The world’s leading facility in neutron science and technology
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2011 has been a year of change and challenges for ILL and true to our past form, this has brought out the best in the Institute. The year began with the prospect of a progressive reduction in funding from our Associates to 2015 as national research budgets were hit by the global recession. Then in March the accident at the Fukushima nuclear power plant in Japan prompted the French Nuclear Safety Authorities – the ASN – to scrutinise yet more closely the ability of all nuclear installations in France to withstand natural disasters, however improbable. It is a testament to the skill and dedication of ILL engineers and support services that the ASN responded in glowing terms to our report, fully endorsing our plans to mitigate the consequences of such events, and envisaging continued operation of our reactor with a horizon of 2030. This result also reflects the foresight of those who originally conceived the reactor design, optimising not only brightness but also robustness with regard to safety:

Furthermore, neutron scattering continues to be a vital, multipurpose tool for science, equipping us to meet the grand technological challenges faced by our society, from clean, renewable sources of energy to new forms of therapy. ILL scientists also responded magnificently to the challenge of external review, presenting their instruments to an expert review panel that reported to our Scientific Council. Their verdict was that the overwhelming majority of our instrumental suite is world-leading, with recommendations of action to be taken to lift the rest to this level.

The evidence for such excellence in terms of scientific publications continues to be very impressive, with yet another record year for high-impact publications, and the strongest demand for beamtime in our history. We welcomed India as a new scientific member this year and have the prospect of further new members next year. News of our scientific achievements is also reaching a much wider audience after an initiative to communicate more effectively with media in our partner countries, with coverage in national newspapers and broadcasters such as the BBC.

Of course our instrument suite continues to be strengthened by our Millennium Programme, which delivered first neutrons on the new small-angle instrument D33, as well as the IN1 upgrade LAGRANGE and increased flux on the cold-neutron Laue instrument LADI; we look forward to welcoming users to these instruments in 2012, as well as to an upgraded IN15 and IN16B.

Despite economic hardship, our upgrades will not end there. We will have to be clever, disciplined and determined to balance our budget over the next few years while keeping up scientific output. The remarkable improvements that the Millennium Programme has brought to date (an increase in the average detection rate across our suite by a factor of twenty over the past decade) will enable us to deliver a service at the limits of what is technically possible for several years without substantial new investment in instruments.

However, we have a longer term responsibility to the scientific community to continue to provide such a service; to this end we are already planning a future wave of developments of instruments and infrastructure to be funded when the economic environment is less harsh. This is very much in keeping with the recommendations this year* of the Neutron Working Group established by our Associates to review the longer term needs and provision of neutrons in Europe – a key point being that a future ESS will only be ready to take on a flagship role well into the next decade. We look forward to closer engagement with EBS in the future, building on a MOU for collaboration signed this year between Richard Wagner, as one of his last actions as Director, and his predecessor at ILL and leader of the ESS project, Colin Carlyle.

Richard led ILL boldly and tirelessly through five remarkably successful years and has taken retirement after a lifetime of service to science. I feel particularly privileged to have been invited to take his place more than 30 years since first coming to ILL as a stagiaire with former Director John White. I leave behind the post of Director of Science which has been filed admirably by the new Associate German Director Helmut Schöber, rising from the ranks through his most recent position as Head of the Time-of-Flight and High Resolution Instrument Group. There has been change too in the Division of Administration where Amin Saidoun has left for pastures new after 5 years with us, while Martin Walter has stepped up to the mark to lead this Division as we find a replacement. We are also very fortunate in being able to continue to enjoy the experience and expertise of both José Luis Martínez as French Associate Director and Head of the Division of Projects and Techniques, and Hervé Guex, Head of the Reactor Division, completing the new management team.

The climate for funding will be cooler over the next few years, but we still have excellent prospects and we have the best combination of instruments and service in the world, and we are blessed with a remarkably skilled and dedicated workforce and a user community that is second to none. Furthermore, neutron scattering continues to be a vital, multipurpose tool for science, equipping us to meet the grand technological challenges faced by our society, from clean, renewable sources of energy to new forms of therapy. We look forward to the challenges – and the rewards – of the future with confidence and enthusiasm.

*http://tinyurl.com/86mm52q
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 NANOMETERS

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 MILLELECTRONVOLTS

The associated energies of millelectronvolts 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 1 μeV (even 1 neV with spin-echo) and 1 eV 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 nuclei in a sample, thereby providing a powerful tool for detecting the nuclear spin order.

ELECTRICALLY NEUTRAL

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 or reaction vessels.

HIGH SENSITIVITY AND SELECTIVITY

The variation of scattering power from nucleus to nucleus in a sample varies in a quasirandom 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 nickel 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.

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 58 M€ to the Institute in 2011, a sum enhanced by significant contributions from the ILL’s Scientific Member countries, Austria, Belgium, the Czech Republic, Denmark, Hungary, Italy, Poland, Slovakia, Spain, Sweden and Switzerland. On 1 January 2011, India also joined the ILL, thus becoming the 12th Scientific Member country. ILL’s overall budget in 2011 amounted to approximately 88 M€.

The ILL 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 worldwide: every year, about 2000 researchers from more than 30 countries visit the ILL to perform over 800 experiments supported by the ILL’s review committee.

The ILL monitors the papers published as a result of our facilities, of which there are more than 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 improving polymer processing. They also provide a unique probe into the phenomena that underpin high-temperature superconductivity or the molecular magnetism that may provide the technology on which the computers of the future are based.

PREPARING FOR THE FUTURE

In 2000, 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); 2002-2007; Phase M1: 2008-2014). We were now looking forward to setting the scene – in the framework of our ILL2020 Vision – for developments still further into the future, in order to maintain the Institute’s world-leading position for another 20 years.
impurities. Real scientific surprises tend to come in disguise are generally due to faulty experimental set-ups or sample to be wary of sudden excitement, for unexpected results are very rarely flashy. Students are taught very early on surprise at the end of the track. But scientific surprises always hope, at the bottom of their hearts, for that big deploy in the conduct of their research, scientists will of all - is driven by excitement. Despite the rigour they Adventur - and science is probably the greatest adventure of all - is driven by excitement. Despite the rigour they deploy in the conduct of their research, scientists will always hope, at the bottom of their hearts, for that big surprise at the end of the track. But scientific surprises are very rarely flashy. Students are taught very early on to be wary of sudden excitement, for unexpected results are generally due to faulty experimental set-ups or sample impurities. Real scientific surprises tend to come in disguise and, like hidden treasures, they are only accessible to those prepared to walk the extra mile.

Science is probably the greatest adventure of all

Systematic preparation for the unexpected may sound paradoxical. On reflection, however, it is not a vain philosophical exercise. It has real implications when it comes to developing rational processes for choosing directions of research or the development of scientific infrastructure. This is particularly true for service-oriented facilities like the ILL, where the anticipation of scientific trends and the selection of experiment proposals is part of daily life. It goes without saying that the ranking of proposals must be based on objective criteria - giving chance a chance is simply not an option. That said, to make the most of our portfolio of beamtime, we should be mixing safe assets with the more adventurous choices capable of delivering surprises. The highest potential for encountering the unexpected lies in those areas we know the least. But this leads to another difficulty - fields of ignorance are intrinsically ill-defined, and it is often only when you see the light that you realise you’ve been in the dark. It seems that we have little room for manoeuvre; we have to design our research in the full light of day, whilst hoping to glimpse unexplored shadowlands. It is only from the top of the mountain that you see all the possible paths.

The 2011 Nobel Prize in Chemistry provides an excellent example of how an unexpected result opened up a completely new area of research. At the beginning of the eighties Daniel Shechtman was naturally aware of this and initially suspected experimental artefacts or poor sample quality. But he could find no flaw in his experimental set-up, or problems with the sample. It takes courage and tenacity to counter coded knowledge. His colleagues rejected his claim, to the point of asking him to leave the research group, despite the fact that the ground had already been prepared by theorists in conceptual terms. Twenty years later, Shechtman's quasicrystals feature as common knowledge in any good text book on solid-state physics. It is still true of course that translational periodicity is incompatible with five-fold symmetry. We are now aware, however, that perfect long-range order leading to Bragg-like scattering can be achieved without translational periodicity, and that this kind of order admits a far broader range of symmetry operations. Neutrons played an important role in the quasicrystal saga that followed Shechtman's discovery and the ILL was always at the heart of it.

The verdict was clear: the micelles had arranged themselves to form quasicrystals (see scientific highlight by Exner et al., p. 34). Due to their distinctly different nature (micelles have no directional bonding for example), colloidal systems provide a completely new angle for the study of quasicrystals. By cross-correlating the properties of ‘soft’ and ‘hard’ quasicrystals we should now be able to focus on identifying the conditions that trigger quasicrystallinity.

Colloidal quasicrystals might well have gone unnoticed on D11, were it not for the bigger and faster detector with higher resolution which had just been installed as part of the ILL’s Millennium Programme. What is the moral of the story? To prepare for the unexpected, don’t forget to sharpen your tools.

Carrying out science is like preparing for a trip in the mountains. First make sure you have the equipment, and then decide on the route. And once you’ve started walking, stay tuned in, and ready for that breathtaking view that could be waiting at the turn of the bend. Well, I hope that’s the feeling you get when you discover the scientific highlights collected in this report!
MAGNETISM

New research has shown that the suprathermal conditions necessary for the development of magnetism in the ill. The study identified a new mechanism for generating magnetic moments in materials, which could lead to the development of new magnetic materials for applications in technology and energy. The research was supported by the ill and is expected to have significant implications for the future of magnetic materials research.

CHEMISTRY AND STRUCTURE

The properties of a new class of materials were studied in detail. These materials exhibit unique magnetic and structural properties that make them promising for applications in electronics and energy storage. The research was conducted using advanced X-ray and neutron spectroscopic techniques and highlights the potential of these materials for future technological applications.

Biocatalysis: article “Design of a highly specific enzyme for the production of biofuels” p.64

Modeling and spectroscopy: article “Identification of new magnetic materials” p.40

SCIENTIFIC HIGHLIGHTS

NUCLEAR AND PARTICLE PHYSICS

Activities in nuclear and particle physics are spanning a wide field of fundamental and applied physics. Especially in nuclear physics several new fields were explored in 2011. In addition to its applications for nuclear spectroscopy and for fundamental physics, the ILL is also active in nuclear astrophysics. This section focuses on the achievements of the ILL in nuclear physics and astrophysics and highlights important developments in these fields.

Chemistry and structure: article “Anisotropic order in perovskite oxynitrides” p.24

Materials science and engineering: article “Detection of collagenous macromolecules in the body using neutron scattering” p.34

Lipids and glasses: article “Dynamics of glycerophospholipids in solution” p.46

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The dynamics of ordered uranium dioxide: an understanding after 45 years

Uranium dioxide (UO$_2$) has the cubic CaF$_2$ fcc structure and orders anti-ferromagnetically at 30K ($T_N$). The first examination of the dynamics of UO$_2$ was reported in 1966 [1] and the strong magnon-phonon interactions, as well as the apparent complexity of the modes, have been investigated many times. Although quadrupolar interactions were already suggested as being important in the dynamics of UO$_2$ as early as 1969 [2], the lack of knowledge of the symmetry of UO$_2$ below $T_N$ as well as the absence of any first-principles theory meant that progress was slow. Even by 1999, when the 3-k ordering and the Jahn-Teller distortion below $T_N$ were well known, the appearance of three strong modes, instead of the two expected, was not understood [3].

The breakthroughs that allowed progress came through experiments with resonant X-rays and a deeper theoretical understanding of the role of higher-order interactions [4]. Unlike neutrons, resonant X-rays are directly sensitive to the ordering of the quadrupoles, and these were measured for both NpO$_2$ and UO$_2$ at the ESRF [4]. The development of the theory led to the prediction that in UO$_2$ it might be possible to observe the pure quadrupole waves through their interaction with normal spin waves [5].

The experiments at the ILL were made on two spectrometers: IN14, a cold-source triple-axis spectrometer with excellent resolution, and IN22, where we have used full polarisation analysis to separate the magnon and phonon modes [6].

Figure 1: Dispersion along the [001] direction of the mixed magnon-phonon modes in UO$_2$ at 2K, near the anti-crossing position at $(Q = (0.0,0.45)$ as measured on IN14. Red coloured peaks indicate spin-wave like, green are mostly phonon. However, there is mixing in the whole region ($0.35 < Q < 0.55$, and at $Q = 0.45$ the excitations have 50% magnetic and 50% vibrational character. The upper inset shows calculated intensity maps in the energy-momentum transfer space. The lower inset shows an extra small peak at $Q = (0.0,0.5)$, which is identified as a quadrupolar-acoustic mode.

In solids with $d$ and $f$ electrons, under certain conditions the orbitals align to form an ordered pattern. Collective excitations of electric quadrupoles, so-called quadrupolar waves.

The upper inset shows calculated intensity maps in the energy-momentum-transfer space. The lower inset shows an extra small peak at $Q = (0.0,0.5)$, which is identified as a quadrupolar-acoustic mode.

In conclusion, for the dynamics of UO$_2$ in the ordered state the acoustic (QA) modes, which are difficult to observe directly. In their pure form, as stated above, their neutron cross section is zero, but the intensity becomes non-zero if they are near in energy to a spin or a phonon mode [5], just as the QA mode picks up weight when it is near the 90 degree mode. We have seen the weak QA mode with IN14 [see figure 1] at the position $Q = (0.6, 6.5)$ meV.

In conclusion, for the dynamics of UO$_2$ in the ordered state the agreement between experiment and theory is excellent after 45 years! The key has been both new experiments and theory, especially a fundamental understanding of the complex role of higher-order multipole modes on the dynamics. Pure quadrupole waves do not couple to the neutron cross section, but if the energy of these excitations is close to those of the pure magnons, then quadrupole modes acquire a magnon component, thus becoming observable by inelastic neutron scattering. It is as if we observe the uranium atomic moments moving on the quadrupole waves, and the modification of their normal dynamical properties proves the existence of the underlying quadrupolar interactions. This work opens the way, both with theory and experiment, to examine systems more complex than UO$_2$, and understand in greater detail higher-order interactions and their effects on dynamic and other properties.
Evidence for charge orbital and spin stripe order in an overdoped manganite

We investigated a single-layered manganite of the La$_{1-x}$Sr$_x$MnO$_y$ series at and above half doping. At half-doping ($x = 0.5$) first checkerboard-like ordering of Mn$^{3+}$ and Mn$^{4+}$ charges develops accompanied by an orbital ordering of $e_g$ electrons on the nominal Mn$^{3+}$ sites. Below $T = 110$ K an antiferromagnetic (AFM) CE-type ordering sets in, which is described by the so-called Goodenough model [3-5]. The excess of Mn$^{4+}$ in overdoped La$_{0.42}$Sr$_{1.58}$MnO$_4$ perturbs such ordering. Several scenarios are possible to arrange the excess of Mn$^{4+}$ into self-organised patterns. Our work aimed to develop a consistent model for the four coupled ordering parameters, as illustrated in figure 2a [5].

In contrast to previous studies, we determined the full neutron diffraction response in (H4) planes of reciprocal space with fixed components by using the Flatcone detector on IN20 [6]. A map of the scattering in the (H4) plane is shown in figure 2 for the half-doped ($x = 0.5$) and for the overdoped ($x = 0.58$) materials at $T = 2$K.

The fully ordered state of La$_{0.42}$Sr$_{1.58}$MnO$_4$ exhibits sharp superstructure reflections as exactly half and quarter-indexed positions.

Different types of reflections can be easily attributed to the different ordering parameters, as illustrated in figure 2a [5]. The same region of reciprocal space is shown in figure 2b for the overdoped compound La$_{0.42}$Sr$_{1.58}$MnO$_4$. The data clearly exhibit diffuse signals which are broadened along the diagonals of the reciprocal lattice. The detailed analysis shows that the centres of scattering arising from the charge, orbital and magnetic ordering of Mn$^{3+}$ become all incommensurate. The charge ordering satellites are displaced by an incommensurability of $\Delta q = 0.08(3)$ in comparison to the position seen for $x = 0.5$. The orbital and magnetic peaks are also displaced along the diagonals and by the same value: $\Delta q^{o_o,oo} = 0.037(2)$, which is half that of the charge order. Surprisingly, the magnetic scattering associated with the Mn$^{3+}$ moments remains commensurate for $x = 0.58$. Magnetic and electronic order in La$_{0.42}$Sr$_{1.58}$MnO$_4$ corresponds thus to a coupling of three incommensurate and one commensurate order parameter. Upon increasing temperature, none of the incommensurate signals is found to shift in position but all intensities decrease.

The complete mapping of the diffraction signals allowed us to develop a consistent model for the four coupled ordering schemes in overdoped La$_{0.42}$Sr$_{1.58}$MnO$_4$ (figure 1c). Since all the incommensurate displacements are found along the diagonals of the cell, the excess Mn$^{4+}$ must be arranged into stripes running along these diagonals. Due to the transverse modulation of the magnetic signal associated with the Mn$^{3+}$ moments, these stripes must interrupt the zigzag chains, as is illustrated in figure 1c. Different magnetic alignment and the orientation of the stripes result in total in four different domain orientations whose contributions need to be superposed to fully simulate the data. The amount of extra Mn$^{4+}$ corresponding to $x = 0.58$ cannot be modelled by Mn$^{4+}$ stripes with a unique distance. Instead, we have to mix blocks according to $x = 0.6$ (33%) and blocks with $x = 0.57$ (66%). Simple Fourier transforms of large supercells of the charge, orbital and magnetic order of the model shown in figure 1c give a perfect description of the positions of the scattering maxima as well as of the characteristic shape of the diffuse signals [6].

In summary, by using the Flatcone detector on IN20 full maps of elastic neutron scattering in an overdoped single-layered manganite La$_{0.42}$Sr$_{1.58}$MnO$_4$ are obtained. These patterns show the tight coupling between the electronic and magnetic ordering and allow to fully explain the complex order. Our observations point to a stripe-type arrangement very similar to such phases in layered cuprates, nickelates and cobaltates [1]. Also manganites exhibit coupled ordering of charge, orbital and spin degrees of freedom; these ordered phases compete with metallic ferromagnetic states giving rise to the colossal magnetoresistivity. Stripe phases have been proposed already long ago for highly doped manganites [2] but no consistent description of the different ordering patterns could be obtained so far.

References


Figure 1: (a) Tetragonal structure [Å / mm] of the single-layered compound La$_{0.42}$Sr$_{1.58}$MnO$_4$. (b) The charge, orbital and spin ordering in the half-doped compound $x = 0.5$ inside the MnO plane (the oxygen atoms are omitted) can be explained by the Goodenough model. (c) Sketch of charge, orbital and spin ordering in La$_{0.42}$Sr$_{1.58}$MnO$_4$. Figure 2: Scattering map of the (H4) plane in the half-doped compound [a] and in the overdoped material [b] at $T = 2$K. The different positions of the superstructure reflections reveal the different ordering parameters [a].
Ce₃Pt₂₃Si₁₁ ferromagnet: unusual magnetic behavior brought to light by neutron studies

Ce₃Pt₂₃Si₁₁ crystallises in a face-centered cubic structure (Pm-3m space group). Recently, we have synthesised very high quality single crystals. Magnetic measurements have shown that Ce₃Pt₂₃Si₁₁ orders ferromagnetically at T_c = 0.44 K with a spontaneous magnetic moment of 2.14 μB/Ce expected for Ce ³⁺ ion [1]. Such a reduction may arise from crystal electric field (CEF) effect and/or from magnetic arrangements more complex than the collinear ferromagnetic one.

Neutron diffraction experiments performed on a single crystal using the unique four-circle dilution cryostat available on the ILL neutron reflector. The transition at T_c was evidenced by the temperature dependence of the (220), (0-20) and (111) reflections (figure 1). In the ferromagnetic phase at 100 mK, the magnetic contribution is observed on top of nuclear reflections with hkl all even. The non-observation of a magnetic contribution for odd reflections indices is a strong constraint. This leads to ferromagnetic couplings between pairs of Ce ions within the 6 Ce ions in the unit cell. Group theory analysis shows that the only non-zero basis vectors, consistent with a ferromagnetic arrangement on the Ce sites, are those of the T₄ irreducible representation. These vectors describe a ferromagnetic arrangement along [001], [010] and [001] axes respectively, while a combination of the three basis vectors leads to a ferromagnetic arrangement along the [111] direction. In very good agreement with the magnetisation process, shown in figure 2a. The refined value of the magnetic moment, 1.2(2) μB per Ce ion, is close to that deduced from the magnetisation measurements (figure 2a). Both determinations strongly indicate a doublet CEF ground state.

The CEF excitations were studied by inelastic neutron scattering on the IN4 time-of-flight spectrometer. For Ce³⁺ ions in cubic symmetry, only fourth degree terms are effective in the CEF Hamiltonian and thus only one parameter, W = ± ECEF/6 has to be considered [2]. A positive (negative) W selects a doublet (quadruplet) as CEF ground state. Unexpectedly, two magnetic excitations are observed at E₁=12 meV and E₂=19.6 meV on the spectra (figure 3), while neutron diffraction experiments show that the structure remains cubic down to 800 mK. Observation of two CEF excitations in a cubic Ce compound was earlier reported in CeAl₃. It was interpreted in terms of an unusual magneto-elastic coupling that gives rise to a quadruplet CEF ground state.

Calculations of the magnetic susceptibility within the CEF formalism show that experimental data are in better agreement with a quadruplet CEF ground state (figure 3). In this case an interpretation similar to that of CeAl₃ should not apply, as the excited doublet cannot be split. The discrepancy between the different experimental observations in Ce₃Pt₂₃Si₁₁, together with an apparent crystal symmetry that remains cubic, can be tentatively explained by the splitting of the quadruplet ground state via a dynamical Jahn-Teller effect [6]. This hypothesis will need further exploring.

References:
Magnetic structures on crossing the phase transition in perovskite LaCrO$_3$

Magnetic structures on crossing the phase transition in perovskite LaCrO$_3$

The spin ordering in a magnetic crystal lowers the symmetry of the whole system, but it is normally within sub groups of the crystal symmetry of the paramagnetic phase [1]. Although the spin structures in perovskite oxides have been classified on the basis of some common crystal structures in the 1960s [2], it remains unknown whether and how spins are ordered in the rhombohedral phase. The pressure-induced phase transition from the orthorhombic phase to the rhombohedral phase in perovskite LaCrO$_3$ provides an excellent opportunity for us to study these problems and to explore whether the spin-spin interaction will be interrupted by the symmetry change.

Figure 1 displays crystal structures of orthorhombic and rhombohedral phases that are commonly seen in perovskite oxides. A first-order phase transition between these two phases can be triggered by either raising temperature or under high pressure. The transition temperature is expected to become lower under pressure. The orthorhombic phase accommodates type-G antiferromagnetic ordering with two possible spin directions.

On crossing the phase transition, however, the abrupt structural change, especially the symmetry change, leaves an open question: is the type-G antiferromagnetic ordering going to collapse in the rhombohedral phase? Resolving this fundamental issue is a challenge in the field of condensed matter science. First of all, neutron diffraction is required in order to reveal the detailed change in both crystal structure and magnetic structure. The sample also needs to be placed inside a high-pressure chamber with the capability of varying temperature on a neutron beamline. Developed in recent years at the ILL, a combination of a Paris-Edinburgh press mounted on a close-cycled refrigerator and high-flux neutron beam at D20 as well as the high-resolution detector is ideal to address this problem. This highly sophisticated experiment can only be made possible in collaboration with the instrument scientists at the ILL. Moreover, the software FULLPROF also developed at the ILL has been used to determine the atomic positions and spin structure from neutron diffraction.

Results of neutron diffraction on LaCrO$_3$ made at different temperatures and pressures are summarised in the phase diagram in figure 2.

The first-order orthorhombic/rhombohedral phase transition temperature is suppressed linearly as pressure increases. It is surprising that the antiferromagnetic ordering survives on crossing the first-order structural transition, which indicates that the symmetry change does not alter the spin-spin superexchange interaction at all.

Although an antiferromagnetic spin arrangement remains on crossing the phase transition, the spin direction changes relative to the crystal structure of the nearest neighbour. Moreover, the canted spin structure, which is allowed in the orthorhombic phase, is prohibited in the rhombohedral phase. This study also reveals the structural change of perovskite LaCrO$_3$ under pressure. The $T_N$ change as a function of pressure can be rationalised by the structural modification under pressure. These new results indicate that the spin direction is always parallel to the rotation axis of the crystal structure with the highest symmetry in the space group. It is also a nice example to show the close correlation between canted spin structure and the crystal structure symmetry. Our new observations have a profound implication in designing new multiferroic materials for information technologies.
Magnetic proximity effect in YBa$_2$Cu$_3$O$_{7-\delta}$ / La$_{2/3}$Ca$_{1/3}$MnO$_3$ superlattices

The interaction between superconducting (SC) and ferromagnetic (FM) orders has been studied widely and is still the subject of ongoing research. The initial theoretical predictions and later experimental proofs of proximity effects have opened the door for potential applications [1,2,3]. Nevertheless, most of this work has been focused on conventional low temperature superconductors, and little is known about the interaction between superconductivity and ferromagnetism in oxide-based materials.

These oxide based superconducting YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and ferromagnetic La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) multilayers have obvious advantages, such as the high $T_c$ of cuprates or the versatile magnetic properties of manganites; these can be tailored by weak perturbations such as external magnetic fields and/or temperature above and below the superconducting and ferromagnetic transition temperatures. We observed anomalous superconductivity-induced changes in the thickness of these ferromagnetically depleted layers, suggesting that they should not be considered as magnetically dead, but may well host some kind of oscillatory magnetic state.

Figure 1a shows the reflectivity curves measured at different temperatures above and below the superconducting and ferromagnetic transition temperatures. $T_{SC} = 88\,K$ and $T_C = 201\,K$ respectively. Sharp and intense superlattice Bragg peaks, a product of the constructive interference between reflections coming from all the interfaces, can be observed, evidencing the high sample quality. At room temperature [green symbols], only the nuclear interaction of the neutrons is relevant and the even-order Bragg peaks are strongly suppressed, as is to be expected for a superlattice with equal layer thicknesses. As the temperature is lowered below $T_{SC}$, the thickness of the depleted layers reduces below $T_{SC}$.

For the curves measured below the Curie temperature (red and blue symbols) intense even-order Bragg peaks are observed, the fingerprint of the reduced symmetry of the magnetic depth profile with respect to the nuclear one [4]. Figure 1b shows the nuclear and magnetic profiles for various temperatures, as obtained from fitting the data [solid lines in figure 1a].

Evidently, the ferromagnetic moment is strongly suppressed on the LCMO side of the interfaces. Although the magnetic nature of these depleted ferromagnetic regions is not yet clear, their very large magnetic roughness and the anomalous evolution of their thickness with temperature suggest an inhomogeneous or oscillatory magnetic state.

Figure 2 shows the temperature dependence of the asymmetry of the third order superlattice Bragg peak. This asymmetry remains very small above 90K; it exhibits a clear anomaly below $T_{SC}$ which reveals that the onset of superconductivity in the YBCO layers gives rise to marked changes in the depleted layers in LCMO. As shown in figure 1b, the thickness of the depleted layers reduces below $T_{SC}$.

Our PNR measurements have revealed a fascinating magnetic proximity effect, unambiguously confirming the presence of a layer on the LCMO side of the interface, where the FM order of the Mn moments is strongly suppressed. In addition, the superconducting-induced change in the thickness of the depleted FM layer is indicative of a sizeable coupling between superconducting and ferromagnetic orders across the interface.

The magnetic proximity effect in YBa$_2$Cu$_3$O$_{7-\delta}$ / La$_{2/3}$Ca$_{1/3}$MnO$_3$ superlattice as obtained from fitting the data (solid lines in figure 1a).

Figure 1: (a) Polariised neutron reflectivity curves as a function of the momentum transfer for a YBCO/LCMO superlattice at $T = 300\,K$, $T = 100\,K$ and $T = 10\,K$. The arrows indicate the position of the superlattice Bragg peaks. The solid lines are the results of the fits. (b) Nuclear and magnetic scattering length density inside the LCMO layer as obtained from the fits.

Figure 2: Asymmetry of the third order Bragg peak $I(1) - I(2) / I(1) + I(2)$, as a function of temperature. Inset: Reflectivity in the vicinity of the third Bragg peak showing large splitting between the different spin channels below TSC.
Anion order in perovskite oxynitrides

Many transition metal oxynitrides adopt the AMX₃ perovskite type crystal structure [1,2]. The properties of perovskites are known to be sensitive to small structural distortions that may arise from tilting or rotations of the MX₆ octahedra. Oxide–nitride anion order is also expected to be important but consistent models have not been reported.

We have investigated anion order in the representative oxynitride perovskites SrNbO₂N and SrTaO₂N using powder neutron diffraction patterns collected on the high resolution instrument D2B at temperatures between 25° and 750° C [1]. At high temperatures (≥300°C for SrNbO₂N or ≥200°C for SrTaO₂N) only the peaks expected from a cubic perovskite are observed. However, refinements of anion site occupancies in a tetragonal model gave a stable fit with the anion distribution shown in figure 1. This sensitivity to anion populations arises from the high neutron scattering contrast between oxygen and nitrogen. The anion order is observed up to the highest measured temperature of 750°C for SrTaO₂N.

At 25°C, SrNbO₂N and SrTaO₂N both adopt a perovskite superstructure in which rotations of MX₆ octahedra are ordered, as evidenced by additional neutron diffraction peaks. Fits to the neutron data reveal that the rotational order axis is correlated with the anion ordering (figure 1). The rotational perovskite superstructure is usually described by the tetragonal space group I₄/mcm, but the observed anion order is predicted to lower symmetry through loss of the c-glide operation.

This is confirmed by electron diffraction studies of both materials, and of other perovskites EuNbO₂N, EuTaO₂N and EuWON₂, which show that the coupling between rotational and anion orders is a common phenomenon in oxynitride perovskites.

The robust partial anion order observed in SrM₂O₃ (M = Nb, Ta) by neutron diffusion is consistent with a well-defined short range order. This is driven by covalent effects which stabilise the cis (180°) configuration of MN₂O₄ octahedra, as nitride is more strongly bonded to the d0 transition metal M cations than oxide. The combination of cis-coordination of each M cation by two nitrides and the linear coordination of each nitride by two M cations results in the formation of zig-zag M-N-M chains within planes of the perovskite lattice as represented in figure 2. The chains are similar to those of organic polymers and are susceptible to disorder as there are two choices for the 90° turn at each M atom, resulting in randomised chains and rings within the planes (figure 2a) that average to the experimentally-observed anion distribution shown in figure 1.

The above principle of local anion order driven by differing M-N and M-O bond strengths predicts local structure across the range of AMO₃-Nₓ perovskites (figure 2b). The preference for the more strongly bonded nitride ligands to be mutually cis results in a symmetry between nitride order in AMO₃-Nₓ and oxide order in the corresponding AMO₃-N₃ₓ composition. Hence, the representations of Mn-N-chains in AMO₃-Nₓ in figure 2a are equally applicable to -M-O- chains in AMO₃-Nₓ. This is corroborated by an independent powder neutron diffraction study of LaNbO₃Nₓ, where an averaged oxo chain order is evident [4].

In conclusion, the oxygen/nitrogen distributions in the perovskites SrNbO₂N and SrTaO₂N determined by neutron diffraction evidence a well-defined local anion order, with ordered cis-metal-nitride chains confined to planes within the 3-dimensional perovskite framework. The anion order controls the axis around which the octahedra rotate to form a superstructure at room temperature. The anion order is robust but the resultant lattice distortions are very small so that high resolution neutron diffraction is necessary to reveal such structures. A wealth of similar local structures is expected across the range of AMO₃-Nₓ perovskites and further work will be needed to elaborate their influence on physical properties such as dielectric behaviour and photocatalysis.
New metal-hydride clusters provide insights into hydrogen storage

One way to solve this problem is to use metal hydrides, metallic compounds that incorporate hydrogen atoms, as a storage medium for hydrogen [1]. In this technique, the metal hydrides can bind additional hydrogen atoms to produce a solid at least one thousand times smaller than the original volume of hydrogen gas. The hydrogen can then later be released from the solid by heating it to a given temperature.

We have synthesised a new class of ‘heterometallic’ hydride clusters (figure 1) that may spur development of lighter and longer-lived fuel-cell devices [2]. The new heterometallic hydride clusters (figure 1) that may spur development of lighter and longer-lived fuel-cell devices [2].

Before and after the addition of hydrogen, and were reinforced by a remarkable real-time study of the hydrogenation process in a single crystal and by DFT calculations. Neutron diffraction studies on two of the hydrogen-loaded complexes using D19 and VIVALDI allowed more detailed discussion of the structure of the metal-hydride frameworks, thanks to the considerably greater sensitivity of neutrons to hydrogen in the neighborhood of heavy metal atoms. For the first yttrium-tungsten Y4W(PMe3)H11 complex (figure 1a) accurate Y-H bond lengths and angles were obtained on the monochromatic D19 instrument, thanks to its new very large detector.

In summary, we have synthesised a new series of heterometallic polyhydride clusters composed of rare-earth and d transition metals. The structures have been determined precisely using D19 and VIVALDI neutron diffractometers. The clusters reversibly add/eliminate hydrogen. Remarkably, the oxidative addition of hydrogen to the Y4Mo cluster proceeds without loss of crystallinity and can be directly followed by X-ray crystallography. This study has shed first-ever light on a class of heterometallic molecular hydride structures whose unique features point the way to breakthroughs in the development of lightweight fuel-cell technology.

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Hydrogen, the most abundant element in the universe, holds great promise as a source of clean, renewable energy, producing nothing but water as a byproduct and thus avoiding the environmental dangers associated with existing mainstream energy sources. However, broad adoption of hydrogen has stalled because in its natural gaseous state the element simply takes up too much space to store and transport efficiently.

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A square-planar iridium(II) complex

We earlier reported the dehydrogenative functionalisation of the amido pincer ligand \([\text{P=N=P} \equiv \text{R}]) which gives synthetic access to an iridium(II) with an open-shell electronic structure. An experiment on the ILL’s VIVALDI using a single crystal of \([\text{IrCl(P=N=P} \equiv \text{R}])\) confirmed the absence of further hydride ligands and of significant Ir···H–C interactions at the vacant coordination sites. The structural features therefore fully support the formulation as a rare Ir(II) complex, stabilised by a novel, rigid ‘pincer-type’ ligand.

This compound provides an excellent platform for establishing isolable, electronically highly unsaturated complexes such as \([\text{IrCl(P=N=P} \equiv \text{R}])\). In turn, these have served as starting materials for obtaining extremely rare species of precious metals with multiply bonded nitrogen, e.g. \([\text{Ir}([\text{N}=\equiv \text{N}]\equiv \text{N})\equiv \text{P} \equiv \text{N}])\), which are currently being evaluated as catalysts for novel N–E (E = H, C, N) coupling reactions [5].

Coordination compounds of the precious metals are of enormous importance as homogeneous catalysts for the transformation of organic substrates. Generally, their electronic structures favour closed-shell states, thus explaining the typical preference of two-electron (oxidative addition/reductive elimination) over one-electron elementary reactions. However, the importance of radical reactivity for platinum metal complexes has recently become more apparent, for example in radical H₂, C–H, and C–C activation reactions or catalytic oxidation. Nonetheless, fully characterised metalloradical complexes of these metals remain comparatively scarce.

References

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Light-emitting dendrimer film morphology: a neutron reflectivity study

For the NR experiments, neat films of 1, 2, and 3 were spin-coated from solutions of concentrations of 20 mg/mL in chloroform onto ITO substrates. The NR measurements were carried out in the time-of-flight mode with a wavelength range of 2-20 Å at an incidence angle of 0.7° on the D17 reflectometer with the samples held under vacuum. NR measurements of the ITO on glass showed that the first layer was 38 Å thick and the bulk layer of ITO was 1490 Å thick and had a SLD of 4.3x10⁻⁶ Å⁻². The second layer was 84 Å thick and had a SLD of 4.3x10⁻⁶ Å⁻² and the bulk layer of ITO was 1480 Å thick and had a SLD of 6.9x10⁻⁶ Å⁻². These parameters for the ITO were fixed during the analysis of the dendrimer films.

The room temperature reflectivity profiles for films of the first-generation, second-generation, and doubly dendronised dendrimers 1, 2, and 3, respectively, are shown in figure 2. In each case the solid markers represent the data points and the solid lines represent the fits achieved from modeling the films.

**Table 1**

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>SLD of bulk material (10⁻³ Å⁻²)</th>
<th>MW of deuterated dendrimer (g/mol)</th>
<th>SLDend</th>
<th>Density of bulk material (g/cm³)</th>
<th>Volume per molecule (Å³)</th>
<th>OH of protonated dendrimer ( Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0 ± 0.1</td>
<td>2011</td>
<td>0.0145</td>
<td>1.26 ± 0.03</td>
<td>2800 ± 100</td>
<td>20.4</td>
</tr>
<tr>
<td>2</td>
<td>4.5 ± 0.1</td>
<td>3997</td>
<td>0.0230</td>
<td>1.07 ± 0.02</td>
<td>6000 ± 100</td>
<td>26.4</td>
</tr>
<tr>
<td>3</td>
<td>4.5 ± 0.1</td>
<td>3768</td>
<td>0.0273</td>
<td>1.03 ± 0.02</td>
<td>6100 ± 100</td>
<td>25.6</td>
</tr>
</tbody>
</table>

**Figure 1:** Structures of the singly first 1 and second generation 2, and doubly dendronised 3, dendrimers where R= d17-2-ethylhexyl.

**Figure 2:** Room temperature reflectivity profiles of dendrimers 1, 2, and 3. The solid lines are the fits from the model. The profiles are offset for clarity.

**Figure 3:** SLD versus position in the film for films of the three dendrimers from the ITO surface to the air interface.

Organic semiconductors are being extensively studied in a range of applications including organic light-emitting diodes for displays and lighting, solar cells, transistors, and sensors. There are three classes or organic semiconductor materials: small molecules, conjugated polymers and most recently dendrimers. Phosphorescent light-emitting dendrimers have attracted significant attention as they have given rise to some of the most efficient solution processed OLEDs [1]. Light-emitting dendrimers are branched macromolecules that have a modular architecture and consist of a core, dendrons (branching units), and surface groups. The core and dendrons are responsible for the optoelectronic properties of the dendrimers while the surface groups provide solubility and processability. The modularity of the dendrimer structure enables independent tuning of the electrical, optical, and processing properties. For all light-emitting organic materials the morphology of the film can play a critical role in device performance as it governs the intermolecular interactions that control charge transport and the photophysical properties. With phosphorescent dendrimers it has been found that the OLED performance is dependent on dendrimer generation and/or the number of dendrons attached to the core complex.

Neutron reflectivity (NR) has been used to study the morphology of conjugated polymer films and the interface with the commonly used anode indium tin oxide (ITO) [2-7]. In this work, we applied NR measurements to study the morphology of phosphorescent dendrimer films [8]. The dendrimers are comprised of fac-tris (2-phenylpyridyl)indium(III) cores (green), biphenyl-based dendrons (blue), and 2-ethylhexyloxy surface groups (red) ([1] not change the photoluminescence properties of the dendrimers. 2-ethylhexyloxy surface groups to provide contrast for the NR property relationships in conjugated light-emitting dendrimer provide useful information on the crucial structure-semiconducting and is consequently more spherical in shape. The NR results differs from 1, in that it has two first-generation dendrons attached per ligand, which we call "doubly dendronised," RO in that it has two first generation dendrons, and RO excluding the bulk glass: the first layer immediately on the surface to the air.

Reflectometer D17

**REFERENCES**

Evidencing hydride species in cerium nickel mixed oxides

About 90% of the hydrogen produced today comes from high temperature steam reforming processes, in large central plants at high temperatures (700 °C–1000 °C), in the presence of a catalyst. The hydrogen produced is used predominantly for petrochemical purposes and raw material in industry. Hydrogen, however, has to be produced, as it is only found in nature in its compound form. In this article we describe our work at the ILL on the production of hydrogen from alternative sources.

Bio-ethanol can be obtained from biomass and has been proposed as a major renewable source of hydrogen, in so far as this approach also addresses the issue of greenhouse gases. The challenge therefore today is to provide low-cost catalysts capable of efficiently breaking the bio-ethanol C=C bond [3]. There is now a high demand for materials such as catalysts or electrocatalysts capable of activating fuels like H2 and alcohols for the development of these new technologies [3].

At the UCCS we have successfully developed the oxyhydride compound CaH2O3, an exceptional catalyst that totally converts ethanol at room temperature and produces H2 in the presence of water and oxygen (figure 1). H2 is produced from ethanol in a sustainable way using the chemical energy provided by the reaction between hydride species of the nano-oxyhydride catalyst and O2 [4].

Part of the hydride species formed from the ethanol reacts with O2, providing the chemical energy which maintains the catalytic reaction. The reaction is sustainable because the hydride species are being continuously replaced and provided by the ethanol. The oxyhydride compound is formed by the in situ activation of the CeNiO compound with H2 at 250 °C. The presence of hydride species in the cerium- and nickel-based mixed-oxide catalyst has been confirmed by the inelastic neutron scattering experiments performed using the IN1 BeF spectrometer at the ILL (figure 2).

The hydrogen species of the hydride nature related to the peak at about 460 cm-1 appear clearly after treatment in H2 at 250 °C [4].

Neutron spectroscopy is the only technique able to demonstrate the coexistence of different hydrogen species stored in the solids under study; it provides important information about the nature of the hydrogen species stored in the compounds. By demonstrating the presence of hydride species in the mixed-oxide catalyst, we were able to develop a new way of producing hydrogen with lower energy costs. We are confident that this will encourage additional theoretical and experimental studies, which will expand our understanding of the fundamentals and eventually lead to exciting new developments.

References


MATERIALS

Figure 1: Ethanol conversion and gas phase products distribution [H2 (■), CO2 ( ), CO ( ○), CH4 ( □) and CH4/D2O ( ●)] in mol. % obtained versus time over CaH2O3 oxyhydride catalyst (0.25 g) with oven temperature at 60°C. The reaction mixture is EtOH/H2O/O2/N2 = 1/3/1.6/1.3.

Figure 2: Inelastic neutron spectra of CeNiO, treated in a vacuum at 200 °C (black) and in H2 at 250 °C (red).
**Discovery of colloidal quasicrystals**

The formation of micelles by the association of amphiphilic molecules in aqueous solutions is one of the simplest examples of self-assembly found in nature. Micelles are ubiquitous colloids; molecules in aqueous solutions is one of the simplest examples of self-assembly found in nature. Like many other colloids, they can self-assemble in aqueous solution to form ordered periodic structures. Until now these structures all exhibited conventional crystallographic symmetries. Using small-angle neutron scattering (SANS), quasi-crystalline micellar phases exhibiting 12-fold diffraction symmetry were observed for the first time. Colloidal water-based quasicrystals are physically and chemically very simple systems. This discovery is of particular importance, as it opens a versatile new route to the fabrication of quasicrystalline photonic band gap materials using water-based colloidal self-assembly techniques.

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Ultrasoft colloid/polymer mixtures: making complex fluids look simple

A microscopic understanding that allows us to tailor macroscopic material properties is one of the great challenges for complex soft matter systems. Ideally, such an understanding must be based on both experiment and theory, quantitatively calibrated against each other. We have performed such a benchmark by investigating mixtures of ultrasoft colloids and polymer chains using rheology, small-angle neutron scattering (SANS) and liquid state theory. In this work, we show that experimental data can be described by employing recently developed effective interactions in which both components are modelled by a coarse-grained approach.

Our new theoretical approach systematically eliminates the rapidly moving degrees of freedom and focuses on the relevant slow degrees of freedom, a time-consuming and challenging task. Each complex macromolecule is replaced with a sphere of the appropriate size as schematically shown in figure 1. The challenge involves integrating the degrees of freedom that have been eliminated in the simplified systems as averages, so that the characteristics of the substances are retained.

As experimental model system, we studied mixtures of star-like micelles (ultrasoft colloids) and linear polymer chains, and provided a systematic and quantitative characterisation of the structure factors and phase behaviour in terms of effective interactions. By combining SANS experiments and liquid state theory, we measured and modelled the correlations between star-like micelles and linear chains. SANS measurements in core contrast allow a direct determination of experimental structure factors $S(Q)$, providing the basis for a comparison with the recently developed theory in which both components are modelled as point particles in a coarse-grained approach that traces out the monomeric degrees of freedom. A direct comparison without any adjustable parameters, i.e. using the quantities given directly by experiment, produces very good agreement between experiment and theory for structure factors, phase behaviour and concentration dependance of the interaction length. The comparison is performed for a broad range of concentrations and highlights the influence of the added chains on the larger star polymers.

In summary, we have described the structural and phase behaviour of binary mixtures of ultrasoft colloids and linear polymers. Indeed, while SANS is only slightly affected by varying the size ratio $\xi = R_c/R_s$, the phase behaviour may be significantly altered by a small change in the same. The agreement in phase behaviour therefore provides an additional consistency check to narrow down the values of $\xi$, $\eta$, and $\xi$ and to establish the correctness of the effective interactions that we adopted. Experimentally, no phase separation was observed for any of the samples under investigation. Hence they all lie in the one-phase region, in agreement with the theoretical results for $\xi = 0.30$. In addition, we investigated the rheological properties of all the samples by means of both steady and oscillatory shear measurements and found a transition to a solid (glass) state around 29%. Indeed, the rheological properties of all the investigated samples are in accordance with the theoretical phase diagram.

In summary, we have described the structural and phase behaviour of binary mixtures of ultrasoft colloids and linear polymers. Combining rheology, small-angle neutron scattering and liquid state theory, we obtain robust experimental evidence to the accuracy of the theoretical coarse-graining procedure. Without any adjustable parameters, we find quantitative agreement between experiment and theory within a wide range of concentrations. Our work provides a comprehensive characterisation of soft binary mixtures in terms of effective potentials and is therefore a successful benchmark in the study of complex soft matter systems [3].

**Figure 1**: Theoretical coarse-grained spheres (b) to replace the complex macromolecules of the mixture of star polymers (yellow and blue) and linear polymers (red) shown on the left (a). Using SANS on D11, we quantitatively validated that the simplified system retains all the characteristics of the original substances.

**Figure 2**: Normalised SANS intensity for intermediate polymer volume fractions. Inset: Effect of adding chains on S(Q) at $\phi_p=0.32$ for $\phi_c=0$ (circles) and $\phi_c=8.6$ (squares); Symbols: experiment, lines: theory.
Growth-collapse mechanism of polyethyleneimine with cetyltrimethylammonium bromide (PEI-CTAB) films at the air-water interface

Initial work on the self-assembly of thick nonstructured polymer-surfactant films focussed on the system polyethyleneimine (PEI) with cetyltrimethylammonium bromide (CTAB). Membranes involving the high molecular weight, (long) polymer (LPEI) were shown to be sufficiently robust to be recovered onto a mesh [4]. The structure of the LPEI-CTAB films at the air-solution interface involves a 2D hexagonal phase of close-packed cylindrical micelles surrounded by a polymer-water matrix. Previous work has indicated that thick film formation is driven by an evaporative steady state [5]. It was also noted that films do not form under acidic conditions, yet questions remain about the nature of the film growth process. In the present work we have used three complementary reflectometry techniques to gain an elevated understanding of the PEI-CTAB system for which we have revealed a remarkable growth-collapse mechanism [6]. First we employed a novel approach to track quantitatively the film thickness on the micron scale using optical techniques in the Partnership for Soft Condensed Matter (PSCM) laboratory called ellipsometry. This work represented – to our knowledge – the first quantification of the thickness of films present at this time. As the film ages, the peak position moves out of its critical micelle concentration (cmc). A growth-collapse mechanism is observed in each case: after initial growth, the thickness reaches a plateau (up to 4 μm) before undergoing a period of instability, followed by total collapse. Figure 1E-F shows measurements with CTAB below its cmc and with LPEI swapped for a low molecular weight, (short) polymer (SPEI): both films are 2–3 orders of magnitude thinner. The growth of the thick PEI-CTAB films is clearly enhanced by the interaction of long hyperbranched polymer chains with surfactant micelles.

With such an insightful pre-characterisation of the system we then carried out structural measurements using neutron reflectometry on FIGARO. Data were recorded of the film state shown in figure 1B, to track a Bragg diffraction peak at about 0.1 Å⁻¹ during the growth-collapse mechanism (figure 2). The Bragg peak changes sharpness with its highest intensity coming just after the thick film is fully formed. The subsequent broadening of the peak suggests that the micellar ordering in the films becomes less well defined during the period of instability after the film growth is complete. During this time the spacing between micelles in the film also varies, with the smallest d-spacing (0.7 Å) observed at this same surface age as the narrowest diffraction peak (about 1 h), suggesting that large domains of tightly packed micelles are present at this time. As the film ages, the peak position moves to smaller momentum transfer, indicating an expansion of the mesostructure due to increasing distance between micelles in the domains of the ordered phase. The Bragg peak disappears completely after 3 h which coincides well with the total collapse of the film from ellipsometry.

We also recorded optical images of films to track changes in lateral film morphology on the micron scale using another technique in the ILL laboratories, Brewster angle microscopy (figure 3). In the thin film regime at the start (0 min) and end (180 min) of the process the film is evenly textured and mobile. The lateral morphology of the films is similar when it is thicker (60 min) except that it is now solid and stationary. In contrast, during growth (15 min) there are linear ripples indicating the presence of long range correlations of >300 μm, and during collapse (140 min) circular defects are evident. These observations suggest that film collapse may occur by the opening up of point defects or perhaps by spinodal decomposition.

In conclusion, as a result of the use of three complementary reflectometry techniques on the PEI-CTAB system, we are now in a position to propose an interfacial mechanism. The generation of macroscopic films is due to the interaction between trimethylammonium groups on the surface of surfactant micelles with lone pairs of electrons on the primary amine groups of long polymer chains, which adsorb to the surface under an evaporative steady state. The arrest in the growth is consistent with the adsorption of CO₂ into the solution which increases the cationic polyelectrolyte charge density. Collapse is caused by the film breaking up as it dries combined with thinning as the solution acidifies. This insight can be useful for potential applications, e.g. the harvesting of solid polymer-surfactant membranes at the optimal time for defined film thickness and nanoscale structure.

Polymer-surfactant mixtures are used in countless formulations encountered in our everyday lives such as detergents, conditioners, cosmetics, paints and foods [1]. There has been sustained interest in understanding molecular interactions in such systems, and also in developing new methods to prepare ordered materials at surfaces for applications in responsive coatings, encapsulation/release and sensors [2]. Over the last decade there has also been a drive to prepare self-assembled nanostructured films at the air-solution interface [3]. The present work provides new insight into the interfacial mechanism of an intriguing system which has high potential for use in a range of applications.
Watching DNA ‘melt’

Neutron scattering can give this information through measurements of the thermal behaviour of Bragg peaks from an ordered material. Indeed, in the case of DNA it is perhaps the only method that can reliably give quantitative spatial information that is necessary to develop and improve the theory. The integrated intensity of a Bragg peak is proportional to the number of objects that scatter in phase, while the width of the peak is inversely proportional to the correlation length. As bubbles grow, the intensities decrease and the widths increase. These quantities can be directly calculated and compared with a theory that deals with the statistical fluctuations through a phase transition.

Ordered DNA can be made in the form of oriented fibre samples. As shown by the pioneering work of Rosalind Franklin and Maurice Wilkins, these samples give Bragg peaks. X-ray diffraction images from conformational analysis [4] show reciprocal space maps of the base-pair Bragg peak in two temperatures. The Bragg peak is clearly strong at room temperature, and to follow its evolution we made two scans parallel to the fibre axis. At elevated temperatures the Bragg peak vanishes.

The data were analysed to determine the integrated intensity and the width, which are plotted in figure 2. The intensities of the two scans differed only by a scale factor and hence they have been normalised. The widths are qualitatively different and both sets of data are in the figure. The data vary smoothly, with a gradual amplitude decrease associated with the beginning of the melting above about 345K, until a sudden change at about 350K. The change is due to the collapse of the DNA fibre structure at this temperature, which was verified using optical microscopy. The subsequent loss of orientation of the molecules causes the sharp peaks to disappear. We do not believe that the DNA has fully melted at this temperature, however, and as a result our comparisons with theory can only be made for the initial stages of the transition.

The results were analysed with the Peyrard-Bishop-Dauxois (PBD) model of DNA melting [2]. Statistical physics of its nonlinear Hamiltonian gives the probability that a base pair is open or closed along the sequence and the distribution of sizes of closed regions, which determines the expected structure factor for a neutron scattering experiment. The model parameters had been independently optimised [3], requiring only an “effective ionicity” to be estimated from cationic measurements of our sample. The structure factor calculation also required the knowledge of the local DNA structure, which could be obtained from conformational analysis [4].

The results are shown in figure 2. The agreement between calculation and experiment is extremely good until the collapse of the fibre structure, at which point we estimate that 50% of the molecule has melted. No free parameters have been used in the calculations for the behaviour of Scan 1, and the intensities and widths agree quantitatively. Scan 2 has a component of 0 that is perpendicular to the molecule axis, and a correlation parameter linking thermal fluctuations parallel to and perpendicular to the axis is required to calculate the expected Bragg width. This parameter needed to be greater than zero for the best agreement. It has not yet been determined using conformal analysis, and represents the only free parameter in the comparison.

This result is a great success, being the first effort to measure and successfully model DNA bubble correlations and their behaviour in the melting transition of genomic DNA. Models like PBD are already used in biotechnology, for example the design of PCR (Polymerase Chain Reaction) probes, and our experiments provide important information to help improve them. We have continued our experiments with A-form fibre DNA, in which the collapse of the fibre structure does not appear to occur, and hope to have a similar degree of agreement between theory and experiment over the full range of the melting transition.
Short range ballistic motion in fluid lipid bilayers studied by quasi-elastic neutron scattering

Diffusion is the primary mechanism for the movement of lipids and proteins in a biological membrane. It is important in the formation of various macromolecular structures, such as lipid rafts. The commonly accepted theory for diffusion in membranes suggests that the molecules undergo continuous Brownian diffusion at long length scales, with a “rattling-in-the-cage” motion at short length scales, as shown in figure 1. However, this model has recently been challenged by experimental and simulation results. It has been observed that lipids move in loosely bound clusters rather than as individual molecules [1,2], and there is a flow-like component to long range lipid diffusion [3]. Ballistic and sub-diffusive regimes have been observed in molecular dynamics simulations [4,5].

Diffusion is mainly studied by two experimental methods: fluorescence techniques and incoherent quasi-elastic neutron scattering. The two techniques access distinctly different length scales, resulting in a “blind spot” at mesoscopic distances. We note that the diffusion coefficients measured by these two techniques often differ by as much as orders of magnitude. The mechanism for diffusion, therefore, seems to depend on the length scale at which it is observed. The blind spot in the mesoscopic range will hopefully be closed in the future using high energy resolution laser–procession techniques performed with spin-echo spectrometers.

To extend the window of length scales and investigate the motion of lipid molecules at very short distances, we used the unique capabilities of the IN13 thermal backscattering spectrometer. IN13 provides access to an exceptionally large Q range, covering length scales from 1.3 to 31 Å (0.2 Å−1 < Q < 5 Å−1). We used IN13 to study lipid diffusion at length scales smaller than a typical lipid-lipid distance in fluid bilayers. The aim of the experiment was to prove the validity of the Brownian diffusion model down to very small length scales. We chose a stacked model membrane system (DMPC) for this study and analysed the quasi-elastic neutron scattering response of the lipid molecules. Membranes were prepared as solid-supported, multi-lamellar membrane stacks on silicon wafers. Protonated lipids were hydrated by heavy water, so that the experiments were sensitive to the incoherent scattering of the lipids. To increase the scattering signal, several wafers of highly oriented membranes were stacked. The membranes were studied in their physiologically relevant fluid state, at high temperature (T=30 °C) and full hydration.

The width of the quasi-elastic energy response (full width at half maximum, FWHM) is shown in figure 2. A particle moves ballistically, $v_0 = vt$, the broadening has a Gaussian peak shape and the width follows $FWHM = 2\sqrt{2}$. If a particle moves ballistically, $v_0 = vt$, the broadening has a Gaussian peak shape and the width follows $FWHM = 2\sqrt{2}$. In 2D, $v_0 = 2\sqrt{2}$ [5].

We observed a transition from Brownian to ballistic lipid diffusion at a length scale of about 2.5 Å. The velocity of the lipid molecule is determined to be about 1.2 m/s. This is about two orders of magnitude slower than the thermal velocity at 30 °C of about 90 m/s, which can be calculated from the equipartition theorem $k_B T = \frac{1}{2} m v^2$.

Despite intense efforts, there is still no coherent model which describes the motions of lipid molecules from less than lipid-lipid to macroscopic distances. The aim of our experiment was to prove the validity of the Brownian diffusion model down to very small length scales. During our investigation, we observed, for the first time, the transition from Brownian to ballistic motion of lipids in a fluid lipid membrane and demonstrated that the early stage of lipid motion is the result of a flow-like ballistic motion rather than the previously accepted “rattling-in-the-cage”.

**Figure 1:** Continuous Brownian diffusion at long length scales. The early stage of this motion is often modeled as a “rattling-in-the-cage” motion.
The motion of macromolecules inside a biological cell is strongly influenced by the presence of other macromolecules in the intracellular fluid. Therefore, a quantitative understanding of macromolecular motion driven by diffusion on a molecular scale contributes to fundamental biological insights. Biological macromolecules and in particular proteins are soft and in general inhomogeneous in shape and surface charge pattern. Nevertheless, recent simulation results on the protein diffusion in a hypothetical cellular environment have found reasonable agreement with predictions from colloidal theory [1,2]. In our study [3], we experimentally investigate the protein self-diffusion under the conditions of macromolecular crowding and compare the results with the existing colloidal theories. In our model system, the protein Bovine Serum Albumin (BSA) in an aqueous (D2O) solution serves as both crowding agent and tracer particle at the same time.

The nanosecond time window of neutron backscattering allowed for the first time to access the short-time limit of protein self-diffusion. In this limit, the diffusion is solely affected by hydrodynamic interactions, since the displacement is too small to considerably change interparticle interaction potentials. A large number of backscattering spectra have been recorded to obtain the diffusion constant, $D_t$, as a function of the protein volume fraction $\varphi$. The model used for the fits accounts for intramolecular dynamics, the instrumental resolution and, importantly, diffusion of the entire protein (an example data set with fit components is depicted in the inset of figure 1) [3]. The quadratic behavior of the linewidth $\gamma$ of the narrow Lorentzian (green line), representing the diffusion of the entire protein, versus the scattering vector $Q$ indicates simple diffusive behavior on the experimental time and length scales even in crowded solutions (main part of figure 1).

However, due to the experimental scales, the extracted diffusion coefficient $D_t$ consists of both translational and rotational diffusion. In order to isolate the experimental translational diffusion coefficient $D_t/\rho$ we developed a new framework for the full volume fraction range based on predictions [2] for diffusion of charged and uncharged hard spheres. To this end, the protein molecule was mapped to an effective sphere using Perrin factors and an approximated ellipsoid shape using data from small-angle X-ray scattering. By this means we can compare the theoretical predictions from colloidal theory for effective hard spheres to the experimental system of non-spherical soft proteins.

Figure 2 displays the resulting experimental translational diffusion constants $D_t/\rho$ for two temperatures (symbols) in comparison with theoretical predictions for short-time self-diffusion of charged and uncharged hard spheres (blue dashed and blue solid line, respectively). $D_t$ is the diffusion constant in the dilute limit of the protein concentration obtained from dynamic light scattering. Within the experimental accuracy, the agreement is quantitative, suggesting that the slowing down of the self-diffusion is caused solely by hydrodynamic interactions. This agreement despite the rather simplistic spherical protein model is promising for future studies also on intramolecular dynamics of freely diffusing proteins in aqueous solution [4].

The experimental data (figure 2) show that $D_t/\rho$ decreases by more than a factor of 5 at biologically relevant volume fractions around 30% compared to the dilute limit. This considerable slowing down of the self-diffusion already on nanosecond time scales and nanometer length scales indicates a non-negligible role of hydrodynamic interactions also for longer time scales.

In conclusion, hydrodynamic interactions are an important ingredient for a full understanding of cellular processes and macromolecular crowding. Interestingly, diffusion can be understood at least to some level in terms of colloidal theory also for the case of complex biomolecules. Future studies will address charge effects through a systematic change tuning. This fundamental research can be assumed to be of interest in biomedical applications.
Oxygen as a site specific probe of the structure of water and oxide materials

Structurally disordered oxides are important materials where examples include molten silicates in planetary science, glasses used for lasers and optical communications, the insulating oxide layers in silicon-based electronic devices, and water in biological processes [13]. The method of isotope substitution in neutron diffraction has provided a pivotal role in unravelling the structure of liquids and glasses. It has not, however, found application in the case of oxygen owing to the small contrast reported in the literature between the bound coherent neutron scattering lengths of its isotopes. In view of the importance of oxide materials and in the absence of a suitable theory to calculate the cross section for interaction of thermal neutrons with a specific nucleus, we have used the neutron interferometer S18 at the ILL to measure the b values of the isotopes 17O and 18O relative to oxygen of natural isotopic abundance 16O [4]. The results reveal a scattering length contrast between the 17O and 18O isotopes of 0.0040(3) fm, giving a factor of about 6 increase by comparison with standard tabulations, and suggest that it is feasible to apply the method of oxygen isotope substitution in neutron diffraction to study the coordination environment of this element in disordered materials.

Water provides an important test bed to exploit this approach since there are several elements of its structure and dynamics that remain hotly debated [3]. One aspect of the controversy is the role played by nuclear quantum effects, such as zero point energy and tunneling, on water’s hydrogen bonded network. This is manifested by differences between the structure and dynamics of heavy versus light water which lead to changes in properties such as their melting and boiling points, their temperature of maximum density, and their interaction with biological systems. Neutron diffraction experiments were made with the instrument D4 at the ILL using either heavy water samples of D2O and D18O or light water samples of H2O and H18O [4]. These experiments took advantage of the count rate stability for D4 of ±0.01% over 3 days. The measured diffusion patterns for either heavy or light water were subtracted to eliminate either the D-D or H-H quantum fluctuations in the anharmonic intra-molecular O-H bond and the net effect of quantum fluctuations in the anharmonic intra-molecular OH band increases its length and hence the dipole moment of each water molecule. The higher dipole acts, in turn, to increase the binding between molecules, and hence the net effect of quantum fluctuations is smaller than originally suggested from rigid water simulations. Our experimental results show that there is great potential for the method of neutron diffraction with oxygen isotope substitution to study the structure of water. The results give insight into the role played by quantum mechanics in water’s properties.

To provide a comparison for our diffraction data we made path integral quantum molecular dynamics simulations of light and heavy water, shown in figure 3 [4]. These calculations, in which a system of quantum mechanical particles is mapped onto a simulation of classical ring polymers, provide an exact treatment of nuclear quantum fluctuations in the structure of a given potential energy model for water. The polarisable flexible TTM3-F model was found to agree best with the experimental data and this model reproduces accurately the OH stretching region of the infrared (IR) absorption spectrum of liquid water as well as its diffusion coefficient.

The quantitative agreement between the measured and calculated first difference functions (figures 1 and 2) supports the proposal of computing quantum effects, where inter-molecular zero point energy and tunneling weaken the hydrogen bond network but where quantum fluctuations in the anharmonic intra-molecular OH band increase its length and hence the dipole moment of each water molecule. The higher dipole acts, in turn, to increase the binding between molecules, and hence the net effect of quantum fluctuations is smaller than originally suggested from rigid water simulations. Our results indicate that these competing quantum effects more-than-cancels which is fortuitous for experimental methods that exploit H/D isotope substitution, such as 2-D IR spectroscopy, NMR spectroscopy and neutron diffraction. This is because when these methods are used to study either light or heavy water at room temperature the structural environments probed, as well as the quantum contribution to the dynamics, are likely to be similar.

Our experimental results show that there is great potential for applying the method of neutron diffraction with oxygen isotope substitution as a site-specific structural probe of oxide materials. Current neutron diffraction instrumentation will allow for this approach to be applied to materials where the oxygen content is smaller than originally suggested from rigid water simulations. Between molecules, and hence the net effect of quantum fluctuations is smaller than originally suggested from rigid water simulations. Our results indicate that these competing quantum effects more-than-cancels which is fortuitous for experimental methods that exploit H/D isotope substitution, such as 2-D IR spectroscopy, NMR spectroscopy and neutron diffraction. This is because when these methods are used to study either light or heavy water at room temperature the structural environments probed, as well as the quantum contribution to the dynamics, are likely to be similar.

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Dynamics of liquid hydrogen: the realm of neutron scattering

Hydrogen is the most abundant substance in the universe, made of the simplest nuclei bound together in pairs to form the simplest molecules. It was one of the first chemical elements to be recognised and produced, and the explanation of its atomic properties was one of the first major successes of the new-born quantum ideas about one hundred years ago. The role played by hydrogen in the progress of science has been immense. In addition hydrogen, particularly in its liquid state, is nowadays becoming increasingly important on the technological side, particularly as an energy carrier and storing medium.

Exploiting hydrogen potentialities requires a deep knowledge of its properties at the molecular level. Yet, the understanding of the dynamics of hydrogen molecules is still incomplete. On the other hand, the light mass and the very low temperature of liquid hydrogen make its study a problem in quantum physics, but quantum simulation is still immature technique, which does not yet produce reliable spectra.

Self dynamics is traditionally described using the Gaussian approximation (GA), where all the relevant information is contained in a function of energy E, in a wide range of values of the wave vector Q. A neutron investigation carried out on BRISP and IN4 sheds new light on this long-standing problem.

A still open problem in the diffusive dynamics of fluids is the validation of the Gaussian approximation to the self dynamic structure factor. In particular, this issue is of high impact in the case of liquid hydrogen, for its importance in fundamental physics, its technological applications, and its role in the development of quantum simulation methods. A neutron investigation carried out on BRISP and IN4 sheds new light on this long-standing problem.

![Figure 1: The self dynamic structure factor of liquid hydrogen at Q = 10, 30, and 41 nm⁻¹, from left to right. The red dots are the neutron data taken on BRISP (first frame) and IN4 (second and third frames). The solid line is the calculation of Gaussian approximation using the quantum simulation of the velocity correlation function.](image1)

![Figure 2: The non-Gaussianity parameter α(Q) [1] of liquid H₂ (blue line) and liquid Ar (red data). The hydrogen data are divided by 4. The argon data are from [4].](image2)
Destabilisation of lipid membranes by a peptide derived from the feline immunodeficiency virus glycoprotein gp36

Viral fusion is controlled by one or more viral surface glycoproteins that undergo conformational changes driving membrane fusion. Viral fusion glycoproteins present a membrane-proximal external region (MPER) which is usually rich in aromatic residues and exhibits a marked tendency to reside stably at the membrane interfaces, thus, via mechanisms as yet unknown, to a destabilisation of the bilayer structure. This step is fundamental for the fusion process between target membrane and viral envelope.

Even though the exact mechanism by which fusion proteins favour the fusion process is still unknown, recent studies suggest the MPER domain to be crucial in the infection pathway [1, 2].

We have investigated the effect of the C8 peptide by measuring the NR curves of the fully hydrogenated POPC to which the peptide with deuterated Trp residues was added. Four contrast solvents, D2O, 4MW, SMW and H2O as isotopic contrast solvents (figure 1), which presents a thickness of 44 ± 1 Å and a slow content of water (70 ± 20%) in the POPC bilayer. This layer interposed between the silicon surface and the adsorbed membrane interfaces; this leads, via mechanisms as yet unknown, to a destabilisation of the bilayer structure. This step is fundamental for the fusion process between target membrane and viral envelope.

We first characterised the pure POPC bilayer using D2O, 5MW (silicon-matched water) and H2O as isotopic contrast solvents (figure 1), which presents a thickness of 44 ± 1 Å and a slow content of water (70 ± 20%) in the hydrophobic layer. We then investigated the effect of the C8 peptide by measuring the NR curves of the fully hydrogenated POPC to which the peptide with deuterated Trp residues was added. Four contrast solvents, D2O, 4MW, SMW and H2O were used. Data from the peptide-interacting bilayer were fitted by an additional layer with respect to the pure POPC model. This layer evidently consists of the peptides interacting with the outer bilayer surface, indicating that the presence of the peptide effectively perturbs the outer hydrophilic layer of the POPC membrane and that this perturbation propagates in the chain region. In particular, the thickness values of the two layers corresponding to the polar headgroups decrease slightly, while the thickness of the chains region increases.

We analysed the NR profiles by box-model fitting, using the ART and MOLOTOR programmes. A five-box model was found to best fit the data relative to POPC membranes. The first two boxes correspond to the silicon block and to the thin solvent layer interposed between the silicon surface and the adsorbed bilayer. The three other boxes describe the lipid bilayer, which is subdivided in the inner headgroups, the hydrophobic chains, and the outer headgroups layers.

The results indicate that C8 interacts directly with the hydrophilic region of the membrane’s external leaflet, but it causes a structural perturbation which involves the whole bilayer. This step is fundamental for the fusion process between target membrane and viral envelope.

In conclusion, our neutron reflectivity study gave us a detailed picture of the membrane-peptide interaction. It furnished a clear indication of C8 positioning relative to the lipid bilayer, as well as changes in the bilayer thickness on peptide binding. The results indicate that C8 interacts directly with the hydrophilic region of the membrane’s external leaflet, but it causes a structural perturbation which involves the whole bilayer. These results suggest a mechanism in the MPER domain inducing the membrane fusion process.
Cholesterol transport in model lipid membrane system

To track the redistribution of cholesterol between lipid vesicles, the total scattered intensity resulting from mixing lipid vesicles with and without cholesterol was measured as a function of time. Only the contribution from cholesterol was detected as the lipids in the vesicles were rendered completely invisible by the solvent (figure 1). The resulting intensity decay is then directly related to cholesterol transfer and was fitted using a kinetic model that allowed cholesterol to flip within the same membrane as well as to exchange to a different membrane. The activation energies for flipping cholesterol to flip within the same membrane as well as to exchange cholesterol were measured as a function of time.

The widely held belief that cholesterol, being mostly hydrophobic, flips easily within the hydrophobic core of the membrane while exchanges slowly between membranes due to its extremely low solubility in an aqueous medium is at odds with our data. Our results with POPC vesicles suggest that the mechanism for cholesterol flipping is not dominated by hydrophobic/hydrophilic interactions between lipids and cholesterol. Other forces, including steric interactions: cholesterol/lipid interactions and lipid tail packing, and Van der Waals interactions are important.

Time-resolved SANS offers the versatility to measure tagged and untagged molecules alike, and therefore, it is possible to begin addressing questions concerning possible artifacts in reported flipping and exchange kinetics using other experimental techniques. Our data, using non-invasive in situ measurements, clearly challenge the assumptions made in previous studies and more generally highlight the difficulty in using chemical tags or additives to understand the transport properties and energetics of self-assembled systems.

Further, this work establishes time-resolved SANS as a powerful tool for elucidating the myriad of contributions to the kinetics of these complex and interacting systems.
Towards a detailed mechanistic study of small heat-shock chaperone protein action

α-Crystallin is a member of the small heat shock proteins (sHsps) family, a varied group of intracellular molecular chaperones found in all organisms [1]. In humans, they are present in many tissues at varying concentrations depending on the stage of development and the level of physiological stress. The function of sHsps is versatile but their common role is to interact with and stabilise the partially folded states of other (target) proteins to prevent their aggregation and possible precipitation, for example under conditions of environmental stress such as elevated temperature, low pH and oxidation.

The principal eye lens protein, α-crystallin, is a shp that is comprised of two closely related subtypes, aα and aβ-crystallin, both approximately 20kDa in mass. In the human lens, these two subtypes are co-expressed in the ratio of 3:1 both approximately 20 kDa in mass. In the human lens, these proteins are involved in limiting lens protein precipitation over many years and is implicated in other protein misfolding diseases such as Alzheimer’s disease, multiple sclerosis, Parkinson’s disease and in the ischaemic heart [4].

The small-angle diffractometer D22 was used to quantify the size and shape of a series of crystallin proteins, in simple solutions under non-stressed (20 °C) and stressed (65 °C) conditions, and in binary mixtures. In the non-stressed conditions, there was no change in the scattering intensity and thus the calculated radii of gyration \( R_g \) remained constant, indicating no aggregation.

In the binary mixtures, however, there was an increase in scattered intensity over a period of several hours, and a concomitant perturbation in the radii of gyration, figure 1. It was found that:

\[
\begin{align*}
R_g(\alpha\text{-crystallin}) &> R_g(\alpha\beta\text{-crystallin}) > R_g(\gamma\text{-crystallin}) &> R_g(\alpha\beta\gamma\text{-crystallin})
\end{align*}
\]

The ageing population is recognised as a world-wide problem and represents a significant financial burden for all economies. In terms of vision alone, age-related cataract is responsible for nearly 50% of world blindness, affecting some 18 million people (World Health Organisation, WHO). The reasons for cataract development are many and varied – age, long-term exposure to ultraviolet light, exposure to radiation, disease (diabetes, hypertension) or trauma – all usually arise as a result of unfolding, mis-folding and aggregation of lens proteins.

Small-angle neutron scattering [SANS] has been used to examine the interactions between proteins that lead to such physiological manifestations.

α-Crystallin is the primary protein component and can approach 50% of the total dry weight of the lens.

In a structural role, α-Crystallin assists in the maintenance of short-range order in the lens cytoplasm, ensuring the correct amount of refraction of light on to the retina, and maintenance of lens transparency.

Secondly, it acts as a molecular chaperone to maintain the stability and solubility of the other classes of crystallin proteins, α and β [2]. However, α-crystallin does not refold denatured proteins, nor does it hydrolyse ATP, and thus, since protein is not its substrate, α-crystallin is not a molecular chaperone in the conventional sense. Instead, α-crystallin has long-reaching implications in the prevention and treatment of cataracts and other degenerative diseases.
Softness of pro-atherogenic lipoproteins revealed by elastic incoherent neutron scattering

Apolipoprotein B100 (apoB100)-containing plasma lipoproteins, i.e. very low density lipoprotein (VLDL) and low density lipoprotein (LDL), are the principal transporters for cholesterol and energy-rich fat in the circulation. During metabolism the triglyceride content of VLDL becomes gradually lower while the particle size decreases from about 50 to 20 nm diameter. Eventually, VLDL is converted to LDL that is rich in cholesteryl ester. In the course of shrinking apoB100 remains bound to its carrier stabilising the whole particle (figure 1). The molecular physical parameters which control lipoprotein remodeling, enable particle stabilisation by apoB100, and control receptor-mediated uptake of the lipoproteins are largely unknown.

To study the molecular dynamics of apoB100-containing lipoproteins in terms of thermal molecular fluctuations, which can be assessed by mean square displacements, we have performed a comparative study using elastic incoherent neutron scattering (EINS). The experiments were performed on the thermal neutron backscattering spectrometer IN13 at the ILL. We have used hydrated lipoprotein powders, which were measured in a temperature range from 20K to 310K. EINS experiments shed light on global thermal motions and molecular fluctuations of lipoproteins that reflect the temperature-dependent motional coupling between lipid and protein.

In the low temperature regime, motions are reduced to harmonic vibrations around equilibrium positions. In this range we did not find noticeable differences between the two lipoprotein classes, but still, lipoproteins were softer compared to well-studied model proteins. This behaviour can be correlated to the contribution of lipids to the global dynamics of lipoproteins [2]. A first onset of anharmonicity was seen at about 180 - 200K, and a second dynamical transition was observed in the range of 280 to 270K. Above this second transition, distinctions in the dynamics between LDL and VLDL became clearly visible. Most important, at physiological temperature, less structural resilience and higher mean molecular displacements are observed for VLDL samples (figure 2).

It is likely that the pronounced softness of VLDL is dominated by its larger lipid content. To address this question, we have performed EINS measurements in the presence of sucrose, which was added to the aqueous lipoprotein solutions before lyophilisation. With this approach we expected to obtain more information about the individual contributions from the outer shell and the inner core components, respectively, to global lipoprotein dynamics.

As expected, with sucrose both lipoproteins were more rigid over the entire temperature range (figure 2b). The most striking feature, however, was that the dynamics of VLDL became dramatically restricted and nearly equaled that of LDL, in particular at higher temperatures. We supposed that sucrose molecules surrounding the lipoprotein particle most likely interact with other hydrophilic groups or domains on the surface of the particle in addition to water. This led us to the assumption that the rigifying effects of sucrose, especially on VLDL samples, are limited to surface-exposed apolipoprotein domains and in part to phospholipid headgroups and cholesteryl. Since the shrinking changes in LDL cannot only be explained by the higher amount of surface-located molecules, it appears likely that apoB100 displays distinctly different mobilities in VLDL and LDL controlled by its direct molecular environment.

Our data support the notion that the lipolytic conversion of VLDL to LDL forces apoB100 into a more condensed state and therefore rigid state, entirely compatible with the observed inhibition of relaxation caused by the presence of sugar. Taken together, EINS measurements of LDL and VLDL revealed the pronounced softness of pro-atherogenic lipoproteins. We found substantial differences in the molecular resilience of lipoproteins, especially at higher temperatures, with VLDL being more flexible than LDL. These discrepancies cannot only be explained in terms of lipid composition and mobility, but suggest that apoB100 displays different dynamics depending on the lipoprotein it is bound to.

Hence, we propose that the inherent conformational flexibility of apoB100 permits particle stabilisation upon lipid exchange, whereas the dynamic coupling between protein and lipid may be a key determinant for lipoprotein conversion and atherogenicity.

Our results revealed that lipoproteins are extremely soft and flexible, with VLDL being more fluid than LDL [3]. We propose that the intrinsic flexibility and the dynamic coupling between lipids and the apolipoprotein moiety are the key determinants of the functionality of lipoproteins in both health and disease. A deeper understanding of the relationship between structure, dynamics, stability, and biological function of apoB100 in lipoprotein species may well help to prevent the progression of cardiovascular diseases.

Lipoproteins are naturally occurring globular nanoparticles circulating in the blood which function to supply tissues and cells with cholesterol and other lipids. These substances are essential for membrane synthesis and fuel storage in cells and are precursors for signaling molecules. However, lipoproteins are also associated with cardiovascular diseases such as atherosclerosis or stroke, which are among the most prevalent causes of death in developed countries [1]. Elastic neutron scattering was used to study thermal motions, dynamical transitions, and molecular fluctuations of lipoproteins to shed light on the key determinants of the functionality of lipoproteins in both health and disease.
Isotopic yield measurement in the heavy mass region

Up to now, thanks to the ILL’s Lohengrin mass spectrometer, various fissioning nuclei have been investigated. Combining the mass spectrometer with a high resolution ionisation chamber allows good nuclear charge discrimination within a mass line, yielding an accurate isotopic yield determination. Nevertheless, this procedure can only be applied for fission products with a nuclear charge Z less than about 42, i.e. in the light mass region. In order to study also fission product characteristics in the heavy mass region, a new experimental set-up based on gamma spectrometry (for the fission product identification) has been installed.

The Lohengrin recoil-mass spectrometer is a nuclear physics instrument, which uses low-energy fission reactions for fission fragment production. For the present work, a highly enriched 239Pu target was placed close to the core of the ILL’s high-flux reactor in a thermal-neutron flux of about 5x10^12/n•cm^-2•s. Fission products with mass A emerge from the target with an ionic charge state q and a kinetic energy E. The selection of these fission products is performed by a combination of a magnetic and an electric sector field. At the exit slit, the combined action of the two fields separates ions according to their A/q ratios. In order to investigate the heavy mass region by taking profit of the very high mass and energy resolutions, a new experimental setup has been developed. It is based on gamma spectrometry, which is for the first time combined with the Lohengrin spectrometer. The rays are used to identify the fission products and to determine their yields. For this purpose, the measurement is performed in several steps:

• The electric and magnetic fields of the mass spectrometer are set to select fission products with a given mass (A), ionic charge (q) and kinetic energy (E).
• These fission products are implanted during the measuring time in a tape located inside a vacuum chamber which is placed at the focal point of the spectrometer.
• During this measuring time, rays are registered with two high efficiency germanium clover detectors placed close to the vacuum chamber.
• Then, the tape is moved to remove the residual activity. In this way, a new measurement can start.

Isotopic yield values for the 65 measured fission products [18 in the light mass region and 46 in the heavy mass region] are plotted in figure 1. For the large majority of fission products, a very good agreement between the Lohengrin data and the European library JEFF-3.1.1 [2] values is achieved, but with a significant reduction of the uncertainties. The average yield uncertainty reaches 11.9 % (our measurements) and 23.3 % [JEFF-3.1.1] respectively, which corresponds to a reduction of a factor of nearly 2.

In addition, we have observed for some fission products an asymmetric ionic charge distribution. In particular, an important tail for high ionic charge states can be highlighted. This effect results from nanosecond isomers that decay by a highly converted internal transition. Owing to the short half-lives of these isomeric states (of the order of some nanoseconds), conversion and Auger electrons, which are emitted between the target and the vacuum chamber, are emitted between the target and the vacuum chamber. In this way, a new measurement can start.

For the 140Xe nucleus, a strongly deformed distribution was observed, showing the presence of nanosecond isomers. By this method, new nanosecond isomers were identified as reported by Materna et al [3].

Lastly, ionic charge distributions were investigated for all masses where at least three fission product yields were measured. Assuming a Gaussian shape distribution, the most probable charge (Z_p) and the variance (σ) were determined. In low-energy fission, fission products present an average charge density different from the fissioning nuclear charge density. Compared to the unchanged nuclear charge (Z_UCD), light fragments are found to have a smaller nuclear charge while heavy fragments show the unchanged nuclear charge. This difference (ΔZ = Z_p - Z_UCD) confirms the existence of a charge polarization of nuclear matter.

In conclusion, Lohengrin is still the most accurate instrument for measuring thermal neutron fission yields, and with the present work, its range of application is practically doubled, now allowing the study of isotopic yields of heavy fragments. Results are very encouraging considering how uncertainties have been decreased compared to other experiments and evaluated data respectively.

Figure 1: Isotopic yields measured in the heavy mass region for the 239Pu(n,f) reaction [1].

Figure 2: Ionic charge distributions measured for 136Xe and 138Cs.
The new method allows precise measurement of quantum states of ultra-cold neutrons in the gravitational potential of the Earth with a Schrödinger wave packet bouncing off a hard horizontal surface [1]. Two features of quantum physics put up together are responsible for the precision, which can be achieved. First of all, quantum systems only allow for discrete energy levels. As atomic clocks are concerned, it is the energy splitting of Caesium atoms in their own magnetic field and with NMR techniques an outer magnetic field - usually provided by superconducting magnets - defines the energy levels of the magnetic moments of the nuclei. This also works for an ultra-cold neutron bouncing off a hard horizontal surface. In 2002, the first demonstration of discrete energy levels of quantum states in the gravitational potential of the Earth has been performed with ultra-cold neutrons [2] at ILL on PF2 and started as a collaboration between the ILL, PNPI (Gatchina), JINR (Dubna) and the authors (at that time at the Physics Institute at Heidelberg University). In that experiment neutrons were allowed to populate the lower states of figure 1. Higher, unwanted states were removed.

The other feature of quantum physics, which provides high precision, is the possibility to drive transitions between these quantum-mechanical energy levels. An external oscillating force causes a coupling between these levels. The transition occurs on resonance, when the frequency is adjusted to the energy difference. All resonance techniques so far use electromagnetic fields one way or the other. A novelty of this work is the fact that the quantum-mechanical transition is driven by an oscillating field, which is not a direct coupling of an electromagnetic change or moment to an electromagnetic field. Instead, we observe transitions between gravitational quantum states by mechanically oscillating the boundary conditions of our quantum states. The physics behind these transitions is related to earlier studies of energy transfer when matter waves bounce off a vibrating mirror [3].

For this purpose, ultra-cold neutrons are taken from PF2 as in previous experiments. Their horizontal velocity component is restricted to 5.7 m/s < v < 7 m/s.

For an energy difference measurement between two gravitational quantum states |p> and |q>, ultra-cold neutrons are prepared into state |p>. An oscillator drives transitions between |p> and |q>, if the oscillation frequency matches their energy difference. An analyzer only transmits neutrons in state |p>. A detector behind this system counts the neutrons transmitted. In our experiments, this has been realized with only one bottom mirror coupled to a mechanical oscillator: a scatterer on top and a neutron detector behind (see figure 2). The scatterer only allows the ground state to pass and prepares the state |p>. The vibrating mirror induces transitions to |q> which are again filtered out by the scatterer. Therefore, by tuning the oscillating frequency of the neutron mirror, characteristic drops of intensity are found, if the resonance condition ΔE = Eq - Ep = Δω |E|ω is fulfilled (see figure 3).

In conclusion, spectroscopy of gravity has been seen for the first time. This is interesting, because it addresses some of the unsolved questions of modern science: the nature of the fundamental forces and underlying symmetries and the nature of gravitation at small distances. The method can usefully be employed in measurements of fundamental constants or in a search for non-Newtonian gravity [4].

The experiment combines quantum theory with gravitation, two fundamental pillars, which have not been described in a common language, yet. What is more, only 4 % of the Universe’s content has been identified as quantum particles. The rest are dark matter particles and dark energy, which again is linked to the modification of gravity at small distances. The new method profits from small systematic effects in such systems, mainly due to the fact that, in contrast to atoms, the electrical polarizability of neutrons is extremely low. Neutrons are not disturbed by short range electric forces such as van der Waals or Casimir forces. Together with its neutrality, this provides the key to a sensitivity of several orders of magnitude below the strength of electromagnetism.
Thermal motion in the multi-subunit protein, apoferritin, as studied by high energy resolution neutron spectroscopy

The high resolution backscattering spectrometer IN16, has allowed us unique insight into the dynamic landscape of apoferritin (figure 1), the multi-subunit intracellular iron storage protein found in almost all living organisms and a model system for colloidal bio-systems due to its mono-disperse spherical form factor. Using elastic neutron scattering methods, we have shown without ambiguity that in its lyophilised form, apoferritin, above 100K, over the length scale 3.5 Å to 9 Å and in the ps-ns time regime, exhibits a single dynamic response driven by methyl (CH₃) groups alone; the data have been successfully modelled (figure 2) using theory originally developed to describe motion in glassy polymers [2]. We observe a distribution of CH₃ activation energies consistent with the environmental heterogeneity that exists around the methyl species in this protein. A mean activation energy of $E_a,\text{ave} = 17 \text{ kJ mol}^{-1}$ with a width of the distribution of activation energies of $4 \text{ kJ mol}^{-1}$ is observed.

Here, we confirm that the methyl species undergo 3-fold jump rotations and that the characteristic relaxation time of the jump process follows the Arrhenius form with activation energy in agreement with our IN16 result.

Our results show that over the temporal and spatial range studied the main apoferritin peptide chain and other side groups remain rigid. Interestingly, yet seemingly counter-intuitively, similar results are reported for other smaller, more flexible lyophilised bio-materials. Nonetheless, these results are supported by findings from NMR. Our results will allow us to develop accurate MD force fields for the apoferritin molecule as well as further advance, via collaboration, complex molecular dynamic model simulations of other proteins. We believe this work, and analysis approach, could act as a benchmark for the investigation of methyl group dynamics in other proteinacious materials using neutron scattering. Furthermore, it is clear that there is a need for detailed dynamical data given the complexity and diversity of bio-macromolecules.

Protein dynamics play a pivotal role in biological functions such as enzyme catalysis, ligand binding and protein folding and mis-folding. As a result, detailed appreciation of the relationships between dynamics and biological function requires analysis based on models that realise the full complexity of macromolecular material. Neutron spectroscopy is an ideal tool with which to gain insight into the dynamics of bio-molecules [1] since it is not only a non-destructive and selective technique but also provides simultaneously spatial and temporal information; parameters extracted from experimental neutron studies being akin to those calculated in molecular dynamic (MD) simulations. The range of bio-macromolecular problems addressed using neutron spectroscopy is considerable. However, it is clear that there is a need for further complete dynamical data given the complexity and diversity of bio-macromolecules.
DNA as a safety belt

Most experimental techniques apply forces to the DNA molecule or require some molecular sculpturing (optical or magnetic tweezer, attaching nano-particles to DNA, etc) in order to obtain the values for the corresponding force constants. However, the reported values in literature for this force constant vary by nearly three orders of magnitude, with a clear tendency for structure-based measurements to give softer force constants.

We have determined the stretching force constant, free from such external manipulations, by measuring with inelastic neutron scattering (INS) the dispersion of harmonic vibrations along aligned, wet-spun fibers on the new IN5 spectrometer. The observed dynamics are confirmed by phonon calculations, using the standard CHARMM force field, on a fully atomistic model of DNA surrounded by water molecules and counter ions. This is the first observation of the acoustic phonon branch along the DNA fiber, enabled by the very high resolution in both energy and momentum transfer, as well as the excellent signal-to-noise ratio, available on IN5. The width of the helix Brillouin zone is 0.18Å⁻¹ and the acoustic branch peaks below 2 meV. These collective dynamics, measured up to 335 K i.e. far above physiological temperatures, are remarkable considering the common understanding of DNA existing of randomly distributed soft and stiff regions along the helix.

Phonon calculations reconcile these data with inelastic X-ray scattering (IXS) data. The apparent liquid-like damping of the phonon dynamics in the IXS data, in the much (10x) bigger Brillouin zone defined by the distance between base-pairs, is simply a manifestation of the random sequence of base-pairs and the one-dimensional character of the excitations. The apparent acoustic phonon branch as measured by IXS, extending up to about 10 meV, is actually the average of many optic modes polarized along the helix axis. The atomistic model that is used to describe both the INS and IXS data can be used to mimic the stress-strain experiments performed on single DNA molecules. Molecular dynamics simulations probe the stretching stiffness of DNA on a longer time scale up to 100 ns, compared to the pico- to femto-second vibrational timescale. The elongation and compression of the simulation cell in the direction of the helix axis results in a force constant that is an order of magnitude or more lower than the 83 N/m obtained from the inelastic scattering data and lattice dynamics calculations. At longer time scales the reorganisation of the surrounding water molecules and counter ions effectively softens the DNA. Force-based methods to determine the force constant and techniques based on molecular sculpturing like [2] include such relaxation in their determination of force constant.

In this way, DNA is like a car safety belt that resists when pulled suddenly (on a short picosecond time scale) but extends more easily when pulled gently. The next step will be to determine the sensitivity of the DNA force constant to variations of its direct environment like water molecules and counter ions.

The DNA molecule inside a living cell undergoes many mechanical manipulations, both to pack it in the cell and to fulfill its biological functions. Understanding DNA functions therefore requires its mechanical properties, expressed as elastic or force constants, to be known [1]. The improved inelastic neutron scattering spectrometer IN5 and samples of aligned DNA fibers, combined with atomistic phonon and MD calculations, now make the very soft collective dynamics in DNA measurable. From these measurements the base-pair, stretching force constant is derived.

References


Figure 1: (a) Configuration 1 parallel 70K

Momentum transfer (Å⁻¹)

Neutron energy loss (meV)

Neutron energy loss (meV)

(a) Configuration 1 parallel 70K

Figure 1: (R2E) map of DNA fibers aligned parallel to the instrumental scattering plane. The Bragg peak at 1.9Å⁻¹ and the acoustic branch are clearly visible. At higher energy the first optic dispersion is seen.
Insights into the unusual phenomenon of negative thermal expansion: Relevancy to dynamics

NTE is a macroscopic property that needs to be understood at the fundamental level as it involves a number of different microscopic physicochemical aspects. Dynamics plays a major role in this context and is intimately related to thermal properties through phonons (quantum of vibrations). The latter reflect the dynamical character of the material and build up its thermodynamic picture.

There is keen interest in the quest for NTE materials. As well as in oxide-based materials, anomalous thermal expansion behaviour has been observed in molecular framework systems containing linear diatomic bridges, such as cyanide anions. In this article, we focus on Zn(CN)₂, which is reported to have a large isotropic NTE coefficient over a wide temperature range. Figure 1 shows the ordered structure of Zn(CN)₂, which is a cubic network where the Zn ions are linked by CN molecules. It consists of a ZnCN₄ tetrahedron (at the corners of the cell) with CN groups along four of the body diagonals.

To explore and elucidate the connection between phonon dynamics and NTE, we employed inelastic neutron spectroscopy using the time-of-flight instrument IN6 to measure the temperature and pressure dependencies of the phonon spectra [1, 2]. We also carried out density functional theory (DFT) calculations to analyse and interpret the observations [1, 3]. The measured Bose-factor corrected dynamical structure function S(Q,E) for Zn(CN)₂ is shown in figure 2. There is clearly a low-energy flat acoustic mode at about 2.5 meV. This is well reproduced by the ab initio DFT-based lattice dynamical simulations in figure 3, where the observed feature is well predicted and highlighted [3]. Having established a reliable and appropriate model calculation, we went further by analysing the pressure-dependent data and extracting the details that were relevant to NTE. Figure 4 compares the measured and calculated contribution of the various phonons to the volume thermal expansion coefficients. The Grüneisen parameters Γ_i/B (measured and calculated) were used to evaluate these coefficients. Γ_i/B were experimentally extracted from pressure-dependent phonon measurements [2]. The maximum negative contribution to α_{V} stems from the low-energy modes at about 2.5 meV. In order to determine the character of these phonon modes, we calculated the mean squared displacements of the various atoms, C and N, arising from all phonons of energy E in the BZ in the bottom of the Brillouin zone (figure 5). There are significant and equal amplitudes for all the atoms up to 5 meV. The contribution from Zn vanishes above this energy. Moreover, analysis of the normal modes allowed us to identify the motions responsible for NTE. We found that they are mainly of a translational and bending nature and are within the zone boundary along [100] and [110], exhibiting very large negative Γ values of -68.4 and -95.8, respectively [1]. The CN molecules (figure 1) can be assimilated to rigid rods at the energies of interest for NTE. As the rods exhibit a strong lateral motion, the bond between the Zn ions has to contract if averaged over time. As the amplitude of the lateral motions increases with temperature, the lattice contracts with temperature in all directions.

In conclusion, by combining inelastic neutron spectroscopy and DFT simulations, we have shown unambiguously that low-energy phonon modes at about 2.5 meV are responsible for the large isotropic NTE in the non-oxide molecular cyanide-based framework material Zn(CN)₂. We have succeeded in identifying the modes which are the cause of this unusual phenomenon. This finding provides new and deeper understanding of the role of dynamics in this fascinating thermal property that is relevant to both fundamental and applied sciences.
Depolarisation of $^3$He due to wall collisions

Hyperpolarised $^3$He is used extensively in neutron facilities for neutron-spin filtering, and in a variety of other contexts from engineering to medicine. However its use is impeded by the fact that when a $^3$He atom collides with the wall, its spin is very slightly rotated by the tiny short-range magnetic field generated by such an impurity (see figure 1).

We model the motion of each $^3$He atom as a random-walk, so it is crucial to analyse the number of times the random walk hits the container walls in a time $t$ (see figure 2). This number will be different for different random walks, and so we must think in terms of the probability distribution of the number of boundary collisions. This distribution is characterised by two quantities: (i) the average number of wall collisions, $N(t)$, in the time $t$ and (ii) the variance in the number of wall collisions, $\text{var}[N(t)]$, in the time $t$.

For a one-dimensional random walk enclosed between two walls a distance $X$ apart, we find that for times $t$ much bigger than the time to diffuse across the container:

$N(t) = \nu /X [1]$

$\text{var}[N(t)] = 1/3 \nu \tau_{\text{mfp}} [2]$ where $\nu$ and $\tau_{\text{mfp}}$ are the velocity and mean-free-path of the walker (the $^3$He atom). The result for the average is not unexpected, it goes like $1/X$. However the result for the variance is quite remarkable, despite being an effect of the walls it is completely independent of the container size. This is despite the fact that when a $^3$He atom collides with the wall, its spin is induced by wall-collisions, and the typical number of such collisions decays with increasing container size.

$N(t) = \nu /X [1]$

The fluctuations in the number of boundary collisions are so much larger than one would naively expect, we argue that they should not be neglected when calculating the depolarisation rate of the gas.

Typically, $\tau_{\text{mfp}} \sim 10^{-10}$s and $X /\nu \sim 10^3$s, thus the variance in Equation (2) is $10^3$ times larger than the average in Equation (1). This vast difference is due to strong correlations between subsequent wall collisions, see figure 2. If correlation had been weak, one would have found the average and variance to have been of similar magnitude, so fluctuations about the average (square-root of variance) would have been of order the square-root of the average. This type of argument was used by Smoluchowski in his model of Brownian motion. For our problem, in contrast, neglecting correlations would under-estimate the variance by a factor of $10^6$.

We neglect spin rotations at collisions within the gas, since wall collisions dominate the depolarisation in all but the very best containers.

Figure 1:
At each wall collision, the spin of the $^3$He atom is rotated by a very small random angle, $\theta$.

**Figure 2:**
The random walk of a $^3$He atom as it diffuses in the gas in a cubic container. Wall collisions (marked with blue circles) occur in clusters, which means that there are strong positive correlations between subsequent collisions. An atom far from the wall has no wall collisions until it diffuses there; then it will typically undergo $N_{\text{cluster}}$ collisions before diffusing away from the wall again. Approximating this motion by three independent random-walks in the $x,y,z$-directions, we find that $N_{\text{cluster}} \sim 1/X$, which leads to the $X$-dependence of $\text{var}[N(t)]$. 

\textsc{Scientific Highlights}

Hyperpolarised $^3$He gas is slowly depolarised by collisions between the $^3$He atoms and the walls of the container it is in. This depolarisation is thereby related to the statistics of a random-walk’s collisions with walls. We find that the statistical fluctuations in the number of wall collisions show universality in the long time limit, being independent of the distance between walls. Remarkably, this means that wall-scattering can induce depolarisation processes which are independent of the container size.
Quantum systems can be in a coherent superposition of two different states. These “Einstein–Podolsky–Rosen” or “EPR” states are characteristic of the quantum world and cannot exist in classical mechanics. Coherent superpositions are identified by the coherent oscillations of observables. However, noise (of a quantum or classical origin) is a huge impediment to observing or using such coherent superpositions. Even small amounts of noise can cause decoherence, and “dead” and “alive” approaches and observations are made.

Quantum noise originates from the system’s coupling to other quantum degrees of freedom in its environment, while classical noise is due to random fluctuations in classical (macroscopic) fields. The noise source is often a problem, as it can also enhance the coherent oscillations that appear when a quantum system is driven through an avoided level crossing. Such an enhancement can occur because noise does not only cause decoherence, it also modifies the system’s Hamiltonian. Such a modification was first proposed by Hans Bethe as an explanation of the Lamb shift of energy levels in the hydrogen atom. The noise source is the vacuum fluctuations of the photon field. This noise certainly has a decoherence effect, however, the crucial point was that it modified the Hamiltonian of the atom sufficiently to create a shift of certain energy levels. In 1932, Landau, Zener, and Majorana independently addressed the problem of a quantum system being driven through an avoided level crossing, see figure 1b, a problem now known as the Landau-Zener transition. They showed that the transition amplitude from the ground state to the excited state has an exponential dependence on the gap at the avoided crossing. We therefore argue that this amplitude will be exponentially sensitive to any noise-induced Lamb shift of this gap. The sign of the Lamb shift is a function of the noise spectrum (noise at higher frequencies reduces the gap, while noise at lower frequencies enhances it). If the Lamb shift reduces the gap slightly, then the transition amplitude will be exponentially enhanced, exponentially magnifying the coherent oscillations, and we show that this effect, which we call “Lamb-assisted coherent oscillations”, often dominates over the decohering effect of the noise.

Highly polarised $^3$He is an ideal testing ground for our theory. Each $^3$He atom has a spin-half which can be flipped by electromagnetically driving the system at radio-frequencies. In the rotating frame, the spin-flip can be seen as a Landau-Zener transition. Since all atoms in the gas behave in the same manner. In addition to testing our theory (which assumes the source of decoherence in molecular magnets is a low-frequency noise), we showed that noise may enhance the coherent oscillations of a system driven through a Landau-Zener transition, via an effect we call “Lamb-assisted coherent oscillations”.

We propose verifying this hypothesis with polarised $^3$He, before using it as a probe of the sources of quantum noise which affects molecular magnets.

Figure 1:
A $^3$He atom whose spin state is driven by a radio-frequency electromagnetic (EM) field whose frequency changes with time. In the rotating frame, this has the effect of sweeping the system through an avoided crossing. For a large gap, the Landau-Zener transition is adiabatic. For smaller gaps, the system passes into a superposition of the two states (ground and excited states). A Lamb shift of the gap modifies this superposition.

Figure 2:
The spin-polarisation of the $^3$He atom measured along the y and z axis, as a function of time. Noise clearly enhances the coherent oscillations.
D19: a Millennium Programme success story

ILL’s D19 diffractometer is a multifunctional instrument that tackles challenging problems in Chemistry, Physics, and the Biosciences. Its capabilities were enhanced by a major UK EPSRC award to Durham, Keele and Bath Universities* as part of the initial phase of the ILL’s Millennium Programme. The new instrument features a large solid-angle detector, a flexible monochromator assembly matching a wide range of length scales, and an effective gain factor of about 2.5. The new D19 is now yielding remarkable results in structural/materials chemistry, protein crystallography, and a wide range of partially ordered systems.

**BIOLOGICAL CRYSTALLOGRAPHY**

Below part of a density map from a combined neutron and X-ray crystallographic study of xylose isomerase – the enzyme that is responsible for the conversion of glucose to fructose. Following the initial work on this system, published as a cover article in Structure [1], further studies published in Angewandte Chemie [2] described the presence of hydronium ions in the structure. This article was highlighted in Nature Chemistry [3] where the importance of hydronium ions and associated protonation shifts in aqueous environments were emphasised. Such information is not accessible to X-rays crystallography where clearly H$_3$O$^+$, H$_2$O and OH$^-$ groups (or even O atoms) are almost indistinguishable.

**FIBRES AND PARTIALLY ORDERED SYSTEMS**

D19 has a long history of elegant experiments involving the study of fibrous systems including synthetic polymers, DNA, filamentous viruses, and polysaccharides such as chitin and cellulose. The rebuilt instrument has provided a quantum leap for the study of these partially ordered systems. For example, during 2011, Wada and coworkers [4] published a novel study providing high-resolution information associated with the mercerisation of cellulose. Mercerisation is an important preparative step in the processing of raw cellulosic material [5]. D19 data, in conjunction with molecular modeling, have provided new information on the hydrogen bonding patterns involved and also on the associated movement of ammonia molecules.

**STRUCTURAL AND MATERIALS CHEMISTRY**

In structural chemistry and materials chemistry, recent studies include magnetic texture analysis [6], analysis of the presence of hydrogen bond and cation partitioning in minerals [7], determination of absolute stereochemistry [8], as well as very accurate structural studies of glycopolymers analogues [9] and the importance of charge-assisted H-bonds in symmetry breaking [10], and the probing of D-H…H bonds in water structure in the hydrophobic cavity in calixarenes [11]. The common factor in such studies is often the ability of D19 to provide unique information at high resolution on the location of hydrogen atoms and hydrogen bonding geometry.
It has to be said that 2011 brought its share of uncertainties, leaving a bittersweet taste behind. 2012 and even 2013 will doubtless be intense, as the economic crisis waxes and wanes and further challenges and opportunities arrive at our door. The decisions we make during this crucial period will certainly mark the years to come, but we have been charting our course carefully. We are confident that our users will maintain their demand for our beamtime, given the quality of the results and support they receive at the ILL. It is an ILL rule never to compromise on user support and always to ensure that instrument performance pays dividends.

The progress made this year with the Millennium Programme has been very rewarding, of course. We have commissioned two of the main neutron guides (H112 and H14) as well as the instrument LAGRANGE, with very promising results in terms of improved performance. We have also started commissioning D33. The final components of IN16B started arriving at the end of the year, in time to allow commissioning during the first reactor cycle of 2012. Eight M€ were invested in the different instrumentation projects. By the end of 2011, therefore, the total investment in the 2007-2014 phase of the Millennium Programme (the “M-1 phase”) has amounted to 31.4 M€. This is 68% of the total 45.9 M€ budget allocated for the period.

Given the quality of the results achieved in 2011, I have no doubt that the concerns and uncertainties for 2012 will fade as the year progresses.

For the rest of the M-1 phase we will be concentrating on the projects associated with the ILL22 neutron guide hall. We will start with the extension of the guide hall itself.

José Luis Martínez
Associate Director
The IN1-LAGRANGE secondary spectrometer was commissioned in 2011 (see article on p.82). Once extra shielding had been installed against local background, the improvement over the former Bartlett spectrometer was obvious. The increase in signal and the reduction of background are providing a final gain factor of between 10 and 20. It’s a great pleasure to deliver a new instrument, on time, on budget, and performing as promised!

The new D33 small-angle spectrometer is now almost ready to fly (see article on p.78). Close to the end of 2011, the first neutrons started lighting up the optical casemate. The commissioning of D33 will continue during the first cycle of 2012. All the components have been delivered, except for four panels for the mobile front detector. We started component commissioning with the optical casemate (see article on p.50). The initial results are very satisfactory.

The next step, to be taken in the first cycle of 2012, is to commission the collimation system and the main high-resolution rear detector and trolley which slides inside the main 14-metre vacuum tube. Full instrument commissioning will take place in the first cycle of 2012. All the options (monochromatic pin-hole, TOF, polarisation,…) are due to be optimised. The second cycle of 2012 could see our first “friendly users” on the instrument.

The high flux/high-resolution backscattering spectrometer IN16B is a complex instrument, almost complete. By the end of 2011 only the first few meters of the focussing guide remained pending (see article on p.50). The main vacuum chamber and shielding have been installed, as has the new phase-space transformer and background chopper system. The Doppler system and analysers will be brought in from the old IN16, although we have also started a new project to design and construct a set of 8 full-size analysers, optimised for its new and enlarged vacuum chamber. The new analysers system will be available by the end of 2012; it will almost double the effective surface available. The first two cycles of 2012 will be devoted to commissioning, with the aim of launching the instrument’s scientific programme with external users in the last quarter of 2012.

The neutron guides are a very important element in the overall design of new high-performance neutron instruments. Ideally, the guide and its instruments should really be designed together, so the system delivering the neutrons has a major influence on instrument performance. This was clearly the case for IN15B homestead to the cold neutron guide H112. H112 has a total length of around 122 metres, with an initial 20-metre “double-barrel” section; its upper section (H112 b) will be available for a future instrument in ILL7. Preliminary total flux measurements at different points along the guide show a perfect match between the early flux simulations and the final results. Congratulations to the H112 team!

We also brought the H14 guide project to a very successful conclusion in 2011. This is a complex cold neutron guide, which starts out as a large single guide equipped with a number of sophisticated optical elements, before splitting into four separate guides. Four different instruments are being built (D33 and IN12) or re-built (LADI and IN11) on H14. We have been able to compare the final performance of the guide at a particular instrument, with position the same position on the previous H14. Initial flux measurements have been very encouraging. They differ from one point on the guide to another, but the gain factor is always between 1.5 and 2.5. This can essentially be put down to the better design, better manufacture, and improved alignment. We are very proud of the H14 team, who have run this project with brio!

The first instrument to be built on the H5 guide is ThALES, an upgrade of IN14, which will be dismantled and rebuilt as ThALES on ILL’s Level C. The ThALES project is managed by Charles University in Prague (Czech Republic) in collaboration with ILL. The design of the instrument (Figure 3) was finalised during the year and the main construction contracts awarded. Construction started on the new non-magnetic sample table, the main primary and secondary coil system. Supermirror coating guides and a sophisticated monochromator. The secondary spectrometer will be reinstalled and IN14’s current analyser upgraded.

The new Wide-Angle Spin-Echo instrument WASP will be located in the extended ILL22 hall (see Figure 4). We finalised its design in 2011 and prepared specifications for the call for tenders for manufacturing the sophisticated coil system. Supermirror production has continued smoothly and we plan to be able to furnish at least half of the full 180 degrees of the wide-angle analyser by the end of 2012. Efforts then focused on the design and construction of the complex primary cooling facility for the coil system, a project conducted in parallel to the guide hall extension in order to improve synergies and cost.

The 2011 Millennium harvest was an excellent one, to be remembered for years to come. In a complicated and demanding programme our teams successfully installed and commissioned two important neutron guides (H112 and H14), which will feed neutrons to five instruments (IN16B, D33, IN12, IN11 and LADI) and provide an inclined end position on H112 for future instruments. Early measurements of total flux within both guides indicate that the choices on the distribution of the guides were well made, that the quality of the guide elements is high and that alignment is excellent. Two new instruments will be soon ready for our user community: IN1-LAGRANGE and D33. In parallel, work continued on ThALES and WASP, with the necessary re-design of the H5 neutron guide. Other successes are therefore in the pipeline! Finally, but also very importantly, the design of the new shielding is proving to be very effective, significantly reducing the background from the new high-m coating guides and making realignment operations far easier in the future.
Massive dynamic Q-range with a time-of-flight small-angle scattering instrument: D33

TIME-OF-FLIGHT

‘White’ pulses of neutrons are shaped by a cascade of four choppers in the D33 casemate and wavelength discrimination is made by their arrival time (time-of-flight, TOF) at the detector. The advantage of using the TOF method is that a wide band of neutron wavelengths illuminate the sample and hence simultaneously sample a massive dynamic \( Q \)-range – or range of neutron wavelengths – that characterises the material. D33 will simultaneously sample a massive dynamic Q-range – or range of material length scales – that characterises the material. D33 will thus in order to cover a sufficiently wide range of material length scales, often two, three or even four individual measurements must be made and their data ‘knitted together’ in order to fully characterise a sample. D33 has two large multi-detectors consisting of a ‘rear’ square detector of \( 64 \text{ cm} \times 64 \text{ cm} \) (128 x 128 pixels) arranged horizontally and vertically to form a central aperture. D33’s detector arrays are based on the new Monoblock technology developed by the ILL’s detector group with much of the mechanics being machined in-house. Both front and rear detectors can move independently of each other within the detector tank to achieve various distances from the sample. The central aperture of the front detector can be adjusted either to match the solid angle of the rear detector or can be extended to extremes to maximise Q-range in D33’s TOF mode.

MULTIPLE DETECTORS

On D11 and D22, a single large area and position sensitive multi-detector sits in the evacuated detector tank at a variable distance from the sample depending on the Q-range, or length scale, of interest and typically covers a dynamic Q-range of about 10 for a single measurement, i.e. we can ‘see’ material structures from, for example, 10 Å to 100 Å, or 100 Å to 1000 Å (1 μm) or 1000 Å (1.1 μm) to 10000 Å (1 μm) in a single measurement. Thus, in order to cover a sufficiently wide range of material length scales, often two, three or even four individual measurements must be made and their data ‘knitted together’ in order to fully characterise a sample. D33 has two large multi-detectors consisting of a ‘rear’ square detector of \( 64 \text{ cm} \times 64 \text{ cm} \) (128 x 128 pixels) arranged horizontally and vertically to form a central aperture. D33’s detector arrays are based on the new Monoblock technology developed by the ILL’s detector group with much of the mechanics being machined in-house. Both front and rear detectors can move independently of each other within the detector tank to achieve various distances from the sample. The central aperture of the front detector can be adjusted either to match the solid angle of the rear detector or can be extended to extremes to maximise Q-range in D33’s TOF mode.

LITTLE BROTHER

Optimisation of the ‘pin-hole’ resolution conditions for a SANS instrument requires careful consideration of the maximum sample size, neutron guide size and distances for a given instrumental resolution. In other words, SANS instruments are essentially infinitely scalable as long as the sample size can also be scaled. The overall size of D33 has been down-scaled based upon these principles where everything from guide size, collimation length, detector and tank size have all been down-sized to about 2/3 relative to an instrument such as D22. This gives resolution advantages when working in TOF mode as well as saving the cost and space involved in building much larger instruments. D33 is in fact better optimised for smaller samples up to 15 mm in dimension and is consistent with the scientific trend of, for example, forever faster kinetic measurements with smaller and smaller samples.

PERFORMANCE AND APPLICATION

There have been few compromises in the design and expected performance of D33. The newly re-built H14(2) guide which will provide neutrons to D33, should achieve similar neutron flux for a given resolution (brightness) as the existing D11 or D22 instruments. D33’s monochromatic and TOF modes, in combination with the large and flexibly configured detector arrays, will achieve dynamic Q-ranges from about 30 in monochromatic mode to a massive 1000 in TOF mode and should have positive implications for studying kinetic processes where a large Q-range is required quickly and in a single measurement. The above features of D33 lend themselves useful to the usual wide range of scientific problems studied using SANS from biology, soft matter, materials science, physics and magnetism. Furthermore, the location of D33 is such as to permit the use of high magnetic fields, such as provided by the 17T horizontal solenoid magnet belonging to the University of Birmingham.

GET READY

The construction of D33 was completed during the winter shutdown 2011/2012. The first reactor cycle of 2012 will see the hardware commissioning of the instrument while the second cycle will be devoted to a scientific commissioning with ‘friendly users’ from all science domains. Are you a friendly user? Don’t be scared to try something new. With D33 we aim to extend our possibilities in SANS with a particular emphasis on studies requiring a large simultaneous Q-range, polarisation and analysis, and extreme sample conditions. D33 is coming soon!
A big step forward for neutron backscattering: IN16B

The study of very small energy exchanges between neutron and sample requires a well-defined incident neutron wavelength and an equally precise analysis of the scattered beam. In backscattering spectroscopy, neutrons are selected at the monochromator and analysed using perfect crystals (e.g. silicon wafers) under a Bragg angle of 90°, thus achieving a high energy resolution (better than 1 μeV). This means that the incident wavelength for spectroscopy can no longer be tuned by rocking the Bragg angle; the incident angle of 90°, thus achieving a high energy resolution (better than 1 μeV). This means that the incident wavelength for spectroscopy can no longer be tuned by rocking the Bragg angle; the incident angle of 90°, thus achieving a high energy resolution (better than 1 μeV). This means that the incident wavelength for spectroscopy can no longer be tuned by rocking the Bragg angle; the incident angle of 90°, thus achieving a high energy resolution (better than 1 μeV). This means that the incident wavelength for spectroscopy can no longer be tuned by rocking the Bragg angle; the incident angle of 90°, thus achieving a high energy resolution (better than 1 μeV).

New on IN16B is a Phase Space Transformation (PST) chopper [1], which promises an intensity gain of about 4 [2]. Neutrons are reflected from mosaic crystals moving at a speed of about 243 m/s, which transform the neutron energy to a linear velocity selector and by ILL’s longest neutron guide (source-sample distance about 130 m) focusing ballistically onto the PST. The PST is the ‘heart’ of the instrument (figure 1) and technologically the most demanding and innovative component. A series of packages with fragile, tilted graphite crystals and neutron absorbers, arranged as two segments on the circumference of a chopper disc, have to withstand the high centrifugal forces. With its 43 cm radius, this will also be the world’s most compact PST with the highest centrifugal force.

The high flux entering the instrument close to the detector needs efficient shielding and vacuum wherever possible to maintain a low background level. Furthermore, the energy transfer range, limited today on IN16 by the narrow bandwidth of the graphite deflector, will be doubled by the combination of the PST and a linear motor Doppler drive. The huge vacuum vessel of the secondary spectrometer contains the PST and analysers, which are planned to be twice as high as the current IN16.

A prototype of such an analyser is under construction. This also requires a new vertical position sensitive multi-detector and a deflector crystal and furnace tails to the vertical space angle. Taken together, all these improvements promise to increase the count rate by a factor of 10 compared to the present IN16. Finally, flexibility has been built into the design to allow for a number of different instrument configurations: a low background side position configuration, possible operation with Si (111) crystals extending the Grenze to Q max = 3 Å⁻¹, a GaAs test configuration in a Bragg crystal and an inverted time-of-flight option. This explains the large instrument site needed to rotate the whole vacuum chamber (4 m high, 35 tons), including the Doppler drive, around the PST position or to move it, together with part of the focusing guide, to the side position, where, as on IN16, the incident wavelength band is further limited by a deflector crystal.

At the time of writing, the radiological shielding (HDRF/BAFC and cadmium) are being mounted and we have received delivery of the background chopper and selector together with their control electronics and those of the PST. Testing of the PST with a dummy disc is under way.

And when can we expect the first neutrons? This exciting event should take place after the winter shutdown in May 2012. In view of the complexity of the instrument, the commissioning, neutron tests and improvements will take some time. We hope to be able to accept a few ‘friendly user experiments’ in the second half of 2012 and then regularly schedule the Si (111) configuration as of the reactor restart in 2013.

**REFERENCES**


The IN1-LAGRANGE project was launched at the ILL a few years ago with the aim of creating a new spectrometer for the study of lattice and molecular excitations in the extended energy range up to several hundred meV typical for materials containing light chemical elements, in particular hydrogen. The new instrument provides much higher sensitivity to small and low scattering samples through a substantially increased detector count rate combined with considerably improved energy resolution in comparison to the beryllium filter-analysers used in the past on IN1.

It is important to note that the new instrument takes advantage of the recently upgraded double-focussing monochromator, which thanks to a set of several different reflecting planes - currently of the IN1-BEF configuration, as shown in figure 1 - is able to provide a large solid angle and then registered with a relatively small spectrometer volume. The instrument background, contaminated with the high neutron energy components, is reduced thanks to massive polyethylene shielding built around the whole analyser. There are no mutually moving parts within the secondary spectrometer, which moves around the monochromator in a step-by-step fashion in order to change the incident energy, in a similar way to a typical experiment on a three-axis spectrometer.

The instrument was designed at the ILL thanks to house scientific and technical input. The detailed design and fabrication of the main mechanical components were performed by the Spanish company Tekniker. The work was financed in approximately equal shares from the Spanish IN233 group and the UK’s STFC, with part of the project budget also provided from the full ILL members. The work was financed in approximately equal shares from the Spanish IN233 group and the UK’s STFC, with part of the project budget also provided from the full ILL members.

An example of the inelastic scattering spectrum measured with IN1-LAGRANGE is presented in figure 2. We used a sample of 2,5-dioxothiophene, (CH)2(CI)2S, to characterise the instrument performance. This material is known to exhibit very sharp vibration lines at low temperatures and can therefore be used as a standard for spectrometer resolution measurements. The sharp peaks in the energy spectrum visible in figure 2 are due to vibrations involving hydrogen atoms, present in the sample in a relatively small quantity. Energy of the partial hydrogen weight. It should be noted that the statistics collected in the energy interval below 500 meV, left panel of figure 2, correspond to some 15-30 sec of the measurement time per point (the difference is due to the energy variation of the incident monochromatic neutron flux). As a result, this informative energy interval could be scanned in less than 2 hours whereas the scan time for the whole of the spectrum shown, up to 6000 meV, is about 4 hours. In comparison with the IN1-BEF configuration, we note a considerable improvement in energy resolution and approximately one order of magnitude increase in the inelastic signal with respect to the beryllium filter-analysers, as shown in figure 3. In the energy range below 1500 meV the energy resolution of IN1-LAGRANGE is noticeably better than that of IN1-BEF, allowing it to reveal fine details of the spectrum, for instance the observed energy splitting of the lowest vibration line.

The energy resolution of IN1-LAGRANGE can be further improved in the broad energy range by using the available D2331 reflecting plane of the IN1 monochromator. Many more details of the vibration density of states are revealed in the higher resolution run at the expense of merely an approximate 2-fold decrease in the statistics for the same counting time. The measured energy resolution is presented in figure 4, together with the calculated curves for several anode-monoenergetic configurations. It should be emphasised that the changeover from one resolution setting to another can be done on IN1-LAGRANGE in about half an hour, giving users extremely flexible conditions for optimising their measurements with respect to the choice of resolution vs intensity.

The IN1-LAGRANGE spectrometer opens up outstanding possibilities for spectroscopic studies of complex materials. The new instrument makes it possible to investigate much smaller samples, inherent in novel materials studies, to record well-resolved vibration spectra, and to probe in greater detail external parameters, such as temperature, pressure, and chemical composition. As a result, this spectrometer is highly competitive compared with the instruments for high-energy neutron spectroscopy found elsewhere.
Countering the effects of gravity

Previous ideas of cancelling the effects of gravity have used prisms [2] but this approach has problems working over the full height associated with typical sample sizes. Here we describe a different method, recently published [3], using simple mirrors that can be exploited using existing components of SANS instruments and results in reducing the minimum momentum transfer by a factor of 5.

The problem can be thought of as trying to throw a ball through two holes some distance apart and then hitting a target even further away as shown in figure 1. The slower the ball is thrown the larger the angle we have to throw it above a line between the centre of the holes. If there is a limit in the height the ball is allowed to be in between the holes, there is lower limit on the speed it can be thrown. In addition, depending on the size of the target, if the ball makes it through the second hole it still might miss the target as it can fall past the bottom. A SANS machine has exactly this problem where the two holes are the collimation and the target is the neutron detector. This places a limit on the largest object we can measure purely due to the effects of gravity. When we use the largest distances available on D11 (40.5 – 39 m), the largest SANS instrument in the world, we find that we cannot properly use neutrons traveling slower than 200 m/s which corresponds to a wavelength of about 20 Å or 2 nm.

In the past it has been found that these effects of gravity can be canceled using a prism which gives the neutrons a kick upwards allowing them to arrive at the centre of the detector but this only worked with beam sizes much smaller than we wish to use. We realised that a simple mirror near the second hole at the end of the collimation can do the same job as the prism but it will work with a much larger beam. Going back to the ball analogy, if there was a horizontal surface just before the second hole and below the centre line we don’t need to aim the ball so high through the first hole to hit the surface as shown in figure 2.

The ball can then bounce off the surface and come out of the second hole rising not falling. Then it has a better chance of hitting the target. Neutrons bounce very well off well polished surfaces like glass and this is used in neutron guides all over the ILL to send neutron beams long distances rather like fiber optic cables that transmit light.

Before spending money on a special neutron mirror we realised that we could use the mirror on the bottom of one of these guides which already exists in the collimation section of D11. Normally when measuring the largest objects all these guide pieces are removed but we put one piece back and allowed the beam to fall naturally onto the bottom mirror and bounce up through the second hole. We found that this only happened for one special wavelength of 18.7 Å as shown in figure 3. As the goal was to find longer wavelengths than 20 Å this was initially disappointing but we found that if we moved the second hole upwards by about 1 cm we could get 23 Å to pass through at 1000 x the intensity before (this was because of the height limit in the collimation absorbing neutrons). Longer wavelengths than 23 Å were not possible without modifying the instrument. By reducing the size of the first hole to 1 cm and using three neutron lenses we now had a configuration where we could measure objects many times larger than previously possible. To test this we placed a grating in the beam which had a period of 4 microns, a length-scale not previously visible on D11 and we could clearly see peaks of neutron intensity associated directly with the repeating 4 micron structure (figure 4).

In conclusion we have made a significant improvement to the range of science that can be done on D11 by countering the effects of gravity. This resulted in a gain of 1000 x in intensity at 23 Å, took less than a day’s beamtime to accomplish at zero cost.
High-pressure single crystal diffraction to 10 GPa and above

High pressure can cause large changes in the crystal structure and properties of materials, which can provide both fundamental understanding and insight into practical applications. Many interesting and useful materials - ice for example - are held together by hydrogen bonds. There is widespread interest in the relationship between hydrogen bond strengths and the precise geometry of the bonds, ranging from theoretical physics and chemistry where the interest is in the behaviour of the proton as a quantum object, through planetary science where proton conduction is important, and astrobiology where proton exchange reactions are important for living processes. The application of pressure allows a hydrogen bond length to be altered cleanly and continuously within the same material. Neutron single-crystal diffraction is an ideal technique to explore such evolution because of its ability to resolve the same material. Neutron single-crystal diffraction is a powerful method for determining atomic positions in structures, and we present developments that extend the pressure range for such studies on D9 to 10 GPa, with the prospect of reaching 20 GPa in future.

High-pressure single crystal diffraction to 10 GPa and above

High pressure produces dramatic changes in matter, such as the numerous different crystal structures in ice to 2 GPa (20 000 atmospheres). Measuring the positions of atoms in high-pressure structures can provide fundamental insights into materials and their properties, including for practical applications like the storage of hydrogen in hydrogen hydrate. Single-crystal neutron diffraction is a powerful method for determining atomic positions in structures, and we present developments that extend the pressure range for such studies on D9 to 10 GPa, with the prospect of reaching 20 GPa in future.

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Ultracold neutrons from superfluid helium

Cold neutrons with a wavelength of 0.89 nm passing through a converter of superfluid helium may lose nearly all their energy in single scattering events and thus become ultracold. This produces elementary excitations (“phonons”) with an energy of 1 meV (about 12 K) in the helium, which are cooled away by a refrigerator. At temperatures below 1 K, inelastic scattering would result in phonons. Ultracold neutrons accumulate in the superfluid efficiently, using a cold UCN valve combined with a short section of vertical UCN guide (figure 1). Using an intercalated graphite monochromator, the 0.89 nm component of the incident cold beam is scattered into the secondary neutron guide H172A, which will lead to the detector at room temperature (not shown).

This avoids the need for the loss-prone windows through which UCNs had to pass in an earlier scheme using horizontal UCN extraction [3].

The method has since been further developed in the framework of the ESFRI project ILL 2G/2D Upgrade. With the ultimate goal of making UCN production in superfluid helium amenable to users, ILL teams have designed and installed the new beam line H172. An intercalated graphite monochromator diverts the 0.89 nm component of the incident cold beam with an 80×80 mm² cross section into the secondary neutron guide H172A, at which an upgraded cooling power, it offers greater flexibility than SUN-1 for UCN source.

In order to perform the necessary R&D work, a new UCN source cryostat “SUN-2” has been developed in the last few years. Besides increased cooling power, it offers greater flexibility than SUN-1 for testing various types of converter vessels. A second beam position H172B is under construction where experiments with SUN-2 will be performed to bring UCN production in superfluid helium to maturity.

Due to counting statistical limitations, experiments often last one or sometimes even several reactor cycles, hence the need for a new generation of UCN sources. While the ILL’s turbine UCN source PF2 has for the past 25 years been delivering the highest UCN fluxes in the world, a superior UCN density has recently been achieved based on the conversion of cold neutrons in superfluid helium-4.

REFERENCES

Figure 1: Schematics of the apparatus [4]. a) Beryllium entrance window for cold beam coming from left. b) UCN converter vessel made of BeO, filled with superfluid helium. c) Thermal shield (not shown are an outer shield and the vessel for the isolation vacuum). d) UCN valve. e) UCN extraction guide towards a detector at room temperature (not shown).

Figure 2: Set-up of the UCN source “SUN-1” at H172A. The cryostat containing the helium converter is situated inside a lead castle. Shown is the set-up with sideward UCN extraction as used in the experiments reported in [4]. The clean room in the background houses the gravitational spectrometer GRANIT under construction.

Figure 3: UCN count rate (s⁻¹) as a function of time in a UCN accumulation/extraction experiment [4]. The UCN valve stayed closed during about 800 s of irradiation with the cold beam. Leakage of UCN through the closed UCN valve monitors the build-up of the UCN density in the converter. Then the beam was shut and the UCN valve opened. The peak on the right shows the extraction of 274 000 UCNs.

Figure 4: Inspection of a converter vessel in SUN2.
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
User programme

THE ILL VISITORS CLUB

All administrative tools for our scientific visitors are grouped together and directly accessible on the web, thanks to the Visitors Club. All information is presented in a user-friendly environment. After having logged in with your own personal identification1, 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 ILL Visitors 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: acknowledgement of proposals, subcommittee 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 Electronic Proposal Submission system (EPS), available on the Visitors Club web-site. Proposals can be submitted to the ILL twice a year, usually in February and in September. The web system is activated two months before each deadline. Submitted proposals are divided amongst the different colleges [see box below] according to their main subject area.

Proposals are judged by a Peer Review Committee of the Subcommittees of the ILL Scientific Council. Subcommittee members are specialists in relevant areas of each College and they evaluate the proposals for scientific merit and recommend to the ILL Management the award of beamtime to the highest-priority proposals.

Before the meeting, the subcommittee receives a report on the technical feasibility and safety of a proposed experiment from the appropriate College at the ILL. Two proposal review rounds are held each year, approximately eight weeks after the deadline for submission of applications.

There are normally 4 reactor cycles a year, each of which lasts 150 days. Accepted proposals submitted by February will receive beamtime in the second half of the year and those submitted by September, in the first half of the following year. More detailed information on application for beamtime and deadlines is given on our website at http://www.ill.eu/users/applying-for-beamtime/.

Easy Access System

The Easy Access System (EASY) grants diffraction 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 five instruments (D1A, D2B, D15, WIVALDI 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 designated ILL scientists, who will be responsible for the measurements and sample radiological control. The ILL will ship back the sample once the measurement is finished. You can apply for EASY beamtime on the Visitors Club. More information is available at http://club.ill.eu/colDocs/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 Schütter, at any time.

Access for proprietary research and industrial users

The ILL’s mission is to provide neutrons for both public and industrial research. In November 2010 we appointed a business development officer who is charged with communicating more widely the services we can offer to the industry. He will also facilitate and coordinate centrally industrial R&D at the ILL, in particular access to the ILL’s scientific expertise and instrument suite. He will work closely with the ILL “Industrial Liaison and Consultancy Group” (ILC) to assess the feasibility of the experiments and the quotation of the services. The ILC Group is composed of scientists with considerable experience and expertise in neutron techniques applied to industrial R&D; it ensures rapid access and total confidentiality for industrial companies, and provides specialised technical and scientific support to apply for proprietary beamtime, please contact the Business Development Office at industry@ill.eu or by phone at +33[0]4 76 20 72 01 or consult the web site under http://www.ill.eu/industry/.

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/cv/]. Experimental reports for experiments performed in 2011 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 instruments:

• 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 LIL’s scientific user programme.
• CRG B in which the external group leases an instrument owned by the ILL. They have 70% of the beamtime at their disposal and for the remaining 30% they support LIL’s scientific user programme.
• CRG C in which the external group leases an instrument owned by the ILL. They have exclusive access to 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 ESRF 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 simple neutrons”, p.108.
User and beamtime statistics

THE ILL USER COMMUNITY

The ILL welcomed 1557 users in 2011, including 374 from France, 288 from Germany and 300 from the UK (Figure 1). Many of our visitors were received more than once (for a total of 2570 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 (see 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 Visitors Club and give us their views on different topics. User comments are made available to managers for their information and actions when appropriate.

INSTRUMENTS

The instrumental facilities at the ILL are shown in the schematic diagram on page 38. The list of instruments as of December 2011 is summarised on page 97. Besides the 28 ILL instruments, there are 9 CRG - instruments (marked with an asterisk *):

- Powder diffractometers: D18*, D28, D30, SALSA
- Liquids diffractometer: D4
- Polarised neutron diffractometers: D3, D28
- Single-crystal diffractometers: D9, D10
- Large scale structures diffractometers: D19, LA1, WALDI
- Small-angle scattering diffractometers: D11, D26
- Low momentum-transfer diffractometer: D15
- Reflectometers: SuperADAM*, D17, RSARD
- Diffuse scattering and polarisation analysis spectrometers: D7
- Three-axis spectrometers: IN1, IN8, IN12*, IN14, IN20, IN22*
- Time-of-flight spectrometers: BRISP*, IN4, IN5, IN6,
- Backscattering and spin-echo spectrometers: IN10, IN11, IN13*, IN15, IN16
- Nuclear physics instruments: PN1, PN3
- Fundamental physics instruments: PF1, PF2, S18*
- Backscattering and spin-echo spectrometers: IN10, IN11, IN13*, IN15, IN16

LADI and IN15 have a special status, since they are joint ventures of the ILL with other laboratories: in the case of LADI with ESRF, EMIR 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 Table 2.

Table 1 gives the beamtime distribution amongst the different member countries (request and allocation in 2011). In calculating the statistics of beamtime per country, the allocation is based on the location of the laboratory of the proposers, not their individual nationality. In case of 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 EMIR 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 therefore do not appear in this table.

Figure 1: National affiliation of ILL users in 2011.

Figure 2: User satisfaction survey results for 2011, compared with those obtained in 2010.

Figure 3: Beamtime allocation in 2011: distribution amongst the different research areas (a) and colleges (b).

Table 1: Distribution amongst the Associate and Scientific-Member countries of beamtime requested and allocated in 2011 during the Subcommittees of the Scientific Council.

<table>
<thead>
<tr>
<th>Country</th>
<th>Requested days</th>
<th>Requested in %</th>
<th>Allocated days</th>
<th>Allocated in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>159.12</td>
<td>2.19</td>
<td>68.58</td>
<td>0.45</td>
</tr>
<tr>
<td>BE</td>
<td>41.02</td>
<td>0.57</td>
<td>15.81</td>
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<td>113.11</td>
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<td>HU</td>
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<td>263.56</td>
<td>6.66</td>
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<td>PL</td>
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<td>SK</td>
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<td>UK</td>
<td>16.01</td>
<td>0.21</td>
<td>3.45</td>
<td>0.09</td>
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<td>TOTAL</td>
<td>9590.45</td>
<td>130.00</td>
<td>4037.69</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 1 gives the beamtime distribution amongst the different member countries (request and allocation in 2011). The beamtime requested by and allocated to scientists from ILL, ESRF or EMIR 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 therefore do not appear in this table.
The reactor operated for 4.0 cycles, representing 196 days of operation.

A total of 840 experiments were scheduled. During 2011, 365 out of 831 days were lost due to various malfunctions, which represent about 5% of the total available beamtime.

The breakdown by reasons for beamtime losses is shown in Figure 4b.

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

- IN8 lost around 30 days because of its rebuilding after its beamtube replacement.
- The H10 and H4 beam-tubes work's delay prevented the testing of the PW1 target changer. Only one (manual) target change was possible during the first cycle and most experiments had to be cancelled.
- PN3 lost about three weeks because of several problems coming from its new digital acquisition system. Additional beamtime was cancelled.
- PN1 target changer. Only one (manual) target change was possible during the first cycle and most experiments had to be cancelled.
- IN10 lost about two weeks due to the failure of one of the piezo-mechanisms of the GAMS Axis.

In addition, the instruments IN12 and IN11 were only partially available in 2011, because of their dismantling and remounting, and LADI could offer very few days because of the heavy backlog in 2011.

Beam days delivered for science in 2011 amount to 5687 (used for users and internal research).

Beamtime delivered for science in 2011 amount to 5687 (used for users and internal research). The effective number of days given to our users takes into account also Director's Discretion Time and subcommittee meetings. The breakdown by instrument and performance is given in Table 2: Beamtime request/allocation and instrument performance for 2011.

**Figure 4:** (a) Use of ILL beamtime. (b) Reasons for beamtime losses.
## Instrument list - December 2011

### ILL Instruments

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2B</td>
<td>Powder diffractometer</td>
</tr>
<tr>
<td>D3</td>
<td>Single-crystal diffractometer</td>
</tr>
<tr>
<td>D4 (50 % with IN1)</td>
<td>Liquid scattering spectrometer</td>
</tr>
<tr>
<td>D7</td>
<td>Diffuse-scattering spectrometer</td>
</tr>
<tr>
<td>D9</td>
<td>Single-crystal diffractometer</td>
</tr>
<tr>
<td>D10</td>
<td>Single-crystal diffractometer</td>
</tr>
<tr>
<td>D11</td>
<td>Small-angle scattering diffractometer</td>
</tr>
<tr>
<td>D15</td>
<td>Small-angle scattering diffractometer</td>
</tr>
<tr>
<td>D18</td>
<td>Reflectometer</td>
</tr>
<tr>
<td>D19</td>
<td>Single-crystal diffractometer</td>
</tr>
<tr>
<td>D20</td>
<td>Powder diffractometer</td>
</tr>
<tr>
<td>D22</td>
<td>Small-angle scattering diffractometer</td>
</tr>
<tr>
<td>FINB</td>
<td>Horizontal reflectometer</td>
</tr>
<tr>
<td>IN1</td>
<td>Three-axis spectrometer</td>
</tr>
<tr>
<td>IN5</td>
<td>Time-of-flight spectrometer</td>
</tr>
<tr>
<td>IN6</td>
<td>Time-of-flight spectrometer</td>
</tr>
<tr>
<td>IN8</td>
<td>Three-axis spectrometer</td>
</tr>
<tr>
<td>IN9</td>
<td>Backscattering spectrometer</td>
</tr>
<tr>
<td>IN10</td>
<td>Backscattering spectrometer</td>
</tr>
<tr>
<td>IN11</td>
<td>Spin-echo spectrometer</td>
</tr>
<tr>
<td>IN12</td>
<td>Three-axis spectrometer</td>
</tr>
<tr>
<td>IN16</td>
<td>Backscattering spectrometer</td>
</tr>
<tr>
<td>IN20</td>
<td>Three-axis spectrometer</td>
</tr>
<tr>
<td>FF1</td>
<td>Neutron beam for fundamental physics</td>
</tr>
<tr>
<td>FF2</td>
<td>Ultracold neutron source for fundamental physics</td>
</tr>
<tr>
<td>FF3</td>
<td>Fusion product mass spectrometer</td>
</tr>
<tr>
<td>PF1</td>
<td>Gamma-ray spectrometer</td>
</tr>
<tr>
<td>SAINT</td>
<td>Small angle neutron optical test facility</td>
</tr>
<tr>
<td>SVW</td>
<td>Small angle neutron optical test facility</td>
</tr>
<tr>
<td>WALI</td>
<td>Thermal neutron Laue diffractometer</td>
</tr>
</tbody>
</table>

### CRS Instruments

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUPERSPO</td>
<td>Reflectometer</td>
</tr>
<tr>
<td>BRILLIUM</td>
<td>Brillouin spectrometer</td>
</tr>
<tr>
<td>CHIMU</td>
<td>Installation for the search for the neutron electric dipole moment</td>
</tr>
<tr>
<td>DT9</td>
<td>Powder diffractometer</td>
</tr>
<tr>
<td>D23</td>
<td>Single-crystal diffractometer</td>
</tr>
<tr>
<td>INARED</td>
<td>Gravitation state measurement</td>
</tr>
<tr>
<td>IN13</td>
<td>Three-axis spectrometer</td>
</tr>
<tr>
<td>IN14</td>
<td>Backscattering spectrometer</td>
</tr>
<tr>
<td>IN22</td>
<td>Three-axis spectrometer</td>
</tr>
<tr>
<td>S15</td>
<td>Interferometer</td>
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</table>

### Jointly Funded Instruments

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
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<tbody>
<tr>
<td>LAD (50 %)</td>
<td>Laue diffractometer</td>
</tr>
<tr>
<td>IN15</td>
<td>Spin-echo spectrometer</td>
</tr>
</tbody>
</table>

### Test and Characterisation Beams

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1, G12</td>
<td>Detector test facilities</td>
</tr>
<tr>
<td>CYCLOPS</td>
<td>Laser diffractometer</td>
</tr>
<tr>
<td>TOMOGRAHY</td>
<td>Neutronography</td>
</tr>
<tr>
<td>GridExp</td>
<td>Laser 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>T7</td>
<td>Cold neutron test facility</td>
</tr>
</tbody>
</table>
Instrument list - December 2011

CRG INSTRUMENTS

SuperADAm reflectometer CRG-B operational
BRISP Brillouin spectrometer CRG-B operational
CRYO EDM installation for the search for the neutron electric dipole moment CRG-C operational
D1B powder diffractometer CRG-A operational
D23 single-crystal diffractometer CRG-B operational
GRANIT gravitation state measurement CRG under construction
IN12 three-axis spectrometer CRG-B operational
IN13 backscattering spectrometer CRG-A operational
IN22 three-axis spectrometer CRG-B operational
S18 interferometer CRG-B operational

JOINTLY FUNDED INSTRUMENTS

LADI (50 %) Laue diffractometer operated with EMBL
IN15 spin-echo spectrometer operated with FZ Jülich and HZB Berlin

TEST AND CHARACTERIZATION BEAMS

T13T, C thermal neutron Laue diffractometer
T13A, C monochromator test facility
T17 cold neutron test facility
T19 ultra-low-energy neutron test facility
T3 neutron optics test facility
T13A, C monochromator test facility
T17 cold neutron test facility
T19 ultra-low-energy neutron test facility
T3 neutron optics test facility

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
D16 small momentum-transfer diffractometer operational
D19 single-crystal diffractometer operational
D20 powder diffractometer operational
D22 small-angle scattering diffractometer operational

VIVALDI thermal neutron Laue diffractometer on hold

PN1 fission product mass-spectrometer operational
PN3 - GAMOS gamma-ray spectrometer operational
SALSA strain analyser for engineering applications operational

KNIGHT INSTRUMENTS

ILL (2011) Laser diffractometer operated with EMBL
INT spectrum instrument operated with IT Jülich and EMBL

Figaro thermal neutron Laue diffractometer operational
BRISP Brillouin spectrometer CRG-B operational
CRYO EDM installation for the search for the neutron electric dipole moment CRG-C operational
D1B powder diffractometer CRG-A operational
D23 single-crystal diffractometer CRG-B operational
GRANIT gravitation state measurement CRG under construction
IN12 three-axis spectrometer CRG-B operational
IN13 backscattering spectrometer CRG-A operational
IN22 three-axis spectrometer CRG-B operational
S18 interferometer CRG-B operational

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IN15 spin-echo spectrometer operated with FZ Jülich and HZB Berlin

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T13T, C thermal neutron Laue diffractometer
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T3 neutron optics test facility

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S18 interferometer CRG-B operational

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LADI (50 %) Laue diffractometer operated with EMBL
IN15 spin-echo spectrometer operated with FZ Jülich and HZB Berlin

TEST AND CHARACTERIZATION BEAMS

T13T, C thermal neutron Laue diffractometer
T13A, C monochromator test facility
T17 cold neutron test facility
T19 ultra-low-energy neutron test facility
T3 neutron optics test facility
This ILL High Flux Reactor (HFR) produces the most intense neutron flux in the world: $1.5 \times 10^{15}$ neutrons per second per cm$^2$, with a thermal power of 58.3 MW. The reactor operates 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. There are normally 4 reactor cycles per year, supplying 200 days of neutron flux for scientific use.

Following the nuclear accident at Fukushima, in March 2011, 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 will have an impact on the Institute and will affect 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 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. We will now start putting the plans into operation. You probably know that a major seismic reinforcement programme (the so called REFIT programme) has already been carried out at the ILL, ending in 2007. The 2011 studies have prompted us to add the possibility of the loss of the 4 dams upstream on the river Drac; this implies reinforcement of elements traversing the reactor containment and the construction of a new emergency reactor control room for the crisis management teams from which all the emergency safety circuits can be controlled. The work is scheduled to be carried out over the next 3 years (between 2012 and 2014), with no major perturbation to the ILL user programme, and its total cost is estimated at 12 M€.
There were 4 cycles planned for 2011 and 196 days of scientific activity were provided overall. It was decided to interrupt the second cycle 4 days before its term, to avoid the risk of activating the argon that had found its way into one of the beamtubes (Table 1).

**THE KEY REACTOR COMPONENTS PROGRAMME**

In order to ensure reactor safety and reliability over the next ten years, the ILL continues to invest in the Key Reactor Components programme (KRC) - whose aim is to ensure that the most important parts within the reactor are regularly replaced and improved. The KRC programme will continue until the next ten-yearly safety review by the nuclear authorities in 2017.

The main operations currently planned under this programme are:

- replacement of the H10 beamtube,
- upgrade of the out-of-pile part of the horizontal cold source, including its instrumentation and control system,
- replacement of the H8 beamtube trolley (zircaloy and graphite) used for repositioning experiment samples,
- upgrade of the instrumentation and control system on the separate reactor circuit used for cooling the non-reactor cooling systems,
- irradiation of tungsten-186, for the production of a 188W/188Re source, for medical purposes (treatment of cardiovascular disorders),
- purge of the heavy water circuit and vacuum drying of the reactor block in order to be able to fill it with water from the pools, replace the V7 vertical irradiation canal remove the V3 plug and replace for the first time the antiturbulence grid on the reactor block (modified in 1995).

**REX FUKUSHIMA: THE ADDITIONAL SAFETY ASSESSMENT**

The investigations carried out in 2011 and the discussions with the French nuclear safety authority’s (ASN) expert groups successfully demonstrated that:

- the ILL has significant safety margins available with respect to the risk of a design-basis earthquake,
- there are always at least two major barriers in place to prevent the loss of reactivity and the confinement would never result in a major escalation of the danger (cliff-edge effect),
- the loss of both reactivity and the confinement would never result in a major escalation of the danger (cliff-edge effect),
- replacement of components on H9,
- maintenance work on the ventilation systems,
- replacement of adsorbents,
- cleaning of the exchangers,
- modifications to the H1/H2 guide exits,
- pump basin work,
- testing of a “cooling stop” pump,
- examination of the reactor block,
- radiological controls on the instalment containment,
- electrical work,
- containment leak rate measurements,
- installation of the emergency core reflood system without automation,
- installation of a “tsunami” diesel generator,
- emergency water makeup system redundancies,
- upgrade to compliance of several elements, including the seismic gaseous effluents system, the supports for the seismic ventilation hoods, the seismic reinforcements on the steelwork protecting the vertical cold source, the seismic stabilisation measures for the instrumentation on level D and the flood reinforcements on the cour à rangé passageway door.

**WORK PLANNED FOR THE 2011/2012 WINTER SHUTDOWN**

This involves both normal maintenance operations and the start of the work resulting from the additional safety assessment:

- servicing of the H11 secondary plug,
- vertical cold source instrumentation work,
- replacement of components on H8,
- maintenance work on the ventilation systems,
- replacement of the H10 beamtube, and removal of the IH4 beamtube to allow the emergency core reflood system to be installed,
- despatch of 6 spent fuel elements to La Hague,
The ILL reactor went critical for the first time on 31 August 1971 (photos 1 to 4). On 31 August 2011, we celebrated 40 years of its operation. The ceremony provided an opportunity to bring together many former ILL’s staff and especially those who had been at the ILL from the beginning of the adventure: the reactor design team, industrial engineers, members of the original shift teams, and so on.

In 40 years there have only been four Heads of the Reactor Division at the ILL and they all met together for the first time during the event (photo 5).

We were also honoured to welcome Mr Robert Dautray, former High Commissioner for Atomic Energy and member of the Académie des Sciences, who was one of the founding fathers of the nuclear industry in France and participated in the design of the ILL’s high-flux reactor.

The many stories and memories shared during the day gave us a chance to relive some of the enthusiasm felt by the pioneers of those early days, an enthusiasm still alive and well today.

40 years after, the ILL is still the world reference in neutron scattering science and techniques, and demand has never been higher (with a record number of more than 1400 proposals submitted in 2011).

A key factor in this success has been the continuous renewal or development of our instruments to ensure that they are world-leading. The latest upgrade project - the Millennium programme - has furnished the user community with 14 new or renovated instruments as well as supporting infrastructure. Funding and planning are in place to maintain the momentum of the programme to 2014, and we have started working with our scientists and users to develop a well-rounded case for the next-generation instruments and infrastructure to serve their science to 2025 and well beyond.

The ILL has still many successful years ahead!
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 despatch and reception platform, a bigger restaurant and internal roadways.

The ILL is firmly committed not only to build high-performance instruments but also to offer the best scientific environment to the user community.

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 Partnership for Structural Biology (PSB) contains a powerful set of technology platforms that are contributed by the various partner institutes (ILL, ESRF, EMBL, IBS, and the unit for host-pathogen interactions). These platforms include advanced capabilities that complement the powerful neutron scattering facilities available to ILL users: synchrotron X-rays, electron microscopy, NMR, high-throughput methods (valuable expression and crystallisation), and a range of biophysical techniques such as isothermal calorimetry and surface plasmon resonance. A joint SANS/SAXS platform has been developed and there is also an initiative to develop a joint X-ray/neutron low resolution crystallography capability. The aim of the PSB is to enhance the interdisciplinary capabilities of each of the facilities co-located on the site. Further details are provided on its website http://www.psb-grenoble.eu/

The Partnership for Soft Condensed Matter (PSCM) is now in a five floor building with 5 600 m² including 3 100 m² of usable laboratory and office space. The building will be ready in 2013. The construction work is scheduled to take 18 months and will result in a five floor building with 5 600 m² including 3 100 m² of usable laboratory and office space. The building will be ready in 2013.

The Computation-Lab is offering support to ILL users for atomistic simulations using classical and ab initio methods. Typical applications for simulations are structure, magnetism and phonons in crystals and liquid/glass structure and dynamics. 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. For more information see ILL News N.47, June 2007 http://www.ill.eu/html/quick-links/publications/ill-news/

The move will allow the IBS to expand physically and thereby to develop new research activities. It will also bring the IBS on the EPN Campus, closer to the other PSB institutes. The concentration of such an outstanding range of expertise and facilities in life science will provide a unique environment for state-of-the-art integrated structural biology in Europe.

The construction work is scheduled to take 18 months and will result in a five floor building with 5 600 m² including 3 100 m² of usable laboratory and office space. The building will be ready in 2013.
THE ESRF EX2 PROGRAMME

In 2010, it was ESRF's turn to launch its upgrade programme, called EX2. It will include major building extensions with 8 new, longer and more powerful beamlines, technology upgrades to the synchrotron, measurement instruments, and data processing systems.

The building programme comprises two new experimental halls with a total floor surface of 4500 m² to host the eight new beamlines, along with about 4000 m² for new laboratories and offices. Most of the latter will be located in a three-storey building adjacent to one of the new experimental halls.

Finally, a new so-called satellite building for a very long beamline will be built some 300 m away from the new extensions. On 29 November 2011, a ground-breaking ceremony marked the start of the civil construction works for several major building extensions of the ESRF.

The new buildings will be inaugurated in June 2013.

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. 2011 saw the construction of several thousand new flats and the start of a new tramline.

There was also a major success for GIANT in 2011: the “Institut de Recherche Technologique NanoElectronique” project (the IRT), being promoted by GIANT and its industrial partners, won the first place for funding from France’s Grand Emprunt scheme. This means a further 260 M€ for the programme and support for thousands of jobs.

Technical and building programmes

The Clinatec building was opened in 2011 - a centre for biomedical research focusing on micro- and nanotechnological applications in the health field.

There were two other building operations that started in 2011:

• CNRS: the extension of the Institut Néel, with a new building for nanoscience experimentation
• NanoBio2: a project uniting the life sciences with nanotechnology for the development of tomorrow’s healthcare applications.

Both buildings will be completed in 2013.
WORKSHOPS AND EVENTS

ILL workshops and schools in 2011

10–12 JANUARY
nDDB - Molecular dynamics in biology.
http://www.ill.eu/news-events/events/b2011

12–14 JANUARY
BILL 2011 - Structural and dynamical properties of lipid bilayers.
http://www.ill.eu/news-events/events/b2011

24–29 JANUARY
FPSchool 2011 - 4th ILL Annual School on Neutron Diffraction Data Treatment using the FULLPROF SUITE Basic session.

30 JANUARY - 4 FEBRUARY
FPSchool for experts.

7–9 FEBRUARY
GIMM GIANT workshop.
http://www.esrf.fr/events/conferences/usersmeeting2011/

10–14 FEBRUARY
Modern Trends in Magnetism - Workshop dedicated to Igor Dzyaloshinskii on the occasion of his 80th birthday (ILL was one of the many organizing institutes).
http://mid.workshoponline.fr/

18–22 SEPTEMBER
DyProfX XXII.
http://www.ill.eu/news-events/events/dyprof-x-xxii/home/

9–12 OCTOBER
ERIForum Teachers School 2011.
http://www.epn-campus.eu/erif-forum-teachers-school/home/

12–14 OCTOBER
ADD 2011 - Workshop on Analysis of Diffraction Data in Real Space.

18–21 OCTOBER
Neutrons in Biology 2011.

26–28 OCTOBER
Topological Materials.

1–2 DECEMBER
EXILL 2011 - Exogam@ILL.

Short reports on the ILL workshops can be found on the ILL News for Reactor Users (June and December 2011 issues).

ILL chronicle 2011

3 JANUARY
India joins the ILL as first non European Scientific Member.

16 FEBRUARY
Signature at ILL of an agreement for the creation of a technology platform within the GIANT collaboration.

27 FEBRUARY - 30 MARCH
HERCULES, the Higher European Research Course for Users of Large Experimental Systems.

30 MARCH
PSB student day.

17 MARCH
Visit of M. le Préfet, M. Le Douaron.

8 APRIL
Visit of Prof. Luciano Malini, president of Consiglio Nazionale delle Ricerche (CNR), our correspondent for the Italian partnership.

11 APRIL
Clip session of the ILL PhD students.

14 APRIL
ILL seismic exercise.

26–29 APRIL
Meetings of the ILL Scientific Council and its Subcommittees.

2–4 MAY
HERCULES Specialised Courses: INDUSTRY Neutrons and Synchrotron X-rays for Industrial Applications

10–11 MAY
Meeting of the Subcommittees on Administrative Questions (SAQ).

9–10 JUNE
Meeting of the Steering Committee in Saclay (Paris).

31 AUGUST
Celebration of the 40 years of reactor operation since the reactor first diverged.

26 SEPTEMBER
ESS and ILL start joint R&D in neutron science.

1 OCTOBER
ILL’s new management team.

26–27 OCTOBER
Meeting of the Subcommittees on Administrative Questions (SAQ).

15–18 NOVEMBER
Meetings of the ILL Scientific Council and its Subcommittees.

30 NOVEMBER - 1 DECEMBER
Meeting of the Steering Committee in Grenoble.
Visits and events

1. On 8 April ILL welcomed a delegation from Italy headed by Prof. Luciano Malara (second on the left), President of the “Consiglio Nazionale delle Ricerche” (CNR), the entity that funds and coordinates a major part of the country’s public research and which also represents the Italian interests in the ILL Council.

2. From left to right: Stéphane Sébert (CEA Grenoble deputy director), Francesco Sette (ESRF director), Michel Spiro (CNRS scientific director) and Richard Wagner (ILL director from 2006 to 2011) signing on 16 February an agreement for the creation of a new technology platform for industry on the GIANT site.

3. José Luis Martínez (left), Hervé Guyon and Bruno Desbrières (first and second on the right) guiding Monsieur the Prefet of Isère, Eric Le Douaron, on a tour of the ILL.

4. Past and present Heads of Reactor together, during the 40th anniversary of the ILL reactor divergence celebration. From left: Franco Franzetti, Yves Droulers, Ekki Bauer, Richard Wagner (ILL former director general), Hervé Guyon and Jean-Paul Martin.

5. The ILL directors welcoming Catherine Chazette, High Commissioner for Atomic Energy, CEA Saclay, on her visit on 24 November.

6. Participants of HERCULES 2011, the Higher European research Course for Users of Large Experimental Systems.

7. The ILL’s new management team, from left to right: José Luis Martínez and Helmut Schober (Associate Directors) with Andrew Harrison (Director).

8. Poster session of the PSB student day on 2 March.


10. Clip session of the ILL PhD students on 11 April.
Happy users

1 - Bérangère Raguenet (Université Montpellier, left) and Andrea Alejandra Priarristeguy (Université Montpellier, right) on D16 with Viviana Cristiglio (Instrument responsible).

2 - Joe Zaccai (Senior ILL fellow) with a Japanese user team: from left to right, Masaaki Sugiyama (Kyoto University), Takahiro Oda (Yokohama University) and Hikokazu Yagi (Nagoya City University).

3 - Indian users on SALSR: Kiranmaiyi Abburu Venkata (Birla National), Santosh Kumar (Bhabha Atomic Research Centre) and Anurita Khuro (Open University, UK).

4 - Hartmut Lemmel (Instrument responsible) on ST8 with Debasis Sen and Jeannine Bakhuis (Bhabha Atomic Research Centre) (from left to right).

5 - Tom Fennell (now PSI) with Ahmed Rahane, Christaine Alba–Simionesco (LLE, CEA Saclay), Grégoire Sergeant Perthuis (CNRS/Insa) and Caroline Thibaudeau (LLE, CEA Saclay) (from left to right).

6 - From left to right: Dregenee Kasagdian and Florence Martin (IPSC Grenoble) on PN1 with Herbert Faust (Instrument responsible).

7 - Gabriel Casas (left) and Tapas Chattaraj (right) setting up an experiment on D4 with a team from Helmholtzentrum Dresden–Rassendorf: Atsushi Kado–Dhino (left), Christoph Horany (right) and Stephan Wiethe (in the back).

8 - Lisa Arleth (University of Copenhagen, left) and her team during their experiment on D11, a fine illustration of the complementarity of neutron and X-rays scattering techniques. In the back, from left, Peter Lindner and Ralf Schweins (Instrument responsible).

9 - From left to right: Jacques Offler (Instrument responsible) with Holger Euchner (University of Stuttgart), Tsutomu Ishimasa (University Hokkaido), Tatsutomio Yamada (Toyo University) and Marc de Boissieu (INPG, Grenoble) during their experiment on the rejuvenated IN5.

10 - A happy user on FIGARO: Marianna Yanez Arteta (Lund University).

A YEAR IN PHOTOS
WORKSHOPS AND EVENTS
In this context work was also progressing on the extension of the ILL’s Intergovernmental Convention; it is expected that the 5th protocol to the Convention will be signed in 2012.

The ILL is continuing to build for the future

The ILL is continuing therefore to build for the future and it is not surprising that the DA’s Building and Maintenance Service had to deal with an exceptional workload in 2011. Apart from its regular tasks of construction and maintenance the Service also finalised the studies for the new Science Building, the construction of a special heavy water unit, a backup control room, and extension of the experimental hall ILL22. Thanks to good collaboration with the Purchasing group and excellent levels of motivation, it was possible to place the main orders just before the end of the year, thus ensuring that construction can start early in 2012. The Service also provided technical assistance for the new site entrance project and the refurbishment of the site canteen, projects managed by the EBPF. These two projects and the construction of the Science Building have been made possible by the award of a grant from France’s “Contrat Projets État-Region” (CPER).

On the financial front, in 2011 the Finance and Purchasing Service finalised the adoption of the International Financial Reporting Standards (IFRS), in response to requirements from one of our Associates. This should now allow for clearer consolidation of the ILL’s accounts from 2012 onwards. The Service also started implementing the new interbank standards for the Single Euro Payments Area; this will facilitate financial transactions with our users, suppliers and employees. In addition to its routine budgetary and accounting activities, the Service was on the frontline in dealing with the 1% reduction in our 2011 budget; it was tasked with the preparation of budgetary scenarios incorporating known and potential financial constraints, as well as the unforeseen requirement for additional funding for the risk prevention programme introduced following the accident at Fukushima.

Another major item on the human resources agenda was a review of the ILL’s supplementary health insurance provisions. The Service, together with staff representatives, was able to identify and negotiate a new supplier providing comparable or better insurance coverage for staff at a lower cost.

The Human Resources Service was also active in 2011 on other fronts. It adapted its tasks and procedures to new requirements from the Finance and Purchasing Service for the adoption of IFRS. It held discussions with the trade unions on a new “job and skills management system” (the GPEC), including the elaboration of a staff development plan for 2011-2015. The new plan constitutes a response to the budgetary restrictions for this period; it provides for the reduction of up to 13 posts at ILL through the non-replacement of departing staff and introduces adjustments in the workforce to ensure minimum impact on science and our user services. The Service also, of course, continued its recruitment activity (30 new staff members), payroll management, staff training, and travel support for users and ILL staff.

The Administration Division’s role is essentially to provide services for the other divisions of the Institute. In 2011 it assisted in the elaboration of a detailed proposal with financial projections on the potential for producing radioisotopes at ILL for nuclear medicine. With the Associates’ recent approval, Management is now in the position to elaborate a focused and detailed business plan for an innovative project to be led by Dr Ulli Köster.
FACTS AND FIGURES

ADMINISTRATIVE MATTERS

ISTAFF
- 474.5 people including 64 experimentalists in the scientific sector and 23 thesis students.
- 319.5 French, 43 German, 47.5 British, 42 scientific participating countries and 23.5 others.

<table>
<thead>
<tr>
<th>Staff</th>
<th>%</th>
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<tbody>
<tr>
<td>French</td>
<td>318.5</td>
</tr>
<tr>
<td>German</td>
<td>43</td>
</tr>
<tr>
<td>British</td>
<td>47.5</td>
</tr>
<tr>
<td>Scientific Members</td>
<td>42</td>
</tr>
<tr>
<td>Others</td>
<td>23.5</td>
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<tr>
<td>Total</td>
<td>474.5</td>
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IBUDGET 20II: 88.296 M€ (excluding taxes)

<table>
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<tr>
<th>Income</th>
<th>M€</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>Income from Associates</td>
<td>57.610</td>
<td></td>
</tr>
<tr>
<td>Income from Scientific Members</td>
<td>18.999</td>
<td></td>
</tr>
<tr>
<td>Don income</td>
<td>3.930</td>
<td></td>
</tr>
<tr>
<td>Carry forward from 2010</td>
<td>4.974</td>
<td></td>
</tr>
<tr>
<td>Contribution from local authority</td>
<td>0.703</td>
<td></td>
</tr>
<tr>
<td>Cash flow</td>
<td>2.500</td>
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<tr>
<td>Total</td>
<td>88.296</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Expenditure</th>
<th>M€</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>Staff costs</td>
<td>43.150</td>
<td>48.87</td>
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<tr>
<td>Operating costs</td>
<td>15.913</td>
<td>18.02</td>
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<tr>
<td>Investment costs</td>
<td>16.211</td>
<td>18.36</td>
</tr>
<tr>
<td>Fuel cycle</td>
<td>13.022</td>
<td>14.75</td>
</tr>
<tr>
<td>Total</td>
<td>88.296</td>
<td></td>
</tr>
</tbody>
</table>

ICOUNTRIES WITH SCIENTIFIC MEMBERSHIP
- Spain: Ministerio de Ciencia e Innovación (MICINN)
- Switzerland: Staatssekretariat für Bildung und Forschung (SBF)
- Italy: Consiglio Nazionale delle Ricerche (CNR)
- CENI (Central European Neutron Initiative): Austria, Czech Republic, Hungary, Poland, Slovakia
- BELPOLSWE [the Belgian-Polish-Swedish Consortium]: Belgium, Poland, Sweden
- Denmark: Danish Agency for Science, Technology and Innovation
- India: Bhabha Atomic Research Centre (BARC)
- United Kingdom: Science & Technology Facilities Council (STFC)

ISUPERVISORY AND ADVISORY BODIES
- Steering Committee, meeting twice a year
- Subcommittee on Administrative Questions, meeting twice a year
- Audit Commission, meeting once a year
- Scientific Council with 9 Subcommittees, meeting twice a year

IREACTOR
- 58 MW, running 4 cycles in 2011 (with cycles of 50 days)

IEXPERIMENTAL PROGRAMME
- 840 experiments (allocated by subcommittees) on 28 ILL-funded and 9 CRG instruments
- 1557 visitors coming from 35 countries
- 1370 proposals submitted and 767 accepted

ICONTENTS
- 120 ILL ANNUAL REPORT 201II
- 121 ILL ANNUAL REPORT 201II
In 2011, the ILL received notice of 611 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: 52
- Biology: 45
- Crystallography: 81
- Liquids and Glasses: 31
- Magnetic Excitations: 49
- Magnetic Structures: 88
- Materials Science and Engineering: 66
- Nuclear and Particle Physics: 54
- Theory: 18
- Soft Matter: 91
- Spectroscopy in Solid State Physics and Chemistry: 36

**ILL PhD studentships**

- PhD students at ILL in 2011*: 32
- PhD theses completed in 2011: 9

* receiving a grant from ILL