


(1) A. Benoît, M. Caussignac, and S. Pujol, Physica B 169 (1991) 457
(2) A. Benoît, M. Caussignac, and S. Pujol, Physica B 197 (1994) 48
(3) S. Triguiermann, I. Smit, Ph. Comes, A. Benoît and G. Guyot, Cryogenics 46 (2006) 268
Slow-neutron mirrors from holographic nanoparticle-polymer composites

Neutron optics theory is based on the one-particle Schrödinger equation, which contains the optical potential for a particular material or, equivalently, the neutron refractive index at a certain neutron wavelength. Provided we can tune the value of the refractive index for neutrons and provide us with destructive refractive-index structures on or materials, dispersive neutron-optical elements become feasible.

A simple one-dimensional grating structure - periodically modulated along a single direction - can be characterised by a modulated refractive index.

The most common grating structures in neutron optics are probably crystals, which are used in a variety of devices, such as monochromators, wavelength analysers, polarisers and beam splitters for neutron interferometry. However, for cold and very cold neutrons, the grating period of crystals is usually much too small. As an alternative, artificial structures are used that offer a wide range of production processes and available materials (see for instance [1-3]). In addition to techniques such as sputter-etching and lithography, artificial grating structures can also be produced by optical holography, where signal and reference light beams are superposed at the position of a photosensitive recording material held between two glass slides, as shown in figure 1. This superposition results in a periodic light-intensity pattern in the recording material which modulates the density of a one of its ingredients, for example via an intensity-dependent photo-polymerisation process. The resulting hologram can be used as neutron diffraction grating (figure 2).

We use nanoparticle-polymer composites as recording materials. The embedded nanoparticles have an average core diameter of about 13 nm with a size distribution of approximately ± 5 %. The nanoparticle sol is dispersed in a (meth)acrylate monomer. A photoinitiator is added to enable the monomer to polymerise on illumination with light.

Before recording, the photoinitiator, the monomer and the nanoparticles are homogeneously distributed in the sample material. Thanks to the photoinitiator, the light-intensity pattern triggers polymerisation in the bright sample regions. This process consumes monomers, which diffuse from dark to bright regions. As a consequence, the nanoparticles move from bright to dark regions, producing an approximately sinusoidal nanoparticle-concentration pattern, which acts as neutron-diffraction grating.

One major advantage of nanoparticle-containing materials is their optical quality and versatility [4], due to the wide range of possible isotopes that can be embedded to select the value of the refractive index. For instance, holographic gratings with superparamagnetic nanoparticles could potentially be used as polarising beam splitters for cold neutrons. Due to the interplay of nuclear and magnetic interactions, such gratings could act as mirrors for one neutron spin state, while being virtually transparent for the other.

Figure 3 shows the results of neutron diffraction experiments carried out at the very cold neutron beam port of PF2 with free-standing NP-polymer film gratings. Here, the glass plates used for preparation and recording are coated with silane so that they can be easily removed from the surface of the polymer sample after recording, thus reducing incoherent scattering and neutron absorption.

This type of free-standing film grating with a periodicity of 0.5 μm, 100 μm thickness and 20 vol% SiO₂ nanoparticle concentration was shown to exhibit 90% reflectivity, i.e. mirror-like behaviour, for a neutron wavelength of about 4.1 nm [5].

**Authors & References**

J. Klepp and M. Fally (University of Vienna, Austria)
P. Geltenbort (ILL)
C. Pruner (University of Salzburg, Austria)
Y. Tomita (University of Electro-Communications, Tokyo, Japan)

A digital constant fraction discriminator for fast timing studies
in the picosecond range

Over the course of two reactor cycles, the EXILL measurement campaign provided the ideal test bench for the development of a new digital constant fraction discriminator implemented in a dedicated FPGA. The new hardware offers a fast algorithm for determining on-line the arrival time of an event with a time resolution in the tenth-of-a-picosecond range. The results obtained with our new digital electronics are comparable to those from equivalent analogue systems.

WHY A DIGITAL CONSTANT FRACTION DISCRIMINATOR?

Thermal or cold neutron capture on different fissioning systems is an excellent method for producing a variety of very neutron-rich nuclei. Since neutrons at these energies bring to the reaction just enough energy to produce fission, the fragments remain neutron-rich due to negligible neutron evaporation, thus allowing detailed nuclear structure studies on exotic nuclei. The de-excitation of nuclear excited states takes place on a timescale ranging from a few femtoseconds to up to several nanoseconds or more. Although longer lifetimes can be measured using fast digitizers with sampling frequencies of 1 or 2 GHz, it is more complex to obtain time resolution in the picosecond range. The conventional approach consists of using a number of analogue constant fraction discriminators (CFD) to determine the start and stop pulses, and time-to-amplitude converters (TAC) to measure the time difference between them. It is easy to see how the complexity of the setup together with instabilities in the analogue electronics might produce errors in the time determination.

THE DIGITAL APPROACH

The incentive for designing a digital CFD is the possibility of producing very accurate pulse-time information. In the ideal case, this signal is precisely related in time to the occurrence of an event, thus eliminating the amplitude-dependent time walk. In order to provide an alternative to the standard analogue approach, we have developed a new real-time digital CFD system. The goal was to maintain the excellent performances of the TAC, capable of time resolution in the 10 ps range. Our design, which is fully implemented in hardware, does not add any dead time to the acquisition chain. The system consists of two main elements: a number of digitizers to match the required number of channels and a digital CFD card providing a real-time CFD algorithm for timing accuracy. A CAEN V1751 (8 channels, 10 bits, 1 GS/s) waveform digitizer [1] samples the analogue signal from the detector. Since the digitizer has several memory buffers for the trigger signals, the acquisition can take place without any loss of events, irrespective of their frequency and duration, at least until the readout rate allows the buffer memory to be emptied. Each channel has an SRAM memory buffer with independent read-write access divided into 1 to 1024 buffers of programmable size. The board houses a daisy-chain optical link capable of transferring data at 80 MB/s. The digital CFD board, shown in Figure 1, consists of a Xilinx Virtex-6T FPGA and including 1 GB of DDR3 shared memory. The board is the result of a joint development project between the company IoXoS in Switzerland and the ILL. Using the board’s edge-to-edge interconnection solution, which provides full PCB front-end area utilization, we are able to communicate with the optical link of the digitizers using the CAEN proprietary protocol CONET2 and to read out the data stored in the circular buffers of the flash ADC at a very high event rate. The main purpose of the digital CFD board is to perform a specific CFD algorithm on the sampled pulse shape to obtain accurate timing in the ps range. In this way, only the digitizer’s time-stamp and the calculated event arrival time are stored in the event-mode data flow, thus reducing considerably the amount of recorded data.

FIRST RESULTS

The left part of Figure 2 shows the results obtained using a pulse generator to reproduce the detector pulses. By sending the same pulse into a different channel of the acquisition chain, it was possible to evaluate the intrinsic time resolution achievable with the adopted electronics and CFD algorithm. After tuning the algorithm’s parameters, we obtained a dispersion of 14 ps. The second part of the test was performed using a 22Na radioactive source placed between two LaBr₃(Ce) detectors. An energy window centered on the 5.4 keV annihilation line was used to select the relevant events from the background to avoid random coincidences. As the two y-lines are emitted at the same time, no lifetime contribution is expected in the time distribution. The latter therefore represents a direct measurement of the intrinsic time resolution of the system. The right part of Figure 2 depicts our results with a FWHM of the time distribution of about 400 ps, which includes all uncertainties concerning the scintillator and photomultiplier, electronics and setup geometry. These results are compatible with those in [2] obtained with an analogue system.

The digital CFD board, a joint development project between the Swiss company IoXoS and the ILL.
The ILL User Support team is dedicated to helping all visiting researchers to make the most of its facilities. If you are coming to the ILL to carry out experiments, the User Office is here to give you the organisational and administrative support you need to successfully perform your experiments.

Neutron beams and instrument facilities are free of charge for proposers of accepted experiments. Scientists affiliated to the Institute’s member countries will also, in general, be assisted with necessary travel and daily subsistence for a limited period.

The User Support Team makes all arrangements for accommodation and will process claims for expenses after you have completed your experiment.

If you would like more information about the Institute’s facilities, application for beamtime, user support and experimental programme, please visit our web site.

http://www.ill.eu/users
THE ILL USER CLUB
All administrative tools for our scientific visitors are grouped together and directly accessible on the web, thanks to the User Club. All information is presented in a user-friendly environment. After having logged in with your own personal identification, you will have direct access to all the available information which concerns you. Users with particular responsibilities have privileged access to other tools, according to their role. The User Club includes the electronic proposal and experimental reports submission procedures, and electronic peer review of proposals. Additional electronic services have also been put in place: acknowledgment of proposals, submissions results, invitation letters, user satisfaction forms and so on.

PROPOSAL SUBMISSION
There are different ways of submitting a proposal to the ILL:
- **Standard submission** – twice a year – via the Electronic Proposal System (EPS).
- **Long-Term Proposals** – once a year – via the Electronic Proposal System (EPS).
- **EASY** access system (EASY) throughout the year.
- **Director’s Discretion Time (DDT)** throughout the year.
- **Special access** for proprietary research and industrial users.

Submission of a standard research proposal
Applications for beamtime should be submitted electronically, via our website at http://www.ill.eu/users/applying-for-beamtime/

**Easy Access System**
The Easy Access System (EASY) grants admission beamtime to scientists from ILL member countries, who need a rapid structural characterisation of samples and data analysis. Access is open all year long, and it does not go through the ILL standard proposal round and consequent peer review system.

The system offers one neutron/day per cycle, on 4 instruments (D1A, D2B, D16 and OrientExpress) to perform very short experiments at room temperature. The users will not be invited to the ILL, but will send their samples to one of two dedicated ILL scientists, who will be responsible for the measurements and sample radiological control. The ILL will ship back the samples once the measurement is finished. You can apply for EASY beamtime on the Visitors Club. More information is available at http://club.ill.eu/Easy/EASY_Guidelines.pdf

**Long-Term Proposals**
Users from ILL member countries can also apply for extended periods of beamtime, by submitting a Long-Term Proposal (LTP). Its purpose is to facilitate the development of instrumentation, techniques or software – which could be beneficial to the ILL community as a whole - through the award of beamtime over several cycles. The total amount of beamtime that may be allocated to LTPs on any particular instrument is capped at 10%, and beamtime is not awarded to LTPs to perform science beyond essential testing.

LTPs can be submitted once a year at the autumn proposal round using the specific LTP application form. The primary criterion for acceptance of a LTP is the excellence of the science that it will ultimately enable. The length of LTP projects is expected to be 3 years typically, with continuation approved at the end of each year, based on an annual report; a final report is also required at the end of the project. More details are given at http://www.ill.eu/users/applying-for-beamtime/

**Submission of a proposal to the Director’s Discretion Time**
This option allows a researcher to obtain beamtime quickly, without going through the peer-review procedure. DDT is normally used for “hot” topics, new ideas, feasibility tests and to encourage new users. Applications for Director’s Discretion Time can be submitted to the Head of the Science Division, Prof. Helmut Schober, at any time.

**Experimental reports**
Users are asked to complete an experimental report on the outcome of their experiments. The submission of an experimental report is compulsory for every user who is granted ILL beamtime. Failure to do so may lead to rejection in case of application for beamtime for a continuation proposal.

All ILL experimental reports are archived electronically and searchable via the web server as PDF files (under http://club.ill.eu/rv/). Experimental reports for experiments performed in 2012 are included in the CD-ROM of this year’s Annual Report.

COLLABORATIVE RESEARCH GROUP INSTRUMENTS
The ILL provides a framework in which Collaborating Research Groups (CRGs) can build and manage instruments at the ILL to carry out their own research programmes. CRGs represent a particularly successful form of long-term international scientific collaboration. They are composed of scientists from one or two research disciplines, and often multinational, carrying out a joint research programme centred around a specific instrument. CRGs enjoy exclusive access to these instruments for at least half of the beamtime available. The CRGs provide their own scientific and technical support and cover the general operating costs of these instruments. If there is demand from the user community and the resources are available, the beamtime reserved for ILL can be made accessible to users via the subcommittees.

There are currently three different categories of CRG instrument:
- **CRG-A** in which the external group leases an instrument owned by the ILL. They have 50% of the beamtime at their disposal and for the remaining 50% they support ILL’s scientific user programme.
- The **CRG-B** category owns their instrument and retains 70% of the available beamtime, supporting the ILL programme for the other 30%.
- Finally, **CRG-C** instruments are used full time for specific research programmes by the external group, which has exclusive use of the beam.

**SUPPORT LABORATORIES**
The opportunities we offer to our users extend beyond the privileges of access to the world’s leading suite of neutron instruments. The ILL - in collaboration with the ESF and other institutes - is actively responding to the needs of scientists unfamiliar with neutron techniques and in need of training and support facilities. New support facilities have been already set up on the ILL site. For more information see the chapter “More than simply neutrons”, p. 106.

**ACCESS FOR INDUSTRIAL USERS**
Besides academic research, ILL’s instruments are used by a wide range of industries from pharmaceutical and chemical companies to materials and process engineering, energy and environment sectors. Neutron techniques are of particular interest in the industrial context as they provide unique and essential informations at the atomic and molecular level.

The Business Development Office (BDO) is the single point of contact for industry to use ILL neutrons scattering instruments. The Business Development Office will match the needs of industrial customers, direct them towards the best technique and scientists and takes cares of the administrative procedures. The BDO will provide to industrial customers a fast proprietary access and confidentiality under specific contract giving access to any of the world leading scientific instruments of the ILL. The BDO may also act a dedicated R&D partnerships for technological research with consortium including academic and industrial partners. Contact Jérôme Beaucour, beaucour@ill.eu

If you are not yet registered in the Visitors Club and you wish to join it, you can register directly at http://club.ill.eu/ev/
THE ILL USER COMMUNITY

The ILL welcomed 1269 users in 2013, including 290 from France, 226 from Germany and 216 from the UK (Figure 1). Many of our visitors were received more than once (for a total of 1767 user visits).

We value feedback from our users as an indicator of how well our facility is fulfilling their needs and to initiate actions when this is not the case (Figure 2).

The User Satisfaction Form is a means of finding out what our users think of the facility. Users who have just finished an experiment at the ILL are asked to complete the questionnaire on the User Club and give us their views on different topics. User comments are made available to managers for their information and actions when appropriate. User feedback rate was about 65% in 2013.

INSTRUMENTS

The instrumental facilities at the ILL are shown in the schematic diagram on page 98. Besides the 28 ILL instruments, there are 9 CRG-instruments (marked with an asterisk *):

- Powder diffractometers: D1B*, D2B, D20, SALSA.
- Fundamental physics instruments: PF1, PF2, S18*.
- Nuclear physics instruments: PN1, PN3.
- Time-of-flight spectrometers: BRISP*, IN4, IN5, IN6.
- Backscattering and spin-echo spectrometers: IN11, IN13*, IN15, IN16B.
- Nuclear physics instruments: PN1, PN3.
- Fundamental physics instruments: PF1, PF2, S18*.

ILL and IN15 have a special status, since they are joint ventures of the ILL with other laboratories: in the case of ILL and EMBL and for IN15 with FZ Jülich and HZB Berlin. Cyto-EDM is a CRG-C instrument and is not available as a ‘user’ instrument.

Details of the instruments can be found on the web at http://www.ill.eu/instruments-support/instruments-groups/.

USER AND BEAMTIME STATISTICS

<table>
<thead>
<tr>
<th>Country</th>
<th>Requested days</th>
<th>Requested in %</th>
<th>Allocated days</th>
<th>Allocated in %</th>
<th>Allocated days</th>
<th>Allocated in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR</td>
<td>1514.79</td>
<td>26.37</td>
<td>787.54</td>
<td>27.81</td>
<td>814.65</td>
<td>26.77</td>
</tr>
<tr>
<td>UK</td>
<td>278.24</td>
<td>5.00</td>
<td>157.03</td>
<td>5.00</td>
<td>158.57</td>
<td>5.02</td>
</tr>
<tr>
<td>DE</td>
<td>276.90</td>
<td>5.00</td>
<td>143.89</td>
<td>4.68</td>
<td>132.57</td>
<td>4.19</td>
</tr>
<tr>
<td>IT</td>
<td>216.79</td>
<td>5.00</td>
<td>127.03</td>
<td>4.19</td>
<td>127.03</td>
<td>4.19</td>
</tr>
<tr>
<td>CA</td>
<td>188.42</td>
<td>3.27</td>
<td>18.81</td>
<td>0.60</td>
<td>18.87</td>
<td>0.60</td>
</tr>
<tr>
<td>AU</td>
<td>138.90</td>
<td>2.43</td>
<td>67.06</td>
<td>2.11</td>
<td>67.06</td>
<td>2.11</td>
</tr>
<tr>
<td>NL</td>
<td>30.18</td>
<td>0.52</td>
<td>19.18</td>
<td>0.61</td>
<td>19.22</td>
<td>0.61</td>
</tr>
<tr>
<td>AU</td>
<td>321.14</td>
<td>5.58</td>
<td>191.13</td>
<td>6.05</td>
<td>172.07</td>
<td>5.44</td>
</tr>
<tr>
<td>IN</td>
<td>113.14</td>
<td>2.00</td>
<td>67.83</td>
<td>2.21</td>
<td>67.83</td>
<td>2.21</td>
</tr>
<tr>
<td>CH</td>
<td>113.14</td>
<td>2.00</td>
<td>67.83</td>
<td>2.21</td>
<td>67.83</td>
<td>2.21</td>
</tr>
<tr>
<td>UK</td>
<td>66.23</td>
<td>1.18</td>
<td>26.21</td>
<td>0.87</td>
<td>25.56</td>
<td>0.82</td>
</tr>
<tr>
<td>SL</td>
<td>176.89</td>
<td>3.13</td>
<td>100.33</td>
<td>3.28</td>
<td>100.33</td>
<td>3.28</td>
</tr>
<tr>
<td>JP</td>
<td>14.89</td>
<td>0.26</td>
<td>9.88</td>
<td>0.31</td>
<td>9.88</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Total: 3735.16

Beamtime allocation in 2013: distribution amongst the different research areas (a) and colleges (b).

Table 1

In 2013, the ratio of accepted to rejected proposals amongst the different research areas and colleges is given in Figure 3. In 2013, the member countries of the ILL were: France, Germany, UK, Austria, Belgium, the Czech Republic, Denmark, Hungary, Italy, Poland, Slovakia, Spain, Sweden, Switzerland and India.

Table 1 gives the beamtime distribution amongst the different member countries (request and allocation in 2013). In calculating the statistics of beamtime per country, the attribution is based on the location of the laboratory of the proposer, not their individual nationality. For a proposal involving laboratories from more than one member country, the total number of days is divided amongst the collaborating countries, and weighted by the number of people for each country. Local contacts are not counted as proposers except when they are members of the research team.

The beamtime requested by and allocated to scientists from ILL, ESRF or EMBL is allocated to the member countries according to a weighting system based on the fractional membership of the country of the institute concerned. When a proposal involves collaboration with a non-member country, the allocated time is attributed entirely to the collaborating member country (or countries) and weighted by the number of people for each member country. Proposals for which all proposers are from non-member countries do not appear in this table. This explains why the total number of allocated days differs from Table 2.

Figure 1

National affiliation of ILL users in 2013.

User satisfaction survey results for 2013, compared with those obtained in previous years.
A more complete view of beamtime use is given in Table 2. Request and allocation of beamtime as well as the number of scheduled experiments refer to standard submissions to the Request and allocation of beamtime as well as the number of scheduled experiments refer to standard submissions to the

**INSTRUMENT PERFORMANCE**

Table 2 also gives a summary of instrument performance for 2013. For each cycle, a record is kept of any time lost from the total available beamtime and the reasons for the lost time are analyzed for all the instruments. The table gives a global summary for the year.

Overall 4184 days were made available to our users in 2013 on ILL and CRG instruments, which represents about 78.5% of the total days of operation. 220 days were used by ILL scientists on ILL and CRG instruments, which represents about 78.5 % of the total available beamtime. In 2013, 432 out of 5327 days were lost due to various malfunctions, which represent about 8 % of the total available beamtime.

Beam days delivered for science in 2013 amount to 4404 (used for users and internal research).

**Detailed comments on the larger beamtime losses (above 25 days) are as follows:**

- NS lost 18 days during the first cycle and 15 days during the second one, because of chopper and chopper electronics failures.
- On PN1, the entire first cycle was lost since no target change could be made: an end-switch contact/cable of the sample changer was damaged during the VS maintenance in the shutdown. The problem was recognised during the first target change, but no repair intervention was possible in the primary casemate during reactor operation.
- GAMS -5 lost 24 days because the AV- system and the He-Ne laser frequency stabilisation were broken; in addition it could not work for 12 days during the second cycle because the antivibrational system was not stable.

**Beamtime request/allocation has standard subcommittees and Director Discretion Time (DDT) together by instrument and instrument performance CRG instruments are in brown.**

---

**EXPERIMENTAL AND USER PROGRAMME**

**USER AND BEAMTIME STATISTICS**

**INSTRUMENT PERFORMANCE**

Table 2 also gives a summary of instrument performance for 2013. For each cycle, a record is kept of any time lost from the total available beamtime and the reasons for the lost time are analyzed for all the instruments. The table gives a global summary for the year.

Overall 4184 days were made available to our users in 2013 on ILL and CRG instruments, which represents about 78.5% of the total days of operation. 220 days were used by ILL scientists on ILL and CRG instruments, which represents about 78.5 % of the total available beamtime. In 2013, 432 out of 5327 days were lost due to various malfunctions, which represent about 8 % of the total available beamtime.

Beam days delivered for science in 2013 amount to 4404 (used for users and internal research).

**Detailed comments on the larger beamtime losses (above 25 days) are as follows:**

- NS lost 18 days during the first cycle and 15 days during the second one, because of chopper and chopper electronics failures.
- On PN1, the entire first cycle was lost since no target change could be made: an end-switch contact/cable of the sample changer was damaged during the VS maintenance in the shutdown. The problem was recognised during the first target change, but no repair intervention was possible in the primary casemate during reactor operation.
- GAMS -5 lost 24 days because the AV- system and the He-Ne laser frequency stabilisation were broken; in addition it could not work for 12 days during the second cycle because the antivibrational system was not stable.

**Beamtime request/allocation has standard subcommittees and Director Discretion Time (DDT) together by instrument and instrument performance CRG instruments are in brown.**

---

**EXPERIMENTAL AND USER PROGRAMME**

**USER AND BEAMTIME STATISTICS**

**INSTRUMENT PERFORMANCE**

Table 2 also gives a summary of instrument performance for 2013. For each cycle, a record is kept of any time lost from the total available beamtime and the reasons for the lost time are analyzed for all the instruments. The table gives a global summary for the year.

Overall 4184 days were made available to our users in 2013 on ILL and CRG instruments, which represents about 78.5% of the total days of operation. 220 days were used by ILL scientists on ILL and CRG instruments, which represents about 78.5 % of the total available beamtime. In 2013, 432 out of 5327 days were lost due to various malfunctions, which represent about 8 % of the total available beamtime.
### INSTRUMENT LIST - DECEMBER 2013

#### ILI INSTRUMENTS

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>D28</td>
<td>powder diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D3</td>
<td>single-crystal diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D4 (50% with IN1)</td>
<td>liquids diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D7</td>
<td>diffuse-scattering spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>D9</td>
<td>single-crystal diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D10</td>
<td>single-crystal diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D11</td>
<td>small-angle scattering diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D16</td>
<td>small momentum-transfer diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D17</td>
<td>reflectometer</td>
<td>operational</td>
</tr>
<tr>
<td>D19</td>
<td>single-crystal diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D20</td>
<td>powder diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D22</td>
<td>small-angle scattering diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>D33</td>
<td>small-angle scattering diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>FIGARO</td>
<td>horizontal reflectometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN1 - LAGRANGE (50% with D4)</td>
<td>small-angle scattering spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN4</td>
<td>time-of-flight spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN5</td>
<td>time-of-flight spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN6</td>
<td>time-of-flight diffractometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN8</td>
<td>three-axis spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN11</td>
<td>spin-echo spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN13</td>
<td>backscattering spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN16</td>
<td>backscattering spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>IN20</td>
<td>three-axis spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>PF1</td>
<td>neutron beam for fundamental physics</td>
<td>operational</td>
</tr>
<tr>
<td>PF2</td>
<td>ultracold neutron source for fundamental physics</td>
<td>operational</td>
</tr>
<tr>
<td>PN1</td>
<td>fusion product mass-spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>PN3 - GAMS</td>
<td>gamma-ray spectrometer</td>
<td>operational</td>
</tr>
<tr>
<td>SALSA</td>
<td>strain analyser for engineering application</td>
<td>operational</td>
</tr>
<tr>
<td>VIVALDI</td>
<td>thermal neutron Laue diffractometer</td>
<td>on hold</td>
</tr>
</tbody>
</table>

#### CRG INSTRUMENTS

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRISP</td>
<td>Brillouin spectrometer</td>
<td>CRG-B operational</td>
</tr>
<tr>
<td>CRYO EDM</td>
<td>installation for the search for the neutron electric dipole moment</td>
<td>CRG-C operational</td>
</tr>
<tr>
<td>D18</td>
<td>powder diffractometer</td>
<td>CRG-A operational</td>
</tr>
<tr>
<td>D23</td>
<td>single-crystal diffractometer</td>
<td>CRG-B operational</td>
</tr>
<tr>
<td>GRANIT</td>
<td>gravitation state measurement</td>
<td>CRG operational</td>
</tr>
<tr>
<td>IN12</td>
<td>three-axis spectrometer</td>
<td>CRG-B operational</td>
</tr>
<tr>
<td>IN13</td>
<td>backscattering spectrometer</td>
<td>CRG-A operational</td>
</tr>
<tr>
<td>IN22</td>
<td>three-axis spectrometer</td>
<td>CRG-B operational</td>
</tr>
<tr>
<td>SuperADAM</td>
<td>reflectometer</td>
<td>CRG-B operational</td>
</tr>
<tr>
<td>S18</td>
<td>interferometer</td>
<td>CRG-B operational</td>
</tr>
</tbody>
</table>

#### JOINTLY FUNDED INSTRUMENTS

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>LADI (50%)</td>
<td>Laue diffractometer</td>
<td>operated with DVBII</td>
</tr>
<tr>
<td>IN15</td>
<td>spin-echo spectrometer</td>
<td>operated with FZ Jülich and HZB Berlin</td>
</tr>
<tr>
<td>GRANIT</td>
<td>gravitation state measurement</td>
<td>operated with LUP (LJF, CNRS)</td>
</tr>
</tbody>
</table>

#### TEST AND CHARACTERISATION BEAMS

<table>
<thead>
<tr>
<th>Beam</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT1, CT2</td>
<td>detector test facilities</td>
</tr>
<tr>
<td>CYCLOPS</td>
<td>Laue diffractometer</td>
</tr>
<tr>
<td>TOMOGRAPHY</td>
<td>neutronography</td>
</tr>
<tr>
<td>OrientExpress</td>
<td>Laue diffractometer</td>
</tr>
<tr>
<td>T3</td>
<td>neutron optics test facility</td>
</tr>
<tr>
<td>T13A, C</td>
<td>monochromator test facility</td>
</tr>
<tr>
<td>T17</td>
<td>cold neutron test facility</td>
</tr>
</tbody>
</table>
INSTRUMENT LIST - DECEMBER 2013

ILL INSTRUMENTS

D2B powder diffractometer operational
D3 single-crystal diffractometer operational
D4 (50% with IN1) liquids diffractometer operational
D7 diffuse-scattering spectrometer operational
D9 single-crystal diffractometer operational
D10 single-crystal diffractometer operational
D11 small-angle scattering diffractometer operational
D12 small-angle scattering diffractometer operational
D16 small momentum-transfer diffractometer operational
D17 reflectometer operational
D19 single-crystal diffractometer operational
D20 powder diffractometer operational
D22 small-angle scattering diffractometer operational
D33 small-angle scattering diffractometer operational
FIGARO horizontal reflectometer operational
IN1- LAGRANGE (50% with D4) three-axis spectrometer operational
IN4 time-of-flight spectrometer operational
IN5 time-of-flight spectrometer operational
IN6 time-of-flight spectrometer operational
IN8 three-axis spectrometer operational
IN11 spin-echo spectrometer operational
IN14 three-axis spectrometer operational
IN16 backscattering spectrometer operational
IN18 backscattering spectrometer operational
IN20 three-axis spectrometer operational
PF1 neutron polarizer device for fundamental sciences operational
PF2 neutron polarizer for fundamental sciences operational
PF3 neutron polarizer device for fundamental sciences operational
PF4 neutron polarizer for fundamental sciences operational
PF5 neutron polarizer for fundamental sciences operational
PF6 neutron polarizer for fundamental sciences operational
PF7 neutron polarizer for fundamental sciences operational
PF8 neutron polarizer for fundamental sciences operational
PH2A neutron polarizer for fundamental sciences operational
PH2B neutron polarizer for fundamental sciences operational
PH2C neutron polarizer for fundamental sciences operational
PH2D neutron polarizer for fundamental sciences operational
PH2E neutron polarizer for fundamental sciences operational
PH2F neutron polarizer for fundamental sciences operational
PH2G neutron polarizer for fundamental sciences operational
PH2H neutron polarizer for fundamental sciences operational
PH2I neutron polarizer for fundamental sciences operational
PH2J neutron polarizer for fundamental sciences operational
PH2K neutron polarizer for fundamental sciences operational
PH2L neutron polarizer for fundamental sciences operational
PH2M neutron polarizer for fundamental sciences operational
PH2N neutron polarizer for fundamental sciences operational
PH2O neutron polarizer for fundamental sciences operational
PH2P neutron polarizer for fundamental sciences operational
PH2Q neutron polarizer for fundamental sciences operational
PH2R neutron polarizer for fundamental sciences operational
PH2S neutron polarizer for fundamental sciences operational
PH2T neutron polarizer for fundamental sciences operational
PH2U neutron polarizer for fundamental sciences operational
PH2V neutron polarizer for fundamental sciences operational
PH2W neutron polarizer for fundamental sciences operational
PH2X neutron polarizer for fundamental sciences operational
PH2Y neutron polarizer for fundamental sciences operational
PH2Z neutron polarizer for fundamental sciences operational

CRG INSTRUMENTS

D23 single-crystal diffractometer CRG-B operational
GRANIT gravitation state measurement CRG operational
IN12 three-axis spectrometer CRG-B operational
IN13 backscattering spectrometer CRG-A operational
IN22 three-axis spectrometer CRG-B operational
SuperADAM reflectometer CRG-B operational
S18 interferometer CRG-B operational

JOINTLY FUNDED INSTRUMENTS

LADI (50%) Laue diffractometer - operated with EMBL
IN15 single-crystal diffractometer - operated with D2B, D4, D7, D9, D10, D11, D12, D16, D17, D19, D20, D22, D33, FIGARO

TEST AND CHARACTERISATION BEAMS

CT1, CT2 detector test facilities
CYCLOPS Laue diffractometer
OrientExpress Laue diffractometer
T3 neutron optics test facility
T13A, C monochromator test facility
T17 cold neutron test facility
"I would like to stress the importance and quality of the safety evaluation report you submitted on 15 September 2011. It corresponded well to the specifications and enabled an analysis to be performed of the robustness of your installations and of your plans for improvements."

The French Nuclear Safety Authority (ASN).

This ILL High Flux Reactor (HFR) produces the most intense neutron flux in the world: 1.5 x 10¹⁵ neutrons per second per cm², with a thermal power of 58.3 MW. The reactor operates on 50-day cycles, with each cycle of operation followed by a shutdown period during which the fuel element is changed and a number of checks are carried out. Occasional longer shutdowns allow for equipment maintenance and upgrades. There are normally 4 reactor cycles per year, supplying 200 days of neutron flux for scientific use.

Following the nuclear accident at Fukushima, Japan, the French Nuclear Safety Authority (ASN) decided to launch additional safety assessments on all French nuclear bases (INBs), including the ILL. This additional safety review has an impact on the Institute and affects its budget over the next years.

The studies performed by the Reactor Division teams analysed the behaviour of the ILL reactor under extreme conditions: the earthquake scenarios envisaged would have caused major damage to a town like Grenoble and would have led to the failure of all the dams on the river Drac, leaving the centre of town under 10 metres of water. On 15 September 2011 ILL submitted the results of its analyses to the IRSN (Institut de Radioprotection et de Sûreté Nucléaire) and the ASN. On 16 November the permanent group of experts for nuclear reactors replied with its conclusions: the ILL’s proposals have been completely accepted. The project plan of work has been well received by the ASN.

Since 2012 we have been putting these plans into operation. You will probably know that a major seismic reinforcement programme (the ‘Refit Programme’) was carried out at ILL, ending in 2007. Unsurprisingly, the 2011 studies demonstrate the robustness of the reactor against maximum expected earthquake conditions.

Since 2012 we have been putting these plans into operation. You will probably know that a major seismic reinforcement programme (the ‘Refit Programme’) was carried out at ILL, ending in 2007. Unsurprisingly, the 2011 studies demonstrate the robustness of the reactor against maximum expected earthquake conditions. However, cumulated with the possibility of the loss of the 4 dams upstream of the river Drac, it has been decided to reinforce elements traversing the reactor containment and to build a new emergency reactor control room from which all the emergency safety circuits can be controlled by the crisis-management teams. The building housing this control room has already been built.

The reinforcement works are programmed over 5 years (from 2012 to 2016) and should have no major impact on the ILL user programme. Its total cost was originally estimated at 12 M€. Following an ASN decision of 6 December 2013 and the studies it requires, the cost is now estimated at 15 M€. The additional work now required involves the installation of a new reactor electronics room, modifications to the ILL 4 office building to minimise any movement during an earthquake, and the replacement of the air intake building.

First of all, I would like to stress the importance and quality of the safety evaluation report you submitted on September 15, 2011. It corresponded well to the specifications and enabled an analysis to be performed of the robustness of your installations and of your plans for improvements."
The main operations planned under this programme are:
- the replacement of the beamtubes,
- the construction of the new heavy water management building and heavy water exchange installations (for the deliveries from Canada of 40m³ of fresh heavy water for the reactor, with the removal of the irritated heavy water).

The programme of work has been defined and is progressing well.
- Test drills have been carried out to define the dimensions of the 2 wells required to guarantee a long-term water supply,
- the structural engineering work for the new control room is finished - the building is dimensioned to resist an earthquake on the Beldonne fault at 7.3 on the Richer scale, and the breach of the 4 dams on the Drac river. The ground floor of this building now accommodates the heavy water unit used for handling the transfers of heavy water between the ILL and Canada.
- The structural engineering work for the new control room is finished - the building is dimensioned to resist an earthquake on the Beldonne fault at 7.3 on the Richer scale, and the breach of the 4 dams on the Drac river. The ground floor of this building now accommodates the heavy water unit used for handling the transfers of heavy water between the ILL and Canada.

The authors have validated our studies, but require additions to the "hard core" system - a new reactor electronics room and reinforcements limiting potential movement of building IL4 in the event of an earthquake, as well as the replacement of the air intake building.

This is a shutdown planned to last from 9 August 2013 to 25 June 2014, with a particularly ambitious work schedule. The programme includes work on the key reactor components and on the projects specified in the authorities' recent instructions following our Safety Assessment; we will also be performing numerous maintenance operations.

We are keen to avoid a second long shutdown before 2016, we will also be preparing the ground for operations to be performed later in the framework of the Safety Assessment.

Maintenance operations:
- dispatch of spent fuel elements to La Hague,
- testing of 2 spare 'coating stop' pumps on the heavy water circuit,
- homogenisation of the anion exchange resins of the primary circuit and reactor pools, to ensure that the active resins generated over the last 20 years meet ANDRA's waste conditioning criteria,
- modifications to the reactor protection circuit,
- inspections of the cold sources' and gaseous decay tanks' pressure is therefore postponed 3 years),
- there are always at least two major barriers in place to prevent and mitigate the accidents to be feared,
- fusion under water would never result in a cliff-edge effect.

MAIN WORK CARRIED OUT IN 2013

Work following the post-Fukushima Safety Assessment:
- installation of bearing piles to secure the work on buildings connecting with the reactor,
- construction of the buildings (ILL 5E and 5F),
- piercing of reactor containment penetrations and fitting bridges for the circuits and cables of the "hard core" system,
- installation of lighting and scaffolding in the space within the twin walling of the reactor containment.

Radioactive Waste and Effluents

The ILL’s activities in 2013 generated waste and effluents respecting the regulatory limits applicable to our installation, as follows:

- Waste stocked in these decay bins is still quite active and does not meet ANDRA’s specification for intermediate level waste.

### Table 1

<table>
<thead>
<tr>
<th>Cycle no.</th>
<th>Start of cycle</th>
<th>End of cycle</th>
<th>Number of days of operation</th>
<th>Number of days scheduled</th>
<th>Number of unscheduled shutdowns</th>
</tr>
</thead>
<tbody>
<tr>
<td>166</td>
<td>19/02/13</td>
<td>06/04/13</td>
<td>40</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>169</td>
<td>29/04/13</td>
<td>13/06/13</td>
<td>42</td>
<td>45</td>
<td>1</td>
</tr>
<tr>
<td>170</td>
<td>25/06/13</td>
<td>09/08/13</td>
<td>45</td>
<td>45</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>128.1</td>
<td>129</td>
<td>1</td>
</tr>
</tbody>
</table>
In order to maintain their ranking on the international scene, European research institutes must optimise their resources and develop synergies at every level.

The ILL is firmly committed not only to build high-performance instruments but also to offer the best scientific environment to the user community and it has established successful collaboration with neighbouring institutes over the years. After the successful Partnership for Structural Biology, we have now launched a Partnership for Soft Condensed Matter.

In parallel, the ILL and the ESRF have been working on plans to transform our joint site into a research campus – the European Photon and Neutron science campus, or EPN-campus for short – with a truly international reputation, and launched an ambitious project to extend the facilities already offered by our international site. The new scientific and technological installations will be complemented with other more general improvements, such as a new Science Building, a new site entrance, a dispatch and reception platform, a bigger restaurant and internal roadways.

In addition, the ILL has teamed up with the other institutes located on the Polygone scientifique science park (where our Institute is located) for the GIANT partnership, a project which aims to develop our neighbourhood into a world-class science and technology park. The GIANT project aims to develop Grenoble’s Polygone Scientifique into a world-class science and technology park.
THE SCIENCE BUILDING

The new Science Building provides 5,000 square metres of floor space across five levels—four floors of offices and labs etc. and one technical floor. In 2013 the construction was achieved and the first people started to move in their new premises. The building provides a number of platforms for promoting the complementary aspects of neutron and synchrotron techniques (p.108), and collectively enhance the visibility of ILL and ESRF in different research fields ranging from Soft Matter to Materials Science to Technology.

Several shared ESRF and ILL initiatives are hosted in the building including:

- The common library
- The theory group
- The Partnership for Soft Condensed Matter
- The common chemistry laboratories

In addition, the ESRF Business Development Office and the ILL Industrial Liaison Office will provide a unique contact point for industry. Further laboratories for sample characterisation and manipulation offer state-of-the-art complementary techniques to neutrons and X-rays.

THE IBS NOW ON SITE

2013 saw the arrival on the EPN campus of the IBS, the Institut de Biologie Structurale. The IBS is a French national research institute with 240 members of staff, including 181 scientists: researchers, teacher-researchers, engineers and technicians. It has five main fields of activity, three being biological in focus, the other two aiming at the development of new technical approaches:

- Immunity and host-pathogen interactions
- Fundamental intracellular processes
- Limits of life
- Membrane proteins
- New methodologies for integrated structural biology

In practice, many of the proteins and other molecules studied at IBS play an important role in life processes. A better knowledge of the mechanisms at play could lead to the development of new medicines.

We could cite as examples research into HIV virus entry mechanisms, or the resistance of bacteria to antibiotics and the design of new antibiotics, amongst many others.

As IBS director, Dr Eva Pebay-Peyroula, said: “The EPN campus, with its 4th generation synchrotron source and high-flux neutron source, provides unique facilities for a structural biology institute. The IBS needs these for its research and integrates their capabilities into its programme of development. In return, the IBS brings with it complementary techniques for the site, such as high-field NMR and electron microscopy. These are tools providing an excellent complement to the neutron and X-ray facilities”.

More information on these can be found on the IBS’s website: http://www.ibs.fr/science/axes-thematiques/

GRENOBLE AND THE FUTURE

The Grenoble Innovation for Advanced New Technologies partnership, or ‘GIANT’, is forging dynamic new links between higher education, research and industry, to foster technological breakthroughs for the future. The city of Grenoble has been supporting the project with the construction of a new 250 hectare town quarter in the neighborhood of ILL.

A tram line is also being extended, with a new terminus which will serve the ILL well, as it will be only 300 metres from the future site entrance. It will take ca 10 mins to go from ILL to Grenoble railway station and 1.5 mins to the town centre.

The current plans are for the tram to be up and running for the end of 2014.
SCIENTIFIC SUPPORT LABORATORIES

PARTNERSHIP FOR SOFT CONDENSED MATTER

Year 2013 saw an ever increasing demand for using the complementary techniques available in the ILL Soft Matter lab and a considerable success in terms of publications including samples prepared and characterised in this lab. The new chemistry lab responsible, David Hall has largely contributed to the running and maintenance of the instrumentation and work is in progress to upgrade the available tools when moving to the Science Building. A new group has been created, the Soft Matter Science & Support group, that includes responsibilities for the chemistry and PSCM labs and initiatives. A new scientist has been hired, Yuri Gerelli, to fill the duties of ILL PSCM coordinator.

By early 2014, the PSCM will be able to host up to 20 scientists and technicians both internal and from Collaborative Partners laboratories working in the new Science Building of the joint ESRF/ILL campus. In these laboratories, scientists will be able to prepare experiments with highly complex self-assembled and non-equilibrium soft matter systems in fields related to nanotechnologies, life sciences, environment as well as renewable energy. Activities within the PSCM initiative in 2013 have included start of negotiations with a number of laboratories, potential Collaborative Partners as well the organisation of a workshop to attract industrial partners. Users wishing to use the facility in conjunction with neutrons or X-rays, electron microscopy, NMR, high-throughput methods (soluble expression and crystallisation), and a range of biophysical techniques such as isothermal calorimetry and surface plasmon resonance.

A joint SAXS/SANS platform has been developed and there is also strong connectivity and collaboration between the ILL and ESRF crystallography groups involved in structural biology and related industrial efforts. The aim of the PSCM is to enhance the interdisciplinary capabilities of all of the facilities co-located on the site. Further details are provided on its website: http://www.psb-grenoble.eu/

The Carl-Ivar Brandén building (CIBB), is the principal focus for the PSCM and its partner organisations.

DEUTERATION LABORATORY

ILL’s Life Science Group is located within the CIBB and contains the Deuteration Laboratory Platform (D-LAB). The group is involved in a wide variety of externally funded programmes that exploit the capabilities of the PEB as well as promoting interdisciplinary structural biology. The group also has a number of programmes for method development relating to sample preparation and data collection using crystallography, SANS, fibre diffraction and dynamics; it is therefore of central importance to the activities of biological work relating to all of the ILL instrument groups. The Deuteration Laboratory was created in 2005 by the French Ministry of Research and Education to provide users with a facility to prepare research grade samples containing deuterium, an isotope of hydrogen. Deuterium is an excellent substitute for hydrogen in many applications and provides a powerful method for distinguishing between hydrogen atoms and deuterium atoms, leading to a number of advantages in the study of materials and biological samples. The facility is open to users who are carrying out research that requires the use of deuterium-containing samples.

The C-LAB

The Computation-Lab offers support to ILL users for atomistic simulations using classical and ab initio methods. Typical applications for simulations are structure, phonons and (some) magnetism in crystals and structure and dynamics in (partially) disordered systems ranging from liquids and glasses to macro/bio-molecular systems. As samples become more complex, simulations can provide key, complementary information that will help to interpret experimental data and understand how systems behave. Scientists and thesis students at the ILL benefit from the software, hardware and expertise of the C-Lab and users can benefit via their local contacts. In order to improve access to simulations for users, they are now able to request simulation support for their neutron scattering experiments on the official ILL proposal forms by ticking the appropriate box. In 11 proposal rounds since Autumn 2007, there have been 390 requests, at an average of 35 requests per round, with the last round being a record with 55 requests. For more information see ILL News N.47, June 2007 & N.50, June 2009 http://www.ill.eu/html/quick-links/publications/ill-news/

The Materials Science Support Laboratory (MSSL) has moved into the Science Building and is already in use. Have the precision saw and polishing equipment.

The Materials Science Support laboratory (MSSL) has been used for the provision of complementary laser reflection data to support publications resulting from neutrons studies at the air/water interface on FIGARO over the last few years.
2013 was a key year for the ILL. It was the year that saw the completion of the vast majority of the Millennium Programme projects and the start of work programmed for the exceptional long shutdown. At the same time the scientific and technical teams were making major progress on preparations to launch the Endurance Programme, an enterprise to ensure that ILL continues to drive the world’s science forward in the ILL's particular domain.

The high point of the year, however, was surely the signature of the Fifth Protocol to the ILL’s Intergovernmental Convention. The Associates' extension of the Convention sent a strong message of confidence to the ILL’s staff and user communities, confirming the Associates’ commitment to the Institute for the next ten years. The Administration Division’s role is to contribute to this mission by providing practical and efficient expertise in areas as varied as the ILL’s human resources, purchasing and finance, legal support, building construction and maintenance.

The Human Resources Service has also been addressing the question of the national balance of staff at the Institute. Following discussions with our Associates we have taken measures to attract more applications from candidates in the Associates’ and Scientific Members’ countries. It is clearly in the ILL’s interest to maintain a healthy diversity of nationalities, not only amongst the scientists but also amongst the technical and administrative staff. These measures should hopefully bear fruit in the years to come.

Finally on staff issues, we attach particular importance to seeking to resolve the difficulties in pension entitlement experienced by staff whose careers have led them to serve in different countries and who are disadvantaged by the lack of harmonisation in pension legislation.

The Administration Division staff were as competent and committed as ever in 2013, and more than ready to receive the new ones. The action taken in this direction together with our purchasing advisors in the partner countries has resulted in a reasonable improvement in industrial return for Germany and the UK, as well as for some of our Scientific Members. We will be continuing with these efforts in the future.

In 2013 our Building and Site Maintenance Service brought the main projects to a successful conclusion. Of these it is the Science Building which stands out in particular, funded by local authority investment (Région Rhône-Alpes, Grenoble-Alpes Métropole, and the city of Grenoble). The aim of this building, which we share with the ESRF, is to foster scientific collaboration. Its presence and facilities will open up scientific partnerships between the ILL’s Associate or Scientific Member countries, as well as with the ESRF’s Members and Scientific Associates. Similarly, the arrival on the EPN Campus of the IBS during the course of the year will further enhance the potential for collaboration. On the technical side, the SAE staff also oversaw the completion of the new ILL SD building, designed to house our new heavy water facilities and an additional reactor control room. At the same time they were busy with the ILL 22 guide hall: the old instruments were dismantled and the hall made ready to receive the new ones.

All of this activity has its legal underpinnings, the signature of the Fifth Protocol in particular of course, but also the renewal of the contracts with the Scientific Members, an operation requiring frequent exchange and negotiation by our legal staff with the different countries involved. The negotiations advanced well and the contracts should be signed in the first few months of 2014.

The Administration Division staff were as competent and committed as ever in 2013, and more than happy to contribute with skills and professionalism to the ILL’s adventure.
**STAFF ON 31/12/2013**

- 497 people, including 62 scientists and 38 thesis students.
  - 338.5 French, 44.5 German, 42.5 British, 44 Scientific Member countries and 27.5 others.

<table>
<thead>
<tr>
<th>Country</th>
<th>%</th>
</tr>
</thead>
</table>
| France           | 338.5| 68.11%
| Germany          | 44.5 | 8.95%
| United Kingdom   | 42.5 | 8.55%
| Scientific Member countries | 44 | 8.85%
| Others           | 27.5 | 5.53%
| Total            | 497  | 100%

**REVISED BUDGET 2013: 100.448 M€ (excluding taxes)**

<table>
<thead>
<tr>
<th>Income</th>
<th>M€</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Income from Associates*</td>
<td>63.180</td>
<td>62.90%</td>
</tr>
<tr>
<td>Own income</td>
<td>20.539</td>
<td>20.45%</td>
</tr>
<tr>
<td>Carry-forward from 2012</td>
<td>6.761</td>
<td>6.73%</td>
</tr>
<tr>
<td>Contribution from 2013</td>
<td>6.776</td>
<td>6.75%</td>
</tr>
<tr>
<td>MEU reserve</td>
<td>0.390</td>
<td>0.39%</td>
</tr>
<tr>
<td>Cash flow</td>
<td>1.220</td>
<td>1.21%</td>
</tr>
<tr>
<td>Total</td>
<td>100.448</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Expenditure</th>
<th>M€</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Staff costs</td>
<td>44.650</td>
<td>44.45%</td>
</tr>
<tr>
<td>Operating costs</td>
<td>13.973</td>
<td>13.75%</td>
</tr>
<tr>
<td>Investment costs</td>
<td>28.310</td>
<td>28.18%</td>
</tr>
<tr>
<td>Fuel cycle</td>
<td>11.713</td>
<td>11.66%</td>
</tr>
<tr>
<td>Total</td>
<td>100.448</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

* Including Fukushima expenses, Millennium Programme & additional Nuclear taxes.

**PURCHASING STATISTICS**

(Figures to end September 2013)

<table>
<thead>
<tr>
<th>Expenditure</th>
<th>M€</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>France (non-captive market)</td>
<td>14.39</td>
<td>59.34%</td>
</tr>
<tr>
<td>Germany</td>
<td>4.08</td>
<td>16.82%</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>1.77</td>
<td>7.30%</td>
</tr>
<tr>
<td>Scientific Members</td>
<td>1.33</td>
<td>5.48%</td>
</tr>
<tr>
<td>Others</td>
<td>2.64</td>
<td>10.05%</td>
</tr>
<tr>
<td>Total</td>
<td>24.33</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Expenditure</th>
<th>M€</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>France captive/residual</td>
<td>12.23</td>
<td>-</td>
</tr>
<tr>
<td>Total captive &amp; non-captive</td>
<td>36.68</td>
<td>-</td>
</tr>
</tbody>
</table>

**COUNTRIES WITH SCIENTIFIC MEMBERSHIP**

- **Spain**
  - Institut Max von Laue - Paul Langevin (ILL).
  - MINECO Ministerio de Economia y Competividad
- **Switzerland**
  - Staatssikterat für Bildung und Forschung (SBF)
- **Italy**
  - Consiglio Nazionale delle Ricerche (CNR).
  - CENI (Central European Neutron Initiative)
  - Consortium composed of:
    - Austria: Österreichische Akademie der Wissenschaften.
    - Czech Republic: Charles University of Prague.
    - Hungary: Research Institute for Solid State Physics and Optics (RISPO) / Budapest on behalf of the Hungarian Academy of Sciences (MTA).
    - Slovakia: Comenius University Bratislava.
- **BELPOLSWENI**
  - BELgian POLish SWEdish Neutron Initiative
  - Sweden: Swedish Research Council (SRC).
  - Poland: Polish Academy of Sciences.
- **India**
  - Bhabha Atomic Research Centre (BARC).
  - Interim scientific membership 01/01/2011 - 31/12/2014.

**SUPERVISORY AND ADVISORY BODIES**

- Steering Committee, which meets twice a year.
- Subcommittees on Administrative Questions, which meets twice a year.
- Audit Commission, which meets once a year, and statutory Auditor.
- Scientific Council with 9 Subcommittees, which meets twice a year.

**REACTOR**

- 58 MW, operating about 3 cycles in 2013 (139 days).
- (with cycles of 30 days)

**EXPERIMENTAL PROGRAMME**

- 603 experiments (allocated by subcommittees) on 28 ILL-funded and 9 CRG instruments.
- 1269 visitors from 46 countries.
- No proposal round in 2013.
ILL WORKSHOPS AND SCHOOLS IN 2013

21 JANUARY 2013
EXILL collaboration meeting.

23-25 JANUARY

18-22 MARCH
ADD 2013, Analysis of Diffraction Data in Real Space.

25-27 MARCH
NPrafPS 2013: ESS Science Symposium on Neutron Particle Physics at long Pulse Spallation Sources.

6-10 MAY
EMBO Practical Course 2013 (Small-angle neutron and X-ray scattering from proteins in solution).

29 MAY
“Les carrières des femmes en science vers l’équité” (sponsored by ILL)

5-6 JULY
Dynamics of Molecules and Materials II.

9 JULY
NW3 Industry workshop 2013.

12-13 OCTOBER
ILL Open Days.

18-23 NOVEMBER
FullProf School 2013.

28 NOVEMBER
Bragg symposium: Crystallography for life.

Short reports on the ILL workshops can be found on the ILL News (December 2013 issue) http://www.ill.eu/top-links/publications/ill-news/

Workshops websites can be found at http://www.ill.eu/news-events/past-events/
A YEAR IN PHOTOS

VISITS AND EVENTS

1 - The ILL has a new British Director General, Bill Stirling (right), who took over his role from Andrew Harrison on 1 January 2014.
2 - Participants to the EU-LI collaboration meeting on 27 January.
3 - Helmut Schober accompanying a delegation of the Swedish Research Council on a visit of the ILL on 4 April.
4 - Karin Schmalz (first on the left) and Ralf Schweins (second from the left) accompanying members of the German committee for research, educational and technology impact assessment, on a visit of the facility on 27 March.
5 - The ILL Scientific Council members at their meeting in November.
6 - Giuseppe Zaccai (IBS, center) has won the prestigious Walter Hägl for his consistent and outstanding work in neutron scattering with a long-term impact on scientific and/or technical neutron scattering.
7 - The three ILL directors welcome the visit from Luxembourg delegation on 28 March: Prof. J. Kreisel (center) and Dr. A. Michels (far from the right).
8 - Clip session of the ILL PhD students on 28 March.
9 - The ILL summer trainees with Anita Schober (first on the left, Human Resource service).
LONG SHUTDOWN

From 9 August 2013 to June 2014, the ILL reactor is shut down. During this period, a number of major projects have been scheduled. Some are part of the modernisation programme; others are the result of the complementary safety assessment performed by the ILL following the accident at Fukushima.

The main operations planned during the shutdown are: the installation of the new instrument THALES and the major upgrade of another four (SuperADAM, D16, D22, IN15), the replacement of two beam tubes - H13 and IH3 - and the replacement of almost all the H5 guides (see p 98-99).

The ILL staff welcomed the Grenoble public to the site during the Open Days on 12 and 13 October.

1 - Philip Gutfreund explaining the principle of diffraction.
2 - Bob Cubitt describing the science done on the small-angle scattering machines.
3 - Bernard Frick on IN16B.
4 - Simon Baudoin during a cryo-demo.
5 - Virginie Guérard, Alain Filhol and Françoise Vauquois enjoying their lunch-break.
A YEAR IN PHOTOS

WORKSHOPS AND EVENTS

1 - Giovanna Fragato (left, senior fellow and head of Soft Matter Science and Support group), Jean Daillant (centre, director of Soleil) and Florent Malloggi (right, CEA) performing a pioneering neutron reflectometry experiment to probe co-polymer layers at flat oil/water interfaces with a new concept for a liquid/liquid sample cell benefiting from a microfluidic set-up.

2 - Joao Cabral (Imperial College, London), regular ILL user and new member of the ILL Scientific Council, setting up his experiment.

3 - Jacques Olivier (ILL scientist, left with Bertrand Toulemon (University of Rennes and new member of the ILL scientific council) and Mariana Verezhak (master student at the University of Rennes), searching for the signature of some specific transition in an incommensurate intercalation compound on D10.

4 - Andrew Wildes, D7 instrument scientist, mounting a sample on the cryostat stick.

5 - Patrick Guenoun (left, Head of the Ions group, CEA, Saclay) and Lucie Besnard (right, PhD student in the same group) during their experiment on FIGARO.

6 - Thomas Sattmann (in the back, Koeln university) and three of his students on D22.

7 - Marcus Appel, III. PhD student, on IN16.

8 - Maria Toutousa (ESRF) mounting an ammonium perchlorate sample on IN10, during this year’s HERCULES practical on “Neutron backscattering”.

9 - Patrick Jürgensten (Stuttgart, Germany) and Govind Pradep (CEA/INAC/SIRAM/PCI Grenoble) on IN16B.

10 - Mark Johnson (second from the right) talking with Soumit S. Mandal, Rikhia Ghosh and Aninda Jiban Bhattacharyya (Indian Institute of Science, Bangalore) about simulations of proteins in nanotubes.

HAPPY USERS
Publication in 2013

In 2013, the ILL received notice of 587 publications by ILL staff and users. They are listed in the CD-ROM of this year's Annual Report.

The distribution by subject is as follows:

- Applied Physics, Instrumentation and Techniques: 45
- Biology: 59
- Crystallography: 99
- Liquids and Glasses: 30
- Magnetic Excitations: 54
- Magnetic Structures: 88
- Materials Science and Engineering: 40
- Nuclear and Particle Physics: 47
- Theory: 6
- Soft Matter: 78
- Spectroscopy in Solid State Physics and Chemistry: 41

ILL PhD Studentships

- PhD students at ILL in 2013*: 45
- PhD theses completed in 2013: 7

* Receiving a grant from ILL.